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# Synthetic Applications of Organotransition-metal Redox Reactions

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## 1 Introduction

The importance of electron-transfer reactions in organotransition-metal chemistry has only been fully recognized in the past few years despite the discovery[1] of the ferrocene–ferrocenium couple as early as 1952. There are several major reasons for this recognition. First, there are now excellent examples of the redox activation of metal or ligand centres leading to the synthesis of otherwise inaccessible species. Such syntheses, for example of metal carbonyl cluster derivatives *via* electron transfer catalysis,[2] are often fast, efficient, and stereo- or regioselective. Second, detailed mechanistic studies[3] have shown that 17- and 19-electron compounds play important roles in a wide range of organometallic reactions; single-electron transfer to or from diamagnetic precursors provides a major route to such radicals. Third, the electronic structures of important classes of complex can be probed by *X*-ray structural studies of redox-related pairs of complexes, an approach pioneered by L. F. Dahl[4] for compounds with metal–metal bonds.

Many of these topics have been recently described in general reviews[5] of organometallic electrochemistry or in more specific accounts of electron-transfer catalysis,[2,6] redox-induced structural changes,[7] areneiron complexes as electron reservoirs,[8] the coordination chemistry of anion radicals,[9] and electrochemical techniques of particular use to the synthetic chemist.[10] However, the synthetic applications of redox-active organometallics have not been specifically reviewed.

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[1] J. A. Page and G. Wilkinson, *J. Am. Chem. Soc.*, 1952, **74**, 6149.

[2] D. Astruc, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 643; and references therein.

[3] D. R. Tyler, *Progr. Inorg. Chem.*, 1988, **36**, 125.

[4] K. A. Kubat-Martin, M. E. Barr, B. Spencer, and L. F. Dahl, *Organometallics*, 1987, **6**, 2570; K. A. Kubat-Martin, B. Spencer, and L. F. Dahl, *Organometallics*, 1987, **6**, 2580; and references therein.

[5] N. G. Connelly and W. E. Geiger, *Adv. Organomet. Chem.*, 1984, **23**, 1; W. E. Geiger and N. G. Connelly, *Adv. Organomet. Chem.*, 1985, **24**, 87; J. C. Kotz, in 'Topics in Organic Electrochemistry', Plenum Press, 1986; J. K. Kochi, *J. Organomet. Chem.*, 1986, **300**, 139; P. Lemoine, *Coord. Chem. Rev.*, 1988, **83**, 169; C. J. Pickett, in 'Electrochemistry', A Specialist Periodical Report, ed. D. Pletcher, The Royal Society of Chemistry, Vol. 8, p. 81, 1983 and Vol. 9, p. 162, 1984.

[6] M. Chanon, *Acc. Chem. Res.*, 1987, **20**, 214.

[7] W. E. Geiger, *Progr. Inorg. Chem.*, 1985, **33**, 275.

[8] M. Lacoste, M. H. Desbois, and D. Astruc, *New J. Chem.*, 1987, **11**, 561; D. Astruc, *Acc. Chem. Res.*, 1986, **19**, 377.

[9] W. Kaim, *Coord. Chem. Rev.*, 1987, **76**, 187.

[10] W. E. Geiger, in 'Inorganic Reactions and Methods', Vol. 15, ed. J. J. Zuckermann, Verlag Chemie, 1986, p. 110; W. E. Geiger and M. D. Hawley, in 'Physical Methods of Chemistry', Vol. 2, ed. R. W. Rossiter, J. Wiley and Sons, 1986, Chapter 1.

It is the aim of this article, therefore, to redress this imbalance. Most of the examples given are from the author's own work but key references are provided to lead the reader into related areas of interest.

Our entry into the area of organometallic electrochemistry effectively began in the early 1970s with the unexpected synthesis[11] of the stable, paramagnetic alkyne complex $[Cr(CO)_2(\eta\text{-}PhC{\equiv}CPh)(\eta\text{-}C_6Me_6)][PF_6]$ from $[NO][PF_6]$ and $[Cr(CO)_2(\eta\text{-}PhC{\equiv}CPh)(\eta\text{-}C_6Me_6)]$ (rather than the diamagnetic nitrosyl $[Cr(CO)(NO)(\eta\text{-}PhC{\equiv}CPh)(\eta\text{-}C_6Me_6)]^+$); the isolation of salts of other radical cations such as $[Cr(CO)_2(PPh_3)(\eta\text{-}C_6Me_6)]^+$,[12] $[V(CO)_3(PPh_3)Cp]^+$ ($Cp = \eta^5\text{-}C_5H_5$),[13] $[Mn(CO)(dppe)Cp]^+$ ($dppe = Ph_2PCH_2CH_2PPh_2$),[14] and $[Fe(CO)\{P(OMe)_3\}_2(\eta\text{-}C_4Ph_4)]^+$ ($C_4Ph_4$ = tetraphenylcyclobutadiene)[15] soon followed. These particular complexes were somewhat disappointing in showing little enhanced reactivity towards nucleophiles or radicals. However, they helped to show that 17-electron cations could be widely anticipated in organometallic chemistry, and the methods developed for their synthesis and isolation provided the experimental basis for all of our subsequent studies, some of which are featured in Sections 2—6 below.

## 2 The Complex Chemistry of the 17-Electron Cation *trans*-$[Fe(CO)_3(PPh_3)_2]^+$

The chemistry of *trans*-$[Fe(CO)_3(PPh_3)_2]^+$ ($1^+$) provides a simple but effective example of the activation of a metal carbonyl complex by one-electron oxidation. Prepared[16] as a green, crystalline $[PF_6]^-$ salt from *trans*-$[Fe(CO)_3(PPh_3)_2]$ (1) and $AgPF_6$, ($1^+$) contrasts with the 17-electron cations noted in Section 1 in being the precursor[16,17] to a wide range of other carbonyl derivatives (Scheme 1). The reaction with $NO_2$ is particularly noteworthy in giving $[Fe(CO)_2(NO)(PPh_3)_2]^+$ *via* the intramolecular linking of coordinated CO and $NO_2$ and the elimination of $CO_2$.

The reactions of ($1^+$) with iodide and iodine, coupled with kinetic studies using stopped flow i.r. spectroscopy, implicate the radical cation in the oxidative elimination[16] of (1) with $I_2$ to give $[FeI_2(CO)_3(PPh_3)]$ (Scheme 2). In addition, the route by which two equivalents of ($1^+$) and one of $I^-$ yield (1) and $[FeI(CO)_3(PPh_3)_2]^+$ [*i.e.* steps (iii) plus (iv) in Scheme 2] is also followed with other diamagnetic reactants. Thus, $[S_2CNMe_2]^-$ and the adduct $CS_2{\cdot}PPh_3$ give the iron(II) dicarbonyls $[Fe(CO)_2(S\text{–}S)(PPh_3)_2]^Z$ ($S\text{–}S = S_2CNMe_2$, $Z = 1$; $S\text{–}S = S_2CPPh_3$, $Z = 2$)[17] respectively.

The cyclic voltammogram of $[Fe(CO)_3(AsPh_3)_2]$ (2) is notably different from that of (1) in showing a completely irreversible oxidation wave in $CH_2Cl_2$. Despite the obvious instability of the cation ($2^+$) its e.s.r. spectrum is readily

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[11] N. G. Connelly and G. A. Johnson, *J. Organomet. Chem.*, 1974, **77**, 341.

[12] N. G. Connelly, Z. Demidowicz, and R. L. Kelly, *J. Chem. Soc., Dalton Trans.*, 1975, 2335.

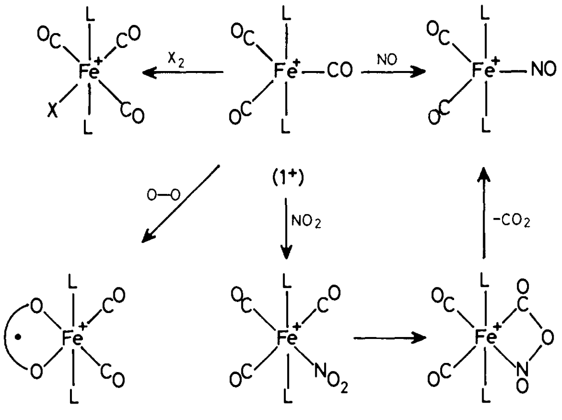
[13] N. G. Connelly and M. D. Kitchen, *J. Chem. Soc., Dalton Trans.*, 1976, 2165.

[14] N. G. Connelly and M. D. Kitchen, *J. Chem. Soc., Dalton Trans.*, 1977, 931.

[15] N. G. Connelly, R. L. Kelly, and M. W. Whiteley, *J. Chem. Soc., Dalton Trans.*, 1981, 34.

[16] P. K. Baker, N. G. Connelly, B. M. R. Jones, J. P. Maher, and K. R. Somers, *J. Chem. Soc., Dalton Trans.*, 1980, 579.

[17] P. K. Baker, K. Broadley, and N. G. Connelly, *J. Chem. Soc., Dalton Trans.*, 1982, 471.



L = PPh₃, X₂ = halogen, O—O = 1,2 diketone

**Scheme 1**

$$[Fe(CO)_3L_2] + I_2 \longrightarrow [Fe(CO)_3L_2]^+ + I\cdot + I^- \qquad (i)$$

$$[Fe(CO)_3L_2] + I\cdot \longrightarrow [Fe(CO)_3L_2]^+ + I^- \qquad (ii)$$

$$[Fe(CO)_3L_2]^+ + I^- \longrightarrow [FeI(CO)_3L_2] \qquad (iii)$$

$$[Fe(CO)_3L_2]^+ + [FeI(CO)_3L_2] \longrightarrow [Fe(CO)_3L_2] + [FeI(CO)_3L_2]^+ \qquad (iv)$$

$$[FeI(CO)_3L_2]^+ + I^- \longrightarrow [FeI_2(CO)_3L] + L \qquad (v)$$

$$L = PPh_3$$

**Scheme 2**

detected when $AgPF_6$ is added to (2) in $CH_2Cl_2$, even at room temperature. Here, the silver(I) ion most probably acts as a 'non-innocent' oxidant, giving the diamagnetic adduct $[Ag\{Fe(CO)_3(AsPh_3)_2\}_2]^+$ (*cf.* $[Ag\{Rh(CO)(PPh_3)Cp\}_2]^+$, Section 3C) which slowly dissociates to give a steady-state concentration of ($2^+$), together with silver metal and (2). The 'non-innocence' of chemical oxidants and reductants is a recurrent theme throughout organometallic electrochemistry and the possibility of reactions which compete with the desired redox process (*e.g.* adduct formation, substitution, *etc.*) should always be borne in mind.

The stable and readily accessible cation ($1^+$) has also lent itself to detailed spectroscopic[18] and electrochemical studies[19,20] which have confirmed the proposed[16] structure and provided evidence that the substitution reactions of 17-electron cations generally occur *via* associative pathways.

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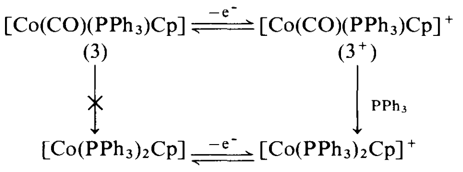
[18] M. J. Therien and W. C. Trogler, *J. Am. Chem. Soc.*, 1986, **108**, 3697.

[19] R. N. Bagchi, A. M. Bond, C. L. Heggie, T. L. Henderson, E. Mocellin, and R. A. Seikel, *Inorg. Chem.*, 1983, **22**, 3007.

[20] M. J. Therien, C.-L. Ni, F. C. Anson, J. G. Osteryoung, and W. C. Trogler, *J. Am. Chem. Soc.*, 1986, **108**, 4037.



**Scheme 3**

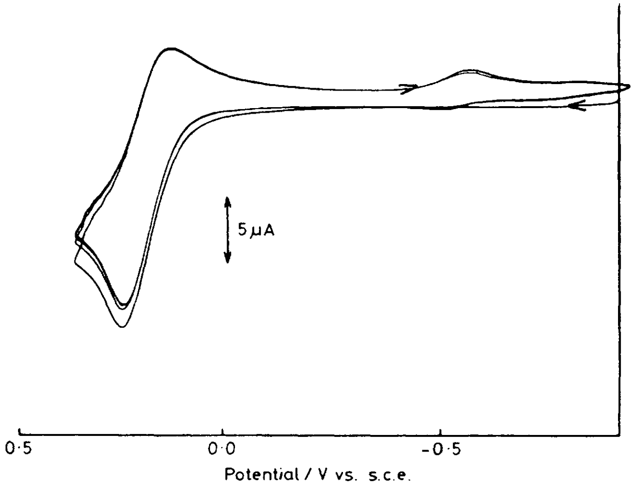


**Figure 1** *Multiple-scan cyclic voltammogram of* [Co(CO)(PPh$_3$)Cp] (3) *in the presence of* PPh$_3$ *in thf*
(Reproduced from *J. Chem. Soc., Dalton Trans.*, 1983, 121)

## 3 The Redox Chemistry of [M(CO)$_2$(η-C$_5$R$_5$)] Derivatives (M = Co or Rh; R = H, Me, or Ph): Synthetic and Structural Consequences

**A. Introduction.**—Although the chemistry of (1$^+$) (Section 2) provides an excellent example of the oxidative activation of a metal carbonyl, the compounds [M(CO)$_{2-n}$L$_n$(η-C$_5$R$_5$)] (M = Co or Rh; L = P- or As-donor; *n* = 0—2; R = H, Me, or Ph), which are isoelectronic with (1), are more versatile in showing that the variation of M, L, *n*, and R can drastically affect the reactivity of the 17-electron cations [M(CO)$_{2-n}$L$_n$(η-C$_5$R$_5$)]$^+$. There are also added bonuses with this set of complexes in that [M(CO)$_2$(η-C$_5$R$_5$)] can be reduced to 19-electron radical anions, and *X*-ray and e.s.r. spectroscopic studies provide a detailed picture of the bonding in the three-membered electron-transfer series [M(CO)$_{2-n}$-L$_n$(η-C$_5$R$_5$)]$^Z$ ($Z$ = 1, 0, and −1).

**B. Cobalt Complexes.**—The oxidative electrochemistry of [M(CO)$_2$(η-C$_5$R$_5$)] (M = Co or Rh, R = H or Me) in CH$_2$Cl$_2$ is complex and depends on the electrode material (Pt or Hg); only in the case of [Co(CO)$_2$(η-C$_5$Me$_5$)]$^+$ is the primary redox product stable enough (at −20 °C) to be detected by e.s.r. spectroscopy.[21] However, the monocarbonyl [Co(CO)($PCy_3$)Cp] (Cy = cyclohexyl) is reversibly oxidized at room temperature and [$FeCp_2$][$PF_6$] gives the stable, green crystalline salt [Co(CO)($PCy_3$)Cp][$PF_6$] whose reactions with halogens, 1,2-diketones, and nitric oxide parallel those of ($1^+$) (Scheme 1).

By contrast, the chemical oxidation of [Co(CO)($PPh_3$)Cp] (3) gives the carbonyl substitution product $[Co(PPh_3)_2Cp]^+$, yields of which are nearly quantitative in the presence of added $PPh_3$. The mechanism of this reaction (Scheme 3) is revealed by the multiple scan cyclic voltammogram (Figure 1) of (3). On the first sweep, a partially reversible oxidation wave is observed at 0.25 V† coupled with a product wave which subsequent sweeps show to be reversible ($E^0 = -0.51$ V). The latter corresponds to the reduction of $[Co(PPh_3)_2Cp]^+$ so that initial one-electron oxidation of (3) to ($3^+$) is followed by rapid substitution to give the bis(phosphine) cation.

The dicarbonyls [$Co(CO)_2(\eta$-$C_5R_5I)$] (R = H or Me) react only very slowly with $PPh_3$ at room temperature, but in the presence of $[FeCp_2]^+$ rapid oxidative substitution again occurs giving $[Co(PPh_3)_2Cp]^+$ and $[Co(CO)(PPh_3)(\eta\text{-}C_5Me_5)]^+$. In all of these reactions, substitution is facilitated by the positive charge generated by one-electron oxidation. This charge not only renders the metal centre more susceptible to nucleophilic attack but also reduces π-back donation to the π*(CO) orbitals, thereby weakening the Co–CO bond.[22]

The oxidative chemistry described above provides not only a synthetic route to new compounds but also evidence to support molecular orbital (m.o.) schemes for the ring–metal bonding in $[M(CO)_2(\eta\text{-}C_5R_5)]$[23] and for the π-bonding of phosphine ligands to transition metals.[24]

*X*-Ray structural studies[25] by McKinney and co-workers on the redox-related pair $[Co(PEt_3)_2Cp]^Z$ ($Z = 0$ or 1) show that the $C_5H_5$ ligand is $\eta^2,\eta^3$-bound to the metal ('allyl-ene' bonding) in the neutral complex (Figure 2a) but more symmetrically bonded (*i.e.* closer to $\eta^5$-$C_5H_5$) in the cation. Just such a structural change is expected on the basis of m.o. calculations[23] which show that the highest occupied molecular orbital (h.o.m.o.) for the neutral complex involves overlap of the $e_1{}^+$ ring orbital (Figure 2b) with the metal $d_{xz}$ orbital. One-electron oxidation results in partial loss of anti-bonding character in bonds C(2)–C(3) and C(4)–C(5), loss of bonding character in bonds C(1)–C(2), C(3)–C(4), and C(1)–C(5), and, therefore, in a more symmetrical ring.

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† Unless stated otherwise, all potential data quoted in this review are relative to the saturated calomel electrode and are taken from cyclic voltammetric measurements at a platinum bead electrode in $CH_2Cl_2$ containing $[NBu^n_4][PF_6]$ as base electrolyte. Under these conditions, the $E^\circ$ value for the ferrocene–ferrocenium couple is 0.47 V. For reversible processes, $E^0$ values {taken as $[(Ep)_{ox} + (Ep)_{red}]/2$} are given; for irreversible processes the oxidation peak potential, $(Ep)_{ox}$, or reduction peak potential, $(Ep)_{red}$, at a scan rate of 200 mV $s^{-1}$, are given.

[21] T. Gennett, E. Grzeszczyk, A. Jefferson, and K. M. Sidur, *Inorg. Chem.*, 1987, **26**, 1856.

[22] K. Broadley, N. G. Connelly, and W. E. Geiger, *J. Chem. Soc., Dalton Trans.*, 1983, 121.

[23] L. R. Byers and L. F. Dahl, *Inorg. Chem.*, 1980, **19**, 277; D. L. Lichtenberger, C. H. Blevins, II, and R. B. Ortega, *Organometallics*, 1984, **3**, 1614.

[24] D. S. Marynick, *J. Am. Chem. Soc.*, 1984, **106**, 4064.

[25] R. L. Harlow, R. J. McKinney, and J. F. Whitney, *Organometallics*, 1983, **2**, 1839.

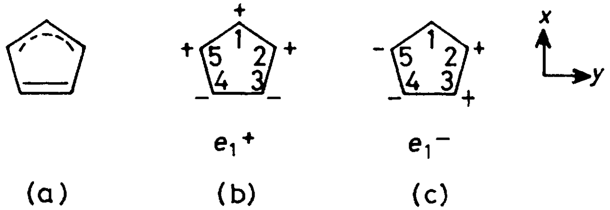

**Figure 2** *(a) The 'allyl-ene' bonding mode for the cyclopentadienyl ligand, and (b) and (c) the* $e_1^+$ *and* $e_1^-$ *ring orbitals involved in the bonding of the ring to the metal in* [M(CO)$_2$(C$_5$R$_5$)] *complexes*

Further inspection[26] of McKinney's structural data showed that oxidation is also accompanied by a shortening of the P–C$_2$H$_5$ bonds, from 1.846(3) to 1.829(3) Å. Again, the change supports m.o. calculations[24] which suggest that the $\pi$-acceptor orbital of a phosphine ligand, PX$_3$, is a hybrid of P 3*d* and P–X $\sigma^*$ components (rather than simply the P 3*d* orbital which was often held to be too high in energy to participate in $\pi$-bonding). Thus, decreased back-bonding in the cation results in depopulation of the P–X $\sigma^*$ orbital.

The reductive electrochemistry of [Co(CO)$_2$($\eta$-C$_5$R$_5$)] is not as extensive as that based on oxidation but nevertheless also leads to insight into bonding. The cyclic voltammogram of [Co(CO)$_2$Cp] shows an irreversible reduction wave, and reaction of the dicarbonyl with sodium amalgam gives the paramagnetic anion [{Co(CO)Cp}$_2$]$^-$.[27] By contrast, the C$_5$Ph$_5$ analogue is reversibly reduced and the mononuclear, 19-electron anion [Co(CO)$_2$($\eta$-C$_5$Ph$_5$)]$^-$ is readily produced at room temperature either electrolytically or chemically using sodium naphthalenide; the thermal stability of this anion probably derives from the sheer bulk of the C$_5$Ph$_5$ ring (cone angle *ca.* 203°).

An analysis of the frozen solution e.s.r. spectrum[28] of [Co(CO)$_2$($\eta$-C$_5$Ph$_5$)]$^-$ showed that the C$_5$-ring is again symmetrically bound to the cobalt atom (*cf.* [Co(PEt$_3$)$_2$Cp]$^+$), and this result is also compatible with the m.o. bonding scheme for [M(CO)$_2$($\eta$-C$_5$R$_5$)] (M = Co or Rh).[23] The l.u.m.o. of the neutral dicarbonyl involves overlap between the $e_1^-$ ring orbital (Figure 2c) and the metal *dyz* orbital. Thus, half population of this l.u.m.o., *via* one-electron reduction, leads to a shortening of bonds C(2)–C(3) and C(4)–C(5) and thence to a more symmetrical C$_5$-ring.

**C. Rhodium Complexes.**—The cyclic voltammogram of [Rh(CO)(PPh$_3$)Cp] (Figure 3) is very different from that of the cobalt analogue (3) in showing[29] an irreversible oxidation wave at *ca.* 0.45 V coupled with a reversible product wave centred at 0.05 V. Thus, it is unsurprising that the chemical oxidation of

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[26] A. G. Orpen and N. G. Connelly, *J. Chem. Soc., Chem. Commun.*, 1985, 1310.

[27] N. E. Shore, C. S. Ilenda, and R. G. Bergman, *J. Am. Chem. Soc.*, 1977, **99**, 1781.

[28] N. G. Connelly, W. E. Geiger, G. A. Lane, S. J. Raven, and P. H. Rieger, *J. Am. Chem. Soc.*, 1986, **108**, 6219.

[29] N. G. Connelly, A. R. Lucy, J. D. Payne, A. M. R. Galas, and W. E. Geiger, *J. Chem. Soc., Dalton Trans.*, 1983, 1879.

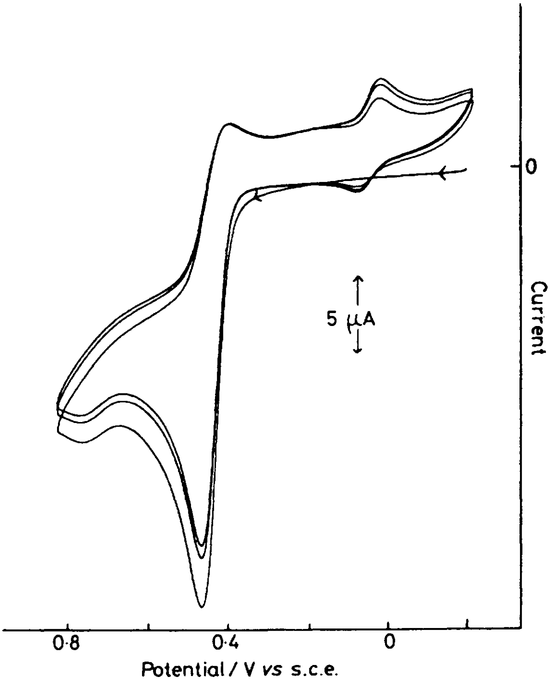

**Figure 3** *Multiple-scan cyclic voltammogram of* [Rh(CO)(PPh$_3$)Cp] *in* CH$_2$Cl$_2$
(Reproduced from *J. Chem. Soc., Dalton Trans.*, 1983, 1879)

[Rh(CO)(PPh$_3$)Cp], with [FeCp$_2$]$^+$ or [N$_2$C$_6$H$_4$F-*p*]$^+$, does not lead to the isolation of the radical cation [Rh(CO)(PPh$_3$)Cp]$^+$ but rather to a secondary product, namely the dicationic fulvalene complex [Rh$_2$(CO)$_2$(PPh$_3$)$_2$($\eta^5$:$\eta'^5$-C$_{10}$H$_8$)]$^{2+}$ [(4) Scheme 4]. The latter is easily reduced, by sodium amalgam or electrolytically, to [Rh$_2$(CO)$_2$(PPh$_3$)$_2$($\eta^5$:$\eta'^5$-C$_{10}$H$_8$)] (5), and both (4) and (5) have been structurally characterized[30] (Figure 4). Compound (4) has the metal–metal bond required to account for the observed diamagnetism, but it is long [2.930(2) Å] and the strain in the structure is also reflected in the bending and twisting of the C$_{10}$H$_8$ bridge. By contrast, the two Rh(CO)(PPh$_3$) groups of (5) are *trans*-disposed with respect to a planar fulvalene ligand.

Both (4) and (5) show one reversible wave in their cyclic voltammogram (the dication is reduced and the neutral molecule is oxidized) at a potential (0.05 V) identical to that of the product wave in Figure 3. The peak separation of 38 mV observed for this wave was thought[30] to indicate simultaneous one-electron transfer at two non-interacting metal centres and to be incompatible with the structural differences between (4) and (5). However, this interpretation was erroneous and the electrochemical data are consistent with an ECE process (E =

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[30] M. J. Freeman, A. G. Orpen, N. G. Connelly, I. Manners, and S. J. Raven, *J. Chem. Soc., Dalton Trans.*, 1985, 2283.

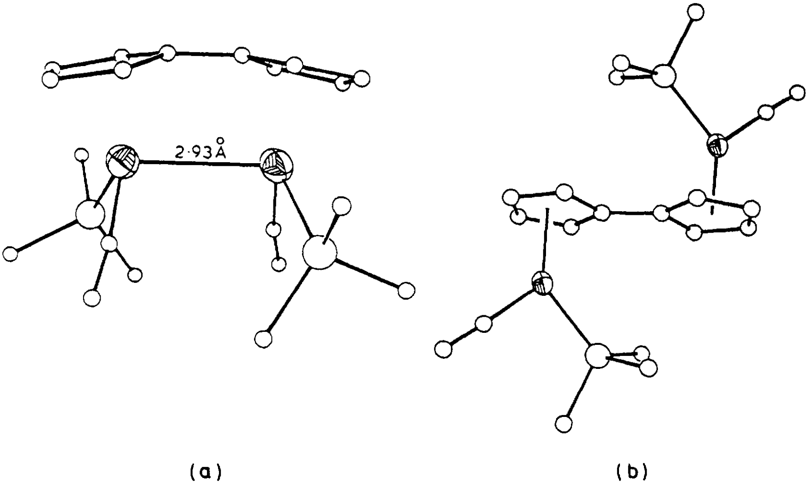
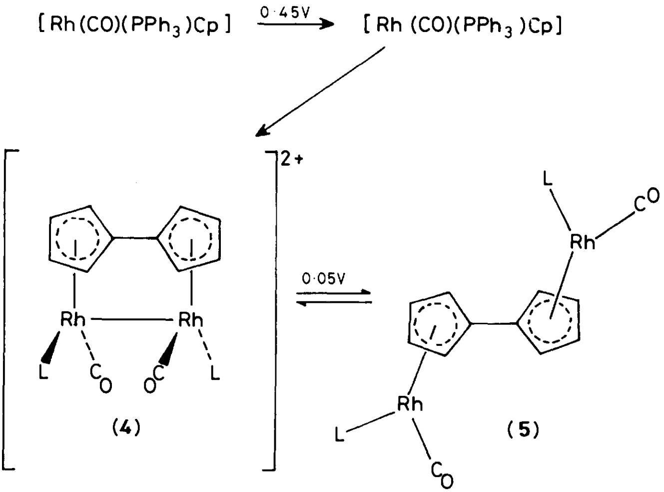


**Figure 4** *The structures of (a) the dication* $[Rh_2(CO)_2(PPh_3)_2(\eta^5:\eta'^5\text{-}C_{10}H_8)]^{2+}$ (4), *and (b) the neutral molecule* $[Rh_2(CO)_2(PPh_3)_2(\eta^5:\eta'^5\text{-}C_{10}H_8)]$ (5)*; hydrogen atoms are omitted for clarity*
(Reproduced from *J. Chem. Soc., Dalton Trans.*, 1985, 2283)



**Scheme 4**

electrochemical, C = chemical) where the intervening chemical step, namely *cis* ⟷ *trans* isomerization, is fast and reversible.[31]

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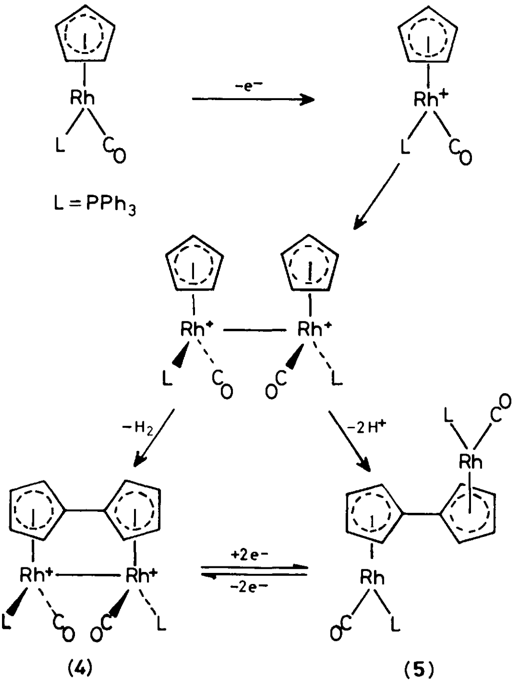
[31] R. Moulton, T. W. Weidman, K. P. C. Vollhardt, and A. J. Bard, *Inorg. Chem.*, 1986, **25**, 1846.



Scheme 5

A fulvalene complex related to (4), namely $[Rh_2(PPh_3)_4(\mu\text{-}C_{10}H_8)]^{2+}$, was prepared by McKinney[32] using $AgBF_4$ to oxidize $[Rh(PPh_3)_2Cp]$. Surprisingly, then, the reaction between $AgPF_6$ and $[Rh(CO)(PPh_3)Cp]$ gives[29] the adduct $[Ag\{Rh(CO)(PPh_3)Cp\}_2][PF_6]$ (6) despite the fact that the silver(I) ion is a strong enough oxidant to bring about electron-transfer and the formation of (4). As in the case of $[Fe(CO)_3(AsPh_3)_2]$ (Section 2), $Ag^+$ acts as a 'non-innocent' oxidant. However, in contrast to $[Ag\{Fe(CO)_3(AsPh_3)_2\}_2]^+$, the adduct (6) is an air-stable, crystalline solid also notable in behaving as a controlled source of the transient radical cation $[Rh(CO)(PPh_3)Cp]^+$. Thus, (6) and NO gas gives $[Rh(NO)(PPh_3)Cp]^+$ [*cf.* the coupling reaction between $(1^+)$ and NO; Scheme 1]; no reaction occurs between nitric oxide and neutral $[Rh(CO)(PPh_3)Cp]$.

The proposed mechanism for the formation of (4) from $[Rh(CO)(PPh_3)Cp]$ is shown in Scheme 5. Intuitively, it should involve C–C rather than Rh–Rh coupling of $[Rh(CO)(PPh_3)Cp]^+$, assuming the positive charge to be localized on the metal centre. However, the oxidation of $[Rh(CO)\{P(OPh)_3\}Cp]$, either electrolytically or with $[FeCp_2]^+$, yields the dimer $[Rh_2(CO)_2\{P(OPh)_3\}_2Cp_2]^{2+}$ which has an unsupported metal–metal bond (2.814 Å) and unlinked cyclo-

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[32] R. J. McKinney, *J. Chem. Soc., Chem. Commun.*, 1980, 603.

pentadienyl rings.[33] Thus, it is more likely that the metal–metal bond of (4) is formed before the cyclopentadienyl rings are coupled; how the $C_{10}H_8$ ligand then results (*i.e.* whether proton or hydrogen atom elimination occurs) is unknown.

The monomeric radical cation $[Rh(CO)(PPh_3)Cp]^+$ has so far proved too reactive to be detected spectroscopically. By contrast, the pentaphenylcyclopentadienyl analogues $[Rh(CO)L(\eta\text{-}C_5Ph_5)]^+$ (L = $PPh_3$ or $AsPh_3$) have been characterized[34] at room temperature in $CH_2Cl_2$ by both i.r. and e.s.r. spectroscopy. The remarkable stability conferred by the $C_5Ph_5$ ring (*cf.* $[Co(CO)_2(\eta\text{-}C_5Ph_5)]^-$, Section 3B) has synthetic consequences in that oxidative substitution reactions, similar to those described for $[Co(CO)_2(\eta\text{-}C_5R_5)]$ (R = H or Me, Section 3B) and dependent on the longevity of intermediate radical cations, can be carried out with $[Rh(CO)_2(\eta\text{-}C_5Ph_5)]$ [but not with the $C_5R_5$ (R = H or Me) analogues)]. The reaction of $[Rh(CO)_2(\eta\text{-}C_5Ph_5)]$ with $P(OPh)_3$ is particularly noteworthy in requiring only a catalytic amount of $[FeCp_2]^+$ as oxidant and in directly yielding the *neutral* complex $[Rh(CO)\{P(OPh)_3\}(\eta\text{-}C_5Ph_5)]$. In the presence of the phosphite ligand the oxidation of $[Rh(CO)_2(\eta\text{-}C_5Ph_5)]$ $[(Ep)_{ox} \approx 1.0$ V] is effected by $[FeCp_2]^+$, the irreversible loss of CO presumably providing the driving force to overcome the thermodynamically unfavourable difference in potentials. Once formed, the long-lived cation $[Rh(CO)\{P(OPh)_3\}(\eta\text{-}C_5Ph_5)]^+$ ($E^0 = 0.67$ V) can also oxidize $[Rh(CO)_2(\eta\text{-}C_5Ph_5)]$, thereby continuing the catalytic cycle and giving $[Rh(CO)\{P(OPh)_3\}(\eta\text{-}C_5Ph_5)]$ as the final product.

Many other examples of this important type of reaction, namely electron-transfer catalysis, are now known, particularly in carbonyl cluster chemistry. Such reactions, however, have been recently reviewed[2] and will not be dealt with further here. Note, however, a new redox-induced pathway[35] by which the two-electron oxidation of a dianion such as $[Fe_5C(CO)_{14}]^{2-}$ in the presence of a Lewis base, L, gives neutral substituted clusters such as $[Fe_5C(CO)_{14}L]$.

## 4 Redox-induced Isomerization

Of the structural changes induced by electron-transfer,[7] the reductive conversion of non-conjugated into conjugated dienes in $[Co(\eta^4\text{-diene})(\eta\text{-}C_5R_5)]$[36] and the oxidative isomerization of Group VI and VII metal carbonyl derivatives have been studied in most detail. This Section concentrates on the latter and in particular on how the isomerization process might play an important part in syntheses involving octahedral carbonyl complexes of manganese and rhenium.

The oxidatively-induced isomerization reactions in question follow an ECEC pathway, represented by the 'square scheme' shown in Scheme 6

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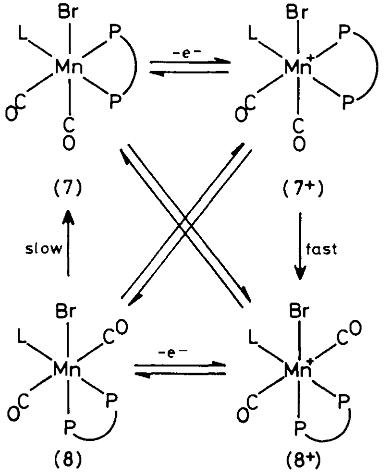
[33] E. Fonseca, W. E. Geiger, T. E. Bitterwolf, and A. L. Rheingold, *Organometallics*, 1988, **7**, 567.

[34] N. G. Connelly and S. J. Raven, *J. Chem. Soc., Dalton Trans.*, 1986, 1613.

[35] S. R. Drake, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc., Chem. Commun.*, 1988, 1033.

[36] W. E. Geiger, T. Gennett, M. Grzeszczuk, G. A. Lane, J. Moraczewski, A. Salzer, and D. E. Smith, *J. Am. Chem. Soc.*, 1986, **108**, 7454.



L = P(OPh)$_3$, P–P = dppm

**Scheme 6**

for the conversion of *cis,cis*-[MnBr(CO)$_2${P(OPh)$_3$}(dppm)] (7; dppm = Ph$_2$PCH$_2$PPh$_2$) into *trans*-[MnBr(CO)$_2${P(OPh)$_3$}(dppm)] (8).[37] As will become apparent, however, the cross-reaction given by equation 1 must also be taken into account.

$$(8) + (7^+) \rightleftharpoons (8^+) + (7) \qquad (1)$$

The kinetic and thermodynamic parameters associated with square schemes can be quantified using either electrochemical or spectroscopic techniques.[38] For example, all of the rate and equilibrium constants for the reactions linking *cis*- and *trans*-[M(CO)$_2$(dppe)$_2$]$^Z$ ($Z = 0$ or 1, M = Mo or W) have been determined.[39] The equilibrium constant for the cross-reaction depends on the redox potentials of the two couples involved, for example (7)–(7$^+$) and (8)–(8$^+$) in Scheme 6. These potentials may differ considerably [*e.g.* 0.31 and 0.89 V for the oxidations of (8) and (7) respectively] or be very similar [*e.g.* 1.06 and 1.10 V for the oxidation of *mer*- and *fac*-[Mo(CO)$_3${P(OPh)$_3$}$_3$];[38] the basis for the variations of redox potential with geometry has been discussed recently.[40]

Oxidative isomerization reactions have long been known to provide simple routes to otherwise inaccessible isomers. For example, the oxidation of *cis,mer*-[MnBr(CO)$_2${P(OMe)$_3$}$_3$][41] or *cis,cis*-[MnBr(CO)$_2$L(P–P)] [L = P(OPh)$_3$,

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[37] N. G. Connelly, K. A. Hassard, B. J. Dunne, A. G. Orpen, S. J. Raven. G. A. Carriedo, and V. Riera, *J. Chem. Soc., Dalton Trans.*, 1988, 1623.

[38] See, for example, A. M. Bond, S. W. Carr, and R. Colton, *Organometallics*, 1984, **3**, 541.

[39] A. Vallat, M. Person, L. Roullier, and E. Laviron, *Inorg. Chem.*, 1987, **26**, 332.

[40] B. E. Bursten and M. R. Green, *Progr. Inorg. Chem.*, 1988, **36**, 393.

[41] R. H. Reimann and E. Singleton, *J. Chem. Soc.. Dalton Trans.*, 1973, 2658.

P–P = dppm, dppe, *etc.*][42] followed by hydrazine reduction of the resulting manganese(II) cations, gave *trans,mer*-[$MnBr(CO)_2\{P(OMe)_3\}_3$] and *trans*-[$MnBr(CO)_2L(P–P)$] respectively. Although such reactions appear straightforward recent studies have uncovered two catalytic processes which considerably complicate matters.

The addition of small quantities of *trans*-[$MnBr(CO)_2\{P(OPh)_3\}(dppm)]^+(8^+)$ to the neutral *trans*-compound (8) results[43] in the quantitative formation of *cis,cis*-[$MnBr(CO)_2\{P(OPh)_3\}(dppm)$] (7). Although the equilibrium (equation 2) lies far to the right, the cross-reaction (equation 1) is thermodynamically favoured by 0.58 V and provides the driving force for the catalytic cycle. The conversion of *trans*- into *cis*-[$Cr(CO)_4\{P(OMe)_3\}_2$] catalysed by *trans*-[$Cr(CO)_4\{P(OMe)_3\}_2]^+$ occurs similarly.[44] In both of these examples the less thermodynamically stable isomer is converted into the more stable isomer.

$$(7^+) \rightleftharpoons (8^+) \tag{2}$$

In the second process the conversion of *fac*-[$Cr(CO)_3\{P(OMe)_3\}_3$] ($E^0 = 0.57$ V) to *mer*-[$Cr(CO)_3\{P(OMe)_3\}_3$] ($E^0 = 0.42$ V) is catalysed by *mer*-[$Cr(CO)_3\{P(OMe)_3\}_3]^+$.[45] Here, although the cross-reaction (equation 3), as written, is thermodynamically unfavourable by 0.15 V, the catalytic cycle is driven by the rapid isomerization of *fac*$^+$ to *mer*$^+$.

$$\text{mer}^+ + \text{fac} \rightleftharpoons \text{mer} + \text{fac}^+ \tag{3}$$

The synthetic implications of these two different catalytic processes have not previously been considered and yet they may be dramatic. Consider, for example, the reduction of ($8^+$). Here, the relative amounts of (7) and (8) produced may depend on the method used to carry out the electron-transfer reaction. Thus, controlled potential electrolysis, which will normally take 10 to 20 minutes for completion, leaves ($8^+$) in contact with (8) thereby facilitating the catalysed formation of (7). By contrast, any method which will result in fast and complete quenching of ($8^+$), for example rapid addition of a soluble reductant to a well-stirred solution of the cation, should result in higher yields of (8). Note also that the all-important cross-reaction is second order so that dilution may attenuate the catalytic cycle and lead to an increased proportion of (8). Such effects may explain the observation that in warm alcohols $NaBH_4$ reduction of *trans,mer*-[$MnBr(CO)_2L_3]^+$ [L = $PMe_2Ph$, $P(OMe)_3$, $P(OEt)_3$, or $P(OMe)_2Ph$] gave the neutral *cis,mer*-isomer in all cases but that hydrazine in a mixture of $CH_2Cl_2$ and 40—60 petroleum ether gave *trans,mer*-[$MnBr(CO)_2L_3$] [L = $P(OMe)_3$ or $P(OEt)_3$].[41]

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[42] F. Bombin, G. A. Carriedo, J. A. Miguel, and V. Riera, *J. Chem. Soc., Dalton Trans.*, 1981, 2049.

[43] N. G. Connelly, S. J. Raven, G. A. Carriedo, and V. Riera, *J. Chem. Soc., Chem. Commun.*, 1986, 992.

[44] A. M. Bond, R. Colton, and T. F. Mann, *Organometallics*, 1988, **7**, 2224.

[45] A. M. Bond, R. Colton, and J. E. Kevekordes, *Inorg. Chem.*, 1986, **25**, 749.

The effects of isomerization in general and the attendant catalytic processes in particular may be relatively straightforward to test and control in the ground-state redox reactions so far described. However, they should also be considered in the excited state, particularly for photoactive rhenium carbonyl complexes such as $[ReX(CO)_3(N{-}N)]$ [X = halide; N–N = 2,2′-bipyridyl (bipy), *o*-phenanthroline (*o*-phen), *etc.*], even though they may be less easily quantified.

The electron-transfer catalysed substitution of $[Re(CO)_3(NCMe)(o\text{-phen})]^+$ with $PPh_3$ to give $[Re(CO)_3(PPh_3)(o\text{-phen})]^+$,[46] and the catalysed reduction of $CO_2$ to CO mediated by $[ReBr(CO)_3(bipy)]$[47] both depend on the reductive quenching of a photogenerated excited state to give a strong reductant, for example $[ReBr(CO)_3(bipy)]^-$ in the second case. In both reactions noted above, the reduction potential for the excited state was estimated from the known values for the ground-state reduction potential and the energy of the incident radiation. However, if isomerization follows photoexcitation a dramatic effect on reduction potential is possible, *i.e.* the excited state may be a much stronger or weaker reductant than assumed. In addition, any such isomerization reaction may well be likened to catalytic processes of the types described above.

A reductively-induced isomerization process has been observed with manganese bipyridyl complexes related to the rhenium compounds mentioned above, but only in the ground state. For example, *cis,cis*-$[Mn(CO)_2(CNBu^t)_2(N{-}N)]^+$ and *fac*-$[Mn(CO)(CNBu^t)_3(N{-}N)]^+$ (N–N = bipy or *o*-phen) give the corresponding *cis,trans*- and *mer*-isomers when treated sequentially with sodium amalgam and air.[48] It is apparent from cyclic voltammetry that the mechanism of this isomerization is not the same as that for the oxidative reaction; a square scheme as simple as that in Scheme 6 seems unlikely. Nevertheless, e.s.r. spectroscopy shows that the reduction step generates radicals which are stable at room temperature.[49,50]

Mixed valence complexes are discussed in more detail in Section 6. However, it is appropriate to note here the redox chemistry of the binuclear cyanide-bridged cations $(9^+)$—$(12^+)$ which undergo oxidative isomerization reactions similar to those relating the neutral mononuclear bromides (7) and (8).

Each of the binuclear complexes is oxidized in two one-electron steps with *trans*-sites oxidized more readily than *cis*-sites, the latter with isomerization [as expected from the redox chemistry of (7) and (8)]. For $(9^+)$ ($E^0$ = 0.61 and 1.22 V) and $(10^+)$ [$E^0$ = 0.66 V and $(Ep)_{ox}$ = 1.55 V] oxidation by $[NO]^+$ gives the mixed-valence dications $(9^{2+})$ and $(10^{2+})$ for which both cyclic voltammetry and i.r. carbonyl spectroscopy suggest two non-interacting sites, *i.e.* trapped valence $[Mn_2]^{3+}$-containing cores. For $(11^+)$, however, where the two oxidation waves are closer in potential [$E^0$ = 0.85 V and $(Ep)_{ox}$ = 1.42 V] isomerization of $(9^{2+})$

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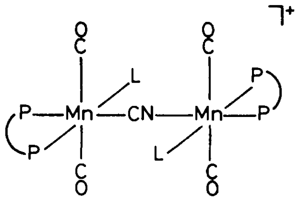
[46] D. P. Summers, J. C. Luong, and M. S. Wrighton, *J. Am. Chem. Soc.*, 1981, **103**, 5238.

[47] C. Kutal, A. J. Corbin, and G. Ferraudi, *Organometallics*, 1987, **6**, 553.

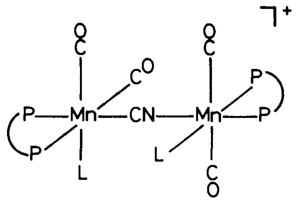
[48] F. J. Garcia Alonso, V. Riera, M. L. Valin, D. Moreiras, M. Vivanco, and X. Solans, *J. Organomet. Chem.*, 1987, **326**, C71.

[49] I. C. Quarmby, Ph.D. Thesis, University of Bristol, 1988.

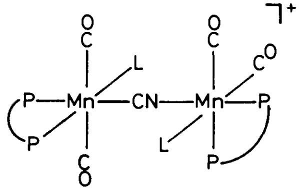
[50] N. G. Connelly, I. C. Quarmby, F. J. Alonso Garcia, and V. Riera, unpublished results.



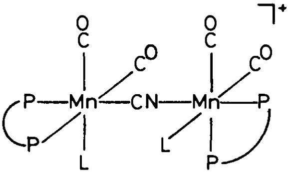
(9+)



(10+)



(11+)



(12+)

L = $P(OPh)_3$, P—P = dppm

seems to occur on formation of ($11^{2+}$), *i.e.* on oxidation of the *trans*-site only.[51] The difference in potential between the two oxidation waves of the binuclear species $[(P\text{-}P)L(CO)_2Mn(\mu\text{-}CN)Mn(CO)_2L'(P\text{-}P')]^+$ can be systematically varied by manipulating the donor–acceptor properties of the ligands [L,L′ = $PEt_3$, $P(OPh)_3$, *etc.*; P–P, P–P′ = dppm, dppe, $Me_2PCH_2CH_2PMe_2$, *etc.*],[49] and the oxidatively-induced isomerization process, readily detected by cyclic voltammetry and i.r. spectroscopy, should provide a simple probe of the mixed-valence properties of the $[Mn_2]^{3+}$-containing oxidation products.

## 5 The Redox Activation of Coordinated Hydrocarbons

**A. C–H Bond Reactions.**—Of the several examples now known of C–H bond cleavage induced by oxidation, three are applicable to a wide range of substrates. In each case the products isolated, usually cationic, are prone to nucleophilic attack at the coordinated hydrocarbon and are therefore precursors to many new organometallic and organic compounds.

The first example involves the $O_2$ oxidation of electron-rich substrates, most commonly 19- and 20-electron areneiron complexes. The reaction is complex, but well understood.[8,52] In all cases, initial one-electron transfer gives the superoxide ion, $O_2^-$; subsequent steps depend on the coordinated arene and may lead to dimerization or to the formation of complexed organic peroxides. With benzylic C–H bonds, however, proton abstraction by $O_2^-$ gives $\eta^5$-benzyls, as shown in Scheme 7 for $[FeCp(\eta^6\text{-}C_6Me_6)]$.

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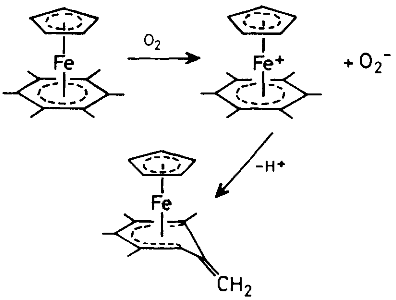
[51] G. A. Carriedo, N. G. Connelly, M. C. Crespo, I. C. Quarmby, and V. Riera, *J. Chem. Soc., Chem. Commun.*, 1987, 1806.

[52] J. R. Hamon and D. Astruc, *Organometallics*, 1988, 7, 1036.



**Scheme 7**

$$\begin{tikzcd}
{[WMe_2Cp_2] + [CPh_3]^+} \arrow[r] & {[WMe_2Cp_2]^+ + \cdot CPh_3} \arrow[dl] \\
{[W(CH_2)MeCp_2]^+ + HCPh_3} \arrow[d] & \\
{[W(CH_2Me)Cp_2]^+} \arrow[r] & {[WH(\eta^2\text{-}C_2H_4)Cp_2]^+}
\end{tikzcd}$$

**Scheme 8**

In the second example, C–H bonds (particularly those of metal alkyls) are activated using the trityl cation $[CPh_3]^+$. This ion is commonly used to abstract hydride ion from coordinated hydrocarbons but it is now apparent that it can also induce C–H bond cleavage *via* an oxidative EC mechanism.

The reaction of $[CPh_3]^+$ with $[WMe_2Cp_2]$ is shown in Scheme 8, with electron loss followed by α-hydrogen atom abstraction by the trityl radical; the EC mechanism is simply proved in that $[WMe_2Cp_2]^+$ is isolable and reacts with $\cdot CPh_3$ to give the same final product, namely the cationic ethylenehydride complex $[WH(C_2H_4)Cp_2]^+$.[53]

In this particular example the initial electron-transfer step is thermodynamically favoured. However, the same type of reaction also occurs[54] between $[CPh_3]^+$ and $[ReR(NO)(PPh_3)Cp]$ ($R = CH_2Ph$, $CH_2CHMe_2$, $CHMePh$, *etc.*), to give carbene or alkene cations such as $[Re(CHPh)(NO)(PPh_3)Cp]^+$ and $[Re(\eta^2\text{-}Me_2C{=}CH_2)(NO)(PPh_3)Cp]^+$. Here, electron-transfer is thermodynamically unfavourable by *ca.* 0.1 to 0.2 V, but the overall reaction is driven to completion by the very rapid, and irreversible, hydrogen atom abstraction. It should be noted that the EC mechanism does not always operate with the trityl cation. Where the difference in redox potential is too unfavourable, for example with $[FeR(CO)_2Cp]$, β-hydride abstraction occurs rather than electron-transfer.[55]

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[53] J. C. Hayes and N. J. Cooper, *J. Am. Chem. Soc.*, 1982, **104**, 5570.

[54] G. S. Bodner, J. A. Gladysz, M. F. Nielsen, and V. D. Parker, *J. Am. Chem. Soc.*, 1987, **109**, 1757.

[55] R. S. Bly, R. K. Bly, M. M. Hossain, G. S. Silverman, and E. Wallace, *Tetrahedron*, 1986, **42**, 1093.

The use of $[CPh_3]^+$ as an oxidant can also lead to the activation of the substituted cyclohexadiene ring of $[Fe(\eta^4\text{-}C_6H_7R)(\eta^6\text{-arene})]$. At room temperature, the *exo*-R group is cleaved but at *ca.* −40 °C, the cation $[Fe(\eta^4\text{-}C_6H_7R)(\eta^6\text{-arene})]^+$ is more stable and the $\cdot CPh_3$ radical is able to abstract the *endo*-hydrogen atom to give $[Fe(\eta^5\text{-}C_6H_6R)(\eta^6\text{-arene})]^+$. Subsequent nucleophilic addition of $R'^-$ to the cation gives difunctionalized cyclohexadienes $[Fe(\eta^4\text{-}C_6H_6RR')(\eta^6\text{-arene})]$.[56]

The third oxidative route to C–H bond cleavage was discovered[57,58] after the reaction of $[CPh_3]^+$ with $[Ru_2(\mu\text{-}CO)(\mu\text{-}CH_2)(\mu\text{-dppm})Cp_2]$ (13), which had been designed to give $[Ru_2(\mu\text{-}CO)(\mu\text{-}CH)(\mu\text{-dppm})Cp_2]^+$ ($14^+$) *via* hydride abstraction, resulted only in poor yields of the carbyne cation in a mixture of products. The realization that $[CPh_3]^+$ might act as an oxidant prompted a cyclic voltammetric study of (13) the results of which are shown in Figure 5. Clearly an EEC, rather than EC, mechanism is operative in that the first wave ($E^0 = 0.24$ V) is fully reversible (Figure 5b) whereas the second [$(Ep)_{ox} = 0.65$ V] is accompanied by a reversible product wave at 1.16 V. On the basis of the electrochemical results, (13) was treated with two equivalents of $[FeCp_2]^+$ as oxidant, in the presence of an excess of lutidine as a proton scavenger, to give near quantitative yields of ($14^+$). Figure 5c confirms that ($14^+$) is oxidized at 1.15 V, *i.e.* at the potential of the product wave in Figure 5a.

Complex ($14^+$) is therefore formed (Scheme 9) by proton loss after double oxidation of (13) to ($13^{2+}$). No C–H bond cleavage occurs after one-electron oxidation; the paramagnetic iron cation $[Fe_2(\mu\text{-}CO)(\mu\text{-}CH_2)(\mu\text{-dppm})Cp_2]^+$ ($15^+$) has been isolated and fully characterized by *X*-ray crystallography[59] and it does not lose H• on treatment with •CPh₃. Hydride abstraction or an EC mechanism of the type shown in Scheme 8 has been assumed[60] for the formation of $[Fe_2(\mu\text{-}CO)(\mu\text{-}CH)(\mu\text{-dppm})Cp_2]^+$ ($16^+$) from $[Fe_2(\mu\text{-}CO)(\mu\text{-}CH_2)(\mu\text{-dppm})Cp_2]$ (15) but neither is correct; complex ($15^+$) gives ($16^+$) only when converted into ($15^{2+}$) with a second equivalent of oxidant.

The double-oxidation deprotonation (EEC) reaction can be used with a range of other hydrocarbon-bridged complexes,[61] leading, for example, to the isolation of $[Ru_3(\mu_3\text{-}C{=}CH_2)(CO)_3Cp_3]^+$ from $[Ru_3(\mu_3\text{-}CMe)(CO)_3Cp_3]$.[58] It also results in C–Me carbon–hydrogen bond activation in the metallacyclononatetraene

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[56] D. Mandon, L. Toupet, and D. Astruc, *J. Am. Chem. Soc.*, 1986, **108**, 1320.

[57] N. G. Connelly, N. J. Forrow, B. P. Gracey, S. A. R. Knox, and A. G. Orpen, *J. Chem. Soc., Chem. Commun.*, 1985, 14.

[58] N. G. Connelly, N. J. Forrow, S. A. R. Knox, K. A. Macpherson, and A. G. Orpen, *J. Chem. Soc., Chem. Commun.*, 1985, 16.

[59] F. J. Collins, S. A. R. Knox, D. A. V. Morton, and A. G. Orpen, unpublished results.

[60] See ref. 29 in B. E. Bursten and R. H. Cayton, *J. Am. Chem. Soc.*, 1986, **108**, 8241; C. P. Casey, M. Crocker, P. C. Vosejpka, P. J. Fagan, S. R. Marder, and M. A. Gohdes, *Organometallics*, 1988, **7**, 670.

[61] See, for example, N. M. Doherty, M. J. Fildes, N. J. Forrow, S. A. R. Knox, K. A. Macpherson, and A. G. Orpen, *J. Chem. Soc., Chem. Commun.*, 1986, 1355; F. M. Collins, Ph.D. Thesis, University of Bristol, 1988.

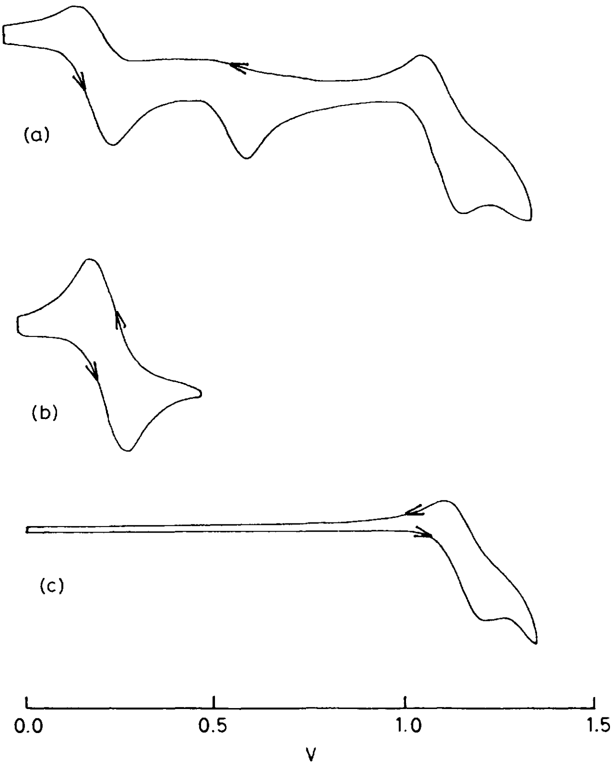

**Figure 5** *Cyclic voltammograms of* $[Ru_2(\mu\text{-}CH_2)(\mu\text{-}CO)(\mu\text{-}dppm)Cp_2]$ (13) (*a*) *from* 0.0 *to* 1.4 V *and* (*b*) *from* 0.0 *to* 0.5 V, *and* (*c*) *of* $[Ru_2(\mu\text{-}CH)(\mu\text{-}CO)(\mu\text{-}dppm)Cp_2]^+$ ($14^+$) *from* 0.0 *to* 1.4 V, *in* $CH_2Cl_2$
(Reproduced from *J. Chem. Soc., Chem. Commun.*, 1985, 14)

complex $[Mo_2(\mu\text{-}C_8Me_8)Cp_2]$ (17); two equivalents of $[FeCp_2]^+$ give $[Mo_2(\mu\text{-}C_8Me_7CH_2)Cp_2]^+$ (18).[62]

**B. Migratory Insertions.**—Probably the first example of oxidatively-induced C–C bond formation involved the synthesis of acetic acid esters, $RCO_2Me$, from $[FeR(CO)_2Cp]$ or $[MoR(CO)_3Cp]$ and a strong oxidant ($Ce^{4+}$ or $Cu^{2+}$) in methanol.[5] The mechanism of this reaction has been elucidated largely *via* chemical and electrochemical studies of the oxidation of species such as $[FeMe(CO)(PPh_3)Cp]$ (19). Once again, this topic has been recently reviewed[63] and will only be treated briefly here.

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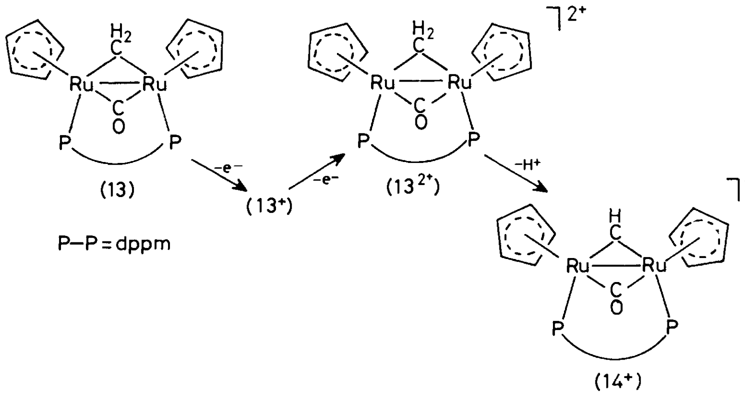
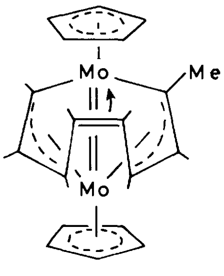
[62] S. G. Bott, N. G. Connelly, M. Green, N. C. Norman, A. G. Orpen, J. F. Paxton, and C. J. Schaverien, *J. Chem. Soc., Chem. Commun.*, 1983, 378.

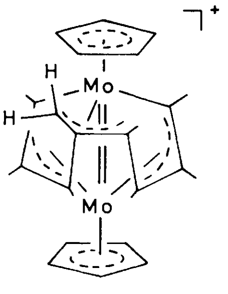
[63] M. N. Golovin, R. Meirowitz, M. M. Rahman, H. Y. Liu, A. Prock, and W. P. Giering, *Organometallics*, 1987, **6**, 2285; M. J. Therien and W. C. Trogler, *J. Am. Chem. Soc.*, 1987, **109**, 5127.



**Scheme 9**



(17)



(18)

The neutral compound (19) only slowly undergoes migratory insertion with CO to give [Fe(COMe)(CO)(PPh$_3$)Cp] (20) but the reaction is catalysed by one-electron oxidants such as [FeCp$_2$]$^+$ or Ag$^+$. Scheme 10 shows the salient features of the redox-based mechanism. Initially, the formation of (20$^+$) from (19$^+$) was thought to occur *via* CO addition to [Fe(COMe)(PPh$_3$)Cp]$^+$ (21$^+$), a 15-electron intermediate. However, it now seems more likely that solvation of (19$^+$) gives the 19-electron complex [FeMe(S)(CO)(PPh$_3$)Cp]$^+$ (22$^+$; S = solvent) which then rearranges to [Fe(COMe)(S)(PPh$_3$)Cp]$^+$ (23$^+$); CO displacement of the solvent then yields (20$^+$).

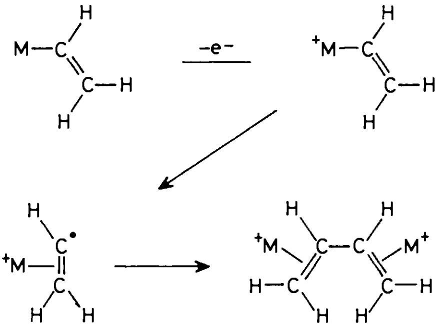
**C. C–C Bond Formation *via* Hydrocarbon Dimerization.**—(i) *General Considerations.* The dimerization of a coordinated π-hydrocarbon can be induced by one-electron oxidation or reduction, as outlined in Schemes 11 and 12 for the simple, as yet hypothetical, examples of σ-vinyl and η$^2$-ethene complexes.

Oxidation (Scheme 11) generates a 17-electron metal centre but a σ–π

$$\begin{tikzcd}[column sep=small]
\begin{matrix}[\mathrm{FeMe(CO)LCp}] \\ (19)\end{matrix} \arrow[r, shift left, "-e^-"] & \begin{matrix}[\mathrm{FeMe(CO)LCp}]^+ \\ (19^+)\end{matrix} \arrow[l, shift left] \arrow[dl, "S"'] \arrow[d] \\
\begin{matrix}[\mathrm{FeMe(S)(CO)LCp}]^+ \\ (22^+)\end{matrix} \arrow[d] & \begin{matrix}[\mathrm{Fe(COMe)LCp}]^+ \\ (21^+)\end{matrix} \arrow[d, "CO"] \\
\begin{matrix}[\mathrm{Fe(COMe)(S)LCp}]^+ \\ (23^+)\end{matrix} \arrow[r, "CO"] & \begin{matrix}[\mathrm{Fe(COMe)(CO)LCp}]^+ \\ (20^+)\end{matrix}
\end{tikzcd}$$

L = $PPh_3$, S = solvent

**Scheme 10**



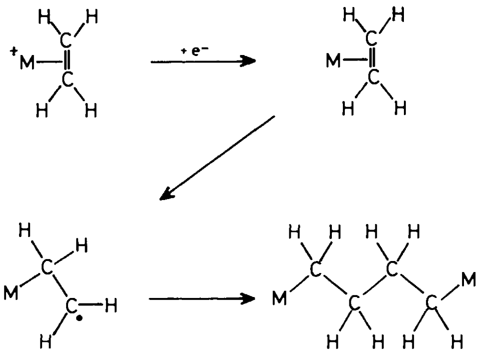
M = 17-electron fragment

**Scheme 11**

rearrangement of the vinyl ligand allows the metal to return to the stable closed-shell configuration while the unpaired electron is placed on the α-carbon atom. Radical–radical coupling then gives the diamagnetic $\eta^2:\eta'^2$-butadiene product. In Scheme 12, a 19-electron species is formed by metal-centred reduction. Then, a π–σ rearrangement can again regenerate an 18-electron configuration and provide the radical site for dimerization.

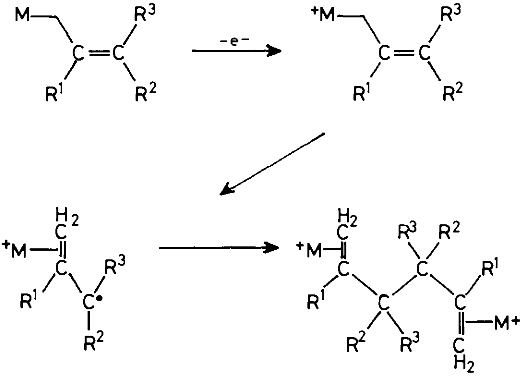
Although these examples are hypothetical they are conceptually useful and helpful in rationalizing the oxidative and reductive dimerizations described in parts (ii) and (iii) below and the more complex redox reactions of coordinated cyclooctatetraene (cot) discussed in part (iv).

(ii) *Oxidative Coupling.* The σ-allyl complexes [$FeR(CO)_2Cp$] (R = $CH_2CR^1{=}CR^2R^3$) react with $AgPF_6$ to give binuclear $\eta^2:\eta'^2$-hexa-1,5-diene complexes (Scheme 13) and a similar reaction occurs with [$Fe(CH_2C{\equiv}CPh)(CO)_2Cp$] to give the $\eta^2:\eta'^2$ complex of 3,4-diphenylhexa-1,2,4,5-tetraene. In



M = 17-electron fragment

**Scheme 12**



M = Fe(CO)$_2$Cp

**Scheme 13**

both cases, the proposed mechanism is very similar to that of Scheme 11 but the reactions are also regiospecific in that coupling occurs between the more highly substituted termini of the three-carbon fragments.[64]

The iodosobenzene oxidation of the carbene cation [Fe(C=CHMe)(dppe)Cp]$^+$ similarly results (Scheme 14) in regiospecific dimerization giving the 2,3-dimethylbuta-1,3-diene-1,4-diylidene complex (24). Here, an oxidative deprotonation step of the type described in Section 5A is thought to precede the formation of [Fe(C≡CMe)(dppe)Cp]$^+$ which subsequently rearranges and then dimerizes.[65] The 17-electron alkyne radical cation intermediate was not detected during the

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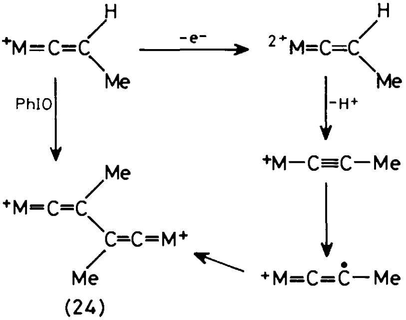
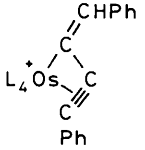
[64] P. S. Waterman and W. P. Giering, *J. Organomet. Chem.*, 1978, **155**, C47.

[65] R. S. Iyer and J. P. Selegue, *J. Am. Chem. Soc.*, 1987, **109**, 910.



M=Fe(dppe)Cp

**Scheme 14**



(25) L = PMe$_3$

reaction but the analogous cycloheptatrienyl complexes [Mo(C≡CR)(dppe)($\eta^7$-$C_7H_7$)]$^+$ (R = Ph, Bu$^n$, *etc.*) have been isolated and fully characterized. Moreover, these paramagnetic cations slowly dimerize to diamagnetic divinylidene dications, [$Mo_2$($\mu$-$C_2R_4$)(dppe)$_2$($\eta^7$-$C_7H_7$)$_2$]$^{2+}$, which are structurally similar to (24). As yet this molybdenum chemistry provides the only example where a paramagnetic monomer and the corresponding diamagnetic dimer are fully characterized.[66]

Although not a dimerization reaction, the formation of (25) from Ag$^+$ and [Os(C≡CPh)$_2$(PMe$_3$)$_4$] may also proceed *via* a mechanism related to that in Scheme 11, *intra*molecular C–C coupling following one-electron oxidation and rearrangement.[67]

(iii) *Reductive Coupling.* Although the reductive coupling of simple $\eta^2$-alkenes (Scheme 12) has not been observed, the alkyne cations [Mo(NCMe)-(MeC≡CMe)$_2$($\eta^5$-L)] (26$^+$) react with magnesium amalgam or [Fe(CO)$_2$Cp]$^-$ to give metallacyclononatetraene, [$Mo_2$($\mu$-$C_8Me_8$)$L_2$] (17; L = Cp), or flyover, [$Mo_2$($\mu$-$C_6Me_6$)$L_2$] (27; L = indenyl), complexes; [68] electrochemical studies show that the radicals (26) are formed in the first step.[69]

The reductive dimerization of cationic cyclic $\eta^5$-dienyls has been long known[5]

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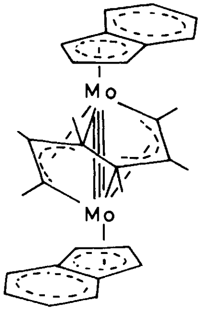
[66] R. L. Beddoes, C. Bitcon, A. Ricalton, and M. W. Whiteley, *J. Organomet. Chem.*, in press.

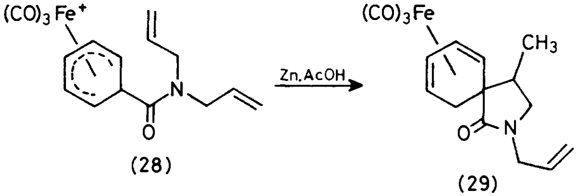
[67] J. Gotzig, H. Otto, and H. Werner, *J. Organomet. Chem.*, 1985, **287**, 247.

[68] M. Green, *Polyhedron*, 1986, **5**, 427.

[69] D. Pufahl, W. E. Geiger, and N. G. Connelly, *Organometallics*, 1989, **8**, 412.



(27)



Scheme 15

to give $\eta^4:\eta'^4$-bidienes but recent studies of the cycloheptadienyl and substituted cyclohexadienyl complexes $[Co(\eta^5\text{-}C_7H_9)Cp]^+$ [70] and $[Fe(CO)_3(\eta^5\text{-}C_6H_6CO_2Me)]^+$ [71] have finally provided good evidence for radical intermediates. In addition, zinc reduction of the diallylamide complex (28) gives the lactam (29) (Scheme 15) in the first example of the intramolecular cross-coupling of a redox-generated radical.[71]

(iv) *Redox-induced C–C Bond Formation and Cleavage in Cyclooctatetraene Complex Chemistry.* One of the earliest[72] and subsequently most thoroughly

**Table 1** *Cyclic voltammetric data for the one-electron oxidation of* $[ML_n(\eta^4\text{-cot})]$

| $ML_n$ | $(Ep)_{ox}/V$ |
|---|---|
| $Fe(CO)_3$ | 0.97 |
| $Fe(CO)_2\{P(OPh)_3\}$ | 0.69 |
| $Ru(CO)_3$ | 0.76 |
| $Co(\eta\text{-}C_5Me_5)$ | 0.10 |
| $Rh(\eta\text{-}C_5H_5)$ | 0.55 |

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[70] W. E. Geiger, T. Gennett, G. A. Lane, A. Salzer, and A. L. Rheingold, *Organometallics*, 1986, **5**, 1352.

[71] A. J. Pearson, Y.-S. Chen, M. L. Daroux, A. A. Tanaka, and M. Zettler, *J. Chem. Soc., Chem. Commun.*, 1987, 155.

[72] N. G. Connelly, M. D. Kitchen, R. F. D. Stansfield, S. M. Whiting, and P. Woodward, *J. Organomet. Chem.*, 1978, **155**, C34.

studied[73] examples of redox-induced C–C bond formation and cleavage is based on the oxidation of $\eta^4$-cot complexes of Fe,[74–77] Ru,[78] Co,[79] and Rh[80] and the electron-transfer reactions of the resulting binuclear, C–C coupled products. All of these reactions, which are generally regio- and stereo-specific, can be rationalized in terms of the 18–17–18-electron and 18–19–18-electron cycles outlined in Schemes 11 and 12. All of the $\eta^4$-cot complexes studied (Table 1) undergo irreversible one-electron oxidation at a platinum electrode, at potentials dependent on the metal and ancillary ligands. All undergo chemical oxidation, with oxidants chosen on the basis of the measured $(Ep)_{ox}$ values in Table 1, to give dimeric dications *via* radical–radical coupling.

The chemical oxidation of $[M(CO)_3(\eta^4\text{-cot})]$, with $Ag^+$ or $[N(C_6H_4Br\text{-}p)_3]^+$ (M = Fe) or with $[FeCp_2]^+$ (M = Ru) gives high yields of the isomeric complexes $[Fe_2(CO)_6(\eta^5{:}\eta'^5\text{-}C_{16}H_{16})]^{2+}$ (31) and $[Ru_2(CO)_6(\eta^2,\eta^3{:}\eta'^2,\eta'^3\text{-}C_{16}H_{16})]^{2+}$ (32) whose mechanism of formation is shown in Scheme 16. The first common intermediate in the two dimerizations, namely $[M(CO)_3(\eta^4\text{-cot})]^+$ ($30^+$), has not been detected but $^{60}Co$ $\gamma$-irradiation of $[Fe(CO)_2L(\eta^4\text{-cot})]$ (L = CO or $PPh_3$) in $CFCl_3$ at 77K results in the observation of e.s.r. spectra not inconsistent with the formation of $[Fe(CO)_2L(\eta^4\text{-cot})]^+$.[81] In addition, the 17-electron cation $[Fe(CO)\{P(OMe)_3\}_2(\eta^4\text{-tpcb})]^+$ (tpcb = tetraphenylcyclobutadiene), which is a stable analogue of ($30^+$; M = Fe), has been fully structurally characterized.[82]

The metal-based paramagnetic cation ($30^+$) rearranges to the allyl-based radical $[M(CO)_3(C_8H_8)]^+$ ($33^+$) which then couples to give the final common intermediate (34). Two different rearrangement pathways then result in (31) and (32), which contain the $\eta^5$-bicyclo[5.1.0]octadienyl and $\eta^2,\eta^3$-cyclooctatrienyl units favoured by iron and ruthenium respectively. Although the intermediate (34) has not been detected for iron or ruthenium, just such species are isolated, as diastereomeric mixtures, when $[Co(\eta^4\text{-cot})(\eta\text{-}C_5Me_5)]$ and $[Rh(\eta^4\text{-cot})Cp]$ are oxidized. Detailed electrochemical studies of $[Rh(\eta^4\text{-cot})Cp]$ have shown that one-electron transfer is followed by a *first*-order reaction which precedes dimerization. It is difficult to envisage any such reaction other than the proposed

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[73] N. G. Connelly, in 'Paramagnetic Organometallic Species in Activation Selectivity, Catalysis', ed. M. Chanon, M. Julliard, and J. C. Poite, Kluwer Academic Publishers, Holland, 1989.

[74] N. G. Connelly, R. L. Kelly, M. D. Kitchen, R. M. Mills, R. F. D. Stansfield, M. W. Whiteley, S. M. Whiting, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1981, 1317

[75] N. G. Connelly, A. R. Lucy, R. M. Mills, J. B. Sheridan, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1985, 699.

[76] N. G. Connelly, M. J. Freeman, A. G. Orpen, J. B. Sheridan, A. N. D. Symonds, and M. W. Whiteley, *J. Chem. Soc., Dalton Trans.*, 1985, 1027.

[77] N. G. Connelly, A. R. Lucy, R. M. Mills, M. W. Whiteley, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1984, 161.

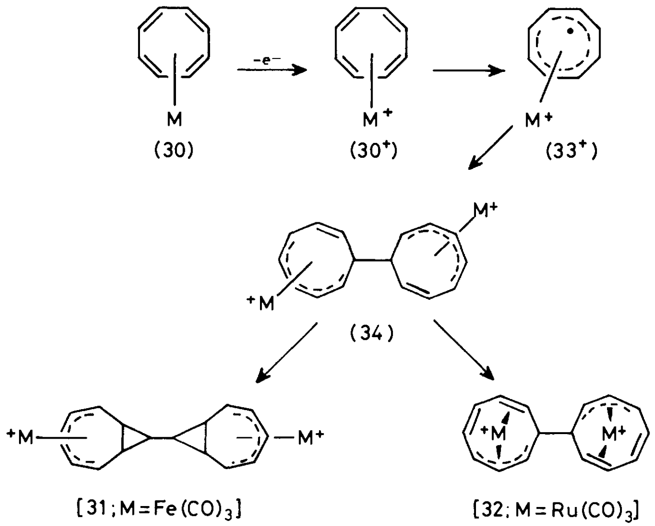
[78] N. G. Connelly, P. G. Graham, and J. B. Sheridan, *J. Chem. Soc., Dalton Trans.*, 1986, 1619.

[79] M. Gilbert, Ph.D. Thesis, University of Bristol, 1988; N. G. Connelly and M. Gilbert, unpublished results.

[80] L. Brammer, N. G. Connelly, J. Edwin, W. E. Geiger, A. G. Orpen, and J. B. Sheridan, *Organometallics*, 1988, 7, 1259.

[81] M. C. R. Symons and N. G. Connelly, unpublished results.

[82] A. G. Orpen, N. G. Connelly, M. W. Whiteley, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, in press.



**Scheme 16**

isomerization of the metal-based 17-electron cation $[Rh(\eta^4\text{-cot})Cp]^+$ to an allyl radical analogous to $(33^+)$.

The dication $[Rh_2(\eta^5{:}\eta'^5\text{-}C_{16}H_{16})Cp_2]^{2+}$ (35) differs from (31) and (32) (and from $[Co_2(\eta^5{:}\eta'^5\text{-}C_{16}H_{16})(\eta\text{-}C_5Me_5)_2]^{2+}$, see below) in slowly isomerizing thermally (Scheme 17), first to an $\eta^2,\eta^3$-bonded complex analogous to the ruthenium dimer (32) and then to the asymmetric species (36) which can only form from one of the two possible diastereomers shown.[80]

Both (31) and $[Co_2(\eta^5{:}\eta'^5\text{-}C_{16}H_{16})(\eta\text{-}C_5Me_5)_2]^{2+}$ (37) undergo redox reactions which result in further C–C bond transformations. Scheme 18 shows the sequence of two-electron steps by which the $C_{16}H_{16}$ hydrocarbon fragment of (31) is converted into three other isomers. The *X*-ray structures of $[Fe_2(CO)_4\{P(OPh)_3\}_2(\eta^5{:}\eta'^5\text{-}C_{16}H_{16})]^{2+}$ [74] [the bis(triphenylphosphite) derivative of (31)] and complexes (38),[83] (39), and (40),[76] also shown in Scheme 18, provide an insight into the origin of the regio- and stereo-selectivity of the redox-induced transformations. A more detailed discussion is given in reference 73 but, as an example, the formation of bond C(3)–C(3′) in (38) requires only a rotation of *ca.* 30° about bond C(1)–C(1′), following reduction of (31), to align the appropriate carbon atoms for coupling.

The twofold symmetry observed for the $C_{16}H_{16}$ ligands in (31) and (38) to (40) led to the assumption that the redox reactions linking the various dimers involved simultaneous one-electron transfer at the two metal centres thereby leading to diradical formation. However, the cobaltocene reduction of (37) gives

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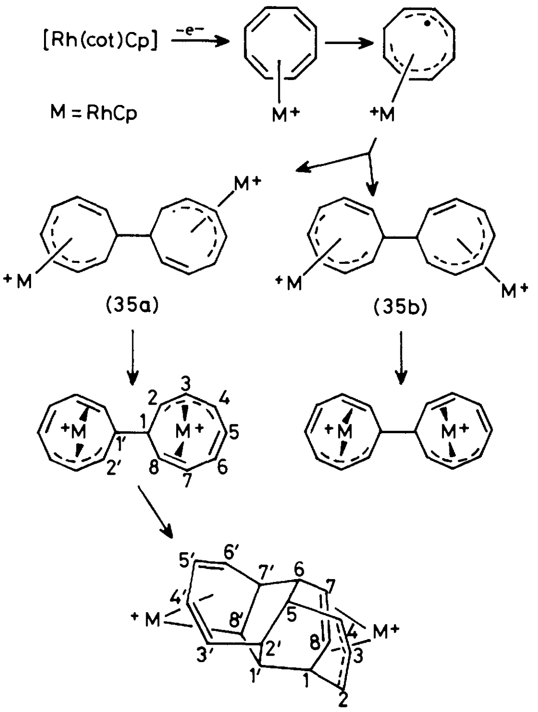
[83] H. A. Bockmeulen, R. G. Holloway, A. W. Parkins, and B. R. Penfold, *J. Chem. Soc., Chem. Commun.*, 1976, 298; B. R. Penfold, personal communication.



(36)

Scheme 17

highly asymmetric $C_{16}H_{16}$ complexes, (41) and (42), the thermolysis of the former leading to a third isomer (43) (Scheme 19). The formation of (41) and (42) is perhaps more consistent, therefore, with a stepwise, ECEC, mechanism, as shown for the $[FeCp_2]^+$ oxidation of (43) to the dication (44) (Scheme 20).[79]

A description of the redox chemistry of cot complexes would be incomplete without reference to Geiger's recent studies of $M_2(\mu\text{-}C_8H_8)$ (M = Ru, Co, or Rh) complexes (Scheme 21) where *reversible* C–C bond transformations are observed. The two-electron oxidation of $[Rh_2(\mu\text{-}C_8H_8)Cp_2]$ (45; M = Co or Rh) leads to the conversion of the $\eta^4{:}\eta'^4$-cot bridge into the twisted $\eta^5{:}\eta'^5$-form in the dication ($45^{2+}$).[84] A second two-electron oxidation, of $[Ru_2(\mu\text{-}C_8H_8)Cp_2]$ (46) which is isostructural and isoelectronic with ($45^{2+}$), then results in complete C–C bond rupture to give the flyover complex ($46^{2+}$).[85] Cyclic voltammetry shows that both two-electron oxidations, of (45) and (46), are irreversible but chemical reduction of the dicationic complexes gives the neutral precursors in near-quantitative yield.

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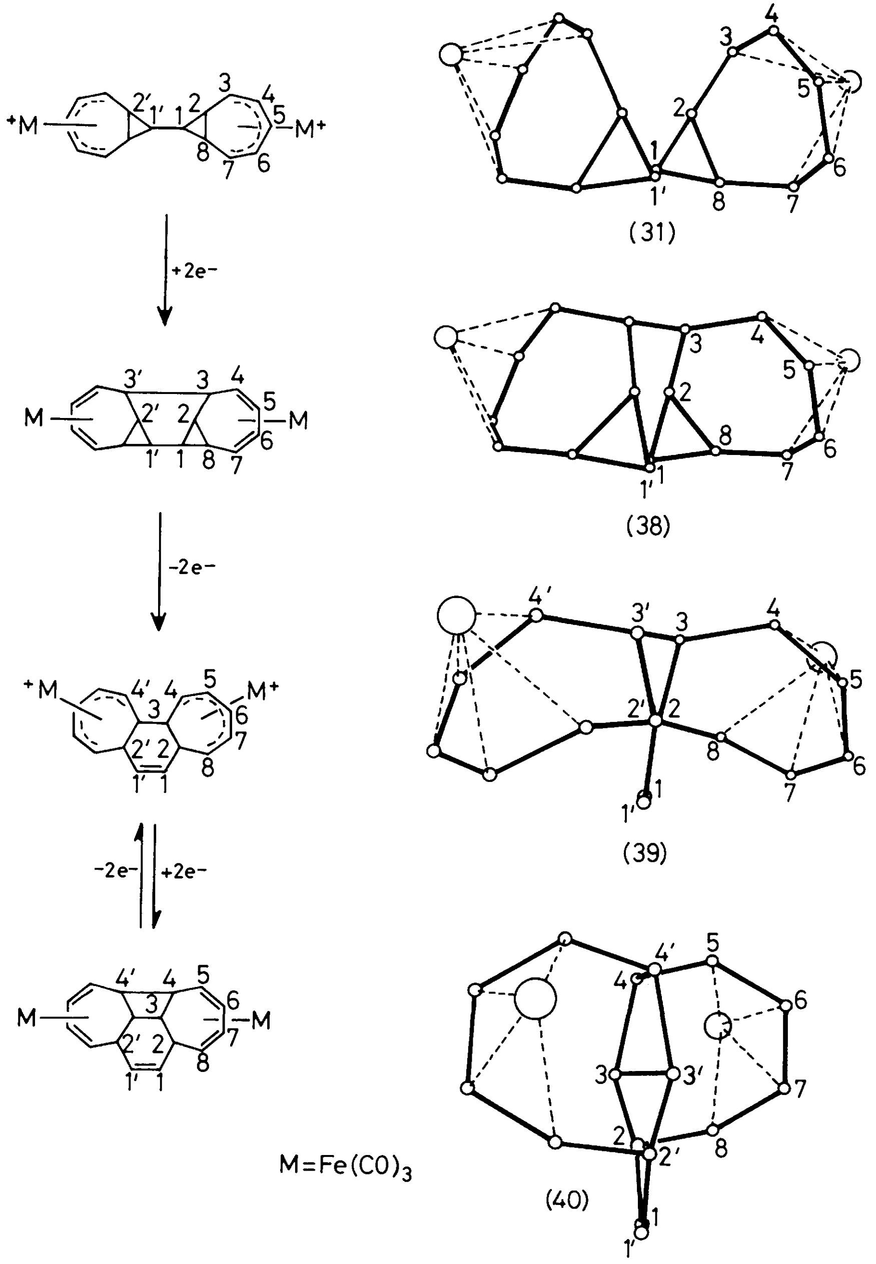
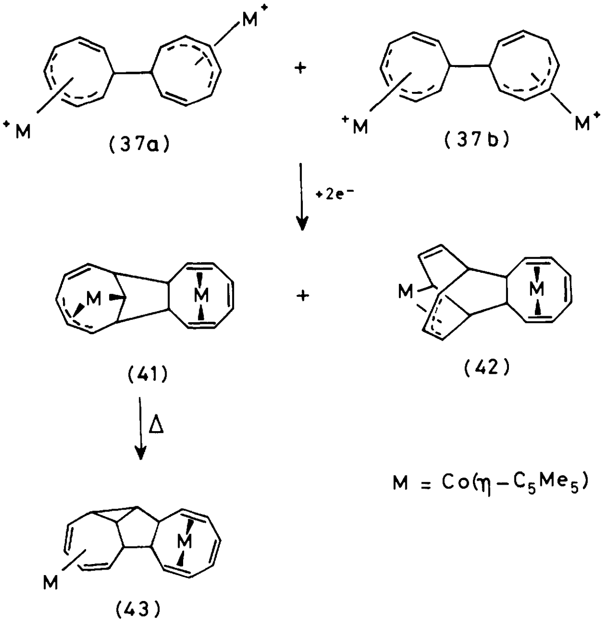
[84] J. Edwin, W. E. Geiger, and A. L. Rheingold, *J. Am. Chem. Soc.*, 1985, **106**, 3052.

[85] J. Edwin, W. E. Geiger, A. Salzer, U. Ruppli, and A. L. Rheingold, *J. Am. Chem. Soc.*, 1987, **109**, 7893.



Scheme 18



Scheme 19

## 6 Mixed-valence Organometallics

Much of the effort expended on understanding and classifying the properties of mixed-valence complexes has involved studies of the oxidation of binuclear metallocenyl complexes such as biferrocene, $[Fe_2(\mu-C_{10}H_8)Cp_2]$, and bis-(fulvalene) diiron, $[Fe_2(\mu-C_{10}H_8)_2]$;[5] the mixed-valence derivatives of these species contain $[Fe_2]^{3+}$ cores. However, the recent work of Astruc on binuclear electron-rich arene complexes[86] such as $[Fe_2(\mu-L)(\eta-C_5Me_5)_2]$ (L = biphenyl, triphenylene, *etc.*) and $[Fe_2(\mu-C_{10}H_8)(\eta^6-C_6R_6)_2]$ (R = H or Me) has considerably extended the range of mixed-valence (and other) states (*e.g.* $[Fe_2]^+$ and $[Fe_2]^{5+}$) available for further detailed study.

Other interesting mixed-valence organometallics can be prepared by the one-electron oxidation of the cyanide-bridged dimanganese complexes $(9^+)$ to $(12^+)$, as described in Section 4, and of $[Cr_2(CO)_4L_2(\mu\text{-biphenyl})]$ where both trapped-valence (L = $PPh_3$) and delocalized ($L_2$ = μ-dppm) bonding is observed.[87] This section, however, highlights attempts to synthesize $[Rh_2]^{3+}$-containing species

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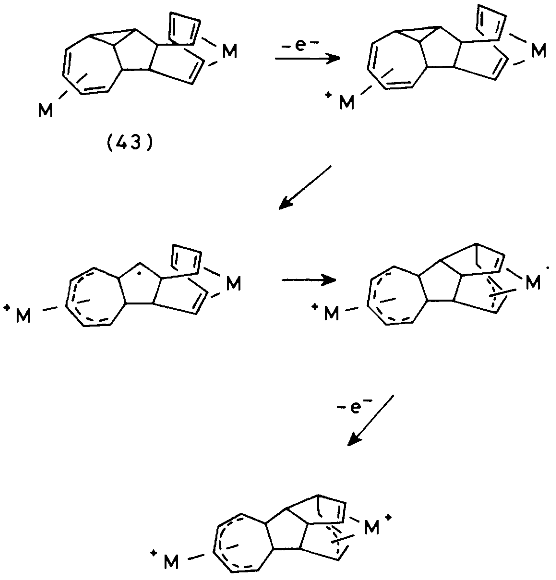
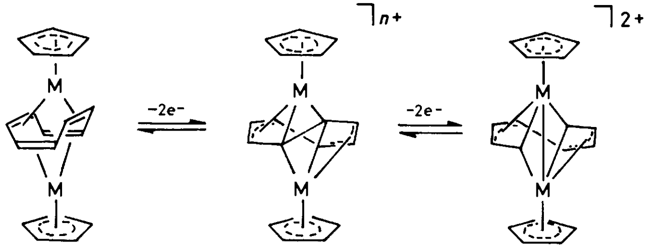
[86] M. Lacoste, F. Varret, L. Toupet, and D. Astruc, *J. Am. Chem. Soc.*, 1987, **109**, 6504; M. H. Desbois, D. Astruc, J. Guillin, J.-P. Mariot, and F. Varret, *J. Am. Chem. Soc.*, 1985, **107**, 5280; M. Lacoste, D. Astruc, M.-T. Garland, and F. Varret, *Organometallics*, 1988, **7**, 2253.

[87] N. Van Order Jr., W. E. Geiger, T. E. Bitterwolf, and A. L. Rheingold, *J. Am. Chem. Soc.*, 1987, **109**, 5680.



M = $Co(\eta-C_5Me_5)$

**Scheme 20**

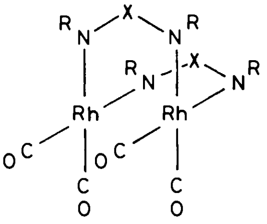


($45$; M = Co,Rh) ($46$; M = Ru, $n = 0$) ($46^{2+}$; M = Ru)

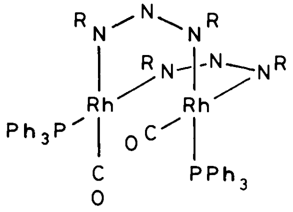
($45^{2+}$, M = Co,Rh, $n = 2$)

**Scheme 21**

derived from ligand-bridged square-planar $Rh^I$ complexes related to $[Rh_2(CO)_4(\mu\text{-}RNXNR)_2]$ (47; R = aryl, X = N or CMe). The attraction of such species derives from their potential ability to bind $\pi$-acceptor ligands (alkenes, alkynes, *etc.*) at the coordinatively unsaturated low oxidation state metal centres



(47)



(48)

while at the same time undergoing photo-induced intramolecular electron-transfer to a reactive excited state.

The complex $[Rh_2(CO)_2(PPh_3)_2(\mu\text{-}RNNNR)_2]$ (48; R = *p*-tolyl), prepared from (43; X = N) and $PPh_3$ by thermal substitution, is oxidized in three, reversible, one-electron steps at a platinum electrode.[88] These electrochemical results, taken with the observation that $[Rh_2(\mu\text{-carboxylate})_4]$ and related $[Rh_2]^{4+}$-containing tetrabridged species can be oxidized to mono-and di-cations,[89] show that the basic face-to-face binuclear structure can exist in at least five different redox states (*i.e.* $[Rh_2]^{2+}$ to $[Rh_2]^{6+}$).

Complex (48) is readily oxidized by $[N_2C_6H_4F\text{-}p]^+$ to the paramagnetic, $[Rh_2]^{3+}$-containing cation ($48^+$). *X*-Ray structural studies on ($48^+$) show a shortened metal–metal interaction [2.69 Å *vs.* 2.96 Å for (48)] consistent with electron removal from an antibonding metal–metal orbital.[88] A delocalized electronic structure for the cation is suggested both by the anisotropic, frozen-solution e.s.r. spectrum of ($48^+$) and by m.o. calculations [which also predict an increased susceptibility to axial coordination when (48) is oxidized].[90]

In order to introduce electronic asymmetry within the $[Rh_2]^{3+}$ core, thereby enhancing the possibility of photoinduced intramolecular electron-transfer, the geometric structure of the dirhodium complex as a whole has been systematically modified. Modest changes may be introduced using the acetamidino-bridged complex (47; X = CMe). Its thermal reaction with $PPh_3$ gives only the tricarbonyl $[Rh_2(CO)_3(PPh_3)\{\mu\text{-}RNC(Me)NR\}_2]$, but this compound undergoes oxidative substitution with ligands, L, in the presence of $[FeCp_2]^+$ (*cf.* Section 3A) to give the asymmetric, but still delocalized, complexes $[Rh_2(CO)_2L(PPh_3)\text{-}\{\mu\text{-}RNC(Me)NR\}_2]^+$ [L = $AsPh_3$, $P(OPh)_3$, *etc.*].[88]

A wide range of highly asymmetric, redox-active dirhodium complexes can be synthesized using $[Rh_2(CO)_2(bipy)(\mu\text{-}RNNNR)_2]$ (49) as the precursor (Scheme 22); formed from (47; X = N) and bipy, (49) differs from the disubstituted complex (48) in containing an $Rh(CO)_2$ group which becomes substitutionally labile in ($49^+$)[91,92]

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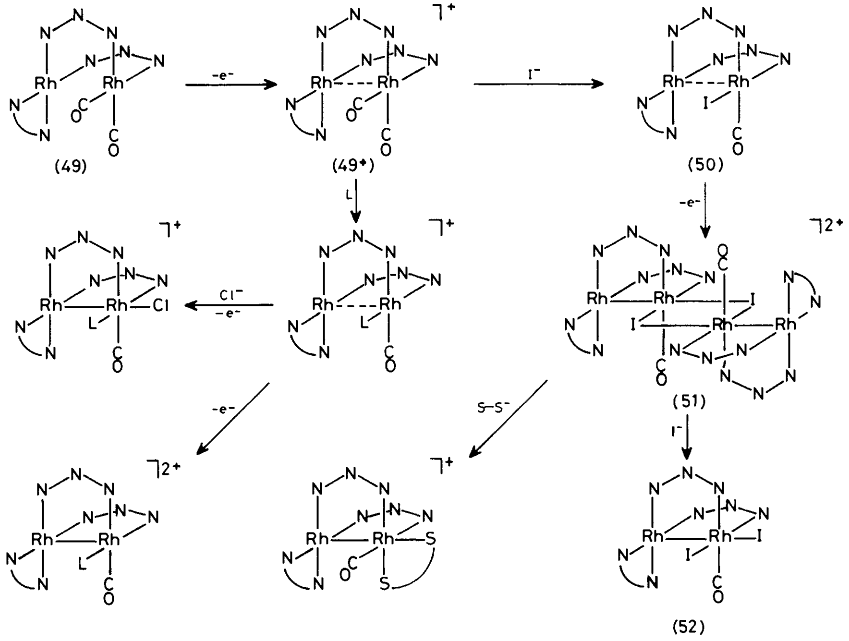
[88] N. G. Connelly, G. Garcia, M. Gilbert, and J. S. Stirling, *J. Chem. Soc., Dalton Trans.*, 1987, 1403; N. G. Connelly, C. J. Finn, M. J. Freeman, A. G. Orpen, and J. S. Stirling, *J. Chem. Soc., Chem. Commun.*, 1984, 1025.

[89] See, for example, T. R. Felthouse, *Progr. Inorg. Chem.*, 1982, **29**, 73, and references therein.

[90] N. G. Connelly, A. G. Orpen, and P. H. Rieger, unpublished results.

[91] N. G. Connelly and G. G. Herbosa, *J. Chem. Soc., Chem. Commun.*, 1987, 246.



**Scheme 22** NNN = *p*-tolylNNNtolyl-*p*, N–N = *2,2′-bipyridyl*, S–S = $S_2CNMe_2$, L = $PPh_3$ *or* $P(OPh)_3$; Rh – – – Rh *and* Rh——Rh *denote one- and two-electron metal–metal bonds in* $[Rh_2]^{3+}$ *and* $[Rh_2]^{4+}$ *cores respectively*

The cyclic voltammetric data in Table 2 show that the oxidation potential for a given dirhodium redox couple can be varied by design by as much as 2.0 V. Thus, bipy complexes with the $[Rh_2]^{4+}$ core become chemically accessible, for example (51) and (52). As predicted by the m.o. calculations noted above, an increase in the oxidation level of the dirhodium core is accompanied by an increase in the susceptibility of the axial sites to coordination, hence the iodide-bridged structure of (51).[92]

The anisotropic e.s.r. spectra of the $[Rh_2]^{3+}$-containing bipy complexes are still consistent with delocalized electronic structures in spite of the molecular asymmetry. However, the reaction of species such as $(49^+)$ with molecular oxygen leads to the observation of e.s.r. spectra consistent with dirhodium superoxide complexes containing the localized $Rh^IRh^{III}(O_2^-)$ arrangement.[93]

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[92] T. Brauns, C. Carriedo, J. S. Cockayne, N. G. Connelly, G. Garcia, and A. G. Orpen, *J. Chem. Soc., Dalton Trans.*, in press.

[93] N. G. Connelly and A. C. Loyns, unpublished results.

**Table 2** *Cyclic voltammetric data*[a] *for dirhodium complexes*

| *Complex* | *Couple* ($E^0$/V) | | |
|---|---|---|---|
| | $[Rh_2]^{2+/3+}$ | $[Rh_2{}^{3+/4+}$ | $[Rh_2]^{4+/5+}$ |
| $[Rh_2(CO)_2(PPh_3)_2(\mu\text{-}L)_2]$[b] | 0.19 | 1.29 | 1.58 |
| $[Rh_2(CO)_2(bipy)(\mu\text{-}L)_2]^+$ | −0.25 | 0.9(I)[c] | — |
| $[Rh_2(CO)(PPh_3)(bipy)(\mu\text{-}L)_2]^+$ | −0.53 | 0.78 | 1.47 |
| $[Rh_2I(CO)(PPh_3)(bipy)(\mu\text{-}L)_2]$ | −1.07 | 0.21 | 1.25, 1.37[d] |
| $[Rh_2(CO)(S_2CNMe_2)(bipy)(\mu\text{-}L)_2]^+$ | — | −0.84 | 1.13 |
| $[Rh_2Cl(CO)(PPh_3)(bipy)(\mu\text{-}L)_2]^+$ | — | −0.56 | 1.28 |

[a] All processes are reversible unless stated otherwise. [b] L = $[RNNNR]^-$, R = *p*-tolyl. [c] Irreversible process; potential is $(Ep)_{ox}$ at a scan rate of 200 $mVs^{-1}$. [d] Potentials for the oxidations of the tetranuclear dication (51) to the $[Rh_4]^{9+}$- and $[Rh_4]^{10+}$-containing tri- and tetra-cations respectively

(These spectra were originally attributed[91] to a concentration-dependant phenomenon but clearly result from the presence of adventitious oxygen in the more dilute samples.) Axial coordination of $O_2$ to $[Rh_2(ap)_4]$ (ap = 2-anilinopyridinato) gives the $Rh^{II}Rh^{III}(O_2{}^-)$ adduct $[Rh_2(ap)_4(O_2)]$,[94] but in the case of ($49^+$) the reaction with oxygen appears to result in carbonyl substitution.[93]

The sequence (49) ⟶ ($49^+$) ⟶ (50) ⟶ (51) ⟶ (52) (Scheme 22) is also notable in linking five well-defined, isolable complexes in an ECEC mechanism for the oxidative elimination reaction of $I_2$ with a $Rh^I$ centre. Such a one-electron transfer mechanism was proposed in Section 2 for the formation of $[FeI_2(CO)_3(PPh_3)]$ from $[Fe(CO)_3(PPh_3)_2]$ and $I_2$, although in that case all the intermediates could not be fully identified. In the present example, the reaction at one rhodium centre is mediated by the second and the paramagnetic intermediates are stabilized by metal–metal bond formation.[92]

Other attempts to vary the electronic properties of species with two or more square-planar rhodium centres have involved the synthesis of paramagnetic A-frame complexes such as $[Rh_2(\mu\text{-}L')L_4]^+$ [$L'$ = 2,3-$(NH)_2C_{10}H_6$ (53) or 1,8-$(NH)_2C_{10}H_6$ (54); $L_2$ = $(CO)(PPh_3)$ or $\eta^4$-diene, diene = cyclooctadiene (cod), norbornadiene, *etc.*],[95] and the trinuclear $[Rh_3]^{4+}$-containing dications [55; R = H or Me, $L_2$ = $(CO)(PPh_3)$ or $\eta^4$-cod].[96] Cation (54) is notable in containing an $[Rh_2]^{3+}$ core prone to axial coordination; reaction with NO gives the stable, diamagnetic nitrosyl adduct $[Rh_2\{\mu\text{-}1,8\text{-}(NH)_2C_{10}H_6\}(NO)(\eta^4\text{-cod})_2]^+$.[95]

## 7 Conclusions and Future Prospects

The examples described in Sections 2 to 6 show that redox-based syntheses, involving 17- and 19-electron radicals as key intermediates, have and will have an important role to play in metal–carbonyl and –hydrocarbon chemistry. However, other important applications of redox-active organometallics are also

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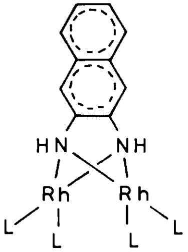
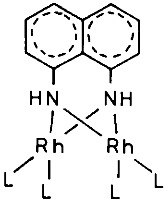
[94] J. L. Bear, C.-L. Yao, F. J. Capdevielle, and K. M. Kadish, *Inorg. Chem.*, 1988, **27**, 3782.

[95] N. G. Connelly, A. C. Loyns, M. J. Fernandez, J. Modrego, and L. A. Oro, *J. Chem. Soc., Dalton Trans.*, 1989, 683.

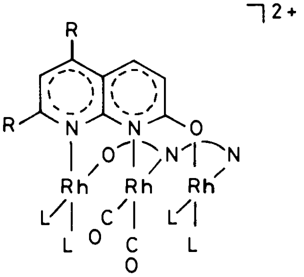
[96] N. G. Connelly, A. C. Loyns, M. A. Ciriano, M. J. Fernandez, L. A. Oro, and B. E. Villarroya, *J. Chem. Soc., Dalton Trans.*, 1989, 689.



(53)



(54)



(55)

coming to light. It is perhaps ironic that ferrocene, whose one-electron oxidation reaction was discovered nearly 40 years ago, features most heavily in such applications. Thus, the couple $[FeCp_2]/[FeCp_2]^+$ is now a IUPAC recommended internal reference potential standard,[97] and plays an integral part in a commercially available biosensor for the determination of blood sugar levels.[98] In addition the ferrocenyl group can be used as a redox-active substituent, for example in macrocyclic ionophores where shifts in the redox potential mirror the binding of group 1A metals.[99] Finally, $[Fe(\eta\text{-}C_5Me_5)_2]$ and tcnq (tetracyanoquinodemethane) give the soluble molecular ferromagnet $[Fe(\eta\text{-}C_5Me_5)_2]$-[tcnq].[100]

Without doubt, chemical, electrochemical, spectroscopic, and structural studies

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[97] G. Gritzner and J. Kuta, *Pure Appl. Chem.*, 1982, **54**, 1527; R. R. Gagne, C. A. Koval, and G. C. Kisensky, *Inorg. Chem.*, 1980, **19**, 2854.

[98] A. E. G. Cass, G. Davis, G. D. Francis, H. A. O. Hill, W. J. Aston, I. J. Higgins, E. V. Plotkin, L. D. C. Scott, and A. P. F. Turner, *Anal. Chem.*, 1984, **56**, 667; J. E. Frew and H. A. O. Hill, *Anal. Chem.*, 1987, **59**, 933A.

[99] See, for example, P. D. Beer, H. Sikanyika, C. Blackburn, and J. F. McAleer, *J. Organomet. Chem.*, 1988, **350**, C15.

[100] J. S. Miller, A. J. Epstein, and W. M. Reiff, *Chem. Rev.*, 1988, **88**, 201.

of redox-active organometallics will continue to provide new and exciting discoveries. Their application should ensure the health and further development of organometallic electrochemistry.

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