

Chemical Redox Agents for Organometallic Chemistry

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The authors (Bill Geiger, left; Neil Connelly, right) have been at the forefront of organometallic electrochemistry for more than 20 years and have had a long-standing and fruitful collaboration.

Neil Connelly took his B.Sc. (1966) and Ph.D. (1969, under the direction of Jon McCleverty) degrees at the University of Sheffield, U.K. Post-doctoral work at the Universities of Wisconsin (with Lawrence F. Dahl) and Cambridge (with Brian Johnson and Jack Lewis) was followed by an appointment at the University of Bristol (Lectureship, 1971; D.Sc. degree, 1973; Readership 1975). His research interests are centered on synthetic and structural studies of redox-active organometallic and coordination complexes and have been presented in more than 150 publications. He is an active but unsuccessful orienteer and an optimistic but often disappointed supporter of Brentford Football Club.

Bill Geiger received his B.S. from Canisius College (1965) and his Ph.D. from Cornell University (with David H. Geske, 1969) and did postdoctoral work at the University of California at Riverside with August H. Maki and at Northwestern University with Donald E. Smith before joining the faculty at Southern Illinois University in 1970. In 1974 he moved to the University of Vermont. His main interest has been in the use of electrochemistry and spectroelectrochemistry to probe the molecular and electronic structures of odd-electron organometallic compounds. Born and raised in Buffalo, he has been an avid fan of the Buffalo Bills since their inception, so he is familiar with near misses.

I. Introduction

A. Scope of the Review

As interest has grown in electron-transfer (ET) reactions of organometallic compounds, so too has the use of chemical oxidizing and reducing agents to effect these transformations. The aim of this review is to show how one-electron oxidants and reductants have been used in preparative chemistry (incorporating both synthetic applications and generation of

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species for *in situ* characterization) in nonaqueous solutions, the usual media for organometallic ET reactions. It is hoped that the information in this review will also be useful to those interested in ET reactions of organic and inorganic systems, which have more often involved the use of labile metal ions such as M(III), M = Fe, Tl¹ (but see ref 2).

A few words are in order about the reagents we have chosen to describe. Given the vast array of molecules and ions known to undergo one-electron processes, some focus in coverage is necessary. We have emphasized reagents in common usage and provide references to show typical applications rather than attempt comprehensive listings. We have also included some less widely known reagents which are, in our opinion, worthy of further development. The subjective nature of such choices is obvious. Finally, we have not treated photochemically-generated reducing agents which, although generally transient species, may have advantages in some applications.³

The reader will note that in places we have referred to personal communications from colleagues. We are grateful to them for providing many practical hints on the preparation and use of the particular reagents with which they are highly experienced. We would also appreciate correspondence from readers who use other valuable oxidants or reductants which we may have inadvertently missed.

B. Benefits of Redox Agents: Comparison with Electrochemical Methods

Brief treatments have previously appeared concerning applications of redox agents in metal dithiolene chemistry^{2a} and in organic ET chemistry.^{2b} In this section we emphasize the comparative benefits and shortcomings in chemical *vs* electrochemical approaches to preparative redox chemistry.

Electrochemical methods are without rival for investigating the *mechanisms* of ET reactions.⁴ In *preparative* applications, however, electrochemical and nonelectrochemical approaches are closer in relative merit. An experimental protocol making use of the complementary aspects of both approaches is often more effective than either individual method.

Controlled potential electrolysis (CPE) is the electrochemical method most often adopted for synthetic-scale redox reactions.⁴ Its versatility (wide range of accessible potentials) and precision (± 1 mV or better in the absence of resistance effects) make CPE ideal for forcing the uptake or release of one or more electrons from a substrate.

The literature of CPE is well-developed for organic, inorganic, and organometallic systems.^{5,6} When CPE is coupled with voltammetric methods such as cyclic voltammetry, polarography (in its various forms), and voltammetry at rotated electrodes, electrochemical methods can initiate and monitor the progress of simple or complex redox processes. Putting aside matters of availability of equipment and the investigator's training in its use, what reasons might one have, then, for using chemical redox agents to effect preparative-scale ET reactions? We now consider some relative advantages and disadvantages of chemical *vs* electrochemical approaches.

1. Advantages of Chemical Redox Agents

a. Absence of Supporting Electrolyte. A post-electrolysis solution contains a supporting electrolyte salt in large (up to 1000-fold) excess over the desired electrode product. If the latter carries a charge, it may have a solubility similar to that of the supporting electrolyte, making separation difficult. Perhaps the greatest advantage of chemical redox agents is that the experimentalist is not confronted with this separation problem in the workup of the reaction solution.

b. Rapid, Large-Scale Preparations. Chemical redox reactions generally yield larger quantities of products in briefer reaction times, and at higher concentrations, when compared with electrolytic preparations. Except for thin-layer electrochemical cells,^{7a,b} which are very limited in the quantities of reagent that can be produced, preparative electrochemical cells have reaction times of tens of minutes, a time frame that may be troublesome if the desired product has limited stability. Homogeneous chemical redox reactions, on the other hand, often proceed as rapidly as solutions of the redox agent and the substrate are mixed.

This time-scale advantage is compromised when the chemical redox reaction is heterogeneous, as occurs with dissolving-metal reductions, for example, or when the reagent is sparingly soluble, for example, when ceric ammonium sulfate is used in CH₂Cl₂. The mass transfer factors which come into play are then analogous to those encountered in electrolysis experiments.

Redox agents are easily adapted to *low-temperature* studies. Several applications are quoted below wherein the redox agent and the substrate are allowed to dissolve and mix just above the melting point of a solvent, conditions very hard to duplicate in practical electrochemical experiments. In electrolysis experiments, lower diffusion coefficients and higher ohmic effects lengthen reaction times at lower temperatures.^{7c}

c. Use of Nonpolar Solvents. The nature of the solvent medium influences the course of ET reactions. In electrochemistry, the use of solvents with polarities significantly less than those of CH₂Cl₂ ($\epsilon = 9$) and THF ($\epsilon = 7$) is quite difficult because the electrolyte salt must dissolve and appreciably dissociate in order to render the solution conducting. Avoiding the requirement of a supporting electrolyte in chemical redox reactions opens opportunities for the use of very low polarity solvents such as pentane and toluene in ET reactions.

Two potential major benefits arise from the use of low-polarity solvents such as aromatic and aliphatic hydrocarbons, one relating to reactivity, the other to solubility. Low-polarity solvents are often relatively noncoordinating and seldom displace ligands from the primary redox product. For this reason, increased chemical stability may often be observed for organometallic complexes in these media.

Rapid precipitation of highly reactive charged products is feasible using nonpolar solvents. A particularly effective use of this strategy arises when both the redox agent and the substrate are soluble

in nonpolar solvents; mixing the solutions or allowing them to diffuse together yields a precipitate of the desired species (A^+ in the case of the oxidation reaction of eq 1). The counterion of the desired species is the redox byproduct, for example, $[\text{CoCp}_2]^+$ when cobaltocene is used as a reductant and $[\text{Ni}(\text{tfd})_2]^{n-}$ ($n = -1$, $\text{tfd} = [\text{S}_2\text{C}_2(\text{CF}_3)_2]^{2-}$) when the neutral reagent ($n = 0$) is used as an oxidant.



2. Disadvantages of Chemical Redox Agents

When compared with electrochemical methods, chemical redox agents have a number of disadvantages, listed here in anticipation of the discussion of individual reagents in sections II and III.

a. Fixed Redox Strength. This is the greatest limitation of chemical redox agents. A given reagent in a given medium has a fixed formal potential so that a range of reagents is required to provide a range of different redox strengths.

b. Chemical Reagents May Be Noninnocent. In this context, an "innocent" reagent is one which engages exclusively in an outer-sphere ET reaction. Whereas electrodes are among the most benign reagents in synthetic applications, chemical redox agents are more likely to engage in inner-sphere electron-transfer processes and to display coordination tendencies, in addition to leaving a potentially reactive byproduct in solution. The nitrosonium cation $[\text{NO}]^+$ is, for example, prone toward inner-sphere ET mechanisms which occasionally result in coordination of the reagent (as NO) to a metal in the oxidizable substrate. Related to the question of reagent innocence is the chemistry of the reagent byproduct in the reaction medium. If Ox is employed as the original redox agent, then the chemistry of Red, the reaction byproduct, must be anticipated or taken into account. The reagent byproduct may have ligating properties, be acidic or basic, or be able to initiate other reactions such as H-atom transfer, causing the desired electron-transfer product to react further.

c. Reagent Byproduct in Reaction Mixture. Even if the reagent byproduct is unreactive, it may still pose difficulties in the spectroscopic characterization and/or isolation of the desired product. Since many applications of chemical redox agents have the purpose of generating spectra of a desired product, the possibility of spectral interference by the reagent byproduct (or the reagent itself) must be considered. Good experimental design anticipates the optical, vibrational, and magnetic resonance spectra of both Ox and Red.

d. Purity and Stability of Reagent. To assure accurate stoichiometry, the degree of purity (*i.e.*, assay) of the redox agent must be known. Furthermore, for reagents which are stored the amount of degradation with time must be known or methods must be available to assay the reagent before reuse.

e. Solubility Compatibility. If homogeneous reactions are desired, the solubilities of the reagent and the substrate must be taken into account.

Table 1. Formal Potentials (V) for the Ferrocene^{+1/0} Couple vs SCE in Selected Electrolytes^a

| solvent | $[\text{NBu}_4][\text{PF}_6]^b$ | $[\text{NEt}_4][\text{PF}_6]^c$ | $[\text{NBu}_4][\text{ClO}_4]^d$ |
|---|---------------------------------|---------------------------------|----------------------------------|
| nitromethane | 0.35 | 0.31 | 0.34 |
| nitrobenzene | | 0.37 | |
| propylene carbonate | 0.38 | 0.36 | 0.34 |
| MeCN | 0.40 | 0.38 | 0.38 |
| DMSO | | 0.43 | 0.45 |
| DMF | 0.45 | 0.46 | 0.47 |
| CH_2Cl_2 | 0.46 | | 0.48 |
| acetone | 0.48 | 0.46 | 0.50 |
| glyme | 0.51 | | |
| THF | 0.56 | | 0.53 |
| others | | | |
| H_2O (0.1 M NaF) | 0.16 V ^e | | |
| MeCN (0.2 M $\text{Li}[\text{ClO}_4]$) | 0.31 V ^f | | |

^a Supporting electrolyte concentration, 0.1 M. ^b Data from W. E. Geiger's laboratory, University of Vermont. ^c Chang, J. P.; Fung, E. Y.; Curtis, J. C. *Inorg. Chem.* **1986**, *25*, 4233. ^d Chang, D.; Malinski, T.; Ulman, A.; Kadish, K. M. *Inorg. Chem.* **1984**, *23*, 817. ^e Bond, A. M.; McLennan, E. A.; Stojanovic, R. S.; Thomas, F. G. *Anal. Chem.* **1987**, *59*, 2853. ^f Kuwana, T.; Bublitz, D. E.; Hoh, G. *J. Am. Chem. Soc.* **1960**, *82*, 5811.

C. Potentials in Nonaqueous Solvents

Formal potentials, E° , are given in this review vs the ferrocene/ferrocenium couple, as recommended by IUPAC.⁸ In most cases, conversions were required from literature values referenced to other couples. Where a choice was involved, we used conversions from data obtained vs the aqueous saturated calomel electrode (SCE), which is reasonably stable in non-aqueous solutions.⁹ Conversions from the SCE scale to $[\text{FeCp}_2]^{+0}$ were based on values compiled in our laboratories or reported in the literature for different solvents (Table 1). In some cases the conversions were circuitous; the correction parameters are listed for each reagent included in Tables 2 (oxidants) and 3 (reductants). We strongly urge workers to report the ferrocene/ferrocenium potential, vs their chosen reference electrode, under the experimental conditions employed.

For most couples, it was judged unnecessary to list formal potentials in more than one solvent. Solvent-based variations in E° tend to be small for larger, coordinatively saturated, reagents such as $[\text{CoCp}_2]$ and $[\text{Fe}(\text{bipy})_3]^{3+}$. Potentials of smaller ions such as Ag^+ or $[\text{NO}]^+$, which are more highly affected by solvent, are more fully reported. It is beyond the scope of this review to be generally concerned about the effects of ion pairing on the formal potentials, although occasional comments on this subject are included. The interested reader may consult the original papers and in-depth treatments of solvation and ion pairing associations for discussions of the general trends expected from such interactions.¹⁰

D. Reversible vs Irreversible ET Reagents

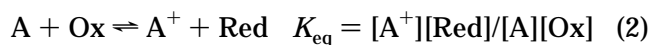
Most of the couples of the ET agents listed in Tables 2 and 3 are reversible so that their potentials,

Table 2. Formal Potentials (V vs Fc) of Selected Oxidizing Agents

| oxidant | solvent | E° | correction | ref |
|--|---------------------------------|-------------|------------|----------|
| [N(C ₆ H ₂ Br ₃ -2,4,6) ₃] ⁺ | MeCN | 1.36 | <i>a</i> | 228 |
| Ce(IV) | HClO ₄ | 1.30 | <i>b</i> | <i>c</i> |
| | H ₂ O | 0.88 | <i>b</i> | <i>c</i> |
| [N(C ₆ H ₃ Br ₂ -2,4) ₃] ⁺ | MeCN | 1.14 | <i>a</i> | 228 |
| [WCl ₆] | CH ₂ Cl ₂ | ca. 1.1 | <i>d</i> | 132 |
| [NO] ⁺ | CH ₂ Cl ₂ | 1.00 | none | 195 |
| [Ru(phen) ₃] ³⁺ | MeCN | 0.87 | <i>e</i> | 108 |
| [NO] ⁺ | MeCN | 0.87 | none | 195 |
| [thianthrene] ⁺ | MeCN | 0.86 | <i>f</i> | <i>g</i> |
| [N(C ₆ H ₄ Br-4) ₃] ⁺ | CH ₂ Cl ₂ | 0.70 | <i>d</i> | <i>h</i> |
| | MeCN | 0.67 | <i>i</i> | <i>j</i> |
| [Fe(bipy) ₃] ³⁺ | MeCN | 0.66 | <i>e</i> | 111 |
| Ag ⁺ | CH ₂ Cl ₂ | 0.65 | <i>d</i> | 63 |
| [Mo(tfd) ₃] | MeCN | 0.55 | <i>f</i> | <i>k</i> |
| [IrCl ₄ (PMe ₂ Ph) ₂] | MeCN | ca. 0.5 | <i>l</i> | 123 |
| [Fe(η -C ₅ H ₄ COMe) ₂] ⁺ | CH ₂ Cl ₂ | 0.49 | none | <i>h</i> |
| [CuTf ₂] | MeCN | 0.40 | <i>f</i> | 88 |
| Ag ⁺ | THF | 0.41 | <i>m</i> | 63 |
| [Ni(tfd) ₂] | CH ₂ Cl ₂ | 0.33 | none | <i>h</i> |
| [PtCl ₆] ²⁻ | H ₂ O | 0.31 | <i>b</i> | <i>n</i> |
| [Fe(η -C ₅ H ₄ COMe)Cp] ⁺ | CH ₂ Cl ₂ | 0.27 | none | <i>h</i> |
| Ag ⁺ | acetone | 0.18 | <i>o</i> | 63 |
| Cl ₂ | MeCN | 0.18 | <i>b</i> | <i>p</i> |
| DDQ | MeCN | 0.13 | <i>i</i> | 308 |
| Br ₂ | MeCN | 0.07 | <i>b</i> | <i>p</i> |
| [N ₂ C ₆ H ₄ NO ₂ -4] ⁺ | sulfolane | ca. 0.05 | <i>f</i> | <i>q</i> |
| Ag ⁺ | MeCN | 0.04 | <i>f</i> | 63 |
| [C ₃ {C(CN) ₂ }] ₃ ⁻ | MeCN | 0.03–0.06 | <i>r</i> | 304 |
| [FeCp ₂] ⁺ | | 0.0 | | |
| [N ₂ C ₆ H ₄ F-4] ⁺ | MeCN | -0.07 | <i>f</i> | <i>q</i> |
| [CPh ₃] ⁺ | MeCN | -0.11 | <i>f</i> | <i>s</i> |
| I ₂ | MeCN | -0.14 | <i>f</i> | <i>t</i> |
| TCNE | MeCN | -0.27 | <i>f</i> | <i>u</i> |
| TCNQ | MeCN | -0.30 | <i>f</i> | <i>u</i> |
| [FeCp* ₂] ⁺ | MeCN | -0.59 | none | <i>h</i> |
| | CH ₂ Cl ₂ | -0.48 | none | <i>h</i> |
| [C ₇ H ₇] ⁺ | MeCN | -0.65 | <i>f</i> | <i>s</i> |

^a Use measured difference from potential of [N(C₆H₄Br-4)₃]⁺ which is 0.70 V vs Fc. ^b Fc = 0.40 V vs NHE in H₂O. ^c Smith, G. F.; Getz, C. A. *Ind. Eng. Chem., Anal. Ed.* **1938**, *10*, 191. ^d Fc = 0.46 V vs SCE (CH₂Cl₂/[NBu₄][PF₆]). ^e Fc = 0.32 V vs sodium SCE. ^f Fc = 0.40 V vs SCE (MeCN/[NBu₄][PF₆]). ^g Hammerich, O.; Parker, V. D. *Electrochim. Acta* **1973**, *18*, 537. ^h Data from authors' laboratories. ⁱ Fc = 0.38 V vs SCE (MeCN/[NET₄][ClO₄]). ^j Reynolds, R.; Line, L. L.; Nelson, R. F. *J. Am. Chem. Soc.* **1974**, *96*, 1087. ^k Davison, A.; Edelstein, N.; Holm, R. H.; Maki, A. H. *J. Am. Chem. Soc.* **1964**, *86*, 2799. ^l 0.9 V vs Ag/AgCl in MeCN/0.1 M NaClO₄; conversion to Fc approximate. ^m Fc = 0.56 V vs SCE (THF/[NBu₄][PF₆]). ⁿ Kravtsov, V. I.; Simakov, B. V. *Elektrokhimiya* **1966**, *2*, 646. ^o Fc = 0.48 V vs SCE (acetone/[NBu₄][PF₆]). ^p Parsons, R. *Handbook of Electrochemical Constants*; Butterworth: London, 1959; p 73. ^q Elofson, R. M.; Gadallah, F. F. *J. Org. Chem.* **1969**, *34*, 854. ^r Fc potential uncertain; no supporting electrolyte specified. ^s Volz, H.; Lotsch, W. *Tetrahedron Letts.* **1969**, 2275. ^t Nelson, I. V.; Iwamoto, R. T. *J. Electroanal. Chem.* **1964**, *7*, 218. ^u Gross-Lannert, R.; Kaim, W.; Olbrich-Deussner, B. *Inorg. Chem.* **1990**, *29*, 5046.

and those of the substrate (A), may be used in the Nernst equation to predict the position of the equilibrium in the model redox reaction of eq 2:



Completeness of the reaction may be judged by the ratio of [A⁺] to [A] when a stoichiometric amount of Ox has been added to a solution of A. Equation 3 describes the relative concentrations of A⁺ and A at the stoichiometric equivalence point in terms of the difference in formal potentials of the oxidizing agent,

Table 3. Formal Potentials (V vs Fc) of Selected Reducing Agents

| reductant | solvent | E° | correction | ref |
|---|---------------------------------|-------------|-------------|----------|
| [C ₁₀ H ₈] ⁻ | THF | -3.10 | <i>a</i> | 366b |
| | glyme | -3.05 | <i>a</i> | 366b |
| | DMF | -2.95 | <i>b</i> | <i>c</i> |
| Na | THF, glyme | -3.04 | <i>a</i> | <i>d</i> |
| Li | NH ₃ | -2.64 | <i>e</i> | <i>f</i> |
| Li(Hg) | H ₂ O | -2.60 | <i>e</i> | <i>g</i> |
| K | NH ₃ | -2.38 | <i>e</i> | <i>f</i> |
| Na(Hg) | nonaqueous | -2.36 | <i>e</i> | <i>h</i> |
| [anthracene] ⁻ | glyme | -2.47 | <i>i</i> | <i>j</i> |
| [FeCp*(η -C ₆ Me ₆)] | dmf | -2.30 | <i>b</i> | 437 |
| Na | NH ₃ | -2.25 | <i>e</i> | <i>f</i> |
| [benzophenone] ⁻ | THF | -2.30 | none | <i>k</i> |
| | DMF | -2.17 | <i>b</i> | <i>l</i> |
| [acenaphthalene] ⁻ | THF | -2.26 | <i>a</i> | 366b |
| | glyme | -2.17 | <i>i</i> | <i>i</i> |
| [FeCp(η -C ₆ Me ₆)] | glyme | -2.09 | <i>m</i> | 402 |
| [CoCp* ₂] ⁻ | CH ₂ Cl ₂ | -1.94 | <i>n</i> | <i>o</i> |
| | MeCN | -1.91 | <i>p</i> | <i>q</i> |
| [Fe(CO) ₂ Cp] ⁻ | THF, MeCN | ca. -1.8 | <i>p, r</i> | 448, 449 |
| | (irr) | | | |
| [CoCp ₂] | CH ₂ Cl ₂ | -1.33 | none | <i>k</i> |
| | glyme | -1.31 | <i>m</i> | 404a |
| [Cr(η -C ₆ H ₆) ₂] | CH ₂ Cl ₂ | -1.15 | none | 8 |
| [FeCp* ₂] | CH ₂ Cl ₂ | -0.59 | <i>n</i> | <i>q</i> |
| | MeCN | -0.48 | <i>p</i> | <i>s</i> |
| hydrazine | DMSO | -0.41 | <i>t</i> | 357 |
| [FeCp ₂] | | 0.0 | | |
| NEt ₃ | MeCN | ca. 0.47 | <i>u</i> | 393 |

^a E° vs [biphenyl]^{0/-}; [biphenyl]^{0/-} = -2.69 V vs SCE (DMF/[NBu₄][ClO₄]) (Grzeszczuk, M.; Smith, D. E. *J. Electroanal. Chem.* **1983**, *157*, 205); Fc = 0.45 vs SCE (DMF/[NBu₄][ClO₄]). ^b Fc = 0.45 V vs SCE (DMF/[NBu₄][PF₆]). ^c Aten, A. C.; Buthker, C.; Hoijtink, G. J. *Trans. Faraday Soc.* **1959**, *55*, 324. ^d Hoijtink, G. J.; de Boer, E.; van der Meij, P. H.; Weijland, W. P. *Recl. Trav. Chim.* **1956**, *75*, 487. ^e Fc = 0.40 V vs NHE in H₂O. ^f Strehlow, H. *The Chemistry of Nonaqueous Solvents*; Lagowski, J. J., Ed.; Academic Press: New York, 1966. ^g Lebed, V. I.; Aleksandrov, V. V. *Russ. J. Phys. Chem.* **1964**, *38*, 1414. ^h Balej, J. *Electrochim. Acta* **1976**, *21*, 953. ⁱ E° vs Ag⁺/Ag; [Cr(η -C₆H₆)₂]⁺⁰ = -1.25 V vs Ag⁺/Ag; Fc = 1.12 V vs [Cr(η -C₆H₆)₂]⁺⁰ (ref 8). ^j Dessy, R. E.; King, R. B.; Waldrop, M. J. *Am. Chem. Soc.* **1966**, *88*, 5112. ^k Data from authors' laboratories. ^l Jensen, B. S.; Parker, V. D. *J. Chem. Soc., Chem. Commun.* **1974**, 367. ^m Fc = 0.51 V vs SCE (glyme/[NBu₄][PF₆]). ⁿ Fc = 0.46 V vs SCE (CH₂Cl₂/[NBu₄][PF₆]). ^o Koelle, U.; Khouzami, F. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 640. ^p Fc = 0.40 V vs SCE (MeCN/[NBu₄][PF₆]). ^q Gennett, T.; Milner, D. F.; Weaver, M. J. *J. Phys. Chem.* **1985**, *89*, 2787. ^r Fc = 0.56 V vs SCE (THF/[NBu₄][PF₆]). ^s Robbins, J. L.; Edelstein, N.; Spencer, B.; Smart, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 1882. ^t Fc = 0.43 V vs SCE (DMSO/[NBu₄][PF₆]). ^u Fc = 0.31 V vs SCE (MeCN/Na[ClO₄]).

Ox, and the substrate, A, where ΔE° (in V) = $E^{\circ}(\text{Ox/Red}) - E^{\circ}(\text{A}^+/\text{A})$.¹¹

$$\log\left\{\frac{[A^+]}{[A]}\right\} = 8.47\Delta E^{\circ} \quad (\text{at } 298 \text{ K}) \quad (3)$$

This relationship allows one to show that in order to obtain 10:1, 100:1, and 1000:1 ratios of the product (A⁺) to the reactant (A) with a stoichiometric amount of Ox the formal potential of the redox agent must be respectively 0.118, 0.236, and 0.354 V positive of the E° of the substrate.

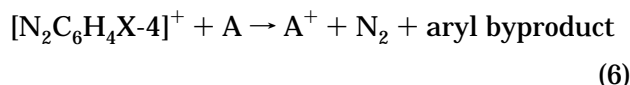
Quantitative predictions cannot be made if the redox agent undergoes chemically irreversible electron transfer. For reagents of this type, the extent of reaction is not predicted by the Nernst equation. Nevertheless, the irreversible potentials (usually peak potentials from slow cyclic voltammetry experi-

ments) listed in Tables 2 and 3 may be used as approximations of the formal potential. Used in this way, irreversible potentials will generally *underestimate* the completeness of the reaction with a substrate, since follow-up reactions after ET have the effect of favoring the overall conversion of reactants to products.¹² In an irreversible electron-transfer reaction, of course, the kinetics of the reaction ultimately controls the degree of redox conversion.

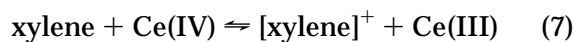
An example of a useful oxidant undergoing irreversible reduction is that of the family of diazonium ions, which rapidly release N₂ (eq 5) after the initial ET (eq 4), giving an aryl radical subject to further coupling or atom abstraction reactions.



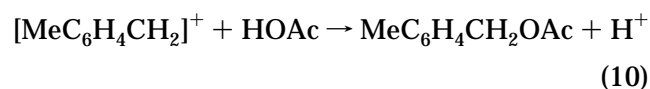
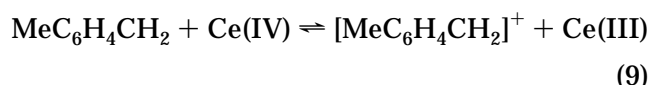
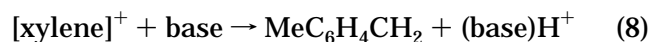
When diazonium salts are used as one-electron oxidants (eq 6), therefore, they will behave as *strong* oxidizing agents than would be predicted by simply using their E_{pk} values as approximations to formal potentials in expressions similar to those of eqs 2 and 3. Other examples will be found throughout the following discussions of the individual reagents.



It is worthwhile noting that the extent of a redox reaction may also increase when the *substrate*, rather than the redox agent, undergoes chemically irreversible ET. Of course, in this situation the ultimate product of the process will not be the primary (initial) ET product. A well-quantified example of such a reaction, namely the oxidation of xylene by excess Ce(IV) in acetic acid, has been discussed by Ebersson.¹³ Because the formal potential of the [xylene]⁺/xylene couple is 1.0 V positive of that of Ce(IV)/Ce(III), the ET reaction of eq 7 is endergonic by *ca.* 23 kcal/mol, resulting in the *electron-transfer* equilibrium itself being strongly in favor of the reactants:



The highly acidic cation, [xylene]⁺, donates a proton to an adventitious base to start a set of exergonic reactions culminating in the production of (4-methylbenzyl)acetate (eqs 8–10).



A special case of “irreversibility” driving an ET reaction arises when the reaction product precipitates from the reaction solution.

E. Categorization of Reagent Strength

In order to facilitate discussion, we thought it useful to define categories of reagent strength on the

Table 4. Suggested Categories for Strengths of Chemical Redox Agents (V vs Fc)

| | oxidants | reductants |
|-------------|-------------|--------------|
| very strong | >0.8 | <-2.5 |
| strong | 0.8–0.2 | -1.5 to -2.5 |
| mild | 0.2 to -0.5 | -0.5 to -1.5 |
| weak | <-0.5 | >-0.5 |

basis of formal potentials. Recognizing that the limits are subjective, we offer the ranges in Table 4 as the basis for discussing a reagent as a weak, mild, strong, or very strong oxidant or reductant.

II. Oxidants

We have chosen to classify the oxidants as “inorganic” or “organic” with further subdivisions according to “type”, *i.e.*, according to charge, magnetic state (para- or diamagnetic), etc. There is, of course, some overlap so that nitrosonium and diazonium salts are considered consecutively as “inorganic” oxidants (given their similar behavior in transition metal chemistry) and alkyl halides are considered with the halogens and main group halides and once again, therefore, under “inorganic” oxidants.

Given the order in which they are discussed, we hope the information provided for each oxidant, namely the synthesis, properties (stability, solubility, spectroscopic), methods of handling, oxidizing power, potential complicating reactions, etc., will enable the reader to choose the most appropriate reagent for a given set of experimental conditions.

Before discussing each reagent individually, we would make one general point. Cationic species, usually in conjunction with inert counteranions, are probably the most widely used oxidants in organometallic chemistry. *The authors do not recommend the use of perchlorate salts under any circumstances. Such salts, of the oxidants themselves or of cationic oxidation products formed therefrom, may be highly and unpredictably explosive.* Although many of the oxidants to be discussed have been prepared as perchlorates, reliable syntheses of salts with other counteranions are invariably available.

A. Inorganic

1. Metal and Metal Complex Oxidants

a. Cations. *i. Ferrocenium Salts.* The ferrocenium ion, [FeCp₂]⁺, is a mild one-electron oxidant, usually regarded as an outer-sphere reagent.¹⁴ Because it is readily available and easily handled it is widely used in both stoichiometric reactions and redox catalysis; salts of a variety of counteranions, including [BF₄]⁻, [PF₆]⁻, [SbF₆]⁻, and [BPh₄]⁻, can be made simply and from cheap precursors. The oxidation potential of the ferrocenium ion can be systematically altered by ring substitution, providing a range of oxidants with $E^{\circ'}$ values varying from -0.63 (for [Fe(η-C₅H₄NMe₂)₂]¹⁵) to 0.64 V (for [Fe(η-C₅H₄CF₃)₂]¹⁶); a table of $E^{\circ'}$ values (*vs* Fc) for various ferrocene derivatives has appeared elsewhere.¹⁷

Ferrocene derivatives with electron-donating substituents are weaker than [FeCp₂]⁺ but may find use

with electron-rich substrates. Thus, $[\text{Fe}(\eta\text{-C}_5\text{H}_4\text{R})\text{-}(\eta\text{-C}_5\text{H}_5)]^+$ ($\text{R} = \text{Bu}^n, \text{Ph}, \text{HgCl}, \text{etc.}$) were employed in kinetic studies of the oxidation of ferrocyclochrome c^{14} (and $[\text{FeCp}^*_2]^+$ is a useful building block in the synthesis of new magnetic materials¹⁸). As yet, the use of ferrocenium ions with electron-withdrawing substituents (stronger oxidants than $[\text{FeCp}_2]^+$) is equally limited; two syntheses employing the acetyl-ferrocenium ion are noted below.

Ferrocenium salts have been prepared by several methods,^{14,19–24} all involving the one-electron oxidation of ferrocene. Surprisingly, full experimental details are not provided in the most widely cited references^{19,20} for the syntheses of $[\text{FeCp}_2][\text{PF}_6]$ and $[\text{FeCp}_2][\text{BF}_4]$ (the two most commonly used ferrocenium salts). The first method¹⁹ readily gives a high yield of the $[\text{PF}_6]^-$ salt and involves FeCl_3 oxidation of ferrocene in aqueous acetone, addition of $[\text{NH}_4][\text{PF}_6]$ to the resulting deep blue solution of the ferrocenium ion, and crystallization of the resulting precipitate from acetone–diethyl ether. Addition of $[\text{NH}_4][\text{BF}_4]$ does not give a precipitate of $[\text{FeCp}_2][\text{BF}_4]$ so readily; the alternative synthesis,²⁰ involving the treatment of ferrocene with *p*-benzoquinone in the presence of $\text{HBF}_4 \cdot \text{OEt}_2$ (aqueous HBF_4 has also been used) provides a more convenient route to this more soluble salt.

These syntheses, detailed in the Appendix, can be used to prepare other ferrocenium salts. The first gives $[\text{FeCp}_2][\text{BPh}_4]$ on addition of NaBPh_4 to the ferrocenium ion solution²³ (see also ref 22). The second has been used to prepare not only $[\text{FeCp}^*_2][\text{BF}_4]$ ²⁵ but also the acyl-substituted ferrocenium salts $[\text{Fe}(\eta\text{-C}_5\text{H}_4\text{COMe})\text{Cp}][\text{BF}_4]$ and $[\text{Fe}(\eta\text{-C}_5\text{H}_4\text{COMe})_2][\text{BF}_4]$ ²⁶ which are considerably stronger oxidants than $[\text{FeCp}_2]^+$ (Table 2). Note, however, that the reaction of *p*-benzoquinone with $[\text{Fe}(\eta\text{-C}_5\text{H}_4\text{COR})_2]$ [$\text{R} = (\text{CH}_2)_5\text{-Me}$] resulted in Michael addition and the formation of benzofuranyl-substituted ferrocenes rather than $[\text{Fe}(\eta\text{-C}_5\text{H}_4\text{COR})_2]^+$.²⁶

Ferrocenium ions with electron-withdrawing substituents (*i.e.*, from less readily oxidized ferrocenes) may also be synthesized by other methods. Details of the preparation²⁷ of $[\text{Fe}(\eta\text{-C}_5\text{H}_4\text{COMe})\text{Cp}][\text{BF}_4]$ ($E^\circ = 0.27$ V) from $[\text{Fe}(\eta\text{-C}_5\text{H}_4\text{COMe})\text{Cp}]$ and AgBF_4 in diethyl ether are given in the Appendix, and $[\text{Fe}(\eta\text{-C}_5\text{Ph}_5)_2][\text{BF}_4]$ ($E^\circ = \text{ca. } 0.3$ V) can be made from $[\text{Fe}(\eta\text{-C}_5\text{Ph}_5)_2]$ and $[\text{NO}][\text{BF}_4]$.²⁸

The crystalline salts $[\text{FeCp}_2][\text{BF}_4]$, $[\text{FeCp}_2][\text{PF}_6]$, and $[\text{FeCp}^*_2][\text{BF}_4]$ are thermally stable, remaining analytically pure (C and H analysis) when stored in air for several months. However, solid $[\text{Fe}(\eta\text{-C}_5\text{H}_4\text{COMe})\text{Cp}][\text{BF}_4]$ is moisture-sensitive and slowly deteriorates (over a period of weeks) even when stored in a desiccator. $[\text{FeCp}_2][\text{BPh}_4]$, used when fluorinated counteranions are undesirable in the final product,²² also slowly decomposes in the solid state in air. It may be stored at -80 °C²⁹ but is best freshly prepared and added to a reaction mixture as a solid. Even then its instability has contributed to the requirement of an excess of the reagent in the oxidatively induced alkyne insertion reaction of the metallacyclobutane complex $[\text{Ir}(\text{CH}_2\text{CHRCH}_2)\text{-}(\text{PhC}\equiv\text{CPh})\text{Cp}^*]$.³⁰ Interestingly, the same reaction does not occur with $[\text{FeCp}'_2][\text{BPh}_4]$ which is more

thermally stable (footnote 16 in ref 22) but a slightly weaker oxidant (by *ca.* 0.1 V).

Ferrocenium ions can be used with a wide range of polar organic solvents, including CH_2Cl_2 ,^{31–34} THF,^{22,35–36} MeOH,³⁷ acetone,³⁸ and MeCN.^{39–41} The solubility of the ferrocenium salt depends on both the solvent and the counteranion. For example, $[\text{FeCp}_2][\text{BF}_4]$ is more soluble than $[\text{FeCp}_2][\text{PF}_6]$ (which is only poorly soluble in cold CH_2Cl_2); $[\text{FeCp}_2][\text{BPh}_4]$ is insoluble in most common organic solvents. In many cases, however, the use of a solution of a ferrocenium salt is unnecessary, and the solid oxidant is added directly to a solution of the substrate. Even though the reaction is then heterogeneous, its rate is usually sufficient. Solvent choice is therefore more often governed by the solubility of the substrate or the stability of the product. For example, oxidative substitution of $[\text{Co}(\text{CO})(\text{PPh}_3)\text{Cp}]$ by PPh_3 in THF in the presence of $[\text{FeCp}_2][\text{PF}_6]$ gives $[\text{Co}(\text{PPh}_3)_2\text{Cp}][\text{PF}_6]$ which is unstable in CH_2Cl_2 .⁴²

The ferrocenium ion almost invariably behaves as an innocent one-electron oxidant, an observation put to good effect in comparative studies of the oxidative activation of C–H bonds by $[\text{CPh}_3]^+$ (a noninnocent oxidant) (section II.B.2.a) and $[\text{FeCp}_2]^+$.^{43–45} The byproduct $[\text{FeCp}_2]$ is readily removed by washing the product with a nonpolar solvent such as hexane or, if necessary, by sublimation. However, excess ferrocenium salt can be difficult to remove from an ionic product. (The authors have detected the ferrocenium ion in the CV of products deemed pure by elemental analysis!) This problem is usually overcome by strictly adhering to the required stoichiometry or by using a slight deficiency of the oxidant (if the substrate is easily removed from its oxidation product). The need for such careful control is illustrated by the reaction between the tautomeric mixture of $[\text{Rh}_2(\mu\text{-NPh})(\text{CO})_2(\mu\text{-dppm})_2]$ and $[\text{Rh}_2(\mu\text{-NHPh})(\text{CO})_2(\mu\text{-dppm})(\mu\text{-Ph}_2\text{PCHPPH}_2)]$ with $[\text{FeCp}_2][\text{PF}_6]$, the products of which depend not only on stoichiometry but also on the order of addition of the reactants.⁴⁶

The stoichiometry of a reaction can sometimes be monitored by ferrocenium ion “titration”. For example, $[\text{FeCp}_2][\text{PF}_6]$ in MeCN was added dropwise to $[\text{RuH}(\text{CO})(\text{PMe}_3)\text{Cp}]$ until a faint green-blue color persisted; the use of 0.71 equiv of the oxidant was consistent with the observed formation of $[\text{RuH}(\text{PMe}_3)(\text{NCMe}_3)_3]^+$, $[\text{Ru}_2(\mu\text{-H})(\text{CO})_2(\text{PMe}_3)_2\text{Cp}_2]^+$, and C_5H_6 in a 1:1:1 ratio. (Other products are formed if $[\text{FeCp}_2][\text{PF}_6]$ and $[\text{RuH}(\text{CO})(\text{PMe}_3)\text{Cp}]$ are reacted in 1:1 or 2:1 ratios.⁴⁰) The use of such a visual “end point” for titration is, however, somewhat subjective and only applicable if the color of the reaction mixture allows. Quantitative titrations should be possible by optical spectrophotometry; data for a range of ferrocenium salts have been reported (*e.g.*, $[\text{FeCp}_2]^+$, $\lambda_{\text{max}} = 617\text{nm}$, $\epsilon = 410$).¹⁴

The ferrocenium ion is particularly useful where selective oxidation is required, for example, in the synthesis of mixed-valence products from bi- or polynuclear species such as $[\text{Ru}(\text{C}\equiv\text{CFC})\text{L}_2\text{Cp}]$ ⁴⁷ and $[\text{Fe}_2(\mu\text{-CH}=\text{CHCH}=\text{CH})(\text{dppe})_2\text{Cp}_2]$ ⁴⁸ which undergo two reversible, sequential redox processes. Selective oxidation of $[\text{Rh}(\text{C}\equiv\text{CPh})\text{L}]$ ($\text{L} = \text{np}_3$ or pp_3) to the

isolable mono- and dications is also accomplished using 1 and 2 equiv of $[\text{FeCp}_2][\text{PF}_6]$, respectively.⁴⁹

In principle, the reversibility of the $[\text{FeCp}_2]^+ / [\text{FeCp}_2]$ couple suggests that the ferrocenium ion can be used only with substrates with formal oxidation potentials negative of 0.0 V. This is the case where the substrate undergoes reversible oxidation (the product distribution is governed by the Nernst equation). However, where this process is irreversible (section I.D), the driving force of the following chemical reaction can lead to oxidation of substrates with E_{ox} more positive than that of the ferrocenium ion. Examples include $[\text{Rh}(\text{CO})\{\text{P}(\text{OPh})_3\}\text{Cp}]$ ($E_{\text{ox}} = 0.23$ V) and $[\text{Rh}(\text{cot})\text{Cp}]$ ($E_{\text{ox}} = 0.08$ V), which are oxidatively dimerized to $[\text{Rh}_2(\text{CO})_2\{\text{P}(\text{OPh})_3\}_2\text{Cp}_2]^{2+}$ ⁵⁰ and $[\text{Rh}_2(\eta^5, \eta^5\text{-C}_{16}\text{H}_{16})\text{Cp}_2]^{2+}$,⁵¹ respectively, and $[\text{RuH}(\text{CO})(\text{PMe}_3)\text{Cp}]$ ($E_{\text{ox}} = 0.35$ V) (see above).⁴⁰

A second strategy for the oxidation of less electron-rich substrates involves the use of ferrocenium ions with electron-withdrawing substituents. Thus, the addition of 1 equiv of $[\text{Fe}(\eta\text{-C}_5\text{H}_4\text{COMe})\text{Cp}]^+$ ($E^\circ = 0.27$ V) to $[\text{Au}\{\text{NC}(\text{Mn}(\text{CO})_2\{\text{P}(\text{OEt})_3\}(\text{dppm})\}_2\}]^+$, which is sequentially oxidized in two one-electron steps ($E^\circ = 0.17$ and 0.45 V), selectively affords the mixed-valence dication $[\text{Au}\{\text{NC}(\text{Mn}(\text{CO})_2\{\text{P}(\text{OEt})_3\}(\text{dppm})\}_2]^{2+}$ whereas $[\text{FeCp}_2]^+$ does not react.⁵² Similarly, oxidatively induced reductive elimination is faster and cleaner when $[\text{RuR}(\text{C}_2\text{Ph})(\text{CO})(\text{PBU}_2\text{Me})_2]$ [$\text{R} = \text{C}_2\text{Ph}$ ($E_{\text{ox}} = 0.28$ V) or CHCHPh ($E_{\text{ox}} = 0.10$ V)] is treated with $[\text{Fe}(\eta\text{-C}_5\text{H}_4\text{COMe})\text{Cp}]^+$ rather than $[\text{FeCp}_2]^+$.⁵³

The stability of the couple $[\text{FeCp}_2]^+ / [\text{FeCp}_2]$ suggests the ferrocenium ion as a potential redox catalyst. It has, indeed, found use with readily oxidized organometallic substrates, for example, in carbonyl insertion (e.g., $[\text{FeMe}(\text{CO})(\text{PPh}_3)\text{Cp}]$ to $[\text{Fe}(\text{COMe})(\text{CO})(\text{PPh}_3)\text{Cp}]$ ⁵⁴ and $[\text{Fe}(\eta\text{-CMe}=\text{CMe}_2)(\text{CO})\{\text{P}(\text{OPh})_3\}\text{Cp}]$ to $[\text{Fe}\{\eta\text{-}(\text{CO})\text{CMe}=\text{CMe}_2\}(\text{CO})\{\text{P}(\text{OPh})_3\}\text{Cp}]$ ⁵⁵) and C–H activation (e.g., of $[\text{IrMe}_2(\text{PPh}_3)\text{Cp}^*]$ to $[\text{IrMe}(\text{C}_6\text{H}_4\text{PPh}_2)\text{Cp}^*]$ ⁵⁶). Its relatively low potential has led to little if any use in organic synthesis (cf. $[\text{N}(\text{C}_6\text{H}_4\text{Br-4})_3]^+$, section II.B.1.a), but substituted ferrocenes with electron-withdrawing substituents are attractive as potential mediators of the electron-transfer-catalyzed oxidation of substrates with E° more positive than 0.0 V. The substituted ferrocenium ions themselves need not be isolable; a catalytic cycle would be sustained if the redox couple is reversible and its members are both inert to side reactions.

ii. Silver(I) Salts. Silver(I) salts are among the most widely used one-electron oxidants, particularly with transition metal complexes but also in organic^{1b} and main group chemistry {e.g., $\text{Ag}[\text{AsF}_6]$ oxidizes⁵⁷ $\text{Te}\{\text{N}(\text{SiMe}_3)_2\}_2$ to the novel Te(III) salt $[\text{Te}\{\text{N}(\text{SiMe}_3)_2\}_2][\text{AsF}_6]$. However, their behavior is neither straightforward nor entirely predictable. Their strength as oxidants can be misjudged if the marked dependence of oxidation potential on solvent is not appreciated and they can participate in a wide range of other reactions, depending on the nature of the substrate and, in part, on the counteranion.

Silver(I) salts are attractive as one-electron oxidants in that they are commercially available with a wide range of counteranions (e.g., $[\text{PF}_6]^-$, $[\text{BF}_4]^-$,

$[\text{SbF}_6]^-$, $[\text{O}_2\text{CCF}_3]^-$, $[\text{O}_3\text{SCF}_3]^-$ (triflate), etc.). Where a less common anion is demanded by the chemistry following electron transfer, the appropriate silver(I) salt can usually be readily prepared. Thus, for example, $\text{Ag}[\text{BPh}_4]$ reacts²² with $[\text{Zr}(\text{CH}_2\text{Ph})_2\text{Cp}_2]$ to give stable $[\text{Zr}(\text{CH}_2\text{Ph})(\text{NCMe})\text{Cp}_2][\text{BPh}_4]$; related $[\text{PF}_6]^-$ salts decompose in solution, with fluorination of the metal center.⁵⁸

Solid silver(I) salts are usually hygroscopic and photosensitive and should therefore be stored in dark, air-free containers. For many purposes, particularly when an excess of the oxidant can be tolerated, the salts can be rapidly weighed in air; for accurate stoichiometric work, or for use with water-sensitive substrates, they are best handled in a glovebag or drybox. A more convenient method to cope with the problem of stoichiometry is to transfer an approximate quantity of the silver salt to a reaction vessel, to dry the contents *in vacuo*, and then to weigh accurately the dried sample. The weight of substrate can then be adjusted to the weight of silver(I) salt taken.

Depending on the counteranion, silver(I) salts may be soluble in a range of organic solvents including CH_2Cl_2 ,^{59,60} acetone,^{61,62} THF,^{63,64} MeCN,^{22,58,62,65,66} alcohols,⁶⁷ and toluene.^{68–70} Because of their moisture and light sensitivity, solutions of the salts are best used immediately (though it is often preferable to use the solid reactant directly). As with the other cationic oxidants described in this review, the anion is often chosen to be noncoordinating; the most commonly used anions are therefore $[\text{BF}_4]^-$ and $[\text{PF}_6]^-$. An important point concerning the latter is that in CH_2Cl_2 , CHCl_3 , or toluene, but not in acetone, MeCN, or THF, hydrolysis of the $[\text{PF}_6]^-$ anion (in the presence of traces of water) is catalyzed⁷¹ by Ag^+ ; byproducts containing species such as $[\text{PO}_2\text{F}_2]^-$, as ligand or counteranion, have been encountered.^{72,73}

Removal of the byproduct of oxidation by silver(I), namely silver metal, is usually straightforward. For solvents in which the product is soluble, filtration through a filter aid such as Celite or Kieselguhr is advisable; the silver metal may be very finely divided. If a reaction is carried out using toluene solutions of both the silver(I) salt and a neutral precursor, a coprecipitate of silver and the cationic product, as a salt of the silver(I) counteranion, may be deposited. Such a strategy can lead to a very simple isolation procedure in that unreacted starting materials can be removed by washing the coprecipitate with toluene; the desired product can then be separated from the insoluble silver metal using a suitable polar solvent as extractant.⁶⁸

The strength of the silver(I) ion as a one-electron oxidant has been variously described, from mild to strong, but of all the reagents described in this review the formal potential of Ag^+/Ag is the most solvent dependent. The potential for the couple Ag^+/Ag is not simply determined in nonaqueous solvents but estimates are available (Table 5). In CH_2Cl_2 , usually regarded as a noncoordinating solvent, $\text{Ag}[\text{PF}_6]$ behaves as a strong oxidant, for example, forming the triarylaminium cation $[\text{N}(\text{C}_6\text{H}_4\text{Br-4})_3]^+$ from $\text{N}(\text{C}_6\text{H}_4\text{Br-4})_3$ ($E^\circ = 0.70$ V). (Note, however, that recent X-ray structural studies⁷⁴ have shown that in the

Table 5. Formal Potentials (V vs Fc) of Ag⁺ and [NO]⁺ Oxidants in Different Solvents

| solvent | Ag ⁺ /Ag ^{a,b} | [NO] ⁺ /NO ^c |
|---------------------------------|------------------------------------|------------------------------------|
| CH ₂ Cl ₂ | 0.65 | 1.00 |
| CH ₃ NO ₂ | | 0.98 |
| DMF | 0.49 | 0.56 |
| H ₂ O | 0.48 | |
| pyridine | 0.43 | |
| THF | 0.41 | |
| acetone | 0.18 | |
| MeCN | 0.04 | 0.87 |

^a Estimate. ^b From ref 63. ^c From ref 195.

solid state, at least, silver(I) can be chelated by CH₂-Cl₂.) By contrast, the silver(I) ion is almost certainly complexed when dissolved in acetone, acetonitrile {-[Ag(NCMe)₂][EF₆] (E = P, Mo, W, and U) has been isolated,⁷⁵ and commercially available [Ag(NCMe)₄][BF₄] has been used⁷⁶ as an oxidant in CH₂Cl₂}, THF, MeOH, and toluene, so that the formal potential is considerably decreased (Table 5). As a qualitative indication of this decrease, Ag[BF₄] is incapable of oxidizing N(C₆H₄Br-4)₃ in toluene, MeCN, or THF; electrochemical studies of Ag[O₂CCF₃] have shown⁶³ that the reduction potential in MeCN is *ca.* -0.6 V more negative than that in CH₂Cl₂.

The solvent dependency of the oxidation potential of Ag(I) can be used to advantage, as in the selective synthesis of the reduced and oxidized forms of the linear trimetallic species [Ag{(NC)Mn(CO)₂{P(OEt)₃}(dppm)}₂]^z.⁵² In CH₂Cl₂, the reaction between *trans*-[Mn(CN)(CO)₂{P(OEt)₃}(dppm)] (*E*^o = 0.03 V) and Ag[PF₆] gives the trication [Ag{(NC)Mn(CO)₂{P(OEt)₃}(dppm)}₂]³⁺, *via* oxidation of the cyanomanganese complex to *trans*-[Mn(CN)(CO)₂{P(OEt)₃}(dppm)]⁺ followed by N-coordination to silver(I). In toluene the reaction affords the monocation [Ag{(NC)Mn(CO)₂{P(OEt)₃}(dppm)}₂]⁺; neither the initial oxidation step nor the oxidation of [Ag{(NC)Mn(CO)₂{P(OEt)₃}(dppm)}₂]⁺ (*E*^o = 0.32 V) occurs.

The solvent-dependent strength of silver(I) is also illustrated by its reactions with [Cr(CNC₆H₄Me-4)₆] (which undergoes three successive one-electron oxidations, at -0.84, -0.15, and 0.64 V⁷⁷). Ag[PF₆] in acetone (*E*^o = 0.18 V) gave either [Cr(CNC₆H₄Me-4)₆]⁺ or [Cr(CNC₆H₄Me-4)₆]²⁺, depending on the stoichiometry of the reaction.⁷⁸ Although stronger oxidants ([NO][PF₆] or SbCl₅) were needed to form the related tricationic complexes [Cr(CNC₆H₃Me₂-2,6)₆]-X₃ (X = [PF₆]⁻ and [SbCl₆]⁻, respectively),⁷⁹ Ag⁺ salts in CH₂Cl₂ (*E*^o = *ca.* 0.65 V) may be sufficiently strong to oxidize [Cr(CNC₆H₄Me-4)₆]²⁺ to [Cr(CNC₆H₄Me-4)₆]³⁺.

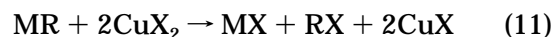
Two complications common to other oxidants can also be encountered in transition metal chemistry. First, the one-electron transfer product will inevitably be more susceptible to nucleophilic attack by donor solvents. Thus [Os(C₆H₄Me-2)₄]⁺ is stable when formed from [Os(C₆H₄Me-2)₄] and Ag[BF₄] in CH₂Cl₂ but not in THF.⁵⁹ Second, the use of a coordinating counteranion (with the cationic oxidant) can lead to binding to the substrate metal center, as in the reactions of *cis*-[Mo(CO)₂(bipy)₂] with AgX (X = NCS, NO₂, or NO₃).⁶⁶

As well as the various complications noted above, a wide variety of reaction modes other than electron transfer can be observed for the silver(I) ion.⁸⁰ First, silver(I) salts are efficient halide abstraction reagents.^{72,81} Second, they may bind to the oxygen,⁸⁰ sulfur {where the reaction of the thiocarbonyl [W(CO)-(CS)(dippe)₂], to give [Ag{(μ-SC)W(CO)(dippe)₂]₂]⁺, contrasts with the simple oxidation of [W(CO)₂(dippe)₂] to [W(CO)₂(dippe)₂]^{+ 61}}, or nitrogen⁵² atoms of coordinated ligands. Third, there are now many examples of the formation of Ag-metal bonds;^{62,82-84} particularly impressive are recent studies⁸⁵ of cluster formation by the sequential condensation of Ag⁺ and [Fe(CO)₄]²⁻ ions, culminating in the one-electron oxidation of [Ag₁₃{Fe(CO)₄]₈]⁴⁺ to [Ag₁₃{Fe(CO)₄]₈]³⁻. In many of these alternative reaction modes, the substrate is redox-active with a formal potential *negative* of that of silver(I); under the experimental conditions described, coordination is preferred even though one-electron transfer is exergonic.

Coordination rather than oxidation is not always a disadvantage. Thus, Ag[O₂CCF₃] and [Os(CO)₃(PPh₃)₂] yielded⁶³ the crystalline adduct [(CF₃CO₂)-AgOs(CO)₃(PPh₃)₂], the slow decay of which gave the short-lived radical cation [Os(CO)₃(PPh₃)₂]⁺, characterized by ESR spectroscopy. Such adducts may be regarded as silver-stabilized radical cations, a concept exploited⁷⁰ in the redox chemistry of [Rh(CO)(PPh₃)Cp] [(*E*_p)_{ox} = *ca.* -0.04 V]. Treatment of this species with Ag[PF₆] in toluene gave the crystallographically characterized salt [Ag{Rh(CO)(PPh₃)Cp}₂][PF₆] which behaved as a stable source of the transient radical cation [Rh(CO)(PPh₃)Cp]⁺ when reacted with NO or NO₂. The "milder" oxidants [FeCp₂]⁺ and [N₂C₆H₄F-4]⁺ react with [Rh(CO)(PPh₃)Cp] to give the fulvalene complex [Rh₂(CO)₂(PPh₃)₂(η⁵,η⁵-C₁₀H₈)]²⁺ by the apparent dimerization of [Rh(CO)(PPh₃)Cp]⁺.

iii. Copper Salts. Although salts of both Cu(I) and, more usually, Cu(II) have been widely used as oxidants in organic chemistry,⁸⁶ organometallic applications are less common. Nevertheless, the reagents are cheap, commercially available with a large number of simple counteranions, and conveniently used with a wide range of organic solvents. Hydrated salts may be employed if the reactants and products are likely to be inert to water, but anhydrous CuCl₂ is simply made by refluxing CuCl₂·2H₂O with thionyl chloride.^{87,88}

Copper(II) halides (hydrated and anhydrous), nitrate, acetate, etc., induce metal-alkyl bond cleavage in [FeR(CO)₂Cp] in CH₂Cl₂⁸⁹ and in ruthenium analogues in MeCN;⁹⁰ the stoichiometry of such reactions, which involve initial one-electron transfer, is given by eq 11. The identity of the oxidant is



[M = Fe(CO)₂Cp or Ru(CO)(PPh₃)Cp, X = halide]

unclear when CuCl₂ reacts with [M₂(CO)₁₀] (M = Mn or Re) in MeCN. In solution, the dichloride rapidly equilibrates with species such as [CuCl]⁺, Cu²⁺, [CuCl₃]⁻, and [CuCl₄]²⁻; the last is certainly not the oxidant and the more positively charged species are favored. Other kinetic studies with [Mn₂(CO)₁₀] were

consistent with $[\text{Cu}(\text{triflate})_2]$ as an outer-sphere oxidant.⁸⁸

Other anhydrous copper(II) oxidants have been used to activate coordinated hydrocarbons. For example, copper acetate induces the oxidative dimerization of $[\text{Re}(\text{C}\equiv\text{CH})\text{L}(\text{NO})\text{Cp}^*]$ ($\text{L} = \text{PPh}_3$) to $[\text{Cp}^*\text{L}(\text{NO})\text{Re}(\mu\text{-C}\equiv\text{CC}\equiv\text{C})\text{ReL}(\text{NO})\text{Cp}^*]$ (which undergoes further oxidation to $[\text{Cp}^*\text{L}(\text{NO})\text{Re}(\mu\text{-C}=\text{C}=\text{C}=\text{C}=\text{C}=\text{C}=\text{C})\text{ReL}(\text{NO})\text{Cp}^*]^{2+}$ with Ag^+)⁹¹ in pyridine and of $[\text{Fe}(\text{CCHMe})(\text{dppe})\text{Cp}]^+$ to $[\text{Cp}(\text{dppe})\text{Fe}\{\mu\text{-C}(\text{Me})\text{C}(\text{Me})=\text{C}(\text{Me})\text{CMe}\}\text{Fe}(\text{dppe})\text{Cp}]^{2+}$ in methanol.⁹²

Copper(I) salts are weaker oxidants than Cu(II) derivatives but may be useful with more electron-rich substrates. Thus, the reaction between copper(I) iodide and the anionic carbene complex $[\text{Mn}\{\text{C}(\text{OEt})\text{CHR}\}(\text{CO})_2\text{Cp}']^-$ in THF results in oxidative coupling, giving the neutral dicarbene derivative $[\text{Cp}'(\text{CO})_2\text{Mn}\{\mu\text{-C}(\text{OEt})\text{CHRCHRC}(\text{OEt})\}\text{Mn}(\text{CO})_2\text{Cp}']$,⁹³ the mixed-metal cluster $[\text{Sb}_2\text{Co}_4(\text{CO})_{10}(\mu\text{-CO})]^{2-}$ gives the monoanion $[\text{Sb}_2\text{Co}_4(\text{CO})_{10}(\mu\text{-CO})]^-$ with $[\text{Cu}(\text{NCMe})_4]^+$.⁹⁴

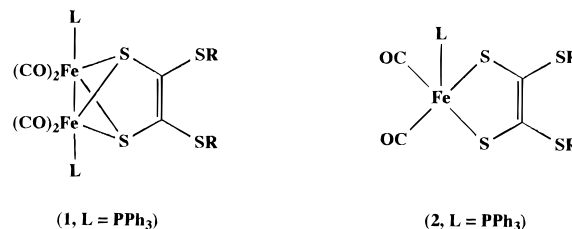
iv. FeCl₃. Both anhydrous and hydrated FeCl_3 are commercially available, but the former may be made by heating the latter under reflux in thionyl chloride,⁸⁸ further purification can be achieved by vacuum sublimation. Hydrated FeCl_3 induces the oxidative coupling of the carbene and alkyl ligands in $[\{\text{RhR}(\mu\text{-CH}_2)\text{Cp}^*\}_2]$ ($\text{R} = \text{Me}, \text{Et}, \text{etc.}$)⁹⁵ but the anhydrous form is normally preferred as the oxidant in organometallic chemistry. The latter is cheap, easily handled (in the absence of moisture), and soluble in organic solvents such as CHCl_3 , ethanol, dioxane, and THF; it may also be added as a solid to substrates dissolved in other solvents. However, it is not ideal for the *in situ* generation of ESR-active species (itself giving rise to a broad signal), and its lability, and those of its reduction products, can lead to the incorporation of chloride. For example, $[\text{M}_2(\text{CO})_{10}]$ is oxidized in MeCN to a mixture of $[\text{MCl}(\text{CO})_5]$ and $[\text{M}(\text{NCMe})(\text{CO})_5]^+$.⁸⁸

In some cases, where the presence of nucleophilic chloride ions is not a problem, the one- (or two-) electron oxidation product can be isolated, for example, *trans*- $[\text{W}(\text{N}_2)_2(\text{PMePh}_2)_4][\text{FeCl}_4]$ from *trans*- $[\text{W}(\text{N}_2)_2(\text{PMePh}_2)_4]$ in dry ethanol.⁹⁶ Where the final product is neutral, separation from the ionic byproducts is particularly facile. Thus, the anions $[\text{Os}_6(\text{CO})_{18}]^{2-}$ (in CH_2Cl_2 , with aqueous FeCl_3) and $[\{\text{Co}(\mu\text{-CO})\text{Cp}\}_2]^-$ (in THF, very slow addition of FeCl_3 to prevent overoxidation to $[\text{Co}(\text{CO})_2\text{Cp}]$) give neutral $[\text{Os}_6(\text{CO})_{18}]$ ⁹⁷ and $[\{\text{Co}(\mu\text{-CO})\text{Cp}\}_2]$,⁹⁸ respectively. Similarly, the oxidation of cluster dianions $[\text{M}_x(\text{CO})_y]^{2-}$ in the presence of L gives $[\text{M}_x(\text{CO})_y\text{L}]$ ($\text{M} = \text{Ru}, \text{Os}, \text{etc.}$)⁸⁴

v. Ce⁴⁺. The cerium(IV) ion is a strong oxidant, usually used as the stable, commercially available salt $[\text{NH}_4]_2[\text{Ce}(\text{NO}_3)_6]$. It is a well-known reagent for organic oxidations^{1b,99} and is also employed in organometallic chemistry to cleave organic products from metal centers.¹⁰⁰ It may, however, also be used more selectively in the isolation of a wide variety of one-electron oxidation products.

The salt $[\text{NH}_4]_2[\text{Ce}(\text{NO}_3)_6]$ is water-soluble and reacts with *cis*- $[\text{Os}(\text{detc})_2(\text{PPh}_3)_2]$ to give *trans*- $[\text{Os}$

$(\text{detc})_2(\text{PPh}_3)_2]^+$ in that solvent.¹⁰¹ However, it is also soluble in alcohols, acetone, acetonitrile, etc., and oxidizes $[\text{B}_6\text{Cl}_6]^{2-}$ (in ethanol) and $[\text{OsCp}_2]$ (in MeCN) to $[\text{B}_6\text{Cl}_6]^-$ ¹⁰² and $[\text{Os}_2\text{Cp}_4]^{2+}$ (the metal-metal bonded dimer of $[\text{OsCp}_2]^+$),¹⁰³ respectively. It may also be added as a solid to a solution of a substrate in the less polar organic solvents more generally useful for synthetic and spectroscopic studies of organometallics. Thus, **1** gives **2** in THF.¹⁰⁴ Alternatively, the use of $[\text{NBu}_4][\text{HSO}_4]$ as a phase-transfer catalyst, which facilitates the oxidation of $[2,2]\text{paracyclophane}$ to its radical cation in CHCl_3 ,¹⁰⁵ may also be applicable for organometallic systems.



vi. [M(L-L)₃]³⁺ ($L\text{-}L = \text{bipy}, \text{phen}, \text{etc.}$). Various cationic coordination complexes of chelating aromatic N-donors, namely $[\text{M}(\text{L-L})_3]^{3+}$ ($\text{M} = \text{Cr}, \text{Fe}, \text{Ru}, \text{Os}, \text{Co}, \text{Ni}; L\text{-}L = \text{bipy}, \text{phen}, \text{etc.}$), can act as one-electron oxidants. Almost invariably, they have been used as their $[\text{ClO}_4]^-$ salts. However, once again we underline the fact that this anion is potentially explosive and recommend the anhydrous $[\text{PF}_6]^-$ salts, synthetic procedures for which are available.¹⁰⁶⁻¹⁰⁸ The Ni(IV) salt $[\text{Ni}(\text{bipy})_3][\text{AsF}_6]_4$ has also been isolated; the tetracation may find use as a very strong oxidant ($E^\circ = 2.06 \text{ V}$).¹⁰⁹

The trications $[\text{M}(\text{L-L})_3]^{3+}$ are generally regarded as outer-sphere reagents,^{88,106,110} their oxidation potentials^{108,111,112} depending mainly on the metal but also varying with the ligand substituents. The nickel complexes are the strongest oxidants,¹¹³ but the iron and cobalt derivatives are the most widely used. Extensive studies have been made of the effects on potential of varying the 4,7-substituents in $[\text{Fe}(\text{phen})_3]^{2+}$. For example, $[\text{Fe}\{\text{phen}(\text{NH}_2)_{2-4,7}\}_3]^{2+}$ is oxidized more readily, by *ca.* 0.9 V, than the parent complex $[\text{Fe}(\text{phen})_3]^{2+}$.^{114,115} The trications $[\text{Fe}(\text{phenX}_{2-4,7})_3]^{3+}$ constitute an array of oxidants in which the potential is modified systematically from 0.66 V ($\text{X} = \text{H}$) to -0.26 V [$\text{X} = \text{NH}(\text{CH}_2)_3\text{NH}_2$]. As yet, they have been largely used as stoichiometric or catalytic electron-transfer oxidants with organic substrates^{112,116,117} although the titanium enolate $[\text{TiCl}\{\text{OC}(\text{H})=\text{CCMe}_2\}\text{Cp}_2]$ is oxidized to a benzofuran.¹¹⁸ When compared^{115,118} with arylammonium salts (section II.B.1.a), $[\text{Fe}(\text{phen})_3]^{3+}$ derivatives are said to be (i) more effective when radical intermediates with relatively high oxidation potentials need to be oxidized in slow ET reactions,¹¹⁶ (ii) as efficient in stoichiometric reactions when the radical intermediates are easily oxidized,¹¹⁷ but (iii) worse in cation radical chain processes since back electron transfer from $[\text{Fe}(\text{phen})_3]^{2+}$ is slower than that with triarylamines.¹¹²

Most studies involving the oxidation of organometallic compounds by $[\text{M}(\text{L-L})_3]^{3+}$ have been mecha-

nistic, for example, the cleavage of main group metal-alkyl bonds^{108,111} and the oxidation of $[\text{Mn}(\text{CO})_5\text{L}]^-$ ($\text{L} = \text{CO}$ or phosphine).¹⁰⁶ However, $[\text{Ru}_3\text{H}_3(\mu_3\text{-CX})(\text{CO})_{9-n}\text{L}_n]$ (e.g., $\text{X} = \text{OMe}$, $\text{L} = \text{PPh}_3$, $n = 2$ or 3) is oxidized to the monocation by $[\text{Fe}(\text{phen})_3]^{3+}$.¹¹⁰

b. Anionic Complexes $[\text{IrCl}_6]^{2-}$ and $[\text{PtCl}_6]^{2-}$.

The hexachloroiridate(IV) dianion $[\text{IrCl}_6]^{2-}$ ($\lambda_{\text{max}} = 487$ nm, $\epsilon = 4060$), usually as the commercially available sodium or potassium salt,¹¹⁹ has been extensively used as an outer-sphere, one-electron oxidant in mechanistic studies of the cleavage of metal-alkyl bonds.¹²⁰ For example, the oxidation of $[\text{PtR}_2(\text{PMe}_2\text{Ph})_2]$ occurs by initial one-electron transfer, though 2 equiv of oxidant are required for complete reaction.¹²¹ Surprisingly, $[\text{IrCl}_6]^{2-}$ does not oxidize $[\text{M}_2(\text{CO})_{10}]$ ($\text{M} = \text{Mn}$ or Re) in MeCN even though the potentials are thermodynamically favorable, an observation ascribed by the authors to the high electrostatic barrier to electron transfer presented by the dianionic charge.^{88,122}

For synthetic purposes it has been less widely used, though in moist MeCN $\text{Na}_2[\text{IrCl}_6]$ induces the oxidative coupling of the methyl and carbene groups of $[\{\text{RhMe}(\mu\text{-CH}_2)\text{Cp}^*\}_2]$ to give propene.⁹⁵ However, as a rare example of a dianionic oxidant it may prove useful in the isolation of salts where the high positive charge of the oxidized product would be balanced by the high negative charge of the Ir(III) counteranion; when used in MeCN (or aqueous solutions), the reduction products are normally $[\text{IrCl}_6]^{3-}$ and/or $[\text{IrCl}_5(\text{NCMe})]^{2-}$.

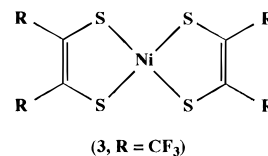
The oxidizing ability of the Ir(IV) center may be altered by varying the ligands, as in *trans*- $[\text{IrCl}_4(\text{PMe}_2\text{Ph})_2]$ ($E^\circ = \text{ca. } 0.5$ V). This neutral oxidant provides an interesting alternative to $[\text{IrCl}_6]^{2-}$ in being soluble in much less polar solvents. It has therefore been used in benzene to oxidize neutral substrates such as $[\text{MCp}_2]$ ($\text{M} = \text{Fe}$ and Ni), the salts $[\text{MCp}_2][\text{IrCl}_4(\text{PMe}_2\text{Ph})_2]$ precipitating directly from the reaction mixture. However, the "inert" anion $[\text{IrCl}_4(\text{PMe}_2\text{Ph})_2]$ can act as a nucleophile; the chloro-bridged Ir(III) complex $[\text{PhMe}_2\text{P}(\mu\text{-Cl})_2\text{Pt}(\text{PPh}_3)_2]^+$ is formed with $[\text{Pt}(\eta\text{-C}_2\text{H}_4)(\text{PPh}_3)_2]$.¹²³

The Pt(IV) complex $[\text{PtCl}_6]^{2-}$ also provides a potentially interesting variation to $[\text{IrCl}_6]^{2-}$ in reacting with Zeise's salt, $[\text{PtCl}_3(\eta\text{-C}_2\text{H}_4)]^-$, as an inner-sphere two-electron oxidant.¹²⁴

c. Neutral Compounds. Neutral metal complex oxidants are uncommon yet potentially extremely useful for the synthesis of charged products in nonpolar, and non-nucleophilic, solvents; mixing stoichiometric quantities of oxidant and substrate in, for example, hexane or toluene should, in principle, lead to the deposition of near-quantitative yields of the electron-transfer salt.

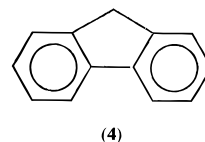
i. $[\text{Ni}(\text{tfd})_2]$ and $[\text{Mo}(\text{tfd})_3]$. The neutral dithiolene complexes $[\text{Ni}(\text{tfd})_2]$ (**3**) and $[\text{Mo}(\text{tfd})_3]$ are strong one-electron oxidants, simply prepared in very high yield from $\text{S}_2\text{C}_2(\text{CF}_3)_2$ and either $[\text{Ni}(\text{CO})_4]$ ¹²⁵ or $[\text{Mo}(\text{CO})_6]$.¹²⁶ That these oxidants have not been widely used may stem from the unattractive synthesis of $\text{S}_2\text{C}_2(\text{CF}_3)_2$ and the involvement of $[\text{Ni}(\text{CO})_4]$ (*highly*

toxic) in the preparation of the nickel compound. Nevertheless, their wider use should be considered.



The crystalline solids are thermally stable in dry air for many years but slowly react with water and should be stored and used under dry conditions. They are soluble in nonpolar solvents and, if necessary, can be repurified by recrystallization from dry benzene ($[\text{Ni}(\text{tfd})_2]$; the use of toluene is to be preferred)¹²⁵ or by continuous (Soxhlet) extraction using pentane ($[\text{Mo}(\text{tfd})_3]$);¹²⁶ the nickel complex is very soluble in CH_2Cl_2 , ensuring homogeneous electron-transfer reactions even at low temperatures.

The products of reduction of $[\text{Ni}(\text{tfd})_2]$ and $[\text{Mo}(\text{tfd})_3]$, namely the monoanions $[\text{Ni}(\text{tfd})_2]^-$ and $[\text{Mo}(\text{tfd})_3]^-$, are inert and unlikely to ion-pair with one-electron oxidation products in solution, even in solvents of low polarity. Thus, the oxidation of $[\text{Cr}_2(\text{CO})_6(\mu\text{-}\eta^6, \eta^6\text{-L})]$ ($\text{L} =$ biphenyl derivative **4**) gave



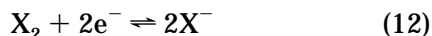
$[\text{Cr}_2(\text{CO})_6(\mu\text{-}\eta^6, \eta^6\text{-L})]^+$ whose mixed-valence behavior was interpreted with the knowledge that the anion would not influence the spectroscopic (IR and ESR) properties of the monocation.¹²⁷ The reaction of $[\text{Mo}(\text{tfd})_3]$ with $[\text{M}_4(\mu_4\text{-E})_4(\eta\text{-C}_5\text{H}_4\text{R})_4]$ ($\text{M} = \text{Cr}$, $\text{E} = \text{S}$ or Se , $\text{R} = \text{Me}$; $\text{M} = \text{Mo}$, $\text{E} = \text{S}$ or Se , $\text{R} = \text{Pr}^i$) in toluene similarly gave the charge-transfer salts $[\text{Mo}(\text{tfd})_3][\text{M}_4(\mu_4\text{-E})_4(\eta\text{-C}_5\text{H}_4\text{R})_4]$ and $[\text{Mo}(\text{tfd})_3]_2[\text{Mo}_4(\mu_4\text{-S})_4(\eta\text{-C}_5\text{H}_4\text{Pr}^i)_4]$.⁹⁷

ii. Transition Metal Hexahalides. High-valent transition metal (d- and f-block) fluorides such as MF_6 ($\text{M} = \text{Mo}$ or W), UF_6 , etc., were recommended as one-electron oxidants by Olah in a review¹²⁸ of new reagents for organic synthesis. Though such reagents have the advantages of ready availability and solubility in organic solvents such as CHCl_3 , CH_2Cl_2 , and THF, they are hydrolyzed, giving HF, and must be used under rigorously dry conditions. As yet, therefore, they have not been widely used as one-electron oxidants in organometallic chemistry although $[\text{MCl}_2\text{Cp}_2]$ ($\text{M} = \text{Mo}$ or W) and $[\text{WF}_6]$ in SO_2 give $[\text{MoCl}_2\text{Cp}_2][\text{WF}_6]$ ¹²⁹ and a mixture of $[\text{WCl}_2\text{Cp}_2]_2[\text{W}_4\text{F}_{18}]$ and $[\text{WCl}_2\text{Cp}_2][\text{WF}_6]_2$, respectively;¹³⁰ $[\text{Ag}(\text{NCMe})_2][\text{EF}_6]$ can be prepared by oxidizing Ag metal with EF_6 ($\text{E} = \text{Mo}, \text{W}$, or U).⁷⁵

The hexachlorides, also strong oxidants (e.g., $E^\circ = \text{ca. } 1.1$ V for $[\text{WCl}_6]$ ^{131,132}), are easier to handle in conventional glassware; WCl_6 oxidizes $[\text{C}_6\text{H}_4\text{Br-4}]_3$ to $[\text{C}_6\text{H}_4\text{Br-4}]_3[\text{WCl}_6]$ (section II.B.1.a) and, in the presence of acetic acid and MOAc ($\text{M} = \text{Na}$ or K), acetoxyates aromatics *via* arene radical cations¹³² (though chlorination reactions can interfere).

2. Main Group Oxidants

a. Halogens and Halides. *i. Halogens.* The halogens Cl₂, Br₂, and I₂ (fluorine may be disregarded as a convenient one-electron oxidant) are readily available, cheap, and easily purified oxidants soluble in a wide variety of organic solvents. Although the differences in formal potentials for the couple of eq 12 are over 0.8 V in aqueous media, the reported potentials span a difference of only about 0.3 V in MeCN (Cl, 0.18 V; Br, 0.07 V; I, -0.14 V). Significant differences are observed, however, in the ET reactivity of the halogens. For example, bromine oxidizes N(C₆H₄R-4)₃ (R = Me or OMe) to the corresponding arylaminium cations [N(C₆H₄R-4)₃]⁺ whereas elec-



trophilic substitution is observed with chlorine. Iodine is insufficiently strong to oxidize such amines,¹³³ unless used in conjunction with a silver(I) salt (see section II.A.1.a.ii), but does effect the one-electron oxidation of both Li[N(PPh₂)₂] and Li[HC(PPh₂)₂], leading to P–P and P–C coupling, respectively.¹³⁴

The solubility of halogens in nonpolar solvents such as toluene and hexane leads to simple synthetic methods for the isolation of pure organometallic oxidation products. For example, the reaction of neutral [Mo(η⁵-C₇H₉)(η-C₇H₇)] with half an equivalent of iodine in toluene gives a precipitate of ionic [Mo(η⁵-C₇H₉)(η-C₇H₇)I] which yields solid [Mo(η⁵-C₇H₉)(η-C₇H₇)]PF₆ when dissolved in water and treated with [NH₄][PF₆];¹³⁵ a similar strategy was adopted for the synthesis of [Mo(dmpc)₃][PF₆].¹³⁶ The iodides themselves may be characterized, but the possible formation of [I₃]⁻ salts should be borne in mind, as in [Co₂(μ-MeC≡CMe)(μ-dppm)₂(CO)₂][I₃].²³ Moreover, both I⁻ and [I₃]⁻ salts, for example, [Ti(η⁴-cot)-Cp]I and [Ti(η⁴-cot)Cp][I₃],¹³⁷ may be isolable (separately or as a mixture) depending on the initial stoichiometry of the reactants. Anionic precursors may also be conveniently oxidized in nonpolar solvents. Thus, the addition of I₂ to a suspension of [NET₄]₂[M(SPh)₄(Mo(CO)₄)₂] in toluene gives solid [NET₄]I and a solution of pure [M(SPh)₄(Mo(CO)₄)₂] (M = Fe or Co).¹³⁸

More robust, but less electron-rich, substrates may be oxidized successfully with chlorine or bromine; for example, [Pt(σ-C₆Cl₅)₄]²⁻ (E' = 0.07 V) in CH₂Cl₂ gives [Pt(σ-C₆Cl₅)₄]⁻¹³⁹ with either halogen in CCl₄. The monoanion can be further oxidized¹⁴⁰ to [Pt(σ-C₆Cl₅)₄] [(E_p)_{ox} = 1.4 V] by an excess of chlorine in the presence of AlCl₃ (as halogen carrier¹⁴¹) in CH₂-Cl₂-CCl₄. Interestingly, [PtPhCl₃(PET₃)₂] in MeNO₂ is inert to chlorine, but addition of AlCl₃ leads to chlorination of the coordinated aryl ring by electrophilic substitution.¹⁴²

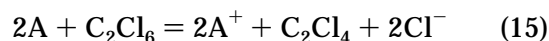
Reactions competing with simple electron transfer are common. The halogens not only act as electrophiles but the halides, formed on halogen reduction, may behave as nucleophiles. Thus, the oxidative addition of I₂ to [Fe(CO)₃(PPh₃)₂], to give [FeI(CO)₃(PPh₃)₂]⁺, involves one-electron oxidation and coordination of I and/or I⁻.¹⁴³ Metal-alkyl bonds are frequently cleaved, giving metal and alkyl halides, as in the halogenation of [FeR(CO)₂Cp].¹⁴⁴

ii. Alkyl Halides and Other Alkylating Agents. Alkyl halides are weak one-electron oxidants, reacting according to eqs 13 and 14; electron-rich sub-



strates such as [Cr(η-arene)₂] and [Mo(dmpc)₃] give the corresponding monocations [Cr(η-arene)₂]⁺¹⁴⁵ and [Mo(dmpc)₃]⁺ (with MeI¹³⁶), respectively. The formation of the radical, R, as a byproduct can result in coupling reactions, as in the formation of both [Co(η⁴-C₅C₅R)Cp] and [CoCp₂]X from [CoCp₂] and RX.¹⁴⁶

The formation of inert C₂Cl₄ as a byproduct (eq 15), rather than alkyl radicals, makes C₂Cl₆ interesting as an alternative to alkyl halide oxidants, as in the oxidation of [CoCp₂] to [CoCp₂]⁺.¹⁴⁷ In common with the alkyl halides, however, the halide ion byproduct may act as a nucleophile toward the oxidation product so that, for example, [{CoClCp*}]₂ is cleanly oxidized to [{CoCl₂Cp*}]₂.¹⁴⁸



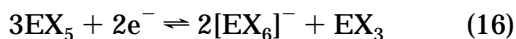
Other alkylating agents may also act as one-electron oxidants. Thus, [OEt₃][BF₄] and MeSO₃F react with [MoCl₂(dppe)₂] in CH₂Cl₂ to give [MoCl₂(dppe)₂]X (X = [BF₄]⁻ and [SO₃F]⁻, respectively), and [ReCl(CO)₃(PPh₃)₂] is similarly oxidized to [ReCl(CO)₃(PPh₃)₂][BF₄].¹⁴⁹

iii. AlCl₃. AlCl₃ is a strong oxidant in CH₂Cl₂ with an oxidation potential estimated to be ca. 1.1 V.¹⁵⁰ However, the mechanism by which it acts is still far from clear, and the identity of the actual oxidant {AlCl₃ itself, the cation [AlCl₂]⁺ (formed by autoionization of AlCl₃ to [AlCl₂][AlCl₄]), or a carbocation such as [CH₂Cl]⁺ (a product of halide abstraction from CH₂Cl₂)}, is unknown.^{151,152} (Indeed, AlCl₃ can function as a reducing agent, for example, toward phenanthrenequinone in THF or glyme!¹⁵²) Nevertheless, it has been widely used to generate cation radicals for ESR spectroscopic studies, mainly from main group organometallics in CH₂Cl₂^{150,153} but also of *p*-dialkoxybenzenes in MeNO₂.¹⁵⁴ In spite of the high sensitivity of AlCl₃ toward water, and the consequent formation of HCl, the highly purified reagent does not seem to be necessary for the acquisition of ESR spectra in CH₂Cl₂.¹⁵⁵ However, it may be purified by vacuum sublimation; it is also commercially available as a 1.0 M solution in PhNO₂, packed under N₂.

Synthetic applications have been far fewer than spectroscopic studies. However, [thianthrene]⁺¹⁵⁶ and a diazasilacylopentene radical cation¹⁵⁷ have been isolated and structurally characterized as [AlCl₄]⁻ salts. Moreover, a mixture of AlCl₃ and Cl₂ (but not chlorine alone) (section II.A.2.a.iii) oxidizes [Pt(σ-C₆-Cl₅)₄]⁻ to [Pt(σ-C₆Cl₅)₄] in CH₂Cl₂-CCl₄¹⁴⁰ (and note that TiCl₃ has been used to oxidize [Pt(σ-C₆Cl₅)₄]²⁻ to [Pt(σ-C₆Cl₅)₄]⁻).¹³⁹

iv. Arsenic and Antimony Pentahalides. The Group 15 pentahalides EX₅ (E = As, X = F; E = Sb, X = F or Cl) are strong oxidants (as well as halogenating agents and halide ion acceptors). They are volatile (AsF₅ is a gas at room temperature and pressure,

SbX₅ are liquids) and moisture-sensitive and must be stored and used in dry conditions (the fluorides give HF with H₂O). Though reactive toward water and other protic solvents such as alcohols, the pentahalides are soluble and stable in solvents such as CH₂Cl₂ and CHCl₃. Electron transfer occurs according to eq 16 though other complex counteranions may appear in isolated salts (see below). If used, the toxicity of arsenic and antimony should be considered.



Of the pentahalides, SbCl₅ has been most widely used. When added as a solution in CH₂Cl₂ to N(C₆H₄-Br-4)₃ or thianthrene in the same solvent, simple one-electron transfer results and the radical cation salts [N(C₆H₄-Br-4)₃][SbCl₆] (section II.B.1.a) and [thianthrene][SbCl₆] (section II.B.1.b) are isolable; aromatic cation radicals (*e.g.*, of perylene, anthracene, etc.) have been generated in the same way for ESR spectroscopic studies, aided by the formation of only diamagnetic reduction byproducts.¹⁵⁸ Organometallic complexes can also undergo one-electron transfer, although subsequent halogenation is common, as in the reaction with [M(CO)₃(η-C₆Me₆)] (M = Mo and W) to give [MCl(CO)₃(η-C₆Me₆)] [SbCl₆];¹⁵⁹ the metal-halide bonds probably result from the reaction between the products of one-electron transfer in that [EX₆]⁻ is a labile source of nucleophilic chloride anions. Moreover, SbCl₅ itself can bind, as a Lewis acid, to the oxidation product. Thus, *cis*-[Mn(CN)(CO)₂{P(OEt)₃}(dppm)] reacts with SbCl₅ in CH₂Cl₂ to give the Mn(II) derivative *trans*-[Mn(CNSbCl₅)(CO)₂{P(OEt)₃}(dppm)] [SbCl₆].¹⁶⁰

Further complications can arise because the antimony-containing reaction products may themselves be oxidants (eq 17), albeit much weaker than EX₅.



For example, [SbCl₆]⁻ oxidizes ferrocene, I⁻, and aromatic amines.¹⁶¹ Moreover, this type of reaction, and the lability of [EX₆]⁻, may give rise to unexpected counteranions such as [SbCl₄]⁻ and [Sb₂Cl₈]²⁻; the latter is found in [Mo₂(μ-Cl)(μ-C₈Me₈)Cp₂]₂[Sb₂Cl₈], the product of the oxidation of [Mo₂(μ-C₈Me₈)Cp₂] with [NPrⁱ₄][SbCl₆].¹⁶²

The pentafluorides, EF₅, are more difficult to handle (in part because of the formation of HF with water) but are stronger oxidants than the chlorides (SbF₅ will oxidize the less electron-rich triarylamines unaffected by SbCl₅, section II.A.2.a.iii) and are less likely to give rise to halogenated byproducts. Accordingly, distillation of EF₅ (E = As and Sb) onto solutions of [MX₂Cp₂] (X = Cl, M = V,^{163,164} Nb,¹⁶⁴ Mo, and W;¹⁶⁵ X = Me, M = Nb and Mo¹⁶⁶) in liquid SO₂ at low temperatures gives high-valent, one- or two-electron oxidation products such as [VCl₂Cp₂]-[AsF₆] and [MoMe₂Cp₂]²⁺. It is noteworthy that [VCl₂Cp₂] and Ag[SbF₆] yield [V(SbF₆)₂Cp₂] and AgCl, *i.e.*, that chloride abstraction occurs with Ag⁺ even though oxidation is favored, and observed, with AsF₅.¹⁶⁴ Moreover, the reaction between [ReCl₂-Cp₂]Cl with a mixture of Ag[SbF₆] and SbF₅ gives [ReCl₂Cp₂][SbF₆]₃ *via* abstraction of the chloride

counteranion with Ag⁺ and oxidation by the pentafluoride.¹⁶⁷

b. Nitrosonium, [NO]⁺, Salts. The use of nitrosonium salts as strong one-electron oxidants in organic^{129,168} and inorganic chemistry¹⁶⁹⁻¹⁷¹ has been briefly reviewed, but they are noninnocent and can participate in a wide range of alternative reactions.

The most commonly used nitrosonium salts, namely [NO][BF₄], [NO][PF₆], and [NO][SbF₆], are commercially available as 95–98% pure solids; a simple laboratory preparation of [NO][BF₄], from amyl nitrite, aqueous HBF₄, and propionic anhydride, is given in ref 172. Many other salts can also be made,^{169,173} for example, [NO][SbCl₆] (from the reaction of NOCl with SbCl₅) and [NO][AsF₆] (by anion exchange between [NO][SbCl₆] and [NBuⁿ₄][AsF₆]).¹⁷⁴

The salts [NO][BF₄] and [NO][PF₆] can be purified by vacuum sublimation (at *ca.* 0.01 mmHg and 220–250 °C^{169,175}), by washing with ethyl acetate or pumping *in vacuo* over P₂O₅,¹⁶⁹ or by recrystallization from MeCN at –20 °C ([NO][BF₄]^{174,176}). They are very moisture-sensitive, decomposing in damp air to give NO₂, etc., and are normally stored in plastic containers; glass is attacked by the corrosive byproducts of decomposition. The bottled salts are best stored in a glovebox or glovebag though they can be kept in a desiccator with the bottle filled with nitrogen or argon after sample removal. We have obtained high product yields from routine syntheses by simply weighing [NO][BF₄] or [NO][PF₆] rapidly in air and adding the solid reagent to the substrate dissolved in a dry and deoxygenated solvent. However, the method outlined in section II.A.1.a.ii (for weighing silver salts) is preferable for stoichiometric reactions, and weighing the reagent in an inert atmosphere or glovebox is recommended when more rigorously dry conditions are required.

Nitrosonium salts are soluble, and stable, in dry MeCN, MeNO₂, or liquid SO₂ but react with diethyl ether, acetone, or THF. They are usually insoluble in CH₂Cl₂ (*e.g.*, [NO][BF₄] and [NO][PF₆]), but [NO][BF₄] does dissolve in the presence of 18-crown-6. They are insoluble in arenes, but the brown charge-transfer adduct [(NO)⁺(C₆Me₆)] is formed on addition of C₆Me₆ to a suspension of [NO][BF₄] in CH₂Cl₂.¹⁷⁶ Such adducts can be crystallized from CH₂Cl₂ or SO₂ and structurally characterized (*e.g.*, [(NO)⁺(C₆H₃-Me₃)] [SbCl₆]);^{174,177} they are weaker oxidants than the uncomplexed [NO]⁺ ion.¹⁷⁶

Nitrosonium salts also dissolve in methanol, forming an equilibrium mixture (eq 18). The use of an alcohol as a solvent, therefore, may lead to protonation rather than one-electron oxidation (though the observation of the formation of [Cr(CO)₂(PhC≡CPh)(η-C₆Me₆)]⁺ from [Cr(CO)₂(PhC≡CPh)(η-C₆Me₆)] and [NO]⁺ in a mixture of MeOH and toluene¹⁷⁸ was the key to the entry of one of us into the field of “organometallic electrochemistry”!).



The nitrosonium ion is a strong oxidant (*e.g.*, it oxidizes [N(C₆H₄-Br-4)₃] (*E*^o = 0.70 V) to [N(C₆H₄-Br-4)₃]⁺, section II.B.1.a)}. Reactions with both inorganic and organic substrates, giving good yields of one-electron oxidation products, have been carried

out in SO_2 ($[\text{MoCl}_2\text{Cp}_2]^{129}$) or, more commonly, in MeCN {octamethylbiphenylene,¹⁷⁴ $[\text{Re}_2\text{Cl}_5(\text{PMePh}_2)_3]^{179}$ *cis*- and *trans*- $[\text{Ta}_6\text{Cl}_{14}(\text{PET}_3)_4]$ (to both the mono- and dications),¹⁸⁰ dithioethers,¹⁷⁵ and aromatic heterocycles such as phenothiazine and phenoxazines¹⁸¹}. Oxidations have also been carried out by addition of a solid salt to a solution of the second reactant, in acetone (a good yield of $[\text{Cr}(\text{NO})(\text{CNBu}^t)_4(\text{PBU}^n)_3]^+$ was obtained¹⁸² despite the reactivity of $[\text{NO}]^+$ toward this solvent^{169,171}), in a mixture of CH_2Cl_2 and MeCN,¹⁸³ and, most usually, in CH_2Cl_2 {e.g., $[\text{Mn}(\text{CO})(\text{CNBu}^t)(\text{dppm})_2]^+$,¹⁸⁴ $[\text{Ru}(\text{CO})_2(\text{PPh}_3)\{\text{P}(\text{O}^i\text{Pr})_3\}(\text{o-C}_6\text{Cl}_4)]^{185}$ $[\text{Fe}(\eta\text{-C}_5\text{Ph}_5)_2]^{186}$ a thiophene-based polymer,¹⁸⁷ $[\text{Ru}(\text{Mes})_4]^+$,¹⁸⁸ and $[\text{Re}_2(\mu\text{-Cl})_2\text{Cl}_4(\text{dppm})_2]^{189}$ }.
 The formation and ready removal of a gaseous byproduct (*i.e.*, NO) in the reaction of $[\text{NO}]^+$ with an oxidizable substrate provides an advantage over other strong oxidants. However, where there is the possibility of competition between oxidation and an alternative pathway, successful product isolation may depend on the efficiency with which NO is removed from the reaction mixture, in the synthesis of radical cations from aromatic heterocycles,¹⁸¹ for example (and see below). Moreover, in the presence of air, the formation of NO_2 , $[\text{NO}_3]^-$, etc., may result in the isolation of other products. For example, in the absence of air $[\text{NO}][\text{PF}_6]$ and $[\text{Re}_2(\mu\text{-S})(\mu\text{-Cl})\text{Cl}_3(\text{CS})(\text{dppm})_2]$ give the monocation $[\text{Re}_2(\mu\text{-S})(\mu\text{-Cl})\text{Cl}_3(\text{CS})(\text{dppm})_2]^+$,¹⁹⁰ but in the presence of air NO_2 is formed and $[\text{Re}_2(\mu\text{-SO}_2)(\mu\text{-Cl})\text{Cl}_3(\text{CS})(\text{dppm})_2]$ results (even with catalytic amounts of $[\text{NO}]^+$ ¹⁹¹).

The nitrosonium ion is far from an innocent oxidant and will often react *via* other pathways, even with easily oxidized substrates.¹⁷⁰ In transition metal chemistry the most common alternative reaction product is a nitrosyl complex. For example, *fac*- or *mer*- $[\text{MnBr}(\text{CO})_3(\text{PMe}_3)_2]$ is oxidized by $[\text{NO}]^+$ to *fac*- $[\text{MnBr}(\text{CO})_3(\text{PMe}_3)_2]^+$ whereas the more electron-rich complex $[\text{MnBr}(\text{CO})\{\text{P}(\text{OMe})_3\}_4]$ yields $[\text{Mn}(\text{CO})(\text{NO})\{\text{P}(\text{OMe})_3\}_4]^{2+}$,¹⁹² $[\text{Fe}(\text{CO})_3(\text{PPh}_3)_2]$ ($E^\circ = -0.06$ V) (easily oxidizable by $[\text{NO}]^+$) undergoes only substitution to $[\text{Fe}(\text{CO})_2(\text{NO})(\text{PPh}_3)_2]^+$.¹⁴³ Studies of the reaction between $[\text{Cr}(\text{CO})_4(\text{L-L})]$ (L-L = dppm or dppe) and $[\text{NO}]^+$ showed¹⁹³ that either oxidation to $[\text{Cr}(\text{CO})_4(\text{L-L})]^+$ or substitution to $[\text{Cr}(\text{CO})_3(\text{NO})(\text{L-L})]^+$ could occur, depending on the efficiency with which NO gas was purged from the reaction mixture. These, and earlier,¹⁹⁴ observations led us to postulate a general mechanism for the reaction of transition metal complex $[\text{ML}_x]$ with $[\text{NO}]^+$ (Scheme 1). The equilibrium involving $[\text{M}(\text{NO})\text{L}_x]^+$, effectively an inner-sphere intermediate, tends toward the formation of $[\text{ML}_x]^+$ if NO is efficiently removed from the reaction medium; nitrosyl complex formation is favored by conditions under which the concentration

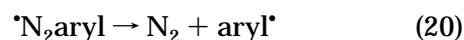
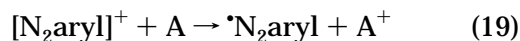
of NO is maximized. (Indeed, the reaction of an oxidized complex, formally a radical, with NO gas provides another route to nitrosyl complexes; $[\text{Cr}(\text{CO})_4(\text{dppe})]^+$ and NO give $[\text{Cr}(\text{CO})_3(\text{NO})(\text{dppe})]^+$.) Thus, whether oxidation or nitrosyl complex formation occurs does not depend simply on the relative redox potentials of $[\text{ML}_x]$ and $[\text{NO}]^+$ but, in addition, on other factors such as the steric and electronic requirements of the metal and ligands in $[\text{M}(\text{NO})\text{L}_x]^+$ and $[\text{ML}_x]$. (Similar comments apply to the oxidation or nitrosation of electron-rich aromatics such as thianthrene.¹⁸¹)
 The nitrosonium ion is also believed to function as an inner-sphere oxidant in organic chemistry,^{168,195} but where one electron-transfer products are observed, intermediates equivalent to $[\text{M}(\text{NO})\text{L}_x]^+$ are less easily verified. However, the recent observation of the formation of R_2NNO (and probably $[\text{R}_2\text{N}=\text{S}]^+$) in the reaction between R_2NSNR_2 ($\text{R}_2\text{N} =$ piperidine or 9-azabicyclo[3.3.1]nonane) and $[\text{NO}][\text{PF}_6]$, but of $[\text{R}_2\text{NSNR}_2]^+$ with $[\text{N}(\text{C}_6\text{H}_4\text{Br-}p)_3]^+$, is good evidence for an inner-sphere process with $[\text{NO}]^+$.¹⁹⁶
 The solvent can also have a marked effect on the outcome of a reaction involving the nitrosonium ion. The formal potential of $[\text{NO}]^+$ is highly solvent dependent, spanning a range of almost 0.5 V (Table 5). Moreover, in acetonitrile halide substitution, as in the formation of $[\text{V}(\text{NCMe})_2\text{Cp}_2]^{2+}$ from $[\text{VCl}_2\text{Cp}_2]$, or solvent addition, as in the formation of $[\text{Mn}(\text{NCMe})(\text{CO})_5]^+$ from $[\text{Mn}_2(\text{CO})_{10}]$,¹⁷⁰ can occur. The dependence of reaction pathway on solvent is, however, much more marked in alcohols. As mentioned above, oxidation can occur in MeOH-toluene mixtures. However, the equilibrium shown in eq 18 is more likely to lead to protonation, as in the formation of $[\text{IrH}(\text{CO})(\text{PPh}_3)\text{Cp}]^+$ from $[\text{Ir}(\text{CO})(\text{PPh}_3)\text{Cp}]$.¹⁷⁰ More irritating, however, is the observation of protonation in apparently dry solvents (due to the formation of H^+ from $[\text{NO}]^+$ and water). The one-electron oxidation of $[\text{Mn}(\text{CN})(\text{CO})_2\{\text{P}(\text{O}^i\text{Pr})_3\}_2(\text{dppm})]$ can be accomplished using $[\text{N}(\text{C}_6\text{H}_4\text{Br-}p)_3]^+$, but $[\text{NO}]^+$ gives *trans*- $[\text{Mn}(\text{CNH})(\text{CO})_2\{\text{P}(\text{O}^i\text{Pr})_3\}_2(\text{dppm})]^{2+}$,¹⁹⁷ underlining the importance of using dry conditions.
c. Arenediazonium Ions, $[\text{N}_2\text{aryl}]^+$. Arenediazonium ions, $[\text{N}_2\text{aryl}]^+$, play an important role in organic synthesis,¹⁹⁸ particularly in metal-catalyzed processes.¹⁹⁹ Many such processes appear to involve initial oxidation, as in eqs 19 and 20, though the mechanism of electron-transfer remains controversial. Inner-sphere processes seem more likely, but kinetic studies suggest outer-sphere oxidation of $[\text{FeCp}^*]_2$ and $[\text{Fe}(\text{CN})_6]^{4-}$.²⁰⁰

of NO is maximized. (Indeed, the reaction of an oxidized complex, formally a radical, with NO gas provides another route to nitrosyl complexes; $[\text{Cr}(\text{CO})_4(\text{dppe})]^+$ and NO give $[\text{Cr}(\text{CO})_3(\text{NO})(\text{dppe})]^+$.) Thus, whether oxidation or nitrosyl complex formation occurs does not depend simply on the relative redox potentials of $[\text{ML}_x]$ and $[\text{NO}]^+$ but, in addition, on other factors such as the steric and electronic requirements of the metal and ligands in $[\text{M}(\text{NO})\text{L}_x]^+$ and $[\text{ML}_x]$. (Similar comments apply to the oxidation or nitrosation of electron-rich aromatics such as thianthrene.¹⁸¹)

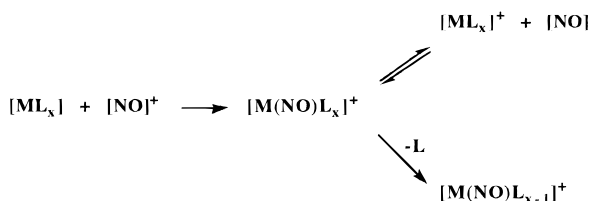
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c. Arenediazonium Ions, $[\text{N}_2\text{aryl}]^+$. Arenediazonium ions, $[\text{N}_2\text{aryl}]^+$, play an important role in organic synthesis,¹⁹⁸ particularly in metal-catalyzed processes.¹⁹⁹ Many such processes appear to involve initial oxidation, as in eqs 19 and 20, though the mechanism of electron-transfer remains controversial. Inner-sphere processes seem more likely, but kinetic studies suggest outer-sphere oxidation of $[\text{FeCp}^*]_2$ and $[\text{Fe}(\text{CN})_6]^{4-}$.²⁰⁰



Scheme 1



Surprisingly little interest has been shown in diazonium salts as stoichiometric one-electron oxidants in organometallic chemistry though they offer many advantages when a mild reagent is required. Moreover, the redox potential can be altered systematically from *ca.* 0.05 to -0.50 V by varying the ring substituents (Table 6).

Table 6. Formal Potentials (V vs Fc) of Arenediazonium Ions [N₂C₆H₄R-4]⁺ ^a

| R | E°/V | R | E°/V | R | E°/V |
|-----------------|------|---|-------|------------------|-------|
| NO ₂ | 0.05 | F | -0.07 | Me | -0.15 |
| Cl | 0.01 | H | -0.10 | NMe ₂ | -0.50 |

^a Potentials from ref 200 and Elofson, R. M.; Gadallah, F. *J. Org. Chem.* **1969**, *34*, 854.

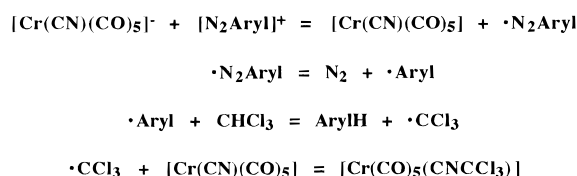
Arenediazonium ions with a wide range of para substituents are simply prepared and readily isolated as stable [BF₄]⁻ and [PF₆]⁻ salts; [N₂C₆H₄NEt₂-4]-[BF₄]⁻ is currently commercially available. The most widely cited preparative methods²⁰¹ involve the synthesis of [BF₄]⁻ salts in an aqueous reaction medium; alternative methods are also available^{198,202} using, for example, BF₃·OEt₂, RNH₂, and ^tBuONO in diethyl ether or CH₂Cl₂.²⁰² In our studies of the oxidation of low-valent transition metal complexes, we have usually used [N₂C₆H₄F-4]X (X = [BF₄]⁻ or [PF₆]⁻). A simple synthesis of the latter, based on the method of Roe,²⁰¹ is given in the Appendix. Note that freshly purchased HPF₆ should be used in this synthesis; older samples of HPF₆ are often severely contaminated with decomposition products. No such problems have been encountered when using HBF₄ to prepare [N₂aryl][BF₄] by the same method.

The simple arenediazonium salts [N₂C₆H₄R-4]X (R = H, Me, F, OMe, or NO₂; X = BF₄ or PF₆) are white or off-white crystalline solids, stable for months if pure, dry, and stored at -10 °C; deliberate thermolysis of [N₂C₆H₄R-4][BF₄]⁻ yields the fluoroarene FC₆H₄R-4. Samples may become colored with age but are easily repurified by dissolution in acetone, filtration, and precipitation with diethyl ether.

Solid salts such as [N₂aryl][BF₄]⁻ and [N₂aryl][PF₆]⁻ may be handled in air. They are soluble in polar solvents such as acetone and acetonitrile but insoluble in CH₂Cl₂. When used with solvents such as THF and CHCl₃, unexpected products resulting from hydrogen atom abstraction reactions may be encountered (see below).

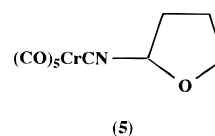
Diazonium ions have been successfully used in the synthesis of a range of 17-electron complexes from their 18-electron analogues, usually by adding the solid salt to the substrate dissolved in CH₂Cl₂^{70,203-207} but also in THF.²⁰⁸ Electron transfer from substrate to [N₂aryl]⁺ is usually rapid at or below room temperature, and the diamagnetic byproducts, nitrogen and the biaryl (formed by dimerization of aryl radicals), are simply removed. Even though the diazonium ion is a mild oxidant, the reduction of [N₂C₆H₄R-4]⁺ is irreversible, and substrates with potentials more positive than that of the oxidant may be oxidized. This can provide an advantage over other mild oxidants, for example, where an equilibrium mixture is formed when the ferrocenium ion reacts with a substrate which is reversibly oxidized at ca. 0.0 V.

The use of arenediazonium salts can also be successful in giving the desired one-electron oxidation product when other oxidants react *via* unexpected pathways. For example, [Rh(CO)(PPh₃)Cp] is oxidatively dimerized to the fulvalene complex [Rh₂(CO)₂(PPh₃)₂(η,η'-C₁₀H₈)] [PF₆]₂ by [N₂C₆H₄F-4] [PF₆]⁻ whereas

Scheme 2

Ag[PF₆] and [NO][PF₆] give [Ag{Rh(CO)(PPh₃)Cp}₂]-[PF₆]⁻ and [Rh(NO)(PPh₃)Cp][PF₆]⁻, respectively.⁷⁰

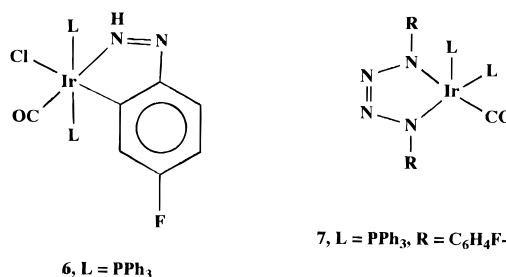
Diazonium salts are often noninnocent one-electron oxidants in organometallic chemistry. For example, one-electron oxidation may be followed by radical coupling; aryl radicals formed by the dissociation of [•]N₂aryl may abstract a hydrogen atom from the solvent and the resulting solvent-based radical couples with the oxidized form of the substrate. Thus, [Cr(CN)(CO)₅]⁻ and [N₂aryl]⁺ react according to Scheme 2 to give functionalized isocyanide complexes such as [Cr(CO)₅(CNR)] [*e.g.*, R = CCl₃ (from CHCl₃)²⁰⁹ or complex **5** (from THF)].²¹⁰ Similar reactions



between [N₂aryl]⁺ and [Mo(CO)₃Tp]⁻ give the chlorocarbene complex [Mo(CCl)(CO)₂Tp'] in CH₂Cl₂²¹¹ or [Mo(η²-COaryl)(CO)₂Tp']^{211,212} when the solvent does not undergo H-atom abstraction.

It is noteworthy that with less hindered polypyrazolylborate ligands [*e.g.*, L = Tp or B(pz)₄] [Mo(CO)₃L]⁻ and [N₂aryl]⁺ give [Mo(CO)₂(N₂aryl)L].²¹³ Many other transition metal complexes likewise give arenediazo complexes²¹⁴ in which the N₂aryl group can act as either a one-electron donor ("doubly bent", isoelectronic with a "bent" nitrosyl ligand) or a three-electron donor ("singly bent", isoelectronic with a "linear" nitrosyl ligand). The factors which govern oxidation as opposed to complexation were discussed during our early studies of [NO]⁺ and [N₂aryl]⁺ as oxidants¹⁹⁴ and are outlined in section II.A.2.b for [NO]⁺.

Arenediazonium ions may also undergo insertion reactions, for example, into M-H bonds ([PtHCl(PEt₃)₃] yields [PtCl(PEt₃)₂(NH:Naryl)]⁺)²¹⁵ or into one M-P bond of [Fe(NO)₂(dppe)] to give [Fe(NO)₂-{PPh₂CH₂CH₂P(Ph)₂N₂C₆H₄F-4}]⁺,²¹⁶ and *ortho*-metalation or dimerization, as in the formation of **6** and **7** from [IrCl(CO)(PPh₃)₂] and [N₂C₆H₄F-4]⁺ in the presence of ethanol or 2-propanol.²¹⁴ Finally, arylation of, or azo coupling with, coordinated hydrocarbons such as chpt and cot may also be observed.^{217,218}



d. Oxygen. Precautions are almost invariably taken to avoid the presence of oxygen during the synthesis of organotransition metal complexes; conventional wisdom has led to the assumption that decomposition to unwanted products is to be expected. Nevertheless, there are good examples where O_2 is used to give well-defined one-electron oxidation products (or secondary products derived therefrom). It should also be noted, given the role of 17-electron species in electron-transfer-catalyzed processes, that adventitious oxygen may play a part in the generation of radical-like intermediates and the acceleration of reactions assumed to proceed solely through diamagnetic intermediates.

Oxygen is, of course, readily available and easily handled. It reacts with $[Cr(\eta\text{-arene})_2]$ to give $[Cr(\eta\text{-arene})_2][OH]^{145}$ and with related binuclear complexes such as $[Cr_2(\mu\text{-biphenyl})(\eta\text{-C}_6\text{H}_6)_2]$ and $[Cr_2(\mu\text{-biphenyl})_2]$ to give the corresponding dications²¹⁹ (*cf.* the use of 4-pyridinecarboxaldehyde, section II.B.5.a). Stoichiometric reactions have been carried out between $[Fe(\eta\text{-C}_6\text{Me}_6)_2]$ and O_2 , the latter added to the former by means of a gas syringe. This reaction is of particular interest in showing the effects of both temperature and ion pairing on the final outcome of an electron-transfer reaction. At -40°C in toluene, 0.5 equiv of O_2 give $[Fe\{\eta^4\text{-C}_6\text{Me}_4(=\text{CH}_2)_2\}(\eta\text{-C}_6\text{Me}_6)]$; oxidation of $[Fe(\eta\text{-C}_6\text{Me}_6)_2]$ is followed by sequential deprotonation of two of the methyl groups by $[O_2]^-$ within the solvent cage. At 20°C in toluene, or at -40°C in THF in the presence of NaPF_6 , the peroxide salt $[Fe(\eta\text{-C}_6\text{Me}_6)_2][O_2]$ results (the higher temperature or presence of the sodium salt leading to the removal of the superoxide anion from the solvent cage before deprotonation can occur²²⁰).

The dioxygenyl salt $[O_2][EF_6]$ ($E = \text{As}$ or Sb) is arguably the strongest one-electron oxidant yet isolated, with an estimated formal oxidation potential for $[O_2]^+/O_2$ of almost 5.0 V.²²¹ It has been used in low-temperature Freon mixtures to oxidize organic compounds to the corresponding cation radicals. For example, $[O_2][\text{AsF}_6]$ and $\text{NMe}(\text{C}_6\text{H}_4\text{OMe-4})_2$ give $[\text{NMe}(\text{C}_6\text{H}_4\text{OMe-4})_2][\text{AsF}_6]$ in CHF_2Cl at -130°C . The redox byproduct, O_2 , and the solvent are allowed to evaporate, leaving behind the desired salt.²²²

Interestingly, the superoxide ion can act as both an oxidant and reductant. Though generally studied in aqueous media, and as such of limited interest for organometallic applications, it has been generated electrochemically in DMSO, pyridine, DMF, and MeCN. It can also be prepared (with difficulty) as the salt $[\text{NMe}_4][O_2]$, which is soluble in aprotic solvents, and is solubilized, as KO_2 , by crown ethers.²²³

e. Acids. There are several examples of acids such as HBF_4 or HPF_6 effecting the one-electron oxidation of electron-rich organometallics. (The corollary is that adventitious acid, perhaps from impure solvents, can initiate unwanted or unexpected electron-transfer-based reactions, as noted above for oxygen.) Thus, $[\text{Mo}(\eta^5\text{-C}_7\text{H}_9)(\eta\text{-C}_7\text{H}_7)]$ ($E^\circ = -0.19\text{ V}$) and $\text{HBF}_4\cdot\text{OEt}_2$ in diethyl ether¹³⁵ and $[\text{Co}(\text{PET}_3)_2(\eta^5\text{-2,4-dimethylpentadienyl})]$ and $\text{HBF}_4\cdot\text{OEt}_2$ or HO_3SCF_3 in THF,²²⁴ gave $[\text{Mo}(\eta^5\text{-C}_7\text{H}_9)(\eta\text{-C}_7\text{H}_7)][\text{BF}_4]$ and $[\text{Co}(\text{PET}_3)_2(\eta^5\text{-2,4-dimethylpentadienyl})]\text{X}$ ($\text{X} = [\text{BF}_4]^-$ or $[\text{O}_3\text{SCF}_3]^-$), respectively. The last reaction contrasts

with that between HBF_4 and the "closed" cyclopentadienyl complex $[\text{Co}(\text{PET}_3)_2\text{Cp}]$ which undergoes protonation at the metal center²²⁵ (a reaction perhaps more generally expected than one-electron oxidation). It is also noteworthy that the ammonium ion may act as an oxidant, although presumably functioning as a proton source. Thus $[\text{Cr}(\eta^5\text{-heptamethylindenyl})_2]$ in toluene reacts with a saturated solution of $[\text{NH}_4][\text{PF}_6]$ in THF to precipitate $[\text{Cr}(\eta^5\text{-heptamethylindenyl})_2][\text{PF}_6]$.²²⁶ Oxyacids may also function as one-electron oxidants. Thus, HNO_3 or H_2O_2 and $[\text{MXYCp}_2]$ ($\text{M} = \text{Mo}$ or W ; $\text{X}, \text{Y} = \text{Cl}, \text{N}_3, \text{NCS}, \text{O}_2\text{-CCF}_3$, etc.) give $[\text{MXYCp}_2]^+$, which may be precipitated as the $[\text{PF}_6]^-$ salt by addition of $[\text{NH}_4][\text{PF}_6]$ to the aqueous solution.²²⁷ Such acids are likely to be much stronger oxidants than HBF_4 or HPF_6 .

B. Organic

1. Radical Cations

a. Triarylamminium Radical Cations, $[\text{N}(\text{aryl})_3]^+$. Triarylamminium radical cations, $[\text{N}(\text{aryl})_3]^+$, with the para positions substituted to deter nucleophilic substitution, are mild to very strong one-electron oxidants used widely in organic chemistry and, to a far lesser extent, in inorganic chemistry. The archetypal arylamminium salt, $[\text{N}(\text{C}_6\text{H}_4\text{Br-4})_3][\text{SbCl}_6]$ (the cation is colloquially known as Magic Blue because of its intense royal blue color), is commercially available, but many other derivatives, with redox potentials spanning the range 0.16–1.72 V (Table 7), can be prepared or generated *in situ* from the corresponding amine. Many of the cations are remarkably stable and can be used not only as stoichiometric reagents but as catalysts in electron-transfer chain processes; the neutral amines are used as mediators in indirect electrosynthesis.^{228,229}

Table 7. Formal Potentials (V vs Fc) of Triarylamminium Cations $[\text{N}(\text{aryl})_3]^+$ ^a

| aryl | E°/V | aryl | E°/V |
|--|-------------|--|-------------------|
| $\text{C}_6\text{H}_4\text{OMe-4}$ | 0.16 | $\text{C}_6\text{H}_4\text{NO}_2\text{-4}$ | 1.20 |
| $\text{C}_6\text{H}_4\text{Me-4}$ | 0.40 | $\text{C}_6\text{H}_4\text{Br}_2\text{-2,4}$ | 1.14 |
| $\text{C}_6\text{H}_4(\text{COMe})\text{-4}$ | 0.90 | $\text{C}_6\text{H}_4\text{Br}_3\text{-2,4,6}$ | 1.36 |
| $\text{C}_6\text{H}_4\text{Br-4}$ | 0.70 | C_6Cl_5 | 1.72 ^b |
| $\text{C}_6\text{H}_4\text{CN-4}$ | 1.08 | | |

^a Potentials from ref 228 unless stated. ^b From ref 237.

Arylamminium salts are prepared from triaryl amines, many of which have been synthesized specifically as radical cation precursors.^{230–233} There are three main preparative procedures, using (i) a silver(I) salt in the presence of iodine,^{233–235} (ii) an $[\text{NO}]^+$ salt,^{181,233,235} or (iii) a higher valent halide, usually SbCl_5 , as the oxidant;^{230,231,233,236,237} the method chosen depends *inter alia* on the oxidation potential of the amine and the counteranion desired. Method i involves the addition of iodine in diethyl ether to a solution of the amine and AgX in the same solvent, extraction of the resulting precipitate into CH_2Cl_2 (to remove silver metal), and precipitation of the salt $[\text{N}(\text{aryl})_3]\text{X}$ with diethyl ether. The $[\text{BF}_4]^-$ and $[\text{PF}_6]^-$ salts of $[\text{N}(\text{C}_6\text{H}_4\text{R-4})_3]^+$ ($\text{R} = \text{Br}$ or OMe) have been prepared in this way though higher yields of the $[\text{PF}_6]^-$ salts are isolable from $[\text{NO}][\text{PF}_6]$ oxidation of the appropri-

ate amine in MeCN.^{233,235} Salts of the $[\text{SbCl}_6]^-$ anion result from the treatment of the amine with SbCl_5 in CH_2Cl_2 ,^{230,236} where SbCl_5 is not strong enough to accomplish amine oxidation, SbF_5 may be used.²³⁷

The stability of solid arylaminium cations depends *inter alia* on the counteranion. Thus, salts of $[\text{N}(\text{C}_6\text{H}_4\text{-Br-4})_3]^+$ with larger anions such as $[\text{PF}_6]^-$, $[\text{SbCl}_6]^-$, and $[\text{WCl}_6]^-$ (prepared by WCl_6 oxidation of the amine) show little sign of deterioration after several weeks whereas the $[\text{BF}_4]^-$ salt ages more rapidly.^{233,235} The difference in stability has been ascribed to the repression of benzidine radical cation formation *via* debromodimerization;²³³ the larger anions prevent the required approach of two cations. The aging of $[\text{N}(\text{C}_6\text{H}_4\text{-Br-4})_3]^+$ also results in further bromination of the aryl groups (Br_2 is eliminated during the dimerization process); mass spectrometry showed that 6-month-old samples of the $[\text{BF}_4]^-$ salt contained tetra- and pentabrominated amines as well as the dimeric product.²³³ Similar variations in stability have been noted for the salts of $[\text{N}(\text{C}_6\text{H}_4\text{-Me-4})_3]^+$.^{234,235} By contrast, $[\text{N}(\text{C}_6\text{H}_4\text{OMe-4})_3]^+$ (a less powerful oxidant, $E^\circ = 0.16$ V) is also stable as the $[\text{BF}_4]^-$ salt.

The results of kinetic studies and product analysis are critically dependent on the use of pure samples of the arylaminium salts.²³³ The extent to which a sample decays may be estimated by optical spectroscopy,^{233,235} (e.g., $[\text{N}(\text{C}_6\text{H}_4\text{-Br-4})_3]^+$, $\lambda_{\text{max}} = 700$ nm; $[\text{N}(\text{C}_6\text{H}_3\text{Br}_2\text{-2,4})_3]^+$, $\lambda_{\text{max}} = 880$ nm);^{230,231} the deterioration of solid $[\text{N}(\text{C}_6\text{H}_4\text{Me-4})_3][\text{PF}_6]$ during 1 week at room temperature is sufficient to be detectable by changes in the UV spectrum.²³⁵ Voltammetry can also be used to assess the purity of aged samples of $[\text{N}(\text{C}_6\text{H}_4\text{-Br-4})_3]^+$ since decomposition products having other degrees of bromine substitution have different E° values. (Such aged samples have, nevertheless, been successfully used as oxidants; the oxidant mixture has been dubbed "The Blues Brothers".)

The solubility of triarylamminium salts depends on both the aryl substituent and the counteranion. For example, $[\text{N}(\text{C}_6\text{H}_4\text{-Br-4})_3][\text{SbCl}_6]$ is slightly less soluble in CH_2Cl_2 than is the perchlorate salt (which is *not* recommended for use).²³⁶ The stability of such solutions depends on the solvent and, as noted above, on the substitution pattern on the aryl groups and on the counteranion. For example, in CH_2Cl_2 , $[\text{N}(\text{C}_6\text{H}_4\text{-Br-4})_3][\text{ClO}_4]$ is stable for 2 days in the absence of O_2 and light but $[\text{N}(\text{C}_6\text{H}_4\text{-Br-4})_3][\text{PF}_6]$ is indefinitely stable in the absence of light and is even stable for several days in laboratory light. In methanol, $[\text{N}(\text{C}_6\text{H}_4\text{-Br-4})_3]^+$ is methoxylated at one ring²²⁸ whereas $[\text{N}(\text{C}_6\text{H}_3\text{Br}_2\text{-2,4})_3]^+$ is stable and undergoes several thousand turnovers during the mediated side-chain oxidation of alkyl-substituted aromatics.²³⁸

Stoichiometric reactions using arylaminium salts are simply accomplished, either by using the isolated salt or by generating the cation *in situ*. Moreover, the byproduct of electron transfer, $\text{N}(\text{aryl})_3$, is easily removed from the oxidation product. If necessary, the electron-transfer reactions of arylaminium cations can be visually "titrated" in that their intense colors (e.g., $[\text{N}(\text{C}_6\text{H}_4\text{-Br-4})_3]^+$, blue; $[\text{N}(\text{C}_6\text{H}_3\text{Br}_2\text{-2,4})_3]^+$, green) are lost immediately on reduction (optical spectroscopy could be used as a more quantitative

method). In contrast to $[\text{NO}]^+$ and Ag^+ analogues (also strong to very strong oxidants in CH_2Cl_2), arylaminium salts are soluble in CH_2Cl_2 .

Unlike $[\text{NO}]^+$ (section II.A.2.b) and Ag^+ (section II.A.1.a.ii), $[\text{N}(\text{C}_6\text{H}_4\text{-Br-4})_3][\text{PF}_6]$ almost always behaves as an innocent one-electron oxidant (but see below). Thus, *cis*- or *trans*- $[\text{Mn}(\text{CN})(\text{CO})_2\{\text{P}(\text{O}(\text{Ph})_3\}_2\text{-dppm})]$ gives *trans*- $[\text{Mn}(\text{CN})(\text{CO})_2\{\text{P}(\text{O}(\text{Ph})_3\}_2\text{-dppm})][\text{PF}_6]$ in CH_2Cl_2 whereas $[\text{NO}][\text{PF}_6]$ yields the protonated complex $[\text{Mn}(\text{CNH})(\text{CO})(\text{CO})_2\{\text{P}(\text{OR})_3\}_2\text{-dppm}][\text{PF}_6]^{197}$ and $\text{Ag}[\text{PF}_6]$ yields $[\text{Ag}\{(\text{NC})\text{Mn}(\text{CO})_2\{\text{P}(\text{OEt})_3\}_2\text{-dppm}\}_2][\text{PF}_6]^{52}$. Similarly, $[\text{N}(\text{C}_6\text{H}_4\text{-Br-4})_3][\text{PF}_6]$ and $[\text{Fe}(\text{CO})_3(\text{PPh}_3)_2]$ yield $[\text{Fe}(\text{CO})_3(\text{PPh}_3)_2][\text{PF}_6]$ whereas Ag^+ appears to form an Ag-Fe -bonded adduct and $[\text{NO}]^+$ or arenediazonium ions yield substitution products such as $[\text{Fe}(\text{CO})_2(\text{NO})(\text{PPh}_3)_2]^+$.¹⁴³ Note, however, that the $[\text{SbCl}_6]^-$ counteranion is not innocent (see section II.A.2.a.iv) and can act as a source of nucleophilic chloride ions (as has also been observed in organic chemistry²³⁹). For example, $[\text{N}(\text{C}_6\text{H}_4\text{-Br-4})_3][\text{SbCl}_6]$ oxidatively cleaves $[\text{Fe}_2(\mu\text{-CO})_2(\text{CO})_2\text{Cp}_2]$ to yield $[\text{FeCl}(\text{CO})_2\text{Cp}]^{240}$ and reacts with $[\text{Mn}(\text{CO})(\text{dppe})\text{Cp}']$ to give $[\text{MnCl}(\text{CO})(\text{dppe})\text{Cp}']^+$ *via* $[\text{Mn}(\text{CO})(\text{dppe})\text{Cp}']^+$.²⁰⁵

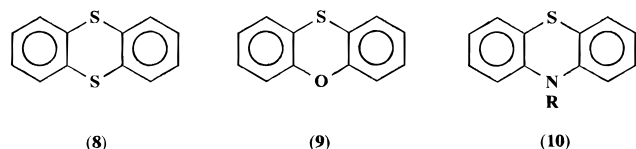
High product yields can be obtained without the need to use the isolated arylaminium cation salts; solutions of $[\text{N}(\text{C}_6\text{H}_4\text{-Br-4})_3]^+$ may be generated *in situ* by treatment of $[\text{N}(\text{C}_6\text{H}_4\text{-Br-4})_3]$ with either $[\text{NO}]^+$ or Ag^+ in CH_2Cl_2 and removal of the byproducts, NO and Ag , by purging the reaction mixture with a stream of nitrogen (or argon) or by filtration, respectively. In this way, $[\text{Fe}(\text{CO})_3(\eta^4\text{-cot})]$ was oxidatively dimerized to $[\text{Fe}_2(\text{CO})_6(\eta^5, \eta^5\text{-C}_{16}\text{H}_{16})][\text{PF}_6]^{2,241}$ and $[\text{Rh}_3(\mu_3\text{-L})_2(\text{CO})_4(\text{PPh}_3)_2]^+$ ($\text{L} = 1,8\text{-naphthyridin-2-onate}$) was oxidized to the mixed-valence complex $[\text{Rh}_3(\mu_3\text{-L})_2(\text{CO})_4(\text{PPh}_3)_2]^{2+,242}$

The applications in organic chemistry of arylaminium cations as catalysts²⁴³⁻²⁴⁸ or as intermediates in indirect electrosynthesis (the amine is added as the mediator)^{228,229} have been extensively reviewed. The solid arylaminium salt is usually used in catalytic applications; efficient catalysis is made possible by the stability of both the amine and its radical cation. However, *in situ* generation of the arylaminium cations is also possible; $[\text{N}(\text{C}_6\text{Cl}_5)_3]^+$ ($E^\circ = 1.84$ V) cannot be isolated but has been generated by SbF_5 oxidation of the amine and used to oxidize *syn*-5,5'-difluorobiadamantylidene ($E^\circ = 1.39$ V) (which is not oxidized by $[\text{N}(\text{C}_6\text{H}_4\text{-Br-4})_3]^+$ or $[\text{N}(\text{C}_6\text{H}_3\text{Br}_2\text{-2,4})_3]^+$).²³⁷ In indirect electroorganic synthesis, the amine is used as a mediator with the cation generated and regenerated by electrolysis; turnovers as high as 2500 cycles have been observed with $[\text{N}(\text{C}_6\text{H}_3\text{Br}_2\text{-2,4})_3]^+$.²²⁹ Far more use has been made in organic chemistry of the possibility of tuning the redox potential of the oxidant; the amine substituent (Table 7) can be systematically altered to achieve selective oxidation. In addition, electron transfer may occur even with an unfavorable potential, subsequent irreversible bond cleavage reactions providing the driving force for the overall reaction.

Finally, arylaminium cations are not always innocent. For example, $[\text{N}(\text{C}_6\text{H}_4\text{-Br-4})_3]^+$ undergoes nucleophilic reactions with chloride and cyanide ions but electron transfer with bromide and iodide ions.

Moreover, substitution is easier with the $[\text{BF}_4]^-$ salt than with the $[\text{SbCl}_6]^-$ salt.²³⁵ Similarly, $[\text{N}(\text{C}_6\text{H}_4\text{-Br-4})_3][\text{BF}_4]$ does not oxidize carboxylates but undergoes acyloxylation at room temperature.²³³ Such side reactions, and the dependence of the reaction pathway on the counteranion, even in solution, can have important consequences for catalysis.²³⁹

b. Thianthrene and Related Radical Cations. Although triarylaminium salts (section II.B.1.a) are the most widely used radical cation oxidants, other such reagents are also available. Of these, the thianthrene cation ($\mathbf{8}^+$) is the most popular although related radical cations of aromatic heterocycles such as phenoxathiin ($\mathbf{9}$), phenothiazine ($\mathbf{10}$, $\text{R} = \text{H}$), *N*-methyl- or *N*-phenylthiazine ($\mathbf{10}$, $\text{R} = \text{Me}$ or Ph), and carbazoles have also been prepared.



The thianthrene radical cation has been isolated as $[\text{AlCl}_4]^-$,¹⁵⁶ $[\text{SbCl}_6]^-$,²⁴⁹ and $[\text{I}_2\text{Cl}_3]^-$ ^{250,251} salts but has most often been used as the perchlorate.^{249,250} The last is, however, explosive, and despite the detailed warnings given on its safe handling,^{249,252} we recommend that it is not used. Rather, the $[\text{BF}_4]^-$ salt, which may be prepared on a large scale from $[\text{NO}][\text{BF}_4]$ and thianthrene in CH_2Cl_2 ²⁵² is to be preferred. (The other salts listed above might also be used if the presence of a halogen-containing counteranion—a source of nucleophilic halide ions—is not a problem.) The purity of [thianthrene] $[\text{BF}_4]$ can be assessed by treatment with NaI in MeCN/CCl_4 and then titration of the released I_2 against sodium thiosulfate,²⁴⁹ or by optical spectroscopy ($\mathbf{8}^+$; in MeCN , $\lambda_{\text{max}} = 546 \text{ nm}$, $\epsilon = 8.5 \times 10^3$,²⁵⁰ in CH_2Cl_2 , $\lambda_{\text{max}} = 548 \text{ nm}$, $\epsilon = 8.9 \times 10^3$ ¹⁵⁶).

The radical cations of other aromatic heterocycles, including $\mathbf{9}$, $\mathbf{10}$, and carbazole, can also be simply prepared as $[\text{BF}_4]^-$ salts using $[\text{NO}][\text{BF}_4]$ ¹⁸¹ and phenoxathiin and SbCl_5 in CH_2Cl_2 give $[\mathbf{9}][\text{SbCl}_6]$.^{253,254} These cations have been used less often than that of thianthrene,²⁵⁵ but the variation in heteroatom and, in some cases, the substituent [*e.g.*, at N in $\mathbf{10}$] could, in principle, lead to the systematic alteration of oxidation potential.

The red to brown salts of the thianthrene cation (the solid $[\text{I}_2\text{Cl}_3]^-$ salt is black) are stable in dry air (the $[\text{AlCl}_4]^-$ salt has been structurally characterized¹⁵⁶) but react with water to give thianthrene and thianthrene *S*-oxide. The pure $[\text{BF}_4]^-$ salt is stable for weeks when dissolved in dry acetonitrile,²⁴⁹ but if generated *in situ*, from thianthrene and $[\text{NO}][\text{BF}_4]$ in CH_2Cl_2 , it deteriorates more rapidly, probably by reacting with NO or NO_2 .

Solutions of thianthrene radical cation salts are purple, giving colorless thianthrene on reduction. Their reactions can therefore be followed visually or, more quantitatively, by optical spectroscopy; the five-line ESR spectrum ($g = 2.0087$ in MeCN ²⁵⁰) of the cation provides another means by which its reactions might be monitored.

The thianthrene cation has been almost exclusively used in investigations of the one-electron-transfer reactions of main group organometallics such as LiPh in THF ,²⁵⁶ MgClPh in ether,²⁵⁶ and HgR_2 in MeCN .^{252,257} In all of these cases, the $[\text{ClO}_4]^-$ salt was used but the less treacherous $[\text{BF}_4]^-$ salt is equally effective, as demonstrated by its reactions with HgR_2 in CH_2Cl_2 .²⁵² As yet the use of aromatic heterocycle radical cations as oxidants in other areas of chemistry has been limited although $[\text{FeCl}(\text{TPP})]$ ²⁵⁴ and neutral actinide porphyrin and phthalocyanin complexes such as $[\text{M}(\text{TPP})(\text{PC})]$ ($\text{M} = \text{U}$ and Th)²⁵³ have been oxidized to the corresponding monocations by $[\mathbf{9}][\text{SbCl}_6]$.

2. Carbocations

a. Trityl, $[\text{CR}_3]^+$ ($\text{R} = \text{Aryl}$), Salts. The trityl cation, $[\text{CPh}_3]^+$, also referred to as the triphenylcarbenium or tritylium ion, has long been known as a reagent for the removal of hydride ion from both organic^{258,259} and organometallic compounds.²⁶⁰ However, it can also function as a one-electron oxidant.

Although the yellow-orange $[\text{BF}_4]^-$, $[\text{PF}_6]^-$, $[\text{AsF}_6]^-$, $[\text{SbCl}_6]^-$, and $[\text{CF}_3\text{SO}_3]^-$ (triflate, Tf) salts of $[\text{CPh}_3]^+$ are commercially available, they are readily made from CPh_3OH and the appropriate acid in acetic or propionic anhydride,²⁵⁸ by the dropwise addition of anhydrous HSbF_6 , $\text{HBF}_4 \cdot \text{Me}_2\text{O}$, or $\text{HPF}_6 \cdot \text{Et}_2\text{O}$ to CClPh_3 in benzene,²⁶¹ or from CClPh_3 and AgPF_6 in CH_2Cl_2 .²³⁴ The triflate salt has also been prepared from CPh_3Cl and Me_3SiTf and converted to $[\text{CPh}_3][\text{BPh}_4]$ (a useful salt in the preparation of cationic, Lewis acidic products which might react with more nucleophilic anions) by metathesis with NaBPh_4 in MeCN .²⁶² In principle, the oxidation potential of $[\text{CPh}_3]^+$ can be systematically altered by ring substitution; the salts $[\text{C}(\text{C}_6\text{H}_4\text{NMe}_2\text{-4})_2\text{Ph}][\text{BF}_4]$,²⁶³ $[\text{C}(\text{C}_6\text{H}_4\text{Me-4})_3][\text{PF}_6]$,²⁶⁴ and $[\text{CPh}_2(\text{C}_6\text{H}_4\text{OMe-4})][\text{BF}_4]$ ^{265,266} have been prepared from the appropriate carbinol $\text{C}(\text{aryl})_3\text{OH}$.²⁵⁸ Trityl salts are usually recrystallized from MeCN at low temperature. Purification may also be accomplished from CH_2Cl_2 -*n*-hexane or MeCN - Et_2O mixtures; large crystals of $[\text{CPh}_3][\text{BF}_4]$, especially suitable for long-term storage, can be grown by layering diethyl ether onto a solution of the salt in MeCN .

Solid salts of $[\text{CPh}_3]^+$ react with moisture, giving colorless CPh_3OH . In the absence of air the solids show no visible signs of decomposition after several months when stored at -10°C ; $[\text{CPh}_3][\text{BPh}_4]$, however, is light sensitive.²⁶² The salt $[\text{CPh}_2(\text{C}_6\text{H}_4\text{OMe-4})][\text{BF}_4]$, a somewhat weaker oxidant ($E^\circ = -0.32 \text{ V}$) than $[\text{CPh}_3][\text{BF}_4]$ ($E^\circ = -0.11 \text{ V}$), is much more stable and does not deteriorate when refrigerated, even in the presence of moist air for 1 year. It may, therefore, be weighed and transferred in air.²⁶⁶ Trityl salts are soluble in dry CH_2Cl_2 , MeCN , or liquid SO_2 but are insoluble in alkane or arene solvents; slow decomposition has been observed in diethyl ether.²⁵⁸ They react with protic solvents such as water and alcohols; in aqueous acetonitrile, $[\text{CPh}_2(\text{C}_6\text{H}_4\text{OMe-4})][\text{BF}_4]$ decomposes 100 times more slowly than $[\text{CPh}_3][\text{BF}_4]$.²⁶⁶

Triarylcarbenium ions are mild one-electron oxidants²⁶⁷ which give $\cdot\text{C}(\text{aryl})_3$ radicals on reduction.

These radicals can often be detected by ESR spectroscopy but form an equilibrium mixture favoring the diamagnetic dimer [e.g., 4-(triphenylmethyl)-1-(diphenylmethylidene)-2,5-cyclohexadiene from $\cdot\text{CPh}_3$]. However, the possible reaction of solvent-based radicals, formed by H-atom abstraction from the solvent by $\cdot\text{C}(\text{aryl})_3$ [giving $\text{CH}(\text{aryl})_3$], with the primary oxidation product should not be discounted [cf. the behavior of aryl radicals formed on reduction of diazonium ions (section II.A.2.c)].

The reactions of trityl cations are normally carried out at low temperature in CH_2Cl_2 or MeCN (though THF has also been used as solvent²⁶⁸). Simple one-electron oxidation products, e.g., $[\text{CpFe}(\mu\text{-cot})\text{CoCp}]^+$ ²⁶⁹ and $[\text{FeMe}\{\text{P}(\text{OMe})_3\}_2\text{Cp}^*]^+$ ²⁷⁰ from $[\text{CpFe}(\mu\text{-cot})\text{CoCp}]$ and $[\text{FeMe}\{\text{P}(\text{OMe})_3\}_2\text{Cp}^*]$, respectively, may result. More often than not, however, other reactions, either following or instead of electron transfer, are observed. Thus, $[\text{CPh}_3]^+$ and $[\text{Re}_2(\mu\text{-H})_4\text{H}_4(\text{PPh}_3)_2]$ give $[\text{Re}_2(\mu\text{-H})_4\text{H}_4(\text{PPh}_3)_2]^+$ in CH_2Cl_2 but $[\text{Re}_2(\mu\text{-H})_4\text{H}_3(\text{NCMe})(\text{PPh}_3)_2]^+$ is isolated from MeCN (in a reaction apparently *not* involving electron transfer).²⁷¹

Trityl cations can act as electrophiles, adding to coordinated hydrocarbons such as the cot ring of $[\text{Fe}(\text{CO})_3(\eta^4\text{-cot})]$,²⁷² or as ligands; the reactions with $[\text{Re}(\text{CO})_5]^-$ and $[\text{Co}\{\eta^5\text{-2,4-bis}(\text{trifluoromethyl})\text{penta-1,3-dienyl}\}\text{Cp}]$ give $[\text{Re}(\text{CO})_4(\eta^3\text{-C}_6\text{H}_5\text{CPh}_2)]$ and $[\text{CoCp}(\eta^5\text{-C}_6\text{H}_5\text{CPh}_2)]^+$,²⁷³ respectively. With $[\text{Fe}(\text{CO})_2(\text{CH}_2\text{SMe})\text{Cp}^*]$, addition at sulfur to give the sulfonium cation $[\text{Fe}(\text{CO})_2\{\text{CH}_2\text{S}(\text{Me})\text{CPh}_3\}\text{Cp}^*]^+$ is followed by decomposition *via* trityl radical loss. Different products result from the reaction with the outer-sphere oxidant, $[\text{FeCp}_2]^+$, suggesting the trityl cation to be an inner-sphere reagent,²⁷⁴ similar conclusions were drawn from comparative studies of the reactions of $[\text{FeCp}_2]^+$ and $[\text{CPh}_3]^+$ or $[\text{C}(\text{tolyl})_3]^+$ with $[\text{RuH}(\text{PPh}_3)_2\text{Cp}]$ ²⁶⁴ and $[\text{MoH}(\text{CO})_2(\text{PPh}_3)\text{Cp}]$,²⁶⁵ respectively.

Extensive studies of the reactions of organometallics with ferrocenium and trityl cations have shed considerable light on the competition between oxidation and hydride abstraction. The formal potential of the oxidant is but one factor which influences the outcome of the reactions of mononuclear transition metal alkyls. Thus, $[\text{WMe}_2\text{Cp}_2]$ ($E^\circ = \text{ca. } -0.8$ V) and $[\text{CPh}_3]^+$ ($E^\circ = -0.11$ V) give $[\text{WH}(\eta\text{-C}_2\text{H}_4)\text{Cp}_2]^+$ by initial electron transfer ($\Delta E = \text{ca. } 0.7$ V) followed by α -hydrogen atom abstraction by $\cdot\text{CPh}_3$.²⁷⁵ Similarly, $[\text{Re}(\sigma\text{-CH}_2\text{CH}_2\text{R})(\text{PPh}_3)(\text{NO})\text{Cp}]$ ($\text{R} = \text{alkyl}$) give²⁷⁶ species such as $[\text{Re}(\text{=CHCH}_2\text{R})(\text{PPh}_3)(\text{NO})(\eta\text{-C}_5\text{H}_5)]^+$ in spite of the endergonic electron-transfer step ($\Delta E = \text{ca. } -0.2$ V); the reaction is driven to completion by the irreversible C–H cleavage following oxidation. If electron transfer is too unfavorable, as in the reaction with $[\text{Fe}(\sigma\text{-alkyl})(\text{CO})_2\text{Cp}]$ ($\Delta E = \text{ca. } -1.0$ V), direct β -hydride abstraction gives $[\text{Fe}(\text{CO})_2(\eta^2\text{-alkene})\text{Cp}]^+$ ²⁷⁷ (although the electron-transfer mechanism can operate in the presence of carbon monoxide).²⁷⁸

Similar comparative studies with hydrocarbon-bridged binuclear organometallics show that the oxidative activation of C–H bonds by $[\text{CPh}_3]^+$ can differ from that by $[\text{FeCp}_2]^+$.^{43–45} For example, $[\text{Mo}_2(\mu\text{-C}_8\text{Me}_8)\text{Cp}_2]$ and $[\text{FeCp}_2]^+$ give $[\text{Mo}_2(\mu\text{-C}_8\text{Me}_7$

$\text{CH}_2)\text{Cp}_2]^+$ by double oxidation (to $[\text{Mo}_2(\mu\text{-C}_8\text{Me}_8)\text{Cp}_2]^{2+}$) followed by proton loss (an EEC mechanism) whereas $[\text{CPh}_3]^+$ gives the same final product but *via* the H-atom abstraction reaction between $[\text{Mo}_2(\mu\text{-C}_8\text{Me}_8)\text{Cp}_2]^+$ and $\cdot\text{CPh}_3$ (an EC process).⁴⁵

Finally, an electron-transfer reaction involving $[\text{CPh}_3]^+$ can lead to a different stereochemistry from a reaction involving direct H⁺ loss. Thus, *exo*-hydride abstraction occurs from a noncoordinated CH_2 group of the hydrocarbon ligand in $[\text{Fe}(\text{CO})_3(\eta^4\text{-cyclohexadiene})]$ whereas $[\text{Fe}(\text{exo-}\eta^4\text{-C}_6\text{H}_7\text{R})(\eta\text{-C}_6\text{H}_6)]$ and $[\text{CPh}_3]^+$ at -50 °C give $[\text{Fe}(\eta^5\text{-C}_6\text{H}_6\text{R})(\eta\text{-C}_6\text{H}_6)]^+$ by loss of an *endo* hydrogen atom after oxidation to $[\text{Fe}(\text{exo-}\eta^4\text{-C}_6\text{H}_7\text{R})(\eta\text{-C}_6\text{H}_6)]^+$.²⁷⁹

b. Tropylium, $[\text{C}_7\text{H}_7]^+$, Salts. The tropylium cation, $[\text{C}_7\text{H}_7]^+$, is a weak oxidant (Table 2) as yet relatively little used in organic²⁶⁷ or organometallic chemistry; the oxidation potential can be varied to some extent by ring substitution.²⁸¹

The colorless salts $[\text{C}_7\text{H}_7][\text{BF}_4]$ and $[\text{C}_7\text{H}_7][\text{PF}_6]$ are commercially available, but the former is readily prepared on a large scale by reacting PCl_5 with chpt in CCl_4 and treating the resulting $[\text{PCl}_6]^-/\text{Cl}^-$ double salt of $[\text{C}_7\text{H}_7]^+$ with HBF_4 .²⁸² Methods involving hydride abstraction from chpt, using $[\text{CPh}_3][\text{BF}_4]$ in MeCN or SO_2 ²⁵⁹ or CPh_3OH and HBF_4 in acetic anhydride,²⁸³ can also be used to prepare the $[\text{AsF}_6]^-$ and $[\text{SbF}_6]^-$ salts; $[\text{C}_7\text{H}_7][\text{SbCl}_6]$ is made directly from chpt, CPh_3Cl , and SbCl_5 in MeCN.²⁸⁴

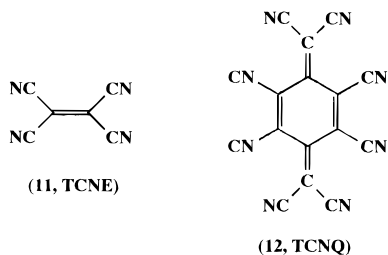
Tropylium salts of complex anions such as $[\text{BF}_4]^-$ and $[\text{PF}_6]^-$ are stable in air and nonhygroscopic (in contrast to simple halide salts such as $[\text{C}_7\text{H}_7]\text{Cl}$). $[\text{C}_7\text{H}_7][\text{BF}_4]$ is soluble in MeCN, SO_2 , and acetone and may be recrystallized from a large volume of ethyl acetate (or from MeCN/ethyl acetate); product loss is extensive during such recrystallization and the purity is little improved.²⁸² It is insoluble in CH_2Cl_2 and forms donor:acceptor complexes with arenes which can undergo photoinduced redox reactions giving the tropyli radical and the arene radical cation.²⁸⁴

Readily oxidized substrates such as $[\text{Re}_2\text{H}_4(\mu\text{-H})_4(\text{PPh}_3)_4]$ and $[\text{Re}(\text{CO})_5]^-$ react with solid $[\text{C}_7\text{H}_7][\text{PF}_6]$ to give $[\text{Re}_2\text{H}_4(\mu\text{-H})_4(\text{PPh}_3)_4]^+$ (in CH_2Cl_2)²⁷¹ and $[\text{Re}_2(\text{CO})_{10}]$ (in THF),²⁸⁵ respectively. Moreover, dianions such as $[\text{Ru}_3(\text{CO})_{11}]^{2-}$ give neutral clusters, $[\text{Ru}_3(\text{CO})_{11}\text{L}]$, when treated with $[\text{C}_7\text{H}_7][\text{BF}_4]$ in the presence of donor ligands, L, such as phosphines.²⁸⁶ Note, however, that $[\text{Ru}_6\text{C}(\text{CO})_{16}]^{2-}$ gives $[\text{Ru}_6\text{C}(\text{CO})_{14}(\eta^6\text{-C}_{14}\text{H}_{14})]$ in which ditropyli, the byproduct of the reduction of $[\text{C}_7\text{H}_7]^+$ (and normally readily removed from the reaction mixture), is bound to one triangular face of the cluster.²⁸⁷ In addition, the tropylium ion itself can act as an electrophile toward coordinated hydrocarbons, for example, the cot rings of $[\text{Fe}(\text{CO})_3(\text{cot})]$ ²⁸⁸ and $[\text{M}(\text{cot})\text{Cp}]$ ($\text{M} = \text{Co}$ and Rh).²⁸⁹

3. Cyanocarbons and Related Electron-Rich Compounds

Many percyanocarbons are one-electron oxidants. However, their redox behavior has been most widely applied to the reconstruction of low-dimensional solids where the *physical* properties (magnetic, conducting, etc.), based largely on the electronic and molecular structure of the reduced (paramagnetic) form of the

percyanocarbon, are of more interest than the *chemical* properties of the oxidation product. Thus, for example, $[\text{FeCp}^*_2][\text{TCNE}]$ is a soluble ferromagnet;²⁹⁰ as a synthetic route to $[\text{FeCp}^*_2]^+$ the reaction of TCNE (**11**) with $[\text{FeCp}^*_2]$ is unimportant.



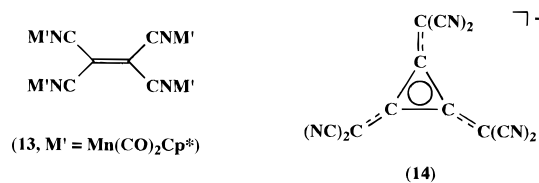
TCNE and 7,7,8,8-tetracyanoquinodimethane (TCNQ, **12**) are the most widely used of the percyanocarbon oxidants. They are commercially available solids which dissolve in a range of polar organic solvents (*e.g.*, MeCN, THF, 1,2-dichloroethane, ethyl acetate, etc.); they may be purified by recrystallization [from 1,2-dichloroethane or chlorobenzene (TCNE), or from ethyl acetate or MeCN (TCNQ)] or by vacuum sublimation. Their reactions may be monitored by IR spectroscopy (in the cyanide stretching region), UV spectroscopy, or by the ESR spectra of the radical anions; full details of such spectra and of other physical properties may be found in refs 291 and 292 (TCNE) and 293 (TCNQ). An important point to note is the toxicity of TCNE.

TCNE and TCNQ are mild oxidants (Table 2) (TCNE, -0.27 and -1.27 V; TCNQ, -0.30 and -0.88 V) which are reduced in two one-electron steps to mono- and dianions (the former have a tendency to dimerize in the solid state). The first process is more generally encountered although $[\text{TCNE}]^-$, obviously a weaker oxidant than TCNE, is capable of oxidizing $[\text{CoCp}^*_2]$; the reaction of the latter with TCNE gives $[\text{CoCp}^*_2]_2[\text{TCNE}]$, a salt of the TCNE dianion.²⁹⁴

TCNE forms charge-transfer complexes with less readily oxidizable substrates such as ferrocene²⁹⁵ and main group metal alkyls, the adducts of the latter sometimes leading to addition reactions to the C=C bond.¹²⁰ Note that $[\text{FeCp}_2]$ is oxidized to $[\text{FeCp}_2]^+$ by the less popular, but stronger, cyanocarbon oxidants hexacyanobutadiene²⁹⁶ and 7,7,8,8-tetrafluoroquinodimethane;²⁹⁷ 2,3-dichloro-5,6-dicyanoquinone (DDQ) is also a stronger oxidant than TCNE (Table 2).²⁹⁸ Complete electron transfer from TCNE occurs with more electron-rich transition metal sandwich compounds to give, for example, $[\text{MCp}^*_2][\text{TCNE}]$ (M = Cr, Mn, Fe, Co and Ni),^{290,294} $[\text{Cr}(\eta\text{-arene})_2][\text{TCNE}]$,²⁹⁹ and $[\text{MoCp}(\eta\text{-C}_7\text{H}_7)][\text{TCNE}]$.¹³⁶ Similar products may be made with TCNQ.

Of the percyanocarbon oxidants, TCNE is probably the least innocent; it has an extensive reaction chemistry with organic,^{291,300} organometallic,²⁹² and coordination³⁰¹ compounds. Many of the reactions with transition metal complexes involve initial one-electron transfer followed by bond formation.¹³⁵ Thus, TCNE may coordinate as an alkene, as in $[\text{Fe}(\eta^2\text{-TCNE})(\text{PPh}_3)(\text{NO})_2]$,³⁰² or *via* up to four N-atoms as in complex **13** (the TCNQ analogue of which is also known).³⁰¹ Fragmentation, for example, to give cyano

and tricyanovinyl units, and cycloaddition to coordinated polyenes²⁹² may also occur.



One less common percyanocarbon is of interest as a rare example of an anionic one-electron oxidant, namely the paramagnetic radical anion of hexacyanotrimethylenecyclopropane, $[\text{C}_3\{\text{C}(\text{CN})_2\}_3]^-$ (**14**) (sometimes confusingly formulated as $[\text{C}_6(\text{CN})_6]^-$). The salt $[\text{NBu}^n_4][\text{C}_3\{\text{C}(\text{CN})_2\}_3]$ is prepared³⁰³ by metathesis of $\text{K}[\text{C}_3\{\text{C}(\text{CN})_2\}_3]$ which is, in turn, synthesized by potassium persulfate oxidation of $\text{Na}_2[\text{C}_3\{\text{C}(\text{CN})_2\}_3]$ ³⁰⁴ in water. The potassium salt is soluble in MeCN and THF/HMPA, and $[\text{NBu}^n_4][\text{C}_3\{\text{C}(\text{CN})_2\}_3]$ is soluble in MeNO₂; the formation of $[\text{C}_3\{\text{C}(\text{CN})_2\}_3]^{2-}$ by reduction could be monitored by the loss of the 13-line ESR spectrum or the maroon color ($\lambda_{\text{max}} = 673, 598, 320$ nm; $\epsilon = 19\,900, 12\,900, 30\,500$)³⁰³ of $[\text{C}_3\{\text{C}(\text{CN})_2\}_3]^-$. Though only a mild oxidant ($E^\circ = \text{ca. } 0.0$ V; see Table 2) $[\text{C}_3\{\text{C}(\text{CN})_2\}_3]^-$ should prove useful in the isolation of dicationic oxidation products, as salts of $[\text{C}_3\{\text{C}(\text{CN})_2\}_3]^{2-}$ {as might be the case in solid $[\text{OsCp}_2^*][\text{C}_3\{\text{C}(\text{CN})_2\}_3]$, formed in the reaction between $[\text{OsCp}_2^*]$ and $[\text{NBu}^n_4][\text{C}_3\{\text{C}(\text{CN})_2\}_3]$ (1:2 ratio)³⁰⁵}.

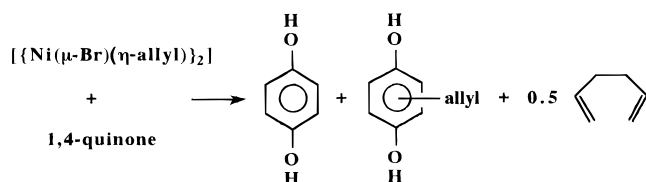
Some variation in oxidation potential is possible in that related carbomethoxytrimethylenecyclopropane derivatives have been prepared. For example, stable yellow crystalline $\text{C}_3\{\text{C}(\text{CO}_2\text{Me})_2\}_3$ may also act as a weak oxidant ($E^\circ = -0.52$ V).³⁰⁴

4. Quinones

Both 1,2- and 1,4-quinones, many of which are commercially available and easily handled, are reduced in two one-electron steps, rendering them potentially useful as one-electron oxidants. As yet, few examples have been reported of the oxidation of organometallics to simple, primary redox products (*i.e.*, A^+ from A). Quinone, semiquinone, or catecholate coordination may occur, either instead of or after electron transfer. Thus, $[\text{Rh}(\text{CO})(\text{PPh}_3)\text{Cp}]$ [$(E_p)_{\text{ox}} = 0.0$ V] and 1,2-O₂C₆Cl₄ ($E^\circ = -0.32$ V) give $[\text{Rh}\{\text{OC}_6\text{Cl}_4\text{OC}(\text{O})\}(\text{PPh}_3)\text{Cp}]$,³⁰⁶ the reaction is endergonic but most likely driven by the irreversible coupling, after electron transfer, of the carbonyl ligand of $[\text{Rh}(\text{CO})(\text{PPh}_3)\text{Cp}]^+$ and the semiquinone anion radical.

The potential associated with the first reduction process is dependent both on pH and on the ring substituents.^{307,308} In the presence of HBF₄, 1,4-benzoquinone ($E^\circ = -0.51$ V³⁰⁸) acts as a simple oxidant toward ferrocene,²⁰ $[\text{FeCp}^*_2]$,²⁵ and $[\text{Fe}(\eta\text{-C}_5\text{H}_4\text{COME})_2]$ ²⁶ giving high yields of the corresponding ferrocenium salts (of the $[\text{BF}_4]^-$ anion). In the case of $[\text{Fe}(\eta\text{-C}_5\text{H}_4\text{COME})_2]$ ($E^\circ = 0.49$ V) the reaction is endergonic. Under the reaction conditions (non-aqueous solvent, HBF₄) the formal potential for the quinone/hydroquinone couple is not strictly known, but it is likely to be *ca.* 0.30 V, as found for aqueous solutions at pH = 0.³⁰⁹

Scheme 3



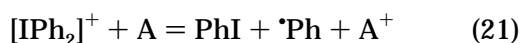
As an illustration of the effect of substituent on the redox potential of quinones, $[\{\text{Ni}(\mu\text{-Br})(\eta\text{-allyl})\}_2]$ is oxidized in DMF, according to the stoichiometry of Scheme 3, by 1,4-benzoquinone and the methyl and dimethyl derivatives ($E^\circ = -1.03$ to -1.15 V) but not by the tri- and tetramethyl analogues ($E^\circ = -1.25$ to -1.33 V).³¹⁰

5. Other Organic Oxidants

a. 4-Pyridinecarboxaldehyde, $\text{NC}_5\text{H}_4\text{CHO}$ -4. 4-Pyridinecarboxaldehyde is a weak one-electron oxidant ($E^\circ = ca. -1.0$ V³¹¹). It is a commercially available liquid but should be distilled before use to remove the carboxylic acid, $\text{NC}_5\text{H}_4\text{CO}_2\text{H}$ -4, and the alcohol, $\text{NC}_5\text{H}_4\text{CH}_2\text{OH}$ -4, which are formed by slow decomposition. It can then be stored under N_2 at $ca. -10$ °C. The primary reduction product dimerizes to give diamagnetic products, presumably the pinacol $\text{NC}_5\text{H}_4\text{CH}(\text{OH})\text{CH}(\text{OH})\text{C}_5\text{H}_4\text{N}$ or the dianion $[\text{NC}_5\text{H}_4\text{CH}(\text{O})\text{CH}(\text{O})\text{C}_5\text{H}_4\text{N}]^{2-}$. 4-Pyridinecarboxaldehyde is particularly useful, therefore, for the *in situ* generation of paramagnetic organometallics for ESR spectroscopic studies, for example, $[\text{Cr}_2(\mu\text{-cot})\text{Cp}_2]^+$ ($E^\circ = -1.2$ V),³⁸ where other oxidants might give paramagnetic reduction products with interfering spectra.

4-Pyridinecarboxaldehyde can also be used in synthesis. Thus, treatment of a mixture of $[\text{Cr}(\eta^6\text{-arene})_2]$ in toluene and KPF_6 in water with the oxidant directly gives a precipitate of $[\text{Cr}(\eta^6\text{-arene})_2]\text{-}[\text{PF}_6]$.³¹² In addition, the reaction of 4-pyridinecarboxaldehyde with $[\text{Cr}_2(\mu\text{-biphenyl})(\eta\text{-C}_6\text{H}_6)_2]$ is highly selective, giving only the monocation $[\text{Cr}_2(\mu\text{-biphenyl})(\eta\text{-C}_6\text{H}_6)_2]^+$ ($E^\circ = -0.82$ V vs Ag/AgCl); it is insufficiently strong to form the dication ($E^\circ = -0.37$ V) though this species is formed exclusively with O_2 ²¹⁹ (section II.A.2.d). Similar selectivity is observed with $[\text{Co}_2(\text{CO})_4\text{L}_2]$ ($\text{L} = [\text{Cr}(\eta\text{-C}_6\text{H}_5\text{PMe}_2)_2]$) which shows three sequential one-electron oxidations; the dication, but not the trication, was isolated.³¹³

b. Diphenyliodonium Cation, $[\text{Ph}_2\text{I}]^+$, and Iodosobenzene, PhIO . Diphenyliodonium salts, $[\text{Ph}_2\text{I}]\text{X}$ ($E^\circ = ca. -0.9$ V³¹⁴), are commercially available as the halides ($\text{X} = \text{Cl}, \text{Br}, \text{or I}$) but may also be made in the laboratory ($\text{X} = \text{Cl},$ ³¹⁵ $[\text{BF}_4], [\text{PF}_6], [\text{AsF}_6], \text{or } [\text{SbF}_6]$ ³¹⁶). The cation $[\text{Ph}_2\text{I}]^+$ is usually used in electrophilic arylation reactions but can also act as a one-electron oxidant toward transition metal complexes, as in eq 21. Although diamagnetic reduc-



tion products are therefore expected, namely iodosobenzene and biphenyl (from the coupling of $\cdot\text{Ph}$), in the reactions so far described, the phenyl radical has invariably abstracted a hydrogen atom from the solvent. Subsequent coupling of the solvent-based

radical with A^+ then occurs, as also observed for arenediazonium ion oxidations (section II.A.2.c). Thus, $[\text{WBr}(\text{N}_2\text{H})(\text{dppe})_2]$, formed *in situ* from $[\text{WBr}(\text{N}_2\text{H}_2)(\text{dppe})_2]^+$ and base, is oxidized by $[\text{IPh}_2]\text{Br}$ to give $[\text{WBr}(\text{N}_2\text{H})(\text{dppe})_2]^+$. Subsequent H-atom abstraction from CH_2Cl_2 or CHBr_3 ,³¹⁷ from CHCl_3 or CBrCl_3 ,³¹⁸ or from CHFBr_2 ,³¹⁹ and coupling of the resulting radicals with $[\text{WBr}(\text{N}_2\text{H})(\text{dppe})_2]^+$ gives $[\text{WBr}(\text{N}_2\text{-CHO})(\text{dppe})_2]$, $[\text{WBr}(\text{N}_2\text{CCl}_2)(\text{dppe})_2]$, and $[\text{W}_2\text{Br}_2(\mu\text{-N}_2\text{CHN}_2)(\text{dppe})_4]^+$, respectively. Likewise, $[\text{IPh}_2]^+$ and $[\text{Mo}(\text{CO})_3\text{Tp}]^-$ gave $[\text{Mo}(\text{CX})(\text{CO})_2\text{Tp}']$ (in CH_2Cl_2 , $\text{X} = \text{Cl}$; in CHBr_3 , $\text{X} = \text{Br}$; in CHI_3 , $\text{X} = \text{I}$) or $[\text{Mo}(\eta^2\text{-COPh})(\text{CO})_2\text{Tp}']$ by direct coupling of the phenyl radical with $[\text{Mo}(\text{CO})_3\text{Tp}']$ (in MeCN).²¹¹

Iodosobenzene, a yellow amorphous powder which slowly decomposes (and explodes when heated above 210 °C³²⁰), has also been used as a one-electron oxidant. With $[\text{Fe}(\text{C}=\text{CHMe})(\text{dppe})\text{Cp}]^+$ it gives $[\text{Fe}_2\{\mu\text{-C}=\text{C}(\text{Me})\text{C}(\text{Me})=\text{C}\}(\text{dppe})_2\text{Cp}_2]^{2+}$ in a reaction unsuccessful with other oxidants such as $[\text{C}_7\text{H}_7]^+$, $[\text{N}_2\text{-Ph}]^+$, and halogens.⁹²

III. Reductants

Far fewer reagents have been reported for the reduction of organometallic complexes, when compared to the large number of oxidants. In part this stems from the smaller number of studies of electron-rich organometallics. However, the difficulty of handling strong reducing agents (especially their inherent sensitivity to oxidation by O_2) undoubtedly also plays a role. As will be seen below, with only a few exceptions (*e.g.*, alkali metals and cobaltocene), most reducing agents have received inadequate attention to demonstrate the breadth and limitations of their use. There is ample need to develop new reducing agents and for more systematic studies of several of those we now discuss.

A. Inorganic

1. Alkali Metals

Although the formal potentials of eq 22 ($\text{M} =$ alkali metal) are not known with great certainty under the

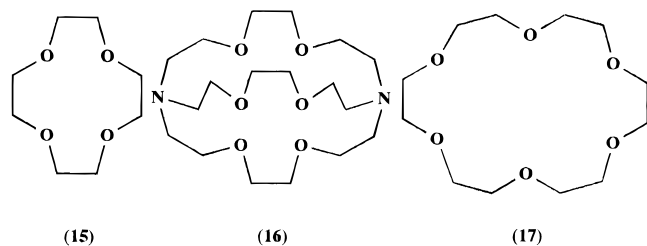


conditions usually applied in organometallic synthesis, they are very negative (*ca.* -3.0 V, Table 3), making the alkali metals extremely powerful reducing agents. Their potentials are quite solvent dependent, as might be expected for a couple in which one redox state (M^+) is much more strongly solvated than the other. For example, E° of Na^+/Na becomes more positive by *ca.* 1.0 V in changing the solvent from DMF to NH_3 . With potentials in the range -2.4 to -3.1 V, alkali metals have proved to be popular reductants. Even dilute amalgams have sufficiently negative potentials to be classified as strong reductants (*e.g.*, 0.1% Na/Hg : -2.2 V).

This family of reagents is subject to an important experimental drawback when applied in a stoichiometric manner on small scales: surface oxide formation, which lowers the reductive efficiency of the metal. Considerable care must be taken to ensure the formation of active metal surfaces for the neces-

sarily heterogeneous reactions involving these metals. Several approaches of increasing rigor have been used to produce reactive surfaces, namely (a) freshly-cut pieces of metal, (b) metallic sands formed by heating the metal in a solvent above the melting point of M, followed by cooling of the mixture while maintaining rapid stirring, and (c) metallic mirrors formed by distillation of metals *in vacuo*. Mixed alkali metal alloys and metal amalgams have also proved popular. Some Na/K alloys are liquids at room temperature, commercially available in high purity, and easily handled under inert atmospheres. However, they present *extreme fire hazards* when exposed to moist air because of their high surface area and reactivity with water. They should be used with *great caution*.

A limited number of solvents may be employed with alkali metals, THF and glyme being the most popular [potentials of the M^+/M couple in nonaqueous solvents have usually been measured by polarographic reduction of the $M(I)$ ion because $M(0)$ will often react with the solvent]. The reductions are often performed in the presence of a macrocycle (a crown ether or cryptand) capable of complexing the M^+ counterion. The complex counterion (e.g., $[M(\text{macrocycle})_n]^+$) tends to stabilize and solubilize³²¹ the electron-transfer salts $[M(\text{macrocycle})_m]_n[A]^{n-}$ ($A =$ target anion) and is particularly useful when seeking larger crystalline forms of the product. The most commonly used macrocycles³²² are 12-crown-4 (**15**) and 2,2,2-cryptand (**16**) for Li^+ ; 2,2,2-cryptand (and 12-crown-5) for Na^+ ; and 18-crown-6 (**17**) for K^+ .



Stoichiometric amounts of potassium sand were successfully employed to reduce neutral complexes with low electron affinities to their corresponding monoanions. $[V(\eta^6\text{-arene})_2]$ ($E^\circ = -3.2$ V)³²³ in THF with 1.1 equiv of potassium gave *ca.* 20% yield of the 18-electron anion $K[V(\eta\text{-arene})_2]$,³²⁴ and $[Ce(\eta\text{-C}_8\text{H}_8)_2]$ in glyme gave an analytically pure precipitate of $K[Ce(\eta\text{-C}_8\text{H}_8)_2]$.³²⁵ In the latter case, 2 equiv of K and higher reaction temperatures (increased solubility of $K[Ce(\eta\text{-C}_8\text{H}_8)_2]$?) gave the pure dianion, $K_2[Ce(\eta\text{-C}_8\text{H}_8)_2]$. Vanadocene, $[VCp_2]$, undergoes a one-electron reduction at -3.30 V in THF.³²⁶ In spite of the very negative potential, $[K(\text{THF})(\text{OEt}_2)][VCp_2]$ was isolated from the reduction of $[VCp_2]$ by potassium and used as a starting material to make organovanadium compounds in low oxidation states.³²⁷

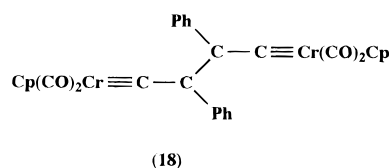
Neutral 17-electron $Co(0)$ complexes have also been successfully reduced to their $18e^-$ analogues; $[CoL_2]$ ($L = \eta^4\text{-1,4-Bu}_2\text{butadiene}$) stirred in THF with K in the presence of 18-crown-6 gave red crystals of $[K(\text{crown})(\text{THF})_2][CoL_2]$.³²⁸ $[Co(\eta\text{-C}_2\text{H}_4)(\text{PMe}_3)_3]$ with K in pentane gave the simple monoanion $K[Co(\eta\text{-C}_2\text{H}_4)(\text{PMe}_3)_3]$ when cyclopentene was present in the

reaction mixture and the dinuclear product $K[\{Co(\eta\text{-C}_2\text{H}_4)(\text{PMe}_3)_3\}_2]$ when it was not.³²⁹

Sodium often provides reducing equivalents for substitution reactions of compounds with metal-halogen bonds. Typical of these applications are the reductions of $[MoCl_4Cp^*]$ by 3 equiv of Na in the presence of phosphine ligands, L. Depending on the stoichiometric ratio of L to the $Mo(V)$ starting material, the $Mo(II)$ complexes isolated are either 18-electron $[MoClL_3Cp^*]$ (with 3 equiv of L)³³⁰ or 16-electron $[MoClL_2Cp^*]$ (with 2 equiv of L).³³¹

Anions of main group organometallics have been isolated after alkali metal reduction of their neutral starting materials. The complex $[Ga_2L_4]$ ($L = 1,3,5\text{-triisopropylphenyl}$) and a suspension of Li powder in diethyl ether containing 12-crown-4 gave $[Li(12\text{-crown-4})_2][Ga_2L_4]$,³³² and the same metal in a slight stoichiometric excess allowed the isolation of blue $[Li(12\text{-crown-4})_2][B(\text{mesityl})_3]$.³³³ The reduction potential of $B(\text{mesityl})_3$ is *ca.* -2.9 V; a second (irreversible) reduction wave at *ca.* -3.5 V³³⁴ provides a rationale for more recent observations in which the dianion of BMe_2Ph has apparently been observed *in situ*.³³⁵ Sodium mirror reduction of BMe_2Ph in THF gave blue solutions typical of $[BR_3]^-$ (λ_{max} 660 nm), but potassium mirrors produced solutions of the purple dianion (λ_{max} 581 nm), albeit in longer reaction times.³³⁵

In some cases, ligand-coupled products were obtained, presumably from one-electron reduction products with considerable ligand radical character. Examples are the reductive coupling of the alkylidene complex $[Cr(=CPh)(CO)_2Cp]$ by Na/K³³⁶ (giving **18**) and the coupling of Cp and Cp* ligands in the Na/Hg reduction of $[RhCpCp^*]^+$.³³⁷ Even though metal

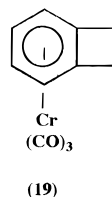


amalgams are considerably weaker reducing agents than M (Table 3), in the last example the potential for Na/Hg in THF is still negative of the reported reduction potential (-2.07 V)³³⁷ of the $Rh(III)$ complex, allowing efficient production of the reduction product. This strategy had been employed much earlier in the reductive coupling of the parent rhenium ion.³³⁸ It may be appropriate to note that a similar ligand-ligand coupling reaction occurs when the cation $[Fe(CO)_3(\eta^5\text{-pentadienyl})]^+$ is reduced by the milder reductant, zinc.³³⁹

Other amalgams (Mg/Hg , Zn/Hg)³⁴⁰ and alloys have also been employed. Among the latter, commercially available Na/Pb should be considered as an alternative to Na/Hg owing to its ease of handling for stoichiometric uses.³⁴¹

In a variation of the usual synthetic method, others have employed the alkali $[K(18\text{-crown-6})][K]$ to reduce $[Mn(CO)_3Cp]$, producing *in situ* the interesting dianion $[Mn(CO)_3(\eta^3\text{-C}_5\text{H}_5)]^{2-}$.³⁴² A ring-slipped dianion has also been produced by the action of Li sand on a fused-ring aromatic chromium tricarbonyl com-

plex, $[\text{Cr}(\text{CO})_3(\eta^6\text{-cyclobutabenzene})]$ (**19**), which underwent electrochemical reduction at -3.0 V.³⁴³

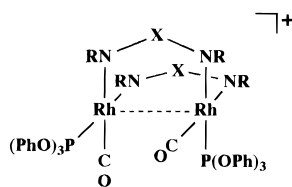


2. Complex Reducing Agents

A host of complex reductants containing main-group metals has been widely used in organic chemistry.³⁴⁴ These reagents are mechanistically complex, and their reactions as one-electron reagents are often unpredictable.^{151a} Nevertheless, the familiarity gained in their use has inspired applications in organometallic ET chemistry, some of which are noted here.

Included in the category of complex reducing agents are lithium alkyls and aryls and simple and complex metal hydrides $\{\text{NaH}, \text{LiAlH}_4, \text{K}[\text{BH}(\text{CH}_2\text{MeEt})_3]$ ("K selectride"), etc. $\}$, virtually all of which are commercially available. One-electron potentials for these reducing agents are generally ill-defined, and even when known the irreversibility of the couples lends uncertainty to their significance in ET applications. Among the compounds for which E° values have been estimated are $[\text{AlH}_4]^-$ (-0.7 V in THF),³⁴⁵ MgBrBu^t (-1.5 V in Et_2O),³⁴⁶ LiBz (-1.4 V in THF/HMPA),³⁴⁷ and $[\text{BH}_4]^-$ (*ca.* -0.6 V in diglyme).³⁴⁸

The borohydride ion, $[\text{BH}_4]^-$, is a mild reducing agent. It is most often used as the sodium salt which may be obtained in high purity by recrystallization from diglyme.³⁴⁹ For example, a suspension of $[\text{Co}_2(\mu\text{-CO})(\mu\text{-NO})\text{Cp}^*_2]^+$ ($E^\circ = -0.7$ V) was successfully reduced to $[\text{Co}_2(\mu\text{-CO})(\mu\text{-NO})\text{Cp}^*_2]$ when treated with an excess of $\text{Na}[\text{BH}_4]$ in THF/pentane.³⁵⁰ Other counterions, however, confer solubility in lower polarity solvents. Since $\text{Na}[\text{BH}_4]$ is insoluble in CH_2Cl_2 , commercially available $[\text{NBu}_4][\text{BH}_4]$ was used to reduce $[\text{Rh}_2(\text{CO})_2\{\text{P}(\text{O}(\text{Ph})_3)_2\}\{\mu\text{-PhNC}(\text{Me})\text{NPh}\}_2]^+$ (**20**) ($E^\circ = -0.43$ V) to $[\text{Rh}_2(\text{CO})_2\{\text{P}(\text{O}(\text{Ph})_3)_2\}\{\mu\text{-PhNC}(\text{Me})\text{NPh}\}_2]$.³⁵¹



(20, X = CMe, R = $\text{C}_6\text{H}_4\text{Me-4}$)

LiAlH_4 can act as a one-electron reductant toward organometallic complexes.³⁵² It gives different reduction products with $[\text{Mo}(\text{CO})_3\text{LCp}^*]^+$ (L = phosphine; $E_p = -2.3$ V for L = PMe_3) under different experimental conditions.^{352c} When a 4:1 ratio of LiAlH_4 :Mo(II) complex was reacted at -20 °C for 1 h, the metal hydrides $[\text{MoH}(\text{CO})_2\text{LCp}^*]$ and $[\text{MoH}(\text{CO})\text{L}_2\text{Cp}^*]$ were isolated in good yield. Reduction of the Mo(II) cation by a substoichiometric amount of LiAlH_4 at -80 °C, however, gave ESR spectroscopic evidence for a radical intermediate. The spectrum

was obtained by distilling THF onto a solid mixture of LiAlH_4 and the Mo(II) complex, letting the reactants mix as the solvent melted, and then quenching the mixture in liquid nitrogen.³⁵²

Lithium aryls and alkyls (LiR) have estimated E° values which vary greatly, depending on the identity of R (*e.g.*, R = Bu^t , *ca.* -2.7 V; R = Cp, *ca.* -0.8 V).^{345,347} *n*-Butyllithium has been used to reduce $[\text{ZrR}_4]$ (R = Me, Bz) to the corresponding dianion, $\text{Li}_2[\text{ZrR}_4]$, which may be polymeric.³⁵³ 1-Norbornyllithium efficiently reduced $[\text{Co}(\text{1-norbornyl})_4]^+$ and allowed the isolation of $[\text{Li}(\text{THF})_4][\text{Co}(\text{1-norbornyl})_4]$ in spite of the very negative potential (-2.02 V) of the $[\text{Co}(\text{1-norbornyl})_4]^{0/-}$ couple.³⁵⁴

3. Hydrazine

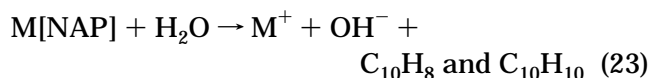
The reducing strength of hydrazine (N_2H_4) in aqueous media is highly pH-dependent. It has been widely employed as a reductant in inorganic chemistry³⁵⁵ but has been little explored under nonaqueous conditions. The anhydrous reagent, an air-sensitive liquid, has been used to reduce octahedral Mn(II) complexes (*e.g.*, $[\text{MnBr}(\text{CO})_2(\text{PMe}_2\text{Ph})_3]^+$ ¹⁹² and $[\text{Mn}(\text{CN})(\text{CO})_2\{\text{P}(\text{O}(\text{Ph})_3)_3\}(\text{dppm})]^+$) to their corresponding Mn(I) analogues in CH_2Cl_2 .³⁵⁶ An advantage of this mild reducing agent ($E_{1/2} = -0.4$ V in DMSO³⁵⁷) is that the redox byproducts are relatively benign (N_2 and unknown H-containing products, possibly H_2O).

B. Organic

1. Metal Naphthalenides

These powerful reductants, which are prepared *in situ*, have formal potentials of *ca.* -3.0 V. THF, glyme, or other ethers are employed as solvents since most other media react with the naphthalene anion, $[\text{NAP}]^-$. Small, freshly cut pieces of an alkali metal dissolve when stirred (using a glass-coated stirring bar) with equimolar naphthalene to produce deep green $\text{M}[\text{NAP}]$. Medium-sized metal chunks have been said to give results superior to those obtained with metal dispersions or sands.³⁵⁸ Although the complete reaction takes several hours, if the green color ($\lambda_{\text{max}} = 463, 735$ nm; $\epsilon = \text{ca. } 2500$)^{359,360} does not immediately appear, the solvent is probably wet or improperly degassed; more rigorous conditions should be sought. Concentrations of 0.1–0.5 M are commonly employed, but under very stringent conditions Beer's law was shown to hold for concentrations of $\text{Na}[\text{NAP}]$ down to less than 10 mM.³⁵⁹ Transfer of the $\text{M}[\text{NAP}]$ solution to that containing the substrate is accomplished with a volumetric syringe. It must be emphasized that all reagents and glassware should be scrupulously dry and oxygen-free to obtain quantitative results. Since the dianion of naphthalene is probably not formed in any significant quantity when NAP is in contact with excess alkali metal,³⁶¹ a constant titre of $\text{M}[\text{NAP}]$ may be aided by using a small excess of the metal in preparation of the reagent stock solution. Stock solutions may be used for several days if adequately protected, but the sensitivity of these reagents to air and moisture precludes a general statement about their shelf lives.

The concentration of M[NAP] in the stock solution is measured by titration. Quenching a solution with excess water, eq 23, followed by titration with stan-



dardized HCl to a phenolphthalein endpoint gives the total base concentration, [B], of the reagent solution. The concentration of B is not, however, equal to the effective M[NAP] concentration unless no hydrolytic decomposition of M[NAP] occurred at any time in the preparation of the stock solution. Since this condition normally cannot be assured, many workers have relied on a double (or "blank") titration method to measure the effective M[NAP] concentration. To this end, quenching the stock solution with an alkyl halide, which destroys M[NAP] *without* liberation of base, provides the blank when titrated with HCl.³⁶² A method for *direct* titration of Li[NAP] against 1,1-diphenylethylene has been described.³⁶³

The naphthalenide anion is ESR-active ($\langle g \rangle = 2.0028$);³⁶⁴ reaction byproducts such as naphthalene and dihydronaphthalene are easily removed by passing the reaction mixture through silica gel.

Although naphthalenides of Li, Na, and K seem to be used interchangeably, in principle the counteranion should affect their reactivities. ESR spectroscopic studies establish that ion pairing between $[\text{C}_{10}\text{H}_8]^-$ and M^+ increases in the order $\text{Li}^+ < \text{Na}^+ < \text{K}^+$.³⁶⁵ The formal potentials of the ion-paired reagents should increase in the same way, *i.e.*, $\text{Li[NAP]} < \text{Na[NAP]} < \text{K[NAP]}$, the lithium reagent therefore being the strongest reductant of the three. Because M[NAP] are only weakly dissociated in ether solvents,³⁶⁶ the effect on the formal potentials is likely to be significant although we are not aware of systematic studies probing this point. Interestingly, the sequence of ion-pairing strength for M[NAP] is opposite to that found for the benzophenone anion radical (section III.B.2). Smaller cations are more effectively complexed by the oxygens of the *solvent* in ether solutions of $[\text{C}_{10}\text{H}_8]^-$, accounting for the lower ion pairing observed for M[NAP] with smaller cations. The solvation effect is insufficient to overcome the major source of ion pairing in the benzophenone anion, which is between the metal and the carbonyl oxygen, with stronger pairing being observed with smaller cations.³⁶⁵

M[NAP] has typically been employed to generate the monoanion of a substrate for the purposes of spectroscopic or X-ray characterization, for example, of metal pyrazolylborates,³⁶⁷ tungsten and titanium alkyls,^{368,369} and metal clusters.³⁷⁰ Dianions have also been suitable targets, including $[\text{W}(\text{C}_2\text{Ph}_2)_3]^{2-}$ from $[\text{W}(\text{CO})(\text{C}_2\text{Ph}_2)_3]$,³⁷¹ $[\text{M}(\text{CO})_5]^{2-}$ from $[\text{M}(\text{CO})_5(\text{NMe}_3)]$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$),³⁷² $[\text{Mn}(\text{CO})_2\text{Cp}]^{2-}$ from $[\text{Mn}(\text{CO})_2(\text{pyr})\text{Cp}]$,³⁷³ and $[\text{Cr}(\text{CO})_3(\eta^4\text{-arene})]^{2-}$ from $[\text{Cr}(\text{CO})_3(\eta^6\text{-arene})]$.³⁴³ In another reaction, using 2 equiv of M[NAP], the monoanion $[\text{Mn}(\text{CO})_3(\eta^4\text{-benzene})^-]$ was produced from the monocation $[\text{Mn}(\text{CO})_3(\eta^6\text{-benzene})]^+$.³⁷⁴ In related studies, reduction of $[\text{Mn}(\text{CO})_3(\eta^5\text{-indenyl})]$ with 2 equiv of K[NAP] in THF gave the dianion $[\text{Mn}(\text{CO})_3(\eta^3\text{-indenyl})]^{2-}$, characterized *in situ* by IR spectroscopy.³⁷⁵ The use of metal encapsulat-

ing agents such as the kryptofix series sometimes aids crystal formation and isolation. Thus, the monoanion $[\text{Mn}(\text{CO})_3(\eta\text{-indenyl})^-]$ was isolated as a thermally unstable salt when $[\text{Mn}(\text{CO})_3(\eta^5\text{-indenyl})]$ was reduced by 1 equiv of K[NAP] in the presence of 18-crown-6.³⁷⁵

The reducing strength of M[NAP] is well exemplified by the results of Cooper *et al.*³⁷² regarding the reduction of $[\text{W}(\text{CO})_5(\text{NMe}_3)]$. The desired dianion $[\text{W}(\text{CO})_5]^{2-}$ was obtained only with K[NAP] or Li[NAP]. The reaction with other strong reducing agents such as Na/Hg, K, sodium benzophenone anion, and sodium anthracenide stopped at the dinuclear dianion, $[\text{W}_2(\text{CO})_{10}]^{2-}$.

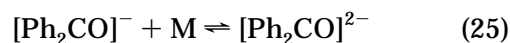
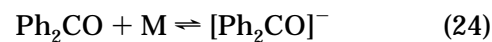
On the other hand, the strength of M[NAP] can sometimes lead to excessive reduction. The reaction of the cluster $[\text{Ni}_3(\mu_3\text{-CO})_2\text{Cp}_3]$ ($E^\circ = -1.4$ V) with K[NAP] gave only decomposition, whereas the milder reductant K[acenaphthalene] gave the desired monoanion $[\text{Ni}_3(\mu_3\text{-CO})_2\text{Cp}_3]^-$.³⁷⁰

Metal naphthalenides are also used to provide reducing equivalents in one-pot reactions which ultimately yield substituted metal complexes in lower oxidation states, as in the reduction of $[\text{TiCl}_3\text{Cp}]$ (4 equiv of Na[NAP] under CO) to give $[\text{Ti}(\text{CO})_4\text{Cp}]^-$ ^{376a} and the production of metallocarboranes from starting ligands and metal halides.^{376b}

The innocence of the metal naphthalenides is not assured when the transition metal is capable of forming metal-arene complexes. Initial reduction products may be labile in the presence of naphthalene, the byproduct of the redox reaction; naphthalene coordination, in a η^4 - or η^6 -mode, is found in the products of the reductions of $[\text{Mn}(\text{CO})_3(\eta^6\text{-benzene})]^+$ and vanadocene, namely $[\text{Mn}(\text{CO})_3(\eta^4\text{-C}_{10}\text{H}_8)]^-$ ³⁷⁴ and $[\text{VCp}(\eta^6\text{-C}_{10}\text{H}_8)]^-$,³⁷⁷ respectively. When $[\text{Mn}(\text{CO})_3(\eta^6\text{-benzene})]^+$ was reduced with potassium anthracenide, substitution of $[\text{Mn}(\text{CO})_3(\eta^4\text{-benzene})^-]$ by anthracene was much slower, enabling studies of the addition reactions of $[\text{Mn}(\text{CO})_3(\eta^4\text{-benzene})^-]$ with diphenylketene.³⁷⁸

2. Benzophenone Anion Radical

Given the strength ($E^\circ = -2.2$ V for the couple $\text{Ph}_2\text{CO}/[\text{Ph}_2\text{CO}]^-$) and ease of preparation of this reagent, the benzophenone radical anion, $[\text{Ph}_2\text{CO}]^-$ (BPA)³⁷⁹ is an under-used reducing agent in organometallic chemistry. It is prepared by the alkali metal (M) reduction of benzophenone (eq 24) in aprotic solvents such as THF, glyme, or liquid ammonia. BPA cannot be used in halocarbon solvents because it reacts rapidly with alkyl halides.³⁸⁰ As discussed below, a possible further complication in the use of BPA is the involvement of the benzophenone dianion (eq 25).



To date, BPA has been used mostly to initiate the electron-transfer-catalyzed substitution reactions of organometallic cluster compounds. Representative examples include the substitution of phosphines for carbonyls in $[\text{Ru}_3(\text{CO})_{12}]$ ³⁸¹ and $[\text{Co}_3(\text{CO})_9(\text{CPh})]$.³⁸²

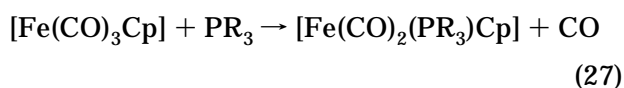
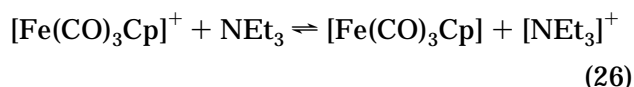
BPA is prepared *in situ* in a dissolving alkali metal reaction;³⁸³ the dark blue monoanion was, interestingly, the first recognized radical anion.³⁸⁴ It displays a multiline ESR spectrum in fluid media³⁸⁵ and must be handled in the rigorous absence of oxygen and water. Contact with the former regenerates neutral Ph₂CO (BPA has been recommended for scavenging the last traces of O₂ from N₂³⁸⁶); with the latter, the coupling product pinacol is formed.³⁸⁷ BPA is routinely employed for the rigorous drying of ether solvents. Optical spectra of BPA have been reported (*e.g.*, $\lambda_{\max} = 630$ nm, $\epsilon = ca. 6 \times 10^3$, in MeCN).³⁸⁸

Of interest in the further development of BPA as a stoichiometric reagent is the question of the possible involvement of the dianion, [Ph₂CO]²⁻, in solutions nominally of the monoanion. Electrochemical measurements show that the dianion is formed at a potential accessible to the alkali metals. The most reliable studies suggest an E° value of *ca.* -2.9 V for the couple [Ph₂CO]⁻/[Ph₂CO]²⁻,³⁸⁹ positive of the potentials of the couples M⁺/M (M = Li, Na, K; Table 3). Evidence that the dianion is present under the synthetic conditions for the production of BPA comes from the color of the solution. With excess metal the solution becomes purple, which is the known color of the dianion.³⁹⁰ Although the addition of the second electron is said to be "slow",³⁹¹ the buildup of [Ph₂CO]²⁻ is likely limited by its propensity to scavenge trace water from the medium. Further work on quantifying this reagent would be welcome.

It is interesting to note that the strength of ion pairing between M⁺ and BPA is K⁺ < Na⁺ < Li⁺, a sequence opposite to that of aromatic hydrocarbon anions such as the naphthalenide ion in ether solvents (section III.B.1).³⁹² One may therefore expect the potassium benzophenone anion to be the strongest reducing agent in the three-metal series.

3. Triethylamine

Triethylamine is a weak reductant (irreversible peak potential, $E_p = +0.47$ V in MeCN³⁹³), whose oxidation byproducts have not been established. In spite of these negative factors, it has seen a few applications in organometallic redox chemistry. For example, in toluene it reduces [MoI₂(NO)Tp'] ($E^\circ = -0.34$ V) to the corresponding monoanion³⁹⁴ and it appears to initiate ET-catalyzed substitution reactions of [Fe(CO)₃(η^5 -L)]⁺ (L = Cp or indenyl)³⁹⁵ and [Mn(CO)₂(NO)Cp']⁺.³⁹⁶ The substitution of a single CO in [Fe(CO)₃Cp]⁺ by phosphine in the presence of NEt₃ is very efficient, considering that the electrochemical reduction potential of [Fe(CO)₃Cp]⁺ ($E_{pc} = -0.60$ V)³⁹⁵ is *ca.* 1.0 V *negative* of the approximate E° of NEt₃. Thus, if NEt₃ does act as an electron-transfer catalyst (according to eqs 26 and 27) the



rapid substitution of 19e⁻ [Fe(CO)₃Cp] by PR₃ (eq 27) and the subsequent oxidation of [Fe(CO)₂(PR₃)Cp] by

another unit of [Fe(CO)₃Cp]⁺ must allow the chain reaction to proceed despite the highly endergonic electron-transfer reaction (eq 26).

4. C₂(NMe₂)₄

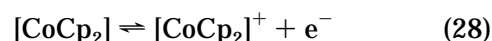
Tetrakis(dimethylamino)ethylene, C₂(NMe₂)₄, reduces TCNE³⁹⁷ and metal carbonyls³⁹⁸ to give salts of the dication [C₂(NMe₂)₄]²⁺, for example, [C₂(NMe₂)₄][TCNE]₂ and [C₂(NMe₂)₄][Co(CO)₄]₂. Though air-sensitive,³⁹⁸ the liquid alkene is commercially available and merits further attention as a two-electron reductant soluble in a wide range of organic solvents (*e.g.*, toluene, diethyl ether, MeCN, and THF).

C. Organometallic

1. Metal Sandwich Complexes

a. Cobaltocene. Cobaltocene, [CoCp₂], is to reductions what the ferrocenium ion is to oxidations: a readily-available metal sandwich complex of moderate redox strength which has become the most popular choice for inducing one-electron changes. This black compound, readily prepared and purified by vacuum sublimation,³⁹⁹ has a number of attractive properties, including solubility in a range of nonpolar and polar solvents. It is air-sensitive in both the solid state and in solution (one study took advantage of this quality by employing [CoCp₂] to scavenge adventitious oxygen, thereby preventing electron-transfer-catalyzed substitution of carbonyls in [Co(CO)₄]).⁴⁰⁰

Cobaltocene should be freshly sublimed (>40 °C, 10⁻⁴ mmHg) before use, but it can be stored for *ca.* 1 week at -10 °C under N₂ without deterioration in its elemental (C and H) analysis. It has a rich chemistry⁴⁰¹ with its facile oxidation ($E^\circ = ca. -1.3$ V) to the corresponding cobaltocenium ion, [CoCp₂]⁺ being relevant here (eq 28); it is almost always an innocent reagent.⁴⁰²



Cobaltocene has been used as a one-electron reducing agent in solvents such as pentane, toluene, THF, CH₂Cl₂,⁴⁰³ acetone, and MeCN. The redox byproduct, [CoCp₂]⁺, generally has poor solubility in relatively nonpolar solvents and is often removed from the reaction mixture by simple filtration. [CoCp₂]⁺ does not usually interfere seriously in visible ($\lambda_{\max} = 409$ nm, $\epsilon = 200$) or ¹H NMR (δ 6.25) spectroscopic studies. It may, however, present an electrochemical interference in the product owing to the two successive one-electron reductions at *ca.* -1.3 and -2.2 V.⁴⁰⁴ Being diamagnetic, [CoCp₂]⁺ is ESR-silent. Unreacted [CoCp₂] is also ESR-silent down to temperatures considerably below that of liquid nitrogen.⁴⁰⁵

Cobaltocene has been employed to reduce mono-cations and dications to neutral complexes by using one or two reducing equivalents, respectively. Evaporation of the reaction mixture followed by extraction with a nonpolar solvent will normally result in facile separation of the desired product from that of the cationic starting material and cobaltocenium ion, especially if a slightly substoichiometric amount of [CoCp₂] is employed. This approach has succeeded

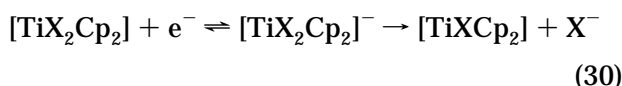
in the preparation of dirhenium complexes,^{406,407} $[M(\eta^4\text{-polymethylthiophene})\text{Cp}^*]$ ($M = \text{Rh, Ir}$),⁴⁰⁸ $[\text{Ru}(\eta^4\text{-Me}_4\text{thiophene})(\eta\text{-C}_6\text{Me}_6)]$,⁴⁰⁹ and $[\text{Ir}_4\text{S}_4\text{Cp}^*_4]$.⁴¹⁰ In the last two cases, the dications $[\text{Ru}(\eta^4\text{-Me}_4\text{thiophene})(\eta\text{-C}_6\text{Me}_6)]^{2+}$ and $[\text{Ir}_4\text{S}_4\text{Cp}^*_4]^{2+}$ underwent two separate one-electron reductions ($E^\circ = -1.0$ and -1.2 V for the Ru complex⁴⁰⁹ and -0.8 and -1.1 V for the Ir cluster⁴¹⁰); both second reduction potentials were sufficiently positive of that of $[\text{CoCp}_2]$ (*ca.* -1.3 V) to assure quantitative formation of the two-electron reduced products. In a related result that is somewhat surprising, the reduction of the trigonal bipyramidal cluster $[\text{Ir}_3\text{S}_2\text{Cp}^*_3]^{2+}$ proceeded to completion with 2 equiv of cobaltocene; the complex $[\text{Ir}_3\text{S}_2\text{Cp}^*_3]$ was isolated in 96% yield even though the formal potentials of the dication, -1.1 and -1.4 V, do not suggest that an equilibrium mixture would favor the neutral cluster.⁴¹⁰

A powerful application of cobaltocene is in the isolation of anions with $[\text{CoCp}_2]^+$ as the counteranion. The most common strategy is to mix solutions of $[\text{CoCp}_2]$ and the neutral substrate, A, in relatively nonpolar media and collect the resulting slightly soluble ET salt $[\text{A}][\text{CoCp}_2]$ (eq 29). This procedure



often results in analytically pure samples even though the anions might be quite air-sensitive.^{191,411–416} Among the anions isolated in this way are $[\text{MoCl}_2(\text{NO})(\eta\text{-C}_5\text{R}_5)]^-$ ($\text{R} = \text{H, Me}$),^{411,417} $[\text{Fe}_4(\text{CO})_{11}(\mu\text{-PR})_2]^-$,⁴¹² and an iron cluster anion $[\text{Fe}_4\text{S}_4(\text{NO})_4]^-$ ⁴¹⁸ (from THF), $[\text{VCl}_3\text{Cp}']^-$,⁴¹³ $[\text{TiCl}_3\text{Cp}]^-$,⁴¹⁴ $[\text{Co}(\text{S}_2\text{N}_2)\text{Cp}]^-$,⁴¹⁵ and a rhenium dinuclear anion¹⁹¹ (from CH_2Cl_2), $[\text{Re}_2\text{Me}_4\text{O}_2]^-$ ⁴¹⁹ (from pentane), Mo(V) polypyrazolylborates,⁴¹⁶ $[\text{TiCl}_2\text{Cp}_2]^-$,⁴²⁰ and $[\text{Co}(\text{CO})_4]^-$ ⁴²¹ (from benzene or toluene), and $[\text{V}(\text{CO})_6]^-$ (from diethyl ether).⁴²¹ In several cases involving cobaltocenium salts of metal carbonylates, strong ion pairing in the ET salts gives rise to unusual chemical and physical properties.^{421,422}

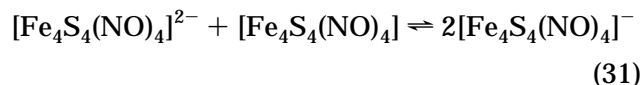
Discussion of two anions of the above group will serve to demonstrate the effectiveness of cobaltocene in isolating salts of unstable anions. The existence of the Ti(III) anions $[\text{TiX}_2\text{Cp}_2]^-$ ($\text{X} = \text{halide}$) had been the subject of debate, based on contrary views of electrochemical results which were ambiguous about halide dissociation from the primary monoanion (eq 30).⁴²³ The isolation of the Ti(III) dichloro and



dibromo derivatives $[\text{CoCp}_2][\text{TiX}_2\text{Cp}_2]$ from toluene proved the existence of the complex anions and allowed systematic studies of their solvolysis in THF. The dichloride proved to be stable in this medium, whereas the dibromide underwent loss of Br^- .⁴²⁰

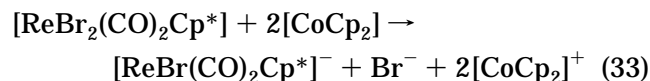
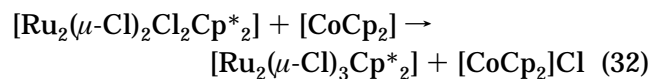
When THF solutions of the metal nitrosyl cluster $[\text{Fe}_4(\mu_3\text{-S})_4(\text{NO})_4]$ were put in contact with sodium amalgam for a few minutes, the secondary product $[\text{Fe}_4(\mu_3\text{-S})_3(\text{NO})_7]^-$ was formed and isolated as the $[\text{AsPh}_4]^+$ salt.⁴¹⁸ When 1 equiv of cobaltocene (or benzophenone anion)⁴²⁴ was used as reductant, the salt $[\text{CoCp}_2][\text{Fe}_4(\mu_3\text{-S})_4(\text{NO})_4]$ was isolated. The for-

mation of two different products is rationalized by the reported potentials of $[\text{Fe}_4\text{S}_4(\text{NO})_4]^z$; two reversible one-electron reductions were observed at *ca.* -0.3 and -1.1 V for the couples $[\text{Fe}_4\text{S}_4(\text{NO})_4]/[\text{Fe}_4\text{S}_4(\text{NO})_4]^-$ and $[\text{Fe}_4\text{S}_4(\text{NO})_4]^-/[\text{Fe}_4\text{S}_4(\text{NO})_4]^{2-}$, respectively. The potential of $[\text{CoCp}_2]$ is sufficiently negative to reduce the cluster to its dianion, but the comproportionation reaction of eq 31 would stop the reduction at the one-electron stage if one reducing equivalent is used.



The dianion, which is generated when the neutral complex is treated with excess reductant (as in the Na/Hg reduction), may, however, be subject to further reactions not apparent on the CV time scale. This is most likely why, under some conditions, the secondary product was formed in the sodium reduction.⁴²⁴

When inherently unstable anions are the redox product, the use of $[\text{CoCp}_2]$ as reductant does not alter the course of their decomposition, as apparent from several studies involving the loss of halide from the initial reduction product (see eqs 32⁴²⁵ and 33⁴²⁶):



A similar strategy has been employed to form metal carbonyls such as $[\text{Mn}_2(\text{CO})_{10}]$, $[\text{Fe}(\text{CO})_5]$, and $[\text{V}(\text{CO})_4(\text{dppe})]$ from halide-containing precursors.^{420,427}

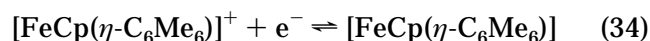
Recognizing that these halide-expulsion reactions are irreversible, it is relevant to mention an analogous study of the reduction of the metal alkylidene complex $[\text{Fe}\{\text{=CMe}(\text{OMe})\}(\text{CO})_2\text{Cp}^*]^+$ (irreversible reduction, $E_p = -1.8$ V in CH_2Cl_2).⁴²⁸ Although the reduction potential disfavors formation of the one-electron reduction product, treatment of the cation with a stoichiometric amount of $[\text{CoCp}_2]$ results in a quantitative yield of $[\text{Fe}(\text{COMe})(\text{CO})_2\text{Cp}^*]$; the same product is formed electrochemically. This is a clear example of irreversibility driving the electron-transfer process despite, in this case, an unfavorable difference of *ca.* 400 mV between E° of cobaltocene and E_p of the iron complex.⁴²⁸ A similar conclusion was drawn with regard to the reaction of $[\text{CoCp}_2]$ with $[\text{Mn}_2(\text{CO})_{10}]$, which gives $[\text{CoCp}_2][\text{Mn}(\text{CO})_5]$.⁴²²

In a few cases, the stronger reductant $[\text{CoCp}^*_2]$ has been used in place of cobaltocene. The permethylated derivative is more air-sensitive than $[\text{CoCp}_2]$, befitting its more negative (by *ca.* 600 mV) potential. Nevertheless, it is thermally stable, easily purified by vacuum sublimation,⁴²⁹ and shares most of the advantageous physical and spectroscopic properties enjoyed by its unsubstituted analogue. Solutions of $[\text{CoCp}^*_2]$ in ether solvents may be prepared for use as needed by reduction of $[\text{CoCp}^*_2]^+$ with alkali metal mirrors (and presumably other reducing agents), followed by filtration of the solution directly into a solution of the reducible substrate.⁴³⁰ $[\text{CoCp}^*_2]$ has

proved to be effective when $[\text{CoCp}_2]$ was too weak to bring about the desired electron-transfer reaction.^{427,430,431} When applied to fullerene reductions, $[\text{CoCp}_2]$ gives $[\text{C}_{60}]^-$ and $[\text{CoCp}^*_2]$ gives $[\text{C}_{60}]^{2-}$.⁴³²

In one of these studies,⁴³¹ precipitation of the salt $[\text{CoCp}^*_2][\text{A}]$ was the apparent driving force for the reaction since the potential for the one-electron reduction of $[\text{W}(\text{CO})_2(\text{NO})(\eta^5\text{-C}_5\text{HPh}_4)]$ (A, -2.2 V) is substantially negative of that of $[\text{CoCp}^*_2]$.

b. $[\text{Fe}(\eta\text{-C}_5\text{R}_5)(\eta\text{-C}_6\text{Me}_6)]$. The 19-electron complex $[\text{FeCp}(\eta\text{-C}_6\text{Me}_6)]$ shares many chemical and physical characteristics with other neutral metal sandwich complex reductants such as $[\text{CoCp}^*_2]$, with which it compares favorably in reducing strength ($E^\circ = -2.09$ V for eq 34). Thanks to the efforts of



Astruc and co-workers, this reagent has already received attention as a reductive trigger for catalytic and stoichiometric reactions. The reader is referred to the review literature for details.⁴³³

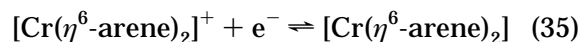
$[\text{FeCp}(\eta\text{-C}_6\text{Me}_6)]$ is prepared in high yield by the action of sodium amalgam on the corresponding 18-electron cation $[\text{FeCp}(\eta\text{-C}_6\text{Me}_6)]^+$ in glyme under argon.⁴³⁴ Although air-sensitive, the deep green compound is thermally stable and sublimates at 70°C at 2×10^{-4} mmHg. It is paramagnetic and displays proton NMR resonances at $+35.0$ ppm (Cp) and -2.15 ppm (CH_3) in toluene- d_8 . ESR-silent in fluid media, it displays a spectrum with a rhombic g -tensor ($g = 2.063, 2.000, 1.864$) at 77 K. It is easily weighed and handled in inert atmospheres, facilitating its stoichiometric use. It is soluble in pentane and other nonpolar solvents and is most often used in ethers. It decomposes in some polar organic solvents.⁴³⁵ The complex may be stored for lengthy periods under an inert atmosphere and re-sublimed as needed.

$[\text{FeCp}(\eta\text{-C}_6\text{Me}_6)]$ has been used to reduce metal sandwich complexes of Ni and Co for which $[\text{CoCp}_2]$ was inadequate.⁴⁰² For example, $[\text{Co}(\eta\text{-C}_4\text{Ph}_4)(\eta\text{-benzene})]^+$ shows a reversible one-electron reduction wave at -1.7 V followed by a second, irreversible, reduction at -2.2 V. Treatment of this cation with $[\text{FeCp}(\eta\text{-C}_6\text{Me}_6)]$ at low temperatures allowed the isolation of $[\text{Co}(\eta\text{-C}_4\text{Ph}_4)(\eta\text{-benzene})]$; with a stronger reductant (0.8% Na/Hg) the same cation gave $[\text{Co}(\eta^3\text{-C}_4\text{Ph}_4\text{H})(\eta\text{-benzene})]$. The latter is apparently formed when the transient anion $[\text{Co}(\eta\text{-C}_4\text{Ph}_4)(\eta\text{-benzene})]^-$ adds a proton from the solvent (THF) or trace water. $[\text{FeCp}(\eta\text{-C}_6\text{Me}_6)]$ has also been used to produce mono-, di-, or trianions of C_{60} by appropriate control of the reaction stoichiometry.⁴³⁶

$[\text{Fe}(\eta\text{-C}_5\text{R}_5)(\eta\text{-C}_6\text{Me}_6)]$ ($\text{R} = \text{H}$ or Me) have been employed in ET-catalyzed substitution reactions of fulvalene-bridged dinuclear complexes.⁴³⁷ For example, the metal-metal-bonded complex $[\text{Mo}_2(\text{CO})_6(\mu\text{-}\eta^5, \eta^5\text{-C}_{10}\text{H}_8)]$ ($E_p = ca. -1.3$ V, irreversible reduction)⁴³⁸ reacts with 0.1–0.2 equiv of $[\text{FeCp}(\eta\text{-C}_6\text{Me}_6)]$ in THF in the presence of PR_3 in $ca. 5$ min to give a complex in which two CO groups have been substituted by phosphines.⁴³⁷ The same reagent with $[\text{W}(\text{CO})_3\text{Ru}(\text{CO})_2(\mu\text{-}\eta^5, \eta^5\text{-C}_{10}\text{H}_8)]$ and PMe_3 gave the zwitterion $[\text{W}(\text{CO})_3\text{Ru}(\text{CO})_2(\text{PMe}_3)(\mu\text{-}\eta^5, \eta^5\text{-C}_{10}\text{H}_8)]$. However, treatment of either $[\text{W}(\text{CO})_3\text{Ru}(\text{CO})_2(\mu\text{-}$

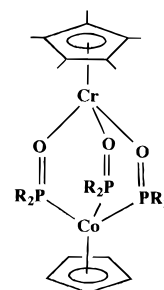
$\eta^5, \eta^5\text{-C}_{10}\text{H}_8)]$ or $[\text{W}(\text{CO})_3\text{Ru}(\text{CO})_2(\text{PMe}_3)(\mu\text{-}\eta^5, \eta^5\text{-C}_{10}\text{H}_8)]$ with $[\text{FeCp}^*(\eta\text{-C}_6\text{Me}_6)]$ gives $[\text{W}(\text{CO})_3\text{Ru}(\text{CO})(\text{PMe}_3)_2(\mu\text{-}\eta^5, \eta^5\text{-C}_{10}\text{H}_8)]$; the more negative E° value of $[\text{FeCp}^*(\eta\text{-C}_6\text{Me}_6)]$ (-2.30 V) triggers electron-transfer-catalyzed substitution of CO by PMe_3 . Although $[\text{FeCp}^*(\eta\text{-C}_6\text{Me}_6)]$ has been used less often than $[\text{FeCp}(\eta\text{-C}_6\text{Me}_6)]$ as a reductant, its very negative potential and its facile synthesis and purification⁴³⁹ make it an interesting target for further development.

c. Others. The sandwich complexes $[\text{Cr}(\eta^6\text{-arene})_2]$ form a class of potentially useful one-electron reducing agents (eq 35). The formal potential of the



parent complex (arene = benzene, $E^\circ = ca. -1.15$, Table 3) is only slightly positive of that of cobaltocene. A number of ring-substituted derivatives can be prepared.⁴⁴⁰ The potentials of $[\text{Cr}(\eta\text{-mesitylene})_2]$ ($E^\circ = -1.3$ V⁴⁴¹) and $[\text{Cr}(\eta\text{-dimethylamino}(\text{benzene}))_2]$ ($E^\circ = -1.5$ V⁴⁴²) show that the reductive power of the reagent is increased when electron-releasing groups are present. The reaction byproduct, $[\text{Cr}(\text{arene})_2]^+$, is ESR-active in both fluid and frozen media,⁴⁴³ in contrast to $[\text{CoCp}_2]^+$ and $[\text{CoCp}_2]$. $[\text{Cr}(\eta\text{-benzene})_2]$, which is commercially available, has been used to prepare metal carbonylates which display significant ion-pairing with $[\text{Cr}(\eta\text{-benzene})_2]^+$. For example, $[\text{Cr}(\eta\text{-benzene})_2]$ and $[\text{Co}_2(\text{CO})_8]$ in benzene give analytically pure $[\text{Cr}(\eta\text{-benzene})_2][\text{Co}(\text{CO})_4]$.⁴²¹

The binuclear complexes $[\text{Cp}^*\text{Cr}(\mu\text{-OPR}_2)_3\text{CoCp}]$ (**21**, $\text{R} = \text{OMe}$ or OEt) are strong reducing agents ($E^\circ = -2.0$ V), with attractive stability and solubility.⁴⁴⁴ Prepared from the corresponding monocations⁴⁴⁵ by Na/Hg reduction in ether solvents, the green neutral complexes ($\lambda_{\text{max}} = 643$ nm) are soluble in a range of solvents including hydrocarbons. Moreover, in spite of their negative potentials they are oxidized only slowly in air, even in solution. Koelle and co-workers have used these reagents to reduce a number of sandwich complexes, including $[\text{CoCp}_2]^+$ and $[\text{FeCp}(\eta\text{-C}_6\text{H}_6)]^+$.⁴⁴⁴ Further developments on the use and properties of these Cr(II) reagents are awaited.



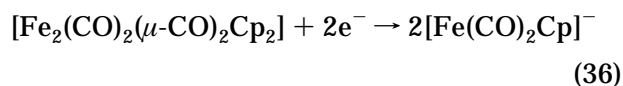
(21, $\text{R} = \text{OMe}$ or OEt)

Ferrocenium ions are common oxidants (section II.A.1.a.i), but the neutral ferrocenes $[\text{Fe}(\eta\text{-C}_5\text{R}_5)_2]$ ($\text{R} = \text{H}$, Me) may be useful as weak reducing agents. For example, the organoborane triple-decker sandwich complex $[\text{Ru}_2(\eta\text{-arene})_2(\text{Et}_2\text{C}_2\text{B}_3\text{H}_3)]$ ($E^\circ = -0.34$ V) was first oxidized with $[\text{FeCp}_2]^+$ ($E^\circ = 0.0$ V); the monocationic complex $[\text{Ru}_2(\eta\text{-arene})_2(\text{Et}_2\text{C}_2\text{B}_3\text{H}_3)]^+$ was spectroscopically characterized and then reduced

back to the neutral starting complex by $[\text{FeCp}^*{}_2]$ ($E^\circ = -0.59$ V). The byproduct of the decamethylferrocene reaction, $[\text{FeCp}^*{}_2]^+$, interferes ($\lambda_{\text{max}} = 780$ nm) in the optical spectrum of the final solution.⁴⁴⁶ Ferrocene was used to prepare $[\text{Rh}_2(\text{CO})(o\text{-O}_2\text{C}_6\text{Cl}_4)\text{-}(\text{bipy})(\mu\text{-RNNNR})_2]$ ($\text{R} = p\text{-tolyl}$) from the corresponding monocation ($E^\circ = +0.06$ V) when cobaltocene failed to give a pure product.⁴⁴⁷

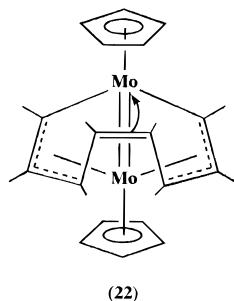
2. Metal Carbonylates

a. $[\text{Fe}(\text{CO})_2\text{Cp}]^-$. The dimer $[\text{Fe}_2(\text{CO})_2(\mu\text{-CO})_2\text{-Cp}_2]$ (Fp_2) and the monomeric anion $[\text{Fe}(\text{CO})_2\text{Cp}]^-$ (Fp^-) are related by a chemically reversible but electrochemically irreversible couple (eq 36):



The anion is a strong one-electron reductant, but it has not been widely used. An anodic wave was reported at $E_{1/2} = -1.74$ V in THF at a mercury electrode,⁴⁴⁸ but since the product of the oxidation was $[\text{Hg}\{\text{Fe}(\text{CO})_2\text{Cp}\}_2]$ this potential is only an approximation of that for the reaction in eq 36. Another estimate of the formal potential associated with eq 36 ($E^\circ = -1.84$ V) was obtained by means of elegant redox equilibration studies.⁴⁴⁹ A value of -1.8 V is used in Table 3. The diiron complex (Fp_2) in eq 36 undergoes an irreversible reduction at *ca.* -2.0 V.^{448,450}

Solutions of Fp^- are prepared by reacting Fp_2 with strong reducing agents such as M/Hg or Na/K in ethers⁴⁵¹ (Fp^- reacts rapidly with alkyl halides and other electrophiles^{452,453}). Its solutions have been used *in situ* to reduce 18-electron cationic Mo(II) alkyne complexes, thereby initiating ligand coupling reactions. Typically, equimolar Fp^- (as an amber-red THF solution of the sodium salt) was stirred with $[\text{Mo}(\text{NCMe})(\eta\text{-alkyne})_2\text{Cp}]^+$ ($E^\circ = -1.96$ V, alkyne = MeC_2Me ⁴⁵⁴) to produce dinuclear metallacyclononatetraene complexes such as **22**.⁴⁵⁵ The redox byproduct, Fp_2 , was separated from the reaction mixture by column chromatography.



One reason for exploring Fp^- more fully for ET reactions is that it is a strong reducing agent which yields a neutral byproduct (Fp_2). This may have advantages in workup procedures and in the choice of counterion available to the target reduction product (if the latter is an anion). Concerning the latter

advantage, several salts $[\text{C}][\text{Fp}]$ (including $\text{C} = \text{Li}$, Na , K , and NBu_4) have been isolated which might facilitate the stoichiometric use of this reagent.^{456,457} Another possible advantage is that both the reagent and its byproduct are diamagnetic, eliminating ESR spectroscopic interference from consideration. However, IR spectroscopic studies should anticipate the carbonyl absorptions of both Fp_2 (2000, 1950, 1800, and 1780 cm^{-1} ⁴⁵⁸) and Fp^- (1865, 1788 cm^{-1} , $[\text{NBu}_4]^+$ salt, in THF⁴⁵⁷).

b. Others. Other metal carbonyl anions, *e.g.*, $[\text{Mn}(\text{CO})_{5-x}\text{L}_x]^-$ ($\text{L} =$ phosphine or phosphite) might offer similar properties as reductants. The formal potentials of the anions decrease from *ca.* -0.5 V ($x = 0$) to -1.8 V [$x = 2$, $\text{L} = \text{P}(\text{alkyl})_3$].⁴⁵⁹ The alkali metal salts $\text{M}[\text{Mn}(\text{CO})_{5-x}\text{L}_x]$, readily prepared by the reaction of $[\text{MnBr}(\text{CO})_{5-x}\text{L}]$ with M/Hg, vary in their solubilities in organic solvents;⁴⁶⁰ $[\text{PPN}][\text{Mn}(\text{CO})_5]$ is soluble in dichloromethane.⁴⁶¹

IV. Conclusions

While studies of the redox activity of organometallic complexes have blossomed in the last two decades, much of the work involving chemical (rather than electrochemical) activation has relied on the use of relatively few, tried and trusted, reagents such as the silver(I), nitrosonium, and ferrocenium cations as oxidants and sodium amalgam, cobaltocene, and metal naphthalenides as reductants.

One aim of this review is to show how such popular redox reagents can be used most effectively. However, it is clear that a wider armory of oxidants and reductants will become necessary as the applications of "organometallic electrochemistry", for example, in directed organic synthesis and catalysis, become more sophisticated. We hope, therefore, that this review will also encourage the use of redox reagents less well known to the inorganic chemistry community. Such reagents include those which are more widely used by organic chemists, for example, the arylaminium cations and the thianthrene radical cation, and others which are far from exotic but virtually ignored. Thus, simple changes to well-tried species can bring great synthetic advantages. For example, if the ferrocenium ion appears to be the most attractive reagent from the viewpoint of reaction workup, but happens to be a slightly weaker oxidant than required, the acetylferrocenium ion may prove to be ideal. Equally, $[\text{CPh}_2(\text{C}_6\text{H}_4\text{OMe-4})]^+$ is a simple derivative of the trityl cation but is considerably more stable and easy to handle.

In order to aid systematic choice we also have provided a "ranking" of reagent strengths according to formal potentials. These potentials were gathered from many sources, and the original data were reported under quite varied experimental conditions. Some errors in our conversion to the ferrocene scale may therefore be anticipated. We emphasize that such difficulties can be avoided in the future if workers always report the potential of the ferrocene/ferrocenium couple (or of another suitable *internal* standard) under their experimental conditions.

V. Appendix: Syntheses of Ferrocenium and Diazonium Salts

A. Ferrocenium Salts

1. Method i. Ferrocenium Tetrafluoroborate, [FeCp₂][BF₄]

To a stirred solution of *p*-benzoquinone (0.70 g, 6.5 mmol) in diethyl ether (20 mL) at room temperature was added HBF₄·OEt₂ (54% in diethyl ether; 3.7 mL, 26.9 mmol). On adding a solution of [FeCp₂] (2.39 g, 12.85 mmol) in diethyl ether (40 mL), a blue solid was immediately precipitated. After the mixture was stirred for 10 min and then allowed to stand for a further 10 min, the blue solid was removed by filtration, washed with diethyl ether (2 × 10 mL), and dried in air. The crude product (yield 3.16 g) was purified by dissolution in acetone (100 mL), filtration, and precipitation by addition of diethyl ether (150 mL) to give a fine blue powder, yield 2.49 g (71%). Anal. Calcd for C₁₀H₁₀FeBF₄: C, 44.0; H, 3.7. Found: C, 44.4; H, 3.7. (The elemental analysis was unchanged on storing the solid in air for 3 months.)

2. Method ii. Ferrocenium Hexafluorophosphate, [FeCp₂][PF₆]

To a stirred solution of [FeCp₂] (5.0 g, 26.9 mmol) in a mixture of water (100 mL) and acetone (40 mL) at room temperature was added anhydrous FeCl₃ (5.9 g, 36.0 mmol). After 15 min the deep blue solution was filtered through Celite and then [NH₄][PF₆] (5.8 g, 35.6 mmol) was added. After 5 min, ethanol (50 mL) was added to aid precipitation of the blue solid which was then removed by filtration (5.6 g). A further 2.4 g of product was obtained from the mother liquors by reduction of the volume of the solvent to ca. 100 mL and then addition of ethanol (50 mL). The two fractions were combined, dissolved in acetone (100 mL), treated with ethanol (200 mL), and cooled to -10 °C for 1 h to give dark blue crystals, yield 5.1 g (57%). Anal. Calcd for C₁₀H₁₀FePF₆: C, 36.3; H, 3.0. Found: C, 36.3; H, 3.1. (The elemental analysis was unchanged on storing the solid in air for 3 months.)

3. Method iii. Acetylferrocenium Tetrafluoroborate, [Fe(η-C₅H₄COMe)Cp][BF₄]

To a stirred solution of [Fe(η-C₅H₄COMe)Cp] (0.39 g, 1.71 mmol) in diethyl ether (150 mL) at room temperature was added solid AgBF₄ (0.32 g, 1.61 mmol). After 0.5 h the blue-green reaction mixture was evaporated to dryness *in vacuo*, and the residue was extracted into CH₂Cl₂ (100 mL). After filtration through Celite, the volume of the dark blue extract was reduced *in vacuo* to ca. 5 mL and diethyl ether (100 mL) was added. The dark blue/green precipitate was then further purified from CH₂Cl₂/diethyl ether to give dark blue microcrystals, yield 0.28 g (51%). Anal. Calcd for C₁₂H₁₂FeBF₄O: C, 45.8; H, 3.8. Found: C, 45.4; H, 3.9.

B. 4-Fluorobenzenediazonium Hexafluorophosphate, [N₂C₆H₄F-4][PF₆]

To a solution of 4-FC₆H₄NH₂ (5.0 mL, 52.7 mmol) in distilled water (15 mL) at 0 °C was added freshly

purchased HPF₆ [25 g (15.1 mL of a 65% solution in water), 111.3 mmol]. To this solution was added dropwise over 1 h a solution of NaNO₂ (3.0 g, 56.6 mmol) in distilled water (20 mL) cooled to ca. 10 °C. After the mixture was stirred for a further 30 min, the off-white precipitate was removed by filtration, washed sequentially with water, ethanol, and diethyl ether (ca. 50 mL of each), and dried in air to give 8.6 g of the crude product. The solid was recrystallized from acetone/ethanol to give white crystals, yield 8.0 g (57%). Anal. Calcd for C₆H₄N₂PF₇: C, 26.9; H, 1.5; N, 10.5. Found: C, 26.8; H, 1.4; N, 10.3. (The elemental analysis was unchanged on storing the solid at -10 °C, under N₂, for 3 months.)

VI. List of Abbreviations

| | |
|--------------------|--|
| bipy | 2,2'-bipyridyl |
| BPA | benzophenone radical anion |
| Bz | benzyl |
| chpt | cycloheptatriene |
| cot | cyclooctatetraene |
| Cp | η ⁵ -C ₅ H ₅ |
| Cp' | η ⁵ -C ₅ H ₄ Me |
| Cp* | η ⁵ -C ₅ Me ₅ |
| CPE | controlled potential electrolysis |
| CV | cyclic voltammetry |
| DDQ | 2,3-dichloro-5,6-dicyanoquinone |
| detc | [S ₂ CNEt ₂] ⁻ |
| DMF | dimethylformamide |
| dmpe | 1,2-bis(dimethylphosphino)ethane |
| DMSO | dimethyl sulfoxide |
| dppm | bis(diphenylphosphino)methane |
| dppe | 1,2-bis(diphenylphosphino)ethane |
| HMPA | hexamethylphosphoramide |
| Mes | mesityl |
| NAP | naphthalene |
| np ₃ | tris(2-(diphenylphosphino)ethyl)amine |
| PC | phthalocyanin |
| phen | 1,10-phenanthroline |
| pp ₃ | tris(2-(diphenylphosphino)ethyl)phosphine |
| pyr | pyridine |
| TCNE | tetracyanoethylene |
| TCNQ | 7,7,8,8-tetracyanoquinodimethane |
| Tf | triflate, [CF ₃ SO ₃] ⁻ |
| tfd | [S ₂ C ₂ (CF ₃) ₂] ²⁻ |
| THF | tetrahydrofuran |
| Tp | [BH(pyrazolyl) ₃] ⁻ |
| Tp' | [BH(3,5-dimethylpyrazolyl) ₃] ⁻ |
| H ₂ TPP | tetraphenylporphyrin |

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