Electrochemistry of Iron and Ruthenium Flyover Bridge Complexes[†]

Domenico Osella,* Mauro Botta, and Roberto Gobetto

Istituto di Chimica Generale ed Inorganica, Università di Torino, 10125 Torino, Italy

Franco Laschi and Piero Zanello*

Dipartimento di Chimica, Università di Siena, 53100 Siena, Italy

The redox chemistry of dimetallacycloheptadiene (flyover bridge) complexes $M_2(CO)_6[C(R)=C(R')-COC(R'')=(R''')]$ (M = Fe or Ru) has been investigated by electrochemical and spectroscopic techniques. For the $Fe_2(CO)_6[(PhC_2Ph)_2CO]$ derivative the bulk of the data indicates a sequence of electrochemical events involving the formation of the monoanion and its decomposition to solvated $[Fe(CO)_3]^-$ and $Fe(CO)_3[(PhC_2Ph)_2CO]$ fragments, which are able to recombine together on electrochemical or chemical reoxidation giving back the parent complex. Electron paramagnetic resonance features of electroreduced solutions of ^{13}CO-enriched sample of $Fe_2(CO)_6[(PhC_2Ph)_2CO]$ and its monophosphine derivative $Fe_2(CO)_5(PPh)_3[(PhC_2Ph)_2CO]$ lend support to the proposed mechanism. The influence of the dienone substituents, R, as well as the effect of the replacement of group V (15) donor ligands for CO on the trend of the electrode potentials is discussed.

Introduction

The reactions between alkynes and iron carbonyls [Fe(CO)$_5$, Fe$_2$(CO)$_9$, Fe$_3$(CO)$_{12}$] or triruthenium dodecacarbonyl [Ru$_3$(CO)$_{12}$] afford a huge number of stable organometallic complexes along with several organic products.[1-3] Usually alkyne oligomerization takes place (with or without concomitant CO insertion) giving rise to interesting and unusual coordination modes of the organic chain over the metallic moiety. Among these oligomerization products, the dimetallacycloheptadiene or "flyover bridge" complexes $M_2(CO)_6[\mu\text{-}C(R)=C(R')XC(R'')=C(R''')]$ (M = Fe, Ru; X = CH$_2$, CO) represent an important class since they are useful precursors in the syntheses of cyclopentadienones, quinones, hydroquinones, and their related six-member heterocycles.[4] Crystal structure determinations of a number of iron compounds, brought about by Piret et al.[5] (R = R' = R'' = R''' = H; X = CH$_2$), by Piron et al.[6] (R = R' = R'' = R''' = Me; X = CO), by Cotton et al.[7] (R = R' = R'' = R''' = Ph; X = CO), and by Pettersen et al.[8] (R = R''' = C≡CS:Me$_3$, R' = R'' = SiMe$_3$; X = CO), pointed out that the Fe$_2$(CO)$_6$ unit is symmetrically bridged by the twisted fulvene or diene chain (see Figure 1). The equivalent environment of the two metallic moieties, early suggested by IR analysis,[1] has been confirmed by Mössbauer studies[9] as well as by variable-temperature ^{13}C NMR studies.[10] The interaction of the fulvene fragment with the Fe$_2$(CO)$_6$ moiety has been described by Thorn and Hoffmann[11] and the overall electronic features have been confirmed for the dienone system by a gas-phase ultraviolet, photoelectron spectroscopy (UV-PES) study coupled with ab initio calculations.[12]

We have been interested in the electrochemistry of transition-metal cluster compounds, which represents one of the most recent aspects of their characterization and is a good test of their catalytic activity as far as reactions involving redox processes are concerned. Since the HOMO

and the LUMO of these systems are generally metal-metal bonding and antibonding in character, respectively, the anodic oxidation and the cathodic reduction very often cause quick and irreversible cluster breakdown. The coordination to the metal skeleton of polydentate ligands as well as organic fragments, which are able to clasp several metal atoms, usually improves the lifetime of the electrogenerated ionic species, when compared with the parent clusters. This is the case of the Co$_3$(CO)$_9$(μ_3-CY)[13] (Y = halogen, alkyl, or aryl radical), HRu$_3$(CO)$_9$(μ_3-R)[14] (R = allyl, allenyl, or acetylido fragment), and Fe$_3$(CO)$_9$(alkyne)[15] series. In this context, flyover bridge complexes might represent interesting candidates since the [M$_2$(CO)$_6$] (M = Fe, Ru) unit interacts with the dienone cap in a multicentered σ/π fashion. Furthermore during their extensive investigation over literally hundreds of organometallic compounds Dessy and co-workers[16] briefly re-

---

(1) Hubel, W. In *Organic Synthesis via Metal Carbonyls*; Wender, I., Pino, P., Eds.; Wiley-Interscience: New York, 1968.

(2) Fehlhammer, W. R.; Stolzenberg, H. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982.

(3) Seddon, E. A.; Seddon, K. R. In *The Chemistry of Ruthenium*; Elsevier; Amsterdam, 1984.

(4) Braye, E. H.; Hoogzand, C.; Hubel, W.; Kruerke, U.; Merènyi, R.; Weiss, E. *Advances in the Chemistry of the Coordination Compounds*; Kirschner, S.; Ed.; Macmillan: New York, 1961.

(5) Piret, P.; Meunier-Piret, J.; Van Meerssche, M. *Acta Crystallogr.* 1965, *19*, 78.

(6) Piron, J.; Piret, P.; Meunier-Piret, J.; Van Meerssche, M. *Bull. Soc. Chim. Belg.* 1969, *78*, 121.

(7) Cotton, F. A.; Hunter, D. L.; Troup, J. M. *Inorg. Chem.* 1976, *15*, 63.

(8) Pettersen, R. C.; Cash, G. G. *Inorg. Chim. Acta* 1979, *34*, 261.

(9) Greatrex, R.; Greenwood, N. N.; Pauson, P. L. *J. Organomet. Chem.* 1968, *13*, 533.

(10) (a) Hickey, J. P.; Wilkinson, J. R.; Todd, L. J. *J. Organomet. Chem.* 1975, *99*, 281. (b) Aime, S.; Milone, L.; Sappa, E. *J. Chem. Soc., Dalton Trans.* 1976, 838.

(11) Thorn, D. L.; Hoffmann, R. *Inorg. Chem.* 1978, *17*, 126.

(12) Casarin, M.; Ajò, D.; Vittadini, A.; Granozzi, G.; Bertoncello, R.; Osella, D. *Inorg. Chem.* 1986, *25*, 511.

(13) (a) Kotz, J. C.; Petersen, J. V.; Reed, R. C. *J. Organomet. Chem.* 1976, *120*, 433. (b) Peake, B. M.; Robinson, B. H.; Simpson, J.; Watson, D. J. *Inorg. Chem.* 1977, *16*, 405.

(14) Zanello, P.; Aime, S.; Osella, D. *Organometallics* 1984, *3* 1374.

(15) Osella, D.; Gobetto, R.; Montangero, P.; Zanello, P., Cinquantini, A. *Organometallics* 1986, *5*, 1247.

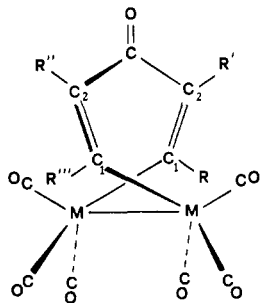**Figure 1.** Structure of flyover bridge complexes under study, M = Fe: R = R' = R'' = R''' = Me (I); R = R' = R'' = R''' = Et (II); R = R''' = Me, R' = R'' = Ph (III); R = R''' = Ph, R' = R'' = Me (IV); R = R'' = Me, R' = R''' = Ph (V); R = R' = R'' = R''' = Ph (VI). M = Ru: R = R'' = Me, R' = R''' = Ph (VII); R = R''' = Ph, R' = R'' = Me (VIII); R = R' = R'' = R''' = Ph (IX).

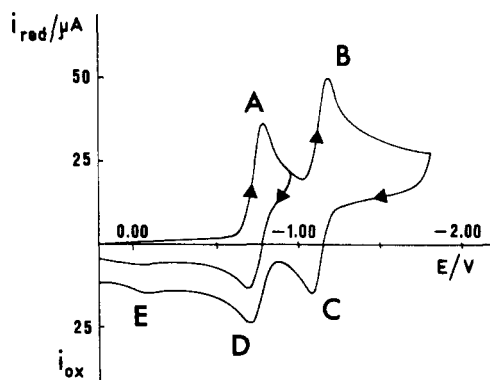**Figure 2.** Cyclic voltammetric response recorded on a MeCN solution containing VI (1.60×10^{-3} mol dm^{-3}) and [NEt$_4$]ClO$_4$ (0.1 mol dm^{-3}) (mercury working electrode; scan rate = 0.2 V s^{-1}).

ported an unusual electrochemical/chemical behavior of some Fe$_2$(CO)$_6$[(RC$_2$R)$_2$CO] complexes, although at that time no precise information on their geometrical and electronic structure was available. Here we report an electrochemical study in nonaqueous solvents of a wide series of flyover bridge derivatives of iron and ruthenium.

Results and Discussion

Cyclic Voltammetric Behavior. Figure 2 shows the cyclic voltammetric response of Fe$_2$(CO)$_6$[(PhC$_2$Ph)$_2$CO] (VI) in acetonitrile (MeCN) solvent at a mercury electrode. As can be seen, two distinct cathodic processes are present at $E_{p(A)} = -0.79$ V and $E_{p(B)} = -1.18$ V, respectively, each displaying a directly associated reoxidation response in the reverse scan. Controlled potential coulometric experiments carried out at a mercury-pool working macroelectrode in correspondence with the first cathodic process ($E_w = -0.90$ V) indicate the consumption of 1 mol of electrons/mol of VI. In addition, the electrolysis directly performed at the potential of the second cathodic step ($E_w = -1.35$ V) leads to the consumption of 2 mol of electrons/mol of VI. Concerning the peak system A/D, the analysis of the cyclic voltammetric responses with scan rates varying from 0.02 to 5 V s^{-1} (at high scan rates the response becomes ill-defined) shows the following features: the anodic to cathodic peak current ratio, $i_{p(D)}/i_{p(A)}$, gradually increases from 0.65 to 0.80; the ratio between the cathodic peak current and the square root of the scan rate, $i_{p(A)}/v^{1/2}$, remains practically constant; the difference between the cathodic peak potential and that of its directly associated
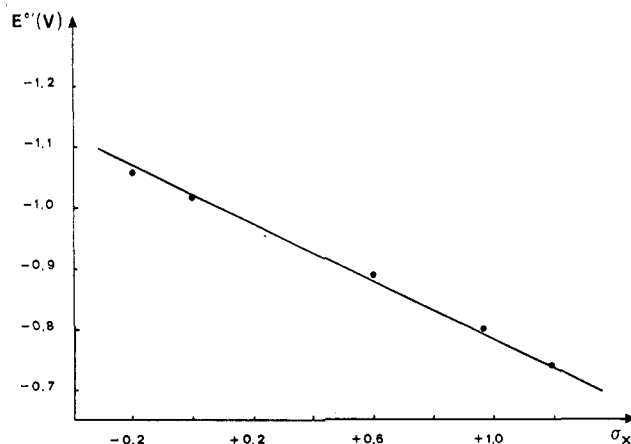

Figure 3. Plot of $E^{o\prime}$ for the reduction 0/1- against the abscissa function σ_x obtained according to eq 1 from the σ^* values of the substituents of the flyover complexes under study. The least-squares slope is 0.23 V, and the correlation coefficient is 0.999.

reoxidation peak, $E_{p(D)} - E_{p(A)} = \Delta E_p$, gradually increases from 85 to 120 mV. All these data are diagnostic of a one-electron quasi-reversible charge transfer complicated by following chemical reactions.[17] Tests at concentrations of VI varying from 5×10^{-4} to 2.2×10^{-3} mol dm^{-3} reveal no substantial change of the above cited parameters, indicating that a first-order reaction follows the charge-transfer process. Making use of the Nicholson's method[18] a half-life of about 20 s can be roughly computed for the electrogenerated monoanion [VI]$^-$.

A formal electrode potential, $E^{o\prime}$, of -0.74 V can be tentatively assigned to the redox couple VI-[VI]$^-$, in view of the impossibility to prevent the chemical complications accompanying this redox change (i.e. to reach the condition $i_{p(D)}/i_{p(A)} = 1$). The analysis of the cyclic voltammograms concerning the second cathodic process occurring at the peak system B/C reveals that this step also involves a one-electron quasi-reversible process ($E^{o\prime} = -1.14$ V) complicated by following chemical reactions, as evidenced by the appearance of the anodic peak E, due to the reoxidation of fragmentation products of the electrogenerated anions. The cathodic behavior of VI at a platinum electrode is slightly different. While the first process is quite similar, the second one appears totally irreversible. Actually this apparent discrepancy, due to different extents of electrochemical reversibility at different electrode materials, is not new and some interpretations have been put forward.[19,20]

In addition, at a platinum electrode, a totally irreversible oxidation process is detectable at $E_p = +1.5$ V, which, by comparison with the response of the one-electron oxidizable ferrocene, can be attributed to a single two-electron step.

The voltammetric picture now described is qualitatively common to all other diiron complexes, and their most significant electrochemical parameters in a few nonaqueous solvents are reported in Table I. The redox potentials are remarkably sensitive to the electronic properties of the substituents R of the cyclopentadienone ligand. Electron-donating groups thermodynamically disfavor the access to the reduced species; on the contrary, electron-

(16) Dessy, R. E.; Pohl, R. L. *J. Am. Chem. Soc.* **1968**, *90*, 1995 and references therein.

(17) Brown, E. R.; Large, R. F., In *Physical Methods of Chemistry*; Weissberger, A., Rossiter, B. W., Eds.; Wiley-Interscience: New York, 1971; Vol. I, Part IIA.

(18) Nicholson, R. S.; Shain, I. *Anal. Chem.* **1965**, *37*, 1351.

(19) Zanello, P.; Cini, R.; Cinquantini, A.; Orioli, P. L. *J. Chem. Soc., Dalton Trans.* **1983**, 2159.

(20) Blanch, S. W.; Bond, A. M.; Colton, R. *Inorg. Chem.* **1981**, *20*, 755.

Table I. Selected Electrochemical Parameters of Diiron Flyover Complexes I-VI in Different Solvents

		redox change						
		0/1-			1-/2- $E°$, V		0/2+	
compounds	no.	$E°$, V	ΔE_p, mV (at 0.2 Vs⁻¹)	$t_{1/2}$, s (mono-anion)	Pt	Hg	$E°$, V	solvent
Fe₂(CO)₆[C(Me)=C(Me)COC(Me)=C(Me)]	I	-1.02	80	20	-1.78[a]	-1.42	+1.62[a]	MeCN
Fe₂(CO)₆[C(Et)=C(Et)COC(Et)=C(Et)]	II	-1.06	70	20	-1.80[a]	-1.39	+1.70[a]	MeCN
		-1.21	110	20	1.89[a]	-1.61[a]		CH₂Cl₂
		-1.00	300		-1.90[a]			THF
Fe₂(CO)₆[C(Me)=C(Ph)COC(Ph)=C(Me)]	III	-0.95	80	40	-1.65[a]		+1.48[a]	MeCN
		-0.97	80	20	-1.70[a]	-1.50[a]		CH₂Cl₂
		-0.81	100		-1.53[a]	-1.32		THF
Fe₂(CO)₆[C(Ph)=C(Me)COC(Me)=C(Ph)]	IV	-0.80	70	70	-1.33[a]	-1.28	+1.47[a]	MeCN
		-0.91	95	30	-1.56[a]	-1.37		CH₂Cl₂
		-0.80	200		-1.58[a]	-1.42		THF
Fe₂(CO)₆[C(Me)=C(Ph)COC(Ph)=C(Me)]	V	-0.88	80	80	-1.53[a]	-1.28	+1.42[a]	MeCN
		-0.96	200	35	-1.78[a]	-1.38		CH₂Cl₂
		-0.85	300		-1.76[a]			THF
Fe₂(CO)₆[C(Ph)=C(Ph)COC(Ph)=C(Ph)]	VI	-0.74	95	20	-1.44[a]	-1.14	+1.50[a]	MeCN
		-0.87	230	30	-1.31	-1.31		CH₂Cl₂
		-0.68	180		-1.48[a]			THF

[a] Peak potential values at 0.2 V s⁻¹ for irreversible processes.

withdrawing ones allow the reduction to occur at more positive potentials. In more quantitative terms, the formal electrode potentials, $E°'$, mainly depend on the field effect of the C_1 substituents. Indeed, a reasonably linear correlation ($r = 0.965$) can be obtained by plotting the sum of the Taft $\sigma*$ values[21] of the C_1 substituents only against $E°'$ values. The best correlation ($r = 0.999$) can be achieved by using as abscissa parameter the optimized function σ_x, obtained according to eq 1 (Figure 3). This

$$\sigma_x = 0.8(\sigma*_R + \sigma*_{R'''}) + 0.2(\sigma*_{R'} + \sigma*_{R''}) \qquad (1)$$

clearly indicates that the transmission of the electronic effect of the substituents is mainly brought about through the Fe–C σ bonds, in agreement with the result of the previous theoretical studies.[12] Furthermore, the HOMO has been shown to possess metal–metal bonding character due to its parentage with the a_1 orbital of the Fe₂(CO)₆ fragment.[11] This accounts for the rapid decomposition of the flyover complexes as a consequence of the two-electron oxidation process, which completely depopulates this orbital.

It is noteworthy that the asymmetric isomer Fe₂(CO)₆-[C(Ph)=C(Me)COC(Ph)=C(Me)] (V), having one methyl and one phenyl substituent close to the diiron skeleton, gives rise to the most long-lived radical anion ($t_{1/2} = 80$ s in MeCN) in the entire series. One could speculate that the kinetic stability of the monoanion is governed by both electronic and steric factors. Thus, the kinetic stability is increased by electron-withdrawing groups (e.g. Ph) as well as by less sterically demanding substituents (e.g. Me); likely a compromise between them, as found in V, leads to the most stable situation.

Exhaustive Electrolysis of Fe₂(CO)₆[(PhC₂Ph)₂CO] (VI). Controlled potential electrolysis at a platinum gauze electrode ($E_w = -0.95$ V, one-electron reduction) of an acetonitrile solution of VI shows a gradual change in color from red to green-brown. At the end of the electrolysis, the solution exhibits at least two prominent oxidation peaks at +0.2 and +0.9 V, respectively, very far from the potential of peak D. This indicates that a drastic fragmentation follows the one-electron reduction in the longer
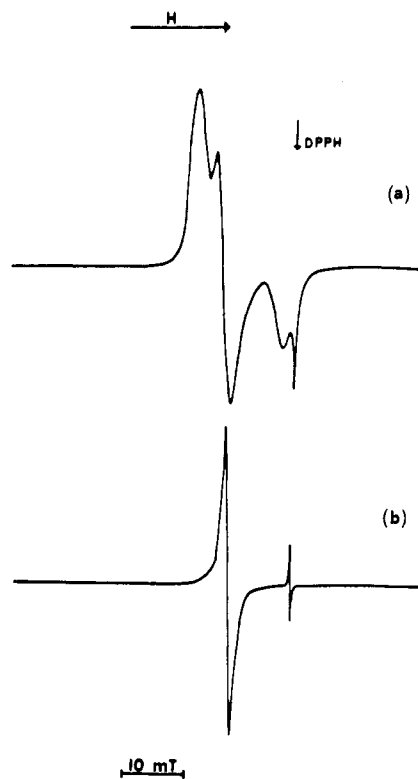
(21) (a) Taft, R. W., Jr. In *Steric Effects in Organic Chemistry*; Newman, M. S., Ed.; Wiley, New York, 1956. (b) $\sigma*$ is by no means a measure of inductive effects but it also contains a resonance component; see for example: Martin, Y. C. In *Quantitative Drug Design*; Marcel Dekker: New York, 1972 and March, J. In *Advances Organic Chemistry*, McGraw-Hill; Tokyo, 1980.

Figure 4. X-band EPR spectra of VI after exhaustive one-electron cathodic reduction at −0.95 V in MeCN, [NEt₄]ClO₄ (0.1 mol dm⁻³) solution: (a) 175 K; (b) room temperature. DPPH (2,2'-diphenylpicrylhydrazyl) is employed as a reference.

time scale electrolysis. The fragments generated in the electroreduction process should be able to recombine together giving back the parent complex; in fact the reoxidation of the solution at +1.0 V affords,[22] after TLC separation workup, VI in yield of about 70%, along with Fe(CO)₃[(PhC₂Ph)₂CO] (5%) and C₄Ph₄CO (tetraphenylcyclopentadienone or tetracyclone) (10%). When the electrochemical reduction/reoxidation cycle is carried out in CH₂Cl₂ solution, the degree of reversibility is remarkably lower (ca. 40%) than that found in MeCN, suggesting that the N-donor solvent plays a role in sta-

(22) Severe electrode fouling of the platinum basket occurs in the electrochemical reoxidation, which needs repeated cleaning by concentrated H₂SO₄.
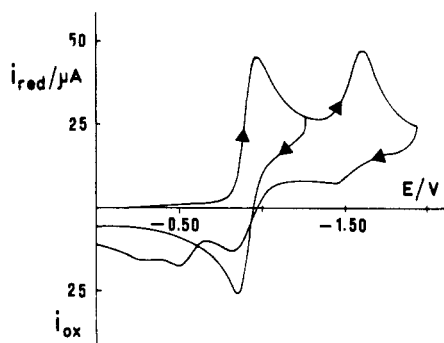
Figure 5. Cyclic voltammetric response recorded at a platinum electrode on a MeCN solution containing C_4Ph_4CO (1.2×10^{-3} mol dm^{-3}) and [NEt_4]ClO_4 (0.1 mol dm^{-3}) (scan rate = 0.2 V s^{-1}).

bilizing the electrogenerated fragments. The reversibility can be obtained also by chemical reoxidation, even if in a minor degree. When the electroreduced solution is exposed to air (O_2) for 1 h or is added to an excess of $AgPF_6$ under N_2 and stirred for 15 min, the parent complex $Fe_2(CO)_6[(PhC_2Ph)_2CO]$ is achieved in 50% and 40% yields, respectively; tetracyclone and $Fe(CO)_3$-[$(PhC_2Ph)_2CO$] again represent the observable byproducts.

EPR Study. More insight in this puzzle comes from an electron paramagnetic resonance (EPR) study of the electroreduced solution. Figure 4 shows the X-band EPR spectra recorded at the end of one-electron bulk electrolysis of VI in acetonitrile at 175 K (a) and at room temperature (b), respectively. The EPR spectrum (trace a) is interpretable on the basis of the presence of two active species: the most abundant one exhibits a well-resolved ortho-rhombic line shape (g_1 = 2.102, g_2 = 2.078, g_3 = 2.007) and the second one a very sharp singlet (g_{iso} = 2.000). At room temperature (trace b) the first signal evolves into a singlet (g_{iso} = 2.061) while the second one remains unaffected. The two singlets are, however, quite different in line width: H_1 = 9.5 G, H_2 = 2.0 G; the low-field peak behavior at low and at room temperature is consistent with a metal-centered paramagnetic species, and its g value is very close to that found for solvated [$Fe(CO)_3$]$^{\bullet-}$ radical.[23] The elusive monoanion $Fe_2(CO)_6[(PhC_2Ph)_2CO]^{\bullet-}$ is expected to display an axial pattern with EPR parameters different from the found orthorhombic ones.

The higher field signal can be confidently assigned to $C_4Ph_4CO^-$, as confirmed by the following electrochemical and EPR analyses of free tetracyclone. It is well-known that cyclopentadienones undergo one-electron reduction processes leading to relatively stable radicals.[24-28] Figure 5 shows the cyclic voltammetric behavior of 2,3,4,5-tetra-phenylcyclopentadienone (tetracyclone) in MeCN solvent. The analysis of the cyclic voltammetric and coulometric data indicates that the organic species undergoes a first quasi-reversible one-electron process ($E^{\circ\prime}$ = -0.89 V), complicated by a very slow chemical reaction,[29] and a
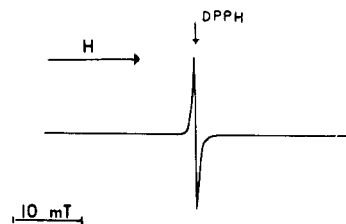
(23) (a) Zotti, G.; Rieke, R. D.; McKennis, J. S. *J. Organomet. Chem.* **1982**, *228*, 281. (b) El Murr, N.; Riveccie, M.; Dixneuf, P. *J. Chem. Soc., Chem. Commun.* **1978**, 552. (c) Dawson, P. A.; Peake, B. M.; Robinson, B. H.; Simpson, J. *Inorg. Chem.* **1980**, *19*, 465. (d) Krusic, P. J.; San Filippo, J., Jr.; Hutchinson, B.; Hance, R. L.; Daniels, L. M. *J. Am. Chem. Soc.* **1981**, *103*, 2129. (e) Peake, B. M.; Symons, M. C. R.; Wyatt, J. L *J. Chem. Soc., Dalton Trans.* **1983**, 1171.

(24) Given, P. H.; Peover, M. E. *J. Chem. Soc.* **1960**, 465.

(25) Oestreich, S.; Broser, W.; Kurreck, H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1977**, *32B*, 686.

(26) Willigen, H.; Geiger, W. E., Jr.; Rausch, M. D. *Inorg. Chem.* **1977**, *16*, 581.

(27) Fox, M. A.; Campbell, K.; Maier, G.; Franz, L. H. *J. Org. Chem.* **1983**, *48*, 1762.

(28) Takano, N.; Takeno, N.,; Morita, M. *Denki Kagaku Oyobi Kogyo Bitswi Kagaku* **1982**, *50*, 964.

Figure 6. X-band EPR spectrum at 175 K of C_4Ph_4CO exhaustively one-electron reduced in MeCN, [NEt_4]ClO_4 (0.1 mol dm^{-3}) solution.
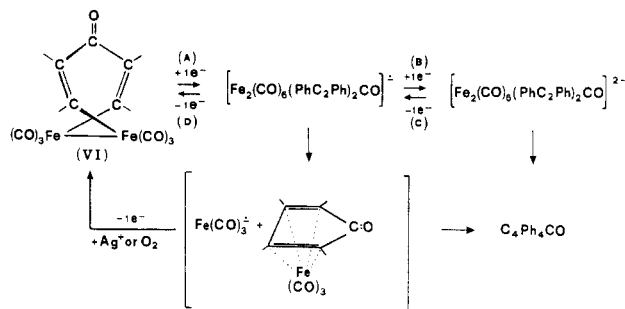

Figure 7. Scheme of the electrochemical events undergone by $Fe_2(CO)_6[C(Ph)=C(Ph)COC(Ph)=C(Ph)]$ (VI) both in CV and electrolysis experiments (substituents of the dienone have been omitted for clarity).

second completely irreversible process (E_p = -1.61 V). After the one-electron exhaustive electrolysis at the potential of the first cathodic step (E_w = -1.00 V) the starting red-violet solution has turned to red-amaranth and the cyclic voltammogram reveals the presence of $C_4Ph_4CO^-$ anion only.

Figure 6 shows the EPR spectrum at 175 K of the electrogenerated tetracyclone radical anion, confirming the identity with the second signal found in the EPR spectrum of electroreduced VI (vide supra). However the tetracyclone seems to be a side product of the decomposition of complex VI, and it is reduced at the potential employed for the electroreduction of VI. Indeed the same amount (ca. 10% based on parent complex VI) is found immediately at the end of the exhaustive electroreduction as well as at the end of the electrochemical or chemical reoxidation cycle.

Further evidence for the presence of [$Fe(CO)_3$]$^-$ in the electroreduced solution of VI comes from EPR tests on an exhaustively 1e electrolyzed solution of ca. 40% ^{13}CO-enriched sample of [$Fe_2(CO)_6(PhC_2Ph)_2CO$] (VI). The low-temperature spectrum exhibits the orthorhombic signal strongly broadened by the unresolved couplings with several ^{13}C nuclei as expected for a iron carbonyl radical.[23d,e] Moreover, the 175 K EPR spectrum of the acetonitrile solution resulting from the exhaustive one-electron electrolysis of $Fe_2(CO)_5(PPh_3)[PhC_2Ph)_2CO]$ (E_w = -1.03 V) exhibits the previously discussed orthorhombic and isotropic signals; in addition, a new broad resonance, partially overlapping with the latter, having a g average value of 2.000 (ΔH = 78.5 G) is detected. When the temperature is raised, this new signal evolves to a sharp doublet centered at g_{iso} = 2.005 with an hyperfine coupling constant $\langle a \rangle$ = 62.0 G. These features can be interpreted in terms of the formation on reduction of three active fragments, namely, [$Fe(CO)_3$]$^{\bullet-}$, [C_4Ph_4CO]$^{\bullet-}$, and $Fe(CO)_2(PPh_3)^{\bullet-}$; the presence of the ^{31}P nucleus ($I = ^1/_2$) is

(29) It is commonly accepted that $C_4Ph_4CO^-$ undergoes a protonation reaction,[24,28] in this case it is likely that a trace of water, present in the nominally anhydrous MeCN, represents the source of protons.
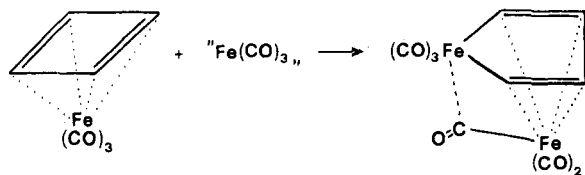
Figure 8. Schematic drawing of the transformation of a π-cyclobutadiene–iron tricarbonyl complex into a ferrole compound (substituents have been omitted for clarity).

responsible for the coupling observed in the last signal. Similar ^{31}P splitting has been reported for the radical anion generated by frozen matrice irradiation of (η^4-cyclohexadiene)Fe(CO)$_2$(PPh$_3$).[30]

An alternative hypothesis could be the fragmentation of VI⁻ into Fe(CO)$_3$ and Fe(CO)$_3$[(PhC$_2$Ph)$_2$CO]⁻ moieties as, in principle, the low-field EPR signal could be attributed to the latter species. However this possibility has to be ruled out. In fact Fe(CO)$_3$[(PhC$_2$Ph)$_2$CO], synthesized according to literature procedures, undergoes in MeCN solution a totally irreversible one-electron reduction (E_p = 1.37 V). The solution resulting from the extensive reduction (E_w = −1.50 V) does not exhibits in CV the complementary peak expected for the oxidation of the monoanion and, most importantly, is EPR silent.

Mechanistic Proposal. From the bulk of these features the sequence of the electrochemical events taking place on both CV and electrolysis time scales can be summarized in Figure 7. The reaction mechanism is consistent with that originally proposed by Dessy and co-workers[16] to account for the chemical reversibility of the process. We differ in the interpretation of the fate of the monoanion Fe$_2$(CO)$_6$[(PhC$_2$Ph)$_2$CO]$^{•-}$ in that its breakdown is suggested in lieu of an unidentified reorganization process. The recombination of the fragments Fe(CO)$_3$$^{•-}$ and Fe(CO)$_3$[(PhC$_2$Ph)$_2$CO] under reoxidation at +1.0 V implies iron–carbon bond modifications, i.e. π bond breaking and σ–π bond making. A similar reaction pathway has been observed when π-cyclobutadiene–iron tricarbonyls complexes are transformed into ferrole compounds[31] by addition of Fe(CO)$_3$ fragments as shown in Figure 8.

Unfortunately, in the case of Fe(CO)$_3$[(PhC$_2$Ph)$_2$CO] we were unable to gain such chemical evidence: indeed the treatment of Fe(CO)$_3$[(PhC$_2$Ph)$_2$CO] with Fe$_2$(CO)$_9$ (a reasonable source of Fe(CO)$_3$ fragments[32]))in toluene solution at +120 °C in a sealed tube or in benzene solution at room temperature under unfiltered UV irradiation (500 W) does not lead to the flyover derivative but only to free tetracyclone and Fe$_3$(CO)$_{12}$. It cannot be, however, excluded that the drastic conditions required for the reaction to occur may cause the decomposition of the flyover derivative as soon as it is formed. When the exhaustive electrolysis is carried out directly at the potential of the second cathodic process (E_w(0/2−) = −1.4 V) at a mercury-pool electrode and the resulting solution is reoxidized by air (O$_2$), chemical reversibility is no longer found. The only identifiable product is free tetracyclone (about 40%) indicating that complete breakdown of the parent flyover complex has taken place in agreement with CV experiments.

As far as the structure of the radical anion [Fe$_2$(CO)$_6$(PhC$_2$Ph)$_2$CO]⁻ is concerned, we propose some specula-
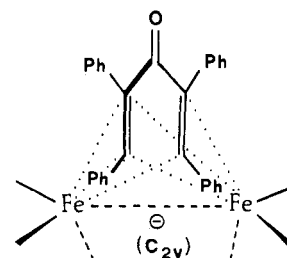
Figure 9. Proposed C_{2v} structure of the elusive anion Fe$_2$-(CO)$_6$[C(Ph)=C(Ph)COC(Ph)=C(Ph)]⁻.
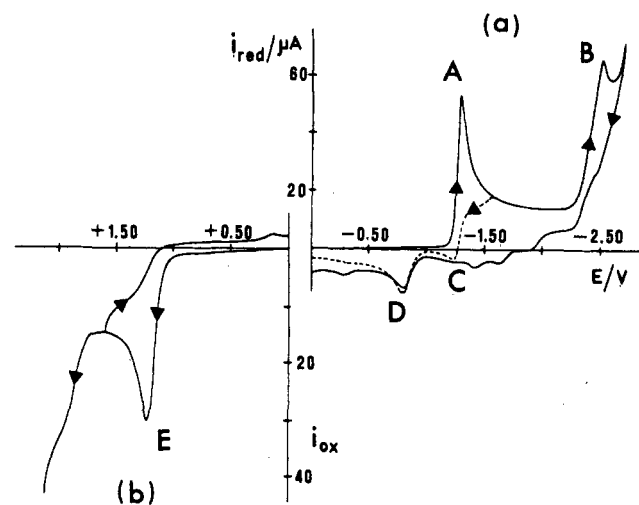
Figure 10. Cyclic voltammetric response recorded on a MeCN solution containing VII (1.90 × 10⁻³ mol dm⁻³) and [NEt$_4$]ClO$_4$ (0.1 mol dm⁻³): (a) cathodic scan at a mercury electrode; (b) anodic scan at a platinum electrode (scan rate = 0.2 V s⁻¹).

tions. The monoanion should represent an ideal transition state from the parent flyover complex to the electrogenerated fragments, according to the mechanism proposed above, and then exhibit a substantial weakening of the Fe–C σ bonds. The ring-opened C_{2v} symmetrical structure (Figure 9), proposed by Thorn and Hoffmann[11] and proved to be operative in the carbonyl exchange process followed by variable temperature NMR spectroscopy,[33] represents an actractive model. This transition state is stabilized by any increase of electron density on the organic chain carried out by the substituents;[11] hence it is likely that the addition of one extra electron greatly enhances its stability. Interestingly enough the LUMO of the C_{2v} structure possesses an antibonding iron–iron character, due to its parentage with the a$_2$ orbital of the Fe$_2$(CO)$_6$ fragment,[11] this accounts for the rupture of the iron–iron bond when the monoanion decomposed in the slow electrolysis time scale. This conformational rearrangement of the intial framework, causing the activation barrier of the heterogeneous charge transfer to increase,[34] is in tune with the CV quasi-reversibility of the 0/1− reduction process.

Ru Derivatives. A slightly different CV behavior is found for the diruthenium derivatives VII–IX. Figure 10 shows the typical voltammogram, anodic and cathodic, respectively, obtained from the diruthenium complex VII. A one-electron reduction process appears at the potentials of the peak system A/C, in which the charge transfer is coupled to a first-order chemical reaction leading to a

(30) Anderson, O. P.; Symons, M. C. R. *Inorg. Chem.* **1973**, *12*, 1932.

(31) (a) Victor, R.; Ben-Shoshan, R. *J. Chem. Soc., Chem. Commun.* **1974**, 93. (b) Davis, R. E.; Barnett, B. L.; Amiet, R. G.; Merk, W.; McKennis, J. S.; Pettit, R. *J. Am. Chem. Soc.* **1974**, *96*, 7108.

(32) Jaouen, G.; Marinetti, A.; Mentzen, B.; Mutin, R.; Saillard, J. Y.;Sayer, B. G.; McGlinckey, M. *J. Organometallics* **1982**, *1*, 753.

(33) Aime, S.; Gobetto, R.; Nicola, G.; Osella, D.; Milone, L.; Rosenberg, E. *Organometallics* **1986**, *5*, 1829.

(34) Tulyathan, B.; Geiger, W. E. *J. Am. Chem. Soc.* **1985**, *107*, 5960.

(35) Bianchini, C.; Mealli, C.; Meli, A.; Sabat, A. Zanello, P. *J. Am. Chem. Soc.* **1987**, *109*, 185.

Table II. Selected Electrochemical Parameters of Diruthenium Flyover Complexes VII–XII

compounds	no.	redox change			solvent
		0/1–		0/1+	
		$E°$, V	$t_{1/2}$, s (monoanion)	$E°$, V	
Ru$_2$(CO)$_6$[C(Me)=C(Ph)COC(Me)=C(Ph)]	VII	–1.25	0.2	–1.24^a	MeCN
		–1.39	0.3	+1.38^a	CH$_2$Cl$_2$
Ru$_2$(CO)$_6$[C(Ph)=C(Me)COC(Me)=C(Ph)]	VIII	–1.19	0.2	+1.14^a	MeCN
		–1.33	0.3	+1.34^a	CH$_2$Cl$_2$
Ru$_2$(CO)$_6$[C(Ph)=C(Ph)COC(Ph)=C(Ph)]	IX	–1.12	0.3	+1.27^a	MeCN
Ru$_2$(CO)$_5$(PPh$_3$)[C(Ph)=C(Me)COC(Me)=C(Ph)]	X	–1.45^a		+1.03^a	MeCN
		–1.57^a		+1.16^a	CH$_2$Cl$_2$
Ru$_2$(CO)$_5$(AsPh$_3$)[C(Ph)=C(Me)COC(Me)=C(Ph)]	XI	–1.36^a		+1.05^a	MeCN
		–1.51^a		+1.29^a	CH$_2$Cl$_2$
Ru$_2$(CO)$_5$(SbPh$_3$)[C(Ph)=C(Me)COC(Me)=C(Ph)]	XII	–1.35^a		+1.07^a	MeCN
		–1.47^a		+1.24^a	CH$_2$Cl$_2$

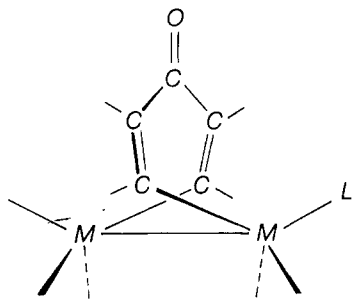^{a} Peak potential values at 0.2 V s^{-1} for irreversible processes.

Figure 11. Structure of the flyover derivatives X–XII (M = Ru, L = PPh, AsPh$_3$, or SbPh$_3$). The position of the ligand L trans to the metal–metal bond is suggested on the basis of a ^{13}C NMR study.[33]

species oxidizable at peak D. At scan rates higher than 20 V s^{-1}, the $i_{p(C)}/i_{p(A)}$ ratio reaches unity, peak D disappears, and the $[E_{p(C)}-E_{p(A)}]$ value is 360 mV at 20 V s^{-1} and 500 mV at 50 V s^{-1}. These data support a quasi-reversible charge transfer, leading to a species having a half-life of about 0.2 s^{-1}. Figure 10 shows a second reduction process, well away from the first reduction peak, detectable only at mercury electrode because of the solvent discharge. It takes place at potential of peak B and corresponds to an irreversible one-electron process.

In the anodic scan an oxidation process occurs at peak E. The analysis of cyclic voltammetric responses indicates that the oxidation process has to be attributed to a one-electron totally irreversible charge transfer. At potentials more positive than peak E other oxidation processes are found, completely nonanalyzable.

No attempt to characterize the products from the one-electron reduction has been performed in the likely hypothesis that the reaction pathway found for the iron derivatives holds also for the ruthenium compounds, although with a minor degree of reversibility. In order to evaluate the effect of the replacement of a CO group by group V (group 15) donor ligands, we have synthesized the monoderivatives of VIII, namely, X–XII, whose solution structures have been inferred by a previous ^{13}C NMR study[32] and shown in Figure 11.

Table II summarizes all significant electrochemical data of the diruthenium flyover complexes. As expected, the presence of ligands having a higher σ donor/π acceptor ratio than that of CO makes the reduction steps thermodynamically less accessible and favors the oxidation steps, causing the former to move toward more negative values and the latter toward less positive values. The substitution also affects the kinetic aspect of the chemical complication

following the charge transfer in that, even at a 50 V s^{-1} scan rate, no reoxidation peak, directly associated to the one-electron cathodic step, can be detected.

Experimental Section

The Fe$_2$(CO)$_6$[C(R)=(R')COC(R'')=C(R''')] (I–VI) and the Ru$_2$(CO)$_5$L[C(R)=C(R')COC(R'')=C(R''')] (L = CO, PPh$_3$, AsPh$_3$, or SbPh$_3$) (VII–XII) flyover derivatives were synthesized from the appropriate alkyne and Fe$_2$(CO)$_9$ or Ru$_3$(CO)$_{12}$, respectively, according to the published procedures.[7,10a,33] Fe(CO)$_3$-[(PhC$_2$Ph)$_2$CO] was prepared from Fe$_2$(CO)$_9$ and tetracyclone according to literature procedures.[36]

The ^{13}CO-enriched Fe$_2$(CO)$_6$[(PhC$_2$Ph)$_2$CO] as well as the monophosphine Fe$_2$(CO)$_5$(PPh$_3$)[(PhC$_2$Ph)$_2$CO] samples were prepared according to literature methods.[33] After crystallization in *n*-heptane at 0 °C, purity of all studied compounds was checked by IR and ^{1}H and ^{13}C NMR spectroscopy.

The IR spectra were recorded on a Perkin-Elmer 580 B instrument and the ^{1}H and ^{13}C NMR spectra on a JEOL GX-270-89 spectrometer. The EPR spectra were obtained from a Bruker 200 D-SRC instrument operating at 9.78 GHz (X-band) equipped with a Bruker variable-temperature ER 411 VT unit. The electrochemical apparatus and the purifications of solvents and supporting electrolytes have been described elsewhere.[35]

Solutions for cyclic voltammetric tests were (1.0–2.0) × 10^{-3} M in the appropriate flyover complex and 0.1 M in supporting electrolyte, namely, [(Et$_4$N)ClO$_4$] in MeCN and [(Bu$_4$N)ClO$_4$] in CH$_2$Cl$_2$ and THF. Solutions for exhaustive electrolyses were (7.0–8.0) × 10^{-3} M in the appropriate flyover complex and 0.15 M in supporting electrolyte. All potentials are referred to the saturated calomel electrode (SCE). Under the actual experimental conditions the ferrocene–ferrocenium couple is located at +0.38 V in MeCN, +0.49 V in CH$_2$Cl$_2$, and +0.56 V in THF.

After bulk electrolyses, separation workup was brought about by SiO$_2$ column chromatography [eluant, petroleum ether (40–70 °C) and CH$_2$Cl$_2$ (3:1 v/v)] or by TLC [absorbent Kieselgel: eluant, petroleum ether (40–70 °C) and 20% diethyl ether]. The identification of Fe(CO)$_3$[(PhC$_2$Ph)$_2$CO] and tetracyclone was achieved by IR and ^{1}H NMR spectroscopy and TLC comparison with autentical samples.[36]

(36) Ogliaruso, M. A.; Romanelli, M. G.; Becker, E. I. *Chem. Rev.* **1965**, *65*, 261.