

Reaction of $[\text{Fe}_3(\text{CO})_{12}]$ with bidentate phosphines: redox behavior of products

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Received 11 January 1996; revised 7 May 1996

Abstract

The reactions of $[\text{Fe}_3(\text{CO})_{12}]$ with the bidentate phosphines 1,2-bis(diphenylphosphino)ethane (dppe), 1,4-bis(diphenylphosphino)butane (dppb), 1,1'-bis(diphenylphosphino)ferrocene (dppf) and 1,4-bis(diphenylphosphino)benzene (dppbz) using trimethylamine N-oxide as decarbonylating agent produce the chelated $[\text{Fe}_3(\text{CO})_8(\mu\text{-CO})_2(\mu,\eta^2\text{-diphosphine})]$ and the new series of symmetrical $[\{\text{Fe}_3(\text{CO})_9(\mu\text{-CO})_2\}_2(\mu,\eta^2\text{-diphosphine})]$ and unsymmetrical $[\text{Fe}_3(\text{CO})_9(\mu\text{-CO})_2(\mu,\eta^2\text{-diphosphine})[\text{Fe}(\text{CO})_4]]$ bridged complexes, in reasonable yield. The complexes were characterized by IR, ^{31}P and ^{13}C NMR spectroscopy, and elemental analysis. Electrochemical studies on these compounds reveal that the substitution of one or more phosphine ligands for carbon monoxide of $[\text{Fe}_3(\text{CO})_{12}]$ results in a more cathodic potential for the first reduction peak, but is insensitive to the σ -donor capabilities of the ligands.

Keywords: Iron; Diphosphine; Electrochemistry; Bridging ligand

1. Introduction

Several reports have described the reaction of mono- and bidentate phosphines with $[\text{M}_3(\text{CO})_{12}]$ ($\text{M} = \text{Ru}, \text{Os}$) [1–9]. The reaction of $[\text{Fe}_3(\text{CO})_{12}]$ with tertiary phosphines generally produces the well-known mono-, di- and trinuclear complexes in very poor yields. Previous attempts to react the monosubstituted trinuclear complex with additional phosphine to afford the disubstituted triiron carbonyl phosphine yielded only the mononuclear iron carbonyl $[\text{Fe}(\text{CO})_4(\text{phosphine})]$ and $[\text{Fe}(\text{CO})_3(\text{phosphine})_2]$ complexes [10].

Herein, we report the synthesis of a new series of triiron carbonyls, derivatives of bidentate phosphine ligands with several coordination modes, using trimethylamine N-oxide as decarbonylating agent, in dichloromethane, at room temperature. The reaction of the title complex with 1,2-bis(diphenylphosphino)ethane (dppe), 1,4-bis(diphenylphosphino)butane (dppb), 1,4-bis(diphenylphosphino)benzene (dppbz) and 1,1'-bis(diphenylphosphino)ferrocene (dppf), under these conditions, produces the complexes $[\text{Fe}_3(\text{CO})_8(\mu\text{-CO})_2(\mu,\eta^2\text{-diphosphine})]$, with the bidentate phosphine acting as a typical chelating bidentate ligand, and $[\text{Fe}_3(\text{CO})_9(\mu\text{-CO})_2(\mu,\eta^2\text{-diphosphine})[\text{Fe}(\text{CO})_4]]$,

$[\{\text{Fe}_3(\text{CO})_9(\mu\text{-CO})_2\}_2(\mu,\eta^2\text{-diphosphine})]$, where the bidentate phosphines act as bridging ligands, with yields in the range 20–30% on the first and third types of complex, and 5–10% on the second.

2. Experimental

2.1. Materials

Triirondodecacarbonyl, $\text{Me}_3\text{NO} \cdot 2\text{H}_2\text{O}$, CDCl_3 and CD_2Cl_2 were purchased from Aldrich and used as received. All manipulations were conducted under argon using Schlenk techniques. Solvents were purified by standard methods [11] and were freshly distilled prior to use.

2.2. Apparatus

Infrared spectra were recorded in solution on a Jasco Model IR-700 and Bomem FTIR spectrophotometers. ^1H , $^{31}\text{P}\{\text{H}\}$ and $^{13}\text{C}\{\text{H}\}$ NMR spectra were obtained on a Bruker Model AC300/P spectrometer operating at 300, 121.5 and 75.45 MHz respectively using tetramethylsilane as internal standard for ^1H and ^{13}C and H_3PO_4 85% as external standard for ^{31}P . Elemental analyses were performed on a Perkin-Elmer Model 2400 CHN apparatus.

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Electrochemical measurements were performed on an EG&G Princeton Applied Research (PAR) M273A electrochemical analyzer interfaced to an IBM computer employing PAR 270 electrochemical software. A standard three-electrode cell was designed to allow the tip of the reference electrode to closely approach the working electrode. Positive feedback IR compensation was applied routinely. All measurements were carried out under argon, in anhydrous deoxygenated solvents; solutions were ca. 1×10^{-3} M with respect to the compounds under study and ca. 1×10^{-1} M with respect to the supporting electrolyte, $[\text{Bu}_4\text{N}][\text{BF}_4]$. A platinum disk working electrode, a platinum wire auxiliary electrode, and a saturated calomel reference electrode (SCE) were used in these experiments. The values of the measurements were calibrated with ferrocene, as internal standard, in known concentration. Under the actual experimental conditions the Fc/Fc^+ couple is located at +0.56 V vs. SCE.

2.3. Syntheses

For all bidentate phosphines used a similar procedure was followed. We present here a general method.

To a mixture of 0.200 g (0.397 mmol) of $[\text{Fe}_3(\text{CO})_{12}]$ and 0.397 mmol of the bidentate phosphines in 20 cm³ of dichloromethane, 0.090 g (0.810 mmol) of $\text{Me}_3\text{NO} \cdot 2\text{H}_2\text{O}$ dissolved in a mixture of 2 cm³ of methanol and 10 cm³ of dichloromethane was added dropwise while argon was bubbled into the solution. After 15 min the black–green solution obtained was filtered through an SiO_2 column ($2 \times 3 \text{ cm}^2$) to destroy excess $\text{Me}_3\text{NO} \cdot 2\text{H}_2\text{O}$, and the solvent was removed under vacuum. The residue was redissolved in a small amount of dichloromethane and the products separated by thin layer chromatography on silica plates, using petroleum–ether (30–60°C)/ CH_2Cl_2 (85:15, v/v) as eluant. The first green fraction eluted was identified as unreacted $[\text{Fe}_3(\text{CO})_{12}]$. The second light-green band eluted was identified as $[\text{Fe}_3(\text{CO})_9(\mu\text{-CO})_2(\mu, \eta^2\text{-diphosphine})][\text{Fe}(\text{CO})_4]$ (diphosphine = dppe, dppf, dppbz), obtained in 5–10% yield.

dppe (1). IR ($\text{CH}_2\text{Cl}_2/\text{pentane}$; νCO , cm^{-1}): 2085 (m), 2052 (m), 2033 (vs), 2011 (vs), 1982 (m), 1946 (s), 1935 (s, sh), 1835 (w), 1795 (w).

dppf (2). IR ($\text{CH}_2\text{Cl}_2/\text{pentane}$; νCO , cm^{-1}): 2085 (m), 2050 (m), 2031 (vs), 2011 (vs), 1980 (m), 1945 (s), 1931 (s, sh), 1830 (w), 1795 (w).

dppbz (3). IR ($\text{CH}_2\text{Cl}_2/\text{pentane}$; νCO , cm^{-1}): 2085 (m), 2051 (vs), 2033 (vs), 2011 (vs), 1981 (m), 1945 (s), 1934 (s, sh), 181832 (w), 1796 (w).

The third black–green band eluted was identified as $[\{\text{Fe}_3(\text{CO})_9(\mu\text{-CO})_2\}_2(\mu, \eta^2\text{-diphosphine})]$ (diphosphine = dppe, dppb, dppf, dppbz), obtained in 20–30% yield.

dppe (4). Anal. Found: C, 42.38; H, 1.74. $\text{C}_{48}\text{H}_{24}\text{O}_{22}\text{P}_2\text{Fe}_6$ Calc.: C, 42.67; H, 1.78%. IR

($\text{CH}_2\text{Cl}_2/\text{pentane}$; νCO , cm^{-1}): 2085 (m), 2033 (vs), 2012 (vs), 1835 (w), 1795 (w).

dppb (5). Anal. Found: C, 43.20; H, 1.98. $\text{C}_{50}\text{H}_{28}\text{O}_{22}\text{P}_2\text{Fe}_6$ Calc.: C, 43.54; H, 2.03%. IR ($\text{CH}_2\text{Cl}_2/\text{pentane}$; νCO , cm^{-1}): 2085 (m), 2033 (vs), 2012 (vs), 1834 (w), 1798 (w).

dppf (6). Anal. Found: C, 44.34; H, 1.84. $\text{C}_{56}\text{H}_{28}\text{O}_{22}\text{P}_2\text{Fe}_7$ Calc.: C, 44.62; H, 1.86%. IR ($\text{CH}_2\text{Cl}_2/\text{pentane}$; νCO , cm^{-1}): 2085 (m), 2033 (vs), 2012 (vs), 1838 (w), 1796 (w).

dppbz (7). Anal. Found: C, 44.32; H, 1.71. $\text{C}_{52}\text{H}_{24}\text{O}_{22}\text{P}_2\text{Fe}_6$ Calc.: C, 44.54; H, 1.72%. IR ($\text{CH}_2\text{Cl}_2/\text{pentane}$; νCO , cm^{-1}): 2085 (m), 2033 (vs), 2012 (vs), 1827 (w), 1793 (w).

The fourth purple band eluted was identified as $[\text{Fe}_3(\text{CO})_8(\mu\text{-CO})_2(\mu, \eta^2\text{-diphosphine})]$ (diphosphine = dppe, dppb, dppf), yield 20–30%.

dppe (8). Anal. Found: C, 50.61; H, 2.83. $\text{C}_{31}\text{H}_{24}\text{O}_{10}\text{P}_2\text{Fe}_3$ Calc.: C, 51.06; H, 2.84%. IR ($\text{CH}_2\text{Cl}_2/\text{pentane}$; νCO , cm^{-1}): 2064 (s), 1998 (vs), 1956 (vw), 1926 (vw), 1789 (w), 1743 (w).

dppb (9). Anal. Found: C, 51.91; H, 3.18. $\text{C}_{38}\text{H}_{28}\text{O}_{10}\text{P}_2\text{Fe}_3$ Calc.: C, 52.17; H, 3.20%. IR ($\text{CH}_2\text{Cl}_2/\text{pentane}$; νCO , cm^{-1}): 2064 (s), 1996 (vs), 1950 (w), 1930 (vw), 1793 (w), 1750 (w).

dppf (10). Anal. Found: C, 55.59; H, 2.95. $\text{C}_{44}\text{H}_{28}\text{O}_{10}\text{P}_2\text{Fe}_3$ Calc.: C, 55.81; H, 2.96%. IR ($\text{CH}_2\text{Cl}_2/\text{pentane}$; νCO , cm^{-1}): 2066 (s), 1998 (vs), 1956 (w), 1931 (vw), 1781 (w), 1738 (w).

3. Results and discussion

3.1. Syntheses

The reactions of $[\text{Fe}_3(\text{CO})_{12}]$ with bidentate phosphines using $\text{Me}_3\text{NO} \cdot 2\text{H}_2\text{O}$ as decarbonylating agent, in 1:1:2 molar ratio, produce the compounds 4–10 in practically the same yield when the reaction is stopped 10–15 min after the addition of decarbonylating agent. However, when the reactions were stirred for 2–3 h after the addition of $\text{Me}_3\text{NO} \cdot 2\text{H}_2\text{O}$, the black–green solutions became purple and the compounds 8–10 were obtained as principal products with yields in the range 20–30%. In this case, a yellow band identified as the bridged mononuclear complexes [e.g. $\{[\text{Fe}(\text{CO})_4]_2(\mu, \eta^2\text{-dppf})\}$]; IR ($\text{CH}_2\text{Cl}_2/\text{pentane}$; νCO , cm^{-1}): 2050 (s), 1980 (m), 1945 (vs), 1931 (vs); ^{31}P NMR (CDCl_3): δ (ppm) 67.4 (s)] was eluted as side products before the chelated purple complexes 8–10. The data are fairly consistent with published values [12]. We believe that these bridged mononuclear complexes were obtained as a consequence of the reaction of the initially formed green bridged products with the excess decarbonylating agent, giving rise to a small amount of the bridged mononuclear complexes and decomposition products, since no increase in yield of purple complexes was

observed for longer reaction times. For shorter reaction times, the bridged mononuclear complexes were not formed. When the iron complex/phosphine/decarbonylating agent molar ratio used was 1:0.5:1, the compounds 4–7 were obtained with yields in the range 20–30% as major products within 10–15 min, together with the unsymmetrical compounds 1–3 in low yields (5–10%).

Compound 10 has previously been obtained, in low yield together with known mono- and dinuclear complexes, in the reaction of $[\text{Fe}_3(\text{CO})_{12}]$ with dppf under more drastic conditions [13]. With the method described here, the reactions were conducted under milder conditions, resulting in an improved yield of the $[\text{Fe}_3(\text{CO})_8(\mu\text{-CO})_2(\mu, \eta^2\text{-diphosphines})]$ (compounds 8–10) together with a new series of triiron carbonyl derivatives where the bidentate phosphines act as bridging ligands.

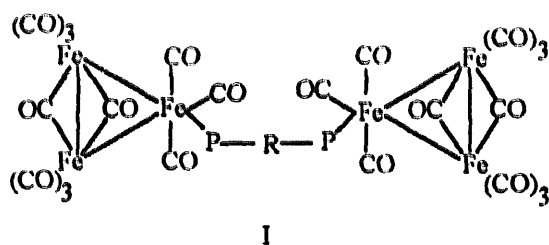
All compounds were reasonably stable in the solid state and in solution, but slowly decomposed when stored for a long period of time under argon in the freezer. They are soluble in polar organic solvents but sparingly soluble in non-polar ones.

3.2. Characterization

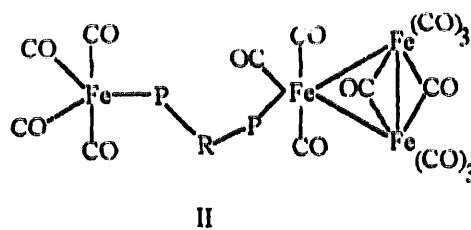
^1H NMR spectra of compounds 1–10 present broad peaks and unfortunately no conclusion could be inferred from these data.

Infrared spectra of derivatives 4–7 exhibit a pattern containing three terminal carbonyl and two bridging carbonyl bands, almost the same as that of unsubstituted $[\text{Fe}_3(\text{CO})_{12}]$ and in agreement with the data for the monosubstituted triphenylphosphine complex $[\text{Fe}_3(\text{CO})_{11}(\text{PPh}_3)]$ [10]. ^{31}P and ^{13}C NMR data for the complexes 4–7 are shown in Table 1.

Compounds 1–3 were identified by IR and ^{31}P NMR spectroscopy only. The infrared spectra of these complexes show two sets of carbonyl absorption bands, corresponding to the mixture of both $[\text{Fe}_3(\text{CO})_{11}]$ and $[\text{Fe}(\text{CO})_4]$ moieties, a result in good agreement with the infrared data found previously for the complexes $[\text{Fe}_3(\text{CO})_{11}(\text{PPh}_3)]$ [10] and $[\{\text{Fe}(\text{CO})_4\}_2(\text{dppf})]$ [12]. This suggests that the compounds are bridged unsymmetrically, where the diphosphines are bound on one side by the $[\text{Fe}_3(\text{CO})_{11}]$ moiety and on the other by the $[\text{Fe}(\text{CO})_4]$ moiety. The ^{31}P NMR spectra at room temperature (see Table 1) present two doublets for 1 and 3 and two singlets for 2. The downfield signals of these complexes are almost identical to the chemical shifts of both dppe complexes of $\text{Fe}(\text{CO})_4$ and mononuclear bridged complexes of dppf previously reported [13,14], and the upfield signals are almost identical to the chemical shifts for the bridged complexes 4–7. These data could confirm the proposed structures (see I and II). Two structures containing chemically equivalent and non-equivalent phosphorus donor atoms can be suggested for the compounds 1–7:



P - R - P = *dppe*, *dppb*, *dppf*, *dppbz*.
Compounds 4–7



P - R - P = *dppe*, *dppf*, *dppbz*.
Compounds 1–3

The singlets at 51.1 4, 47.0 5, 49.3 6 and 55.4 ppm 7 can be assigned to the structure I, in which the two phosphorus atoms in the equatorial position remain in a chemically equivalent environment. The doublets centered at 51.2 ppm ($J_{\text{P-P}} = 35.0$ Hz) and 70.2 ppm ($J_{\text{P-P}} = 35.0$ Hz) for 1, 55.1 ppm ($J_{\text{P-P}} = 3.6$ Hz) and 73.5 ppm ($J_{\text{P-P}} = 3.6$ Hz) for 3 and the singlets at 49.6 and 67.2 ppm for 2 can be ascribed to the structure II, in which both the $[\text{Fe}_3(\text{CO})_{11}]$ and $[\text{Fe}(\text{CO})_4]$ groups are

present in the same molecule, forming an unsymmetrical product.

The room temperature ^{13}C NMR spectra for complexes 4–7 show a broad singlet at 217.9 ppm for 4, 218.1 ppm for 5, 218.0 ppm for 6 and 217.8 ppm for 7 owing to the overall scrambling processes of the carbonyls occurring within each $[\text{Fe}_3(\text{CO})_{11}]$ moiety of the bridged complexes. All the compounds exhibit simple spectra in the ligand region, as expected for these atoms

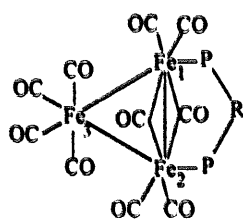
Table 1
 $^{31}\text{P}(\text{H})$ and $^{13}\text{C}(\text{H})$ NMR data for the complexes 1–7

Compound	^{31}P (δ , ppm) ^a	^{13}C (δ , ppm) ^a
$[\text{Fe}_3(\text{CO})_9(\mu\text{-CO})_2(\mu,\eta^2\text{-dppe})\text{Fe}(\text{CO})_4]$ 1	51.2 (u, $J_{\text{P-P}} = 35$ Hz) 70.2 (d, $J_{\text{P-P}} = 35$ Hz)	
$[\text{Fe}_3(\text{CO})_9(\mu\text{-CO})_2(\mu,\eta^2\text{-dppf})\text{Fe}(\text{CO})_4]$ 2	49.6 (s) 67.2 (s)	
$[\text{Fe}_3(\text{CO})_9(\mu\text{-CO})_2(\mu,\eta^2\text{-dppbz})\text{Fe}(\text{CO})_4]$ 3	55.1 (d, $J_{\text{P-P}} = 3.6$ Hz) 73.5 (d, $J_{\text{P-P}} = 3.6$ Hz)	
$[(\text{Fe}_3(\text{CO})_9(\mu\text{-CO})_2)_2(\mu,\eta^2\text{-dppe})]$ 4	51.1 (s)	CO: 217.9 (s, br); phenyl: 129.4 (d, $J_{\text{P-C}} = 42.4$ Hz, C_{ipso}), 131.8 (t, $J_{\text{P-C}} = 4.6$ Hz, C_{ortho}), 131.3 (s, C_{para}), 129.2 (t, $J_{\text{P-C}} = 4.9$ Hz, C_{meta}); ethyl: 24.2 (m)
$[(\text{Fe}_3(\text{CO})_9(\mu\text{-CO})_2)_2(\mu,\eta^2\text{-dppb})]$ 5	47.0 (s)	CO: 218.1 (s, br); phenyl: 131.6 (d, $J_{\text{P-C}} = 43.8$ Hz, C_{ipso}), 132.0 (d, $J_{\text{P-C}} = 9.2$ Hz, C_{ortho}), 131.0 (s, C_{para}), 128.9 (d, $J_{\text{P-C}} = 9.8$ Hz, C_{meta}); butyl: 29.5 (d, $J_{\text{P-C}} = 26.6$ Hz), 24.8 (d, $J_{\text{P-C}} = 15.4$ Hz)
$[(\text{Fe}_3(\text{CO})_9(\mu\text{-CO})_2)_2(\mu,\eta^2\text{-dppf})]$ 6	49.3 (s)	CO: 218.0 (s, br); phenyl: 132.9 (d, $J_{\text{P-C}} = 43.4$ Hz, C_{ipso}), 132.8 (d, $J_{\text{P-C}} = 10.2$ Hz, C_{ortho}), 131.1 (s, C_{para}), 128.4 (s, $J_{\text{P-C}} = 10.3$ Hz, C_{meta}); cyclopentadienyl: 80.4 (d, $J_{\text{P-C}} = 42.8$ Hz, C_{ipso}), 74.1 (d, $J_{\text{P-C}} = 10.8$ Hz, $1C_2$), 73.8 (d, $J_{\text{P-C}} = 7.8$ Hz, C_5)
$[(\text{Fe}_3(\text{CO})_9(\mu\text{-CO})_2)_2(\mu,\eta^2\text{-dppbz})]$ 7	55.4 (s)	CO: 217.8 (s, br); phenyl: 133.0 (d, $J_{\text{P-C}} = 52.1$ Hz, C_{ipso}), 131.1 (s, C_{para}), 129.0 (d, $J_{\text{P-C}} = 10.8$ Hz, C_{meta}); benzyl: 132.7 (t, $J_{\text{P-C}} = 9.8$ Hz, C_α), 131.9 (d, $J_{\text{P-C}} = 45.2$ Hz, C_{ipso})

^a Spectra in CDCl_3 . Subscript a and b refer to the α (adjacent to the phosphine group) and β cyclopentadienyl carbon atoms respectively. C_α refers to the *ortho* carbon atoms (adjacent to the phosphine group) in the benzyl group.

in a symmetrical bridge due to the structure I, except for the complex 4 that presents peaks of a system AA'X.

Table 2 summarizes the ^{31}P and ^{13}C NMR results for compounds 8–10. IR, ^{31}P and ^{13}C NMR spectra of these complexes are in agreement with previously reported results [13] for the $[\text{Fe}_3(\text{CO})_9(\mu\text{-CO})_2(\mu,\eta^2\text{-dppf})]$ complex, and we therefore attribute the same structure for the complexes 8–10 as shown below:



III
 P - R - P = *dppe*, *dppb*, *dppf*.

All compounds exhibit a single absorption in the ^{31}P NMR spectra at room temperature, at 53.3 ppm for 8, 40.6 ppm for 9 and 41.5 ppm for 10, as expected for equatorially-disubstituted derivatives. The room temperature ^{13}C NMR spectra show, for all complexes, three peaks in the intensity ratio 6:2:2. The broad peak at 228.2 ppm for 8, 229.1 ppm for 9 and 230.8 ppm for 10 arises from the four terminal and two bridging car-

bonyls bound to the Fe_1 and Fe_2 (see III) [13]. The singlet at 218.6 ppm for 8, 218.8 ppm for 9, and 216.3 ppm for 10 was assigned to the two axial carbonyls, and the singlet at 207.6 ppm for 8, 207.5 ppm for 9 and 206.9 ppm for 10 was ascribed to the two equatorial carbonyls of the iron atom *trans* to the Fe–P bonds (Fe_3 in III) [15,16]. These reveal the presence of only one independent scrambling process occurring with the non-equivalent carbonyls bound to the Fe_1 and Fe_2 iron atoms (see III).

Lowering the temperature down to -70°C , the ^{13}C NMR spectrum of 9 at the carbonyl region shows six broad absorptions at 261.7, 259.5, 218.7, 215.6, 213.5 and 207.6 ppm in the intensity ratio 1:1:2:2:2:2. The broad peaks at 261.7 and 259.5 ppm were assigned to two non-equivalent bridging carbonyls. No P–CO coupling was observed for the two bridging carbonyl, perhaps owing to the low spectrum resolution at this temperature. The peaks at 218.7 and 207.6 ppm were attributed to the two axial and two equatorial carbonyls respectively, bound to the iron atom *trans* to the Fe–P bonds (Fe_3 in III). No shift of these last two peaks was observed relative to the room temperature spectrum. The absorptions at 215.6 and 213.5 ppm can be assigned to the two pairs of terminal carbonyls bound to Fe_1 and Fe_2 (see III). These results are in good agreement with the results reported earlier for disubstituted phosphite triiron carbonyl complexes [15,16]. The single absorption observed in the room temperature ^{31}P NMR spectrum starts to broaden as the temperature is decreased,

Table 2
 $^{31}\text{P}\{\text{H}\}$ ^a and $^{13}\text{C}\{\text{H}\}$ ^a NMR data for the complexes 8–10

Compound	^{31}P (δ , ppm)	^{13}C (δ , ppm)
$[\text{Fe}_3(\text{CO})_8(\mu\text{-CO})_2(\mu,\eta^2\text{-dppe})]$ 8	53.25 (s)	CO: 228.2 (br), 218.6 (s), 207.6 (s); phenyl: 134.5 (d, $J_{\text{P-C}} = 45.0$ Hz, C_{ipso}), 132.2 (d, $J_{\text{P-C}} = 9.5$ Hz, C_{ortho}), 130.7 (d, $J_{\text{P-C}} = 1.7$ Hz, C_{para}), 128.9 (d, $J_{\text{P-C}} = 9.9$ Hz, C_{meta}); ethyl: 23.8 (d, $J_{\text{P-C}} = 25.4$ Hz)
$[\text{Fe}_3(\text{CO})_8(\mu\text{-CO})_2(\mu,\eta^2\text{-dppb})]$ ^b 9	40.62 (s)	CO: 229.1 (br), 218.8 (s), 207.5 (s); phenyl: 137.7 (d, $J_{\text{P-C}} = 42.7$ Hz, C_{ipso}), 132.4 (d, $J_{\text{P-C}} = 9.1$ Hz, C_{ortho}), 130.6 (s, C_{para}), 129.1 (d, $J_{\text{P-C}} = 9.5$ Hz, C_{meta}); butyl: 25.5 (d, $J_{\text{P-C}} = 21.7$ Hz), 22.0 (d, $J_{\text{P-C}} = 9.6$ Hz)
$[\text{Fe}_3(\text{CO})_8(\mu\text{-CO})_2(\mu,\eta^2\text{-dppf})]$ 10	41.47 (s)	CO: 230.8 (br), 216.3 (s), 206.9 (s); phenyl: 137.6 (d, $J_{\text{P-C}} = 42.7$ Hz, C_{ipso}), 132.7 (d, $J_{\text{P-C}} = 10.1$ Hz, C_{ortho}), 130.1 (s, C_{para}), 128.2 (d, $J_{\text{P-C}} = 10.1$ Hz, C_{meta}); cyclopentadienyl: 77.6 (d, $J_{\text{P-C}} = 43$ Hz, C_{ipso}), 74.6 (d, $J_{\text{P-C}} = 8.8$ Hz, C_a), 72.3 (d, $J_{\text{P-C}} = 5.8$ Hz, C_b)

^a Spectra in CDCl_3 . Subscript a and b refer to the α (adjacent to the phosphine group) and β cyclopentadienyl carbon atoms.

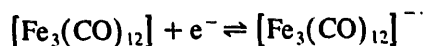
^b Spectrum in CD_2Cl_2 .

and at -70°C two signals of the same intensity are detected at 47.7 and 32.4 ppm. This observation confirms the non-equivalence of the iron atoms Fe_1 and Fe_2 at this temperature, probably owing to distortion of the structure III. An attempt to carry out more extensive variable temperature NMR studies was unsuccessful due to the fact that at temperatures below -70°C crystals began to deposit from the solution.

3.3. Electrochemistry

The cyclic voltammogram at a platinum disk electrode in 1,2-dichloroethane (DCE) solution, at room temperature, of $[\text{Fe}_3(\text{CO})_{12}]$ shows two well-defined reduction peaks in freshly prepared solutions, with $E_{1/2}$ values of -0.33 and 0.71 V vs. SCE, corresponding to one electron each. These results are in accordance with

previous work [17]. The first reduction step can therefore be assigned to the formation of a radical anion



Thus $[\text{Fe}_3(\text{CO})_{12}]$ forms a radical anion that has reasonable stability on the cyclic voltammetric timescale. Reduction of the radical anion at more negative potentials was found to be chemically irreversible. The presence of additional peaks in the reverse scan of the voltammogram suggests that fragmentation of the $[\text{Fe}_3(\text{CO})_{12}]^{\cdot -}$ unit accompanies the addition of a second electron. The reduction of the radical anion is therefore described by the equation [18]

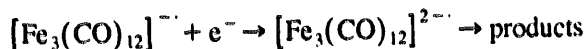


Table 3 summarizes the electrochemical data for the bridged complexes 4–7 and chelated complexes 8–10.

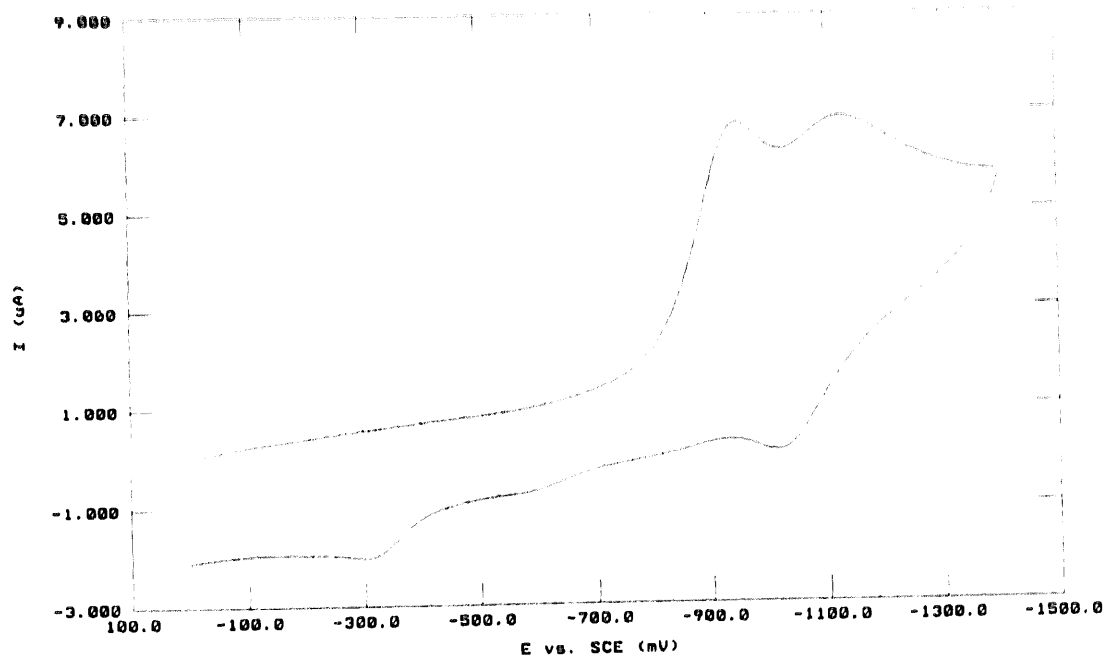


Fig. 1. Cyclic voltammetric responses of a 1,2-dichloroethane solution of 5 at a Pt electrode, scan rate 200 mV s^{-1} .

Table 3
Voltammetric data^{a,b} for the complexes 4–10

Compound	Reduction	Further reduction	Oxidation	
	E_p^{r1}	E_p^{r2}	E_p^{ox2c}	Further E_p^{ox}
$[\text{Fe}_3(\text{CO})_{12}]$	-0.330 ^d	-0.714		
4	-0.812	-1.25	-0.490	
5	-0.938	-1.12	-1.02	-0.316
6	-0.807	-1.33	-0.350	
7	-0.635			
8	-0.930	-1.09	-0.962	-0.259
9	-0.865	-1.12	-1.01	-0.306
10	-0.892	-1.22		-0.423

^a In volts vs. SCE. Superscript 1 (as in E_p^{r1}) refers to a first reduction process; superscript 2 to further processes.

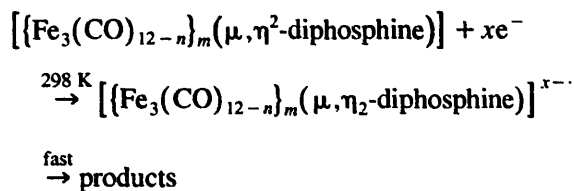
^b Scan rates 200 mV s^{-1} for all complexes.

^c E_p^{ox2} refers to fragmentation peaks on the reverse scan.

^d Reversible peaks.

The cyclic voltammetric responses of these compounds at a platinum disk electrode in DCE solution, at room temperature, are characterized by two chemically irreversible reduction processes. The first corresponds to a two-electron reduction to the radical anions $[\mathbf{4-6}]^{2-}$ (one-electron reduction for each non-interacting $[\text{Fe}_3(\text{CO})_{11}]$ moiety) and to a one-electron reduction to the radical anions $[\mathbf{8-10}]^{\cdot-}$. The second was attributed to the reduction step of the fragments generated by the decomposition of the radical anion species in the first process. Figs. 1 and 2 show the cyclic voltammograms for complexes **5** and **9** as examples. At room temperature, the electrochemistry is complicated by the con-

comitant decomposition of the radical anion and the first irreversible reduction step is



$$n = 2, m = 1, x = 1 \text{ or } n = 1, m = 2, x = 2$$

This same scheme was found for the monosubstituted phosphine and mono- and disubstituted phosphites at triiron dodecacarbonyl complexes studied earlier in dichloromethane [18]. The chelated complex **7** undergoes a single chemically irreversible one-electron reduction peak (EC mechanism) at more anodic potentials (see Table 3). The peak current of the reduction of **7** is about half as high as that of the corresponding peak current of **4-6**. This suggests some electronic interaction between the two Fe_3 cores, since the presence of π -unsaturation in the dppbz chain allows some degree of delocalization, provided that the M–P σ -bonding allows this delocalization through the unoccupied d-orbitals of the phosphorus atoms [19]. Unfortunately, the I – E response of **7** is complicated by subsequent fast chemical reactions, leading to M–P bond breaking that prevents proper electrochemical analyses. However, studies with more stable complexes on reduction, comprising bidentate phosphines with π -unsaturation in the chain that permit some degree of delocalization, are in progress in our laboratory.

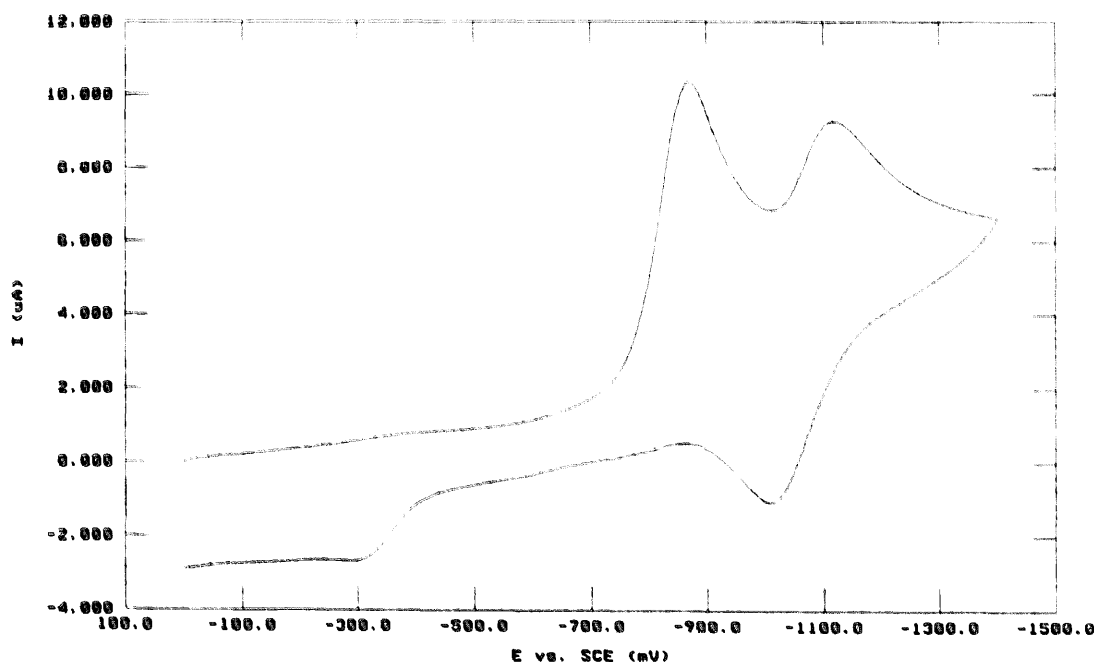


Fig. 2. Cyclic voltammetric responses of a 1,2-dichloroethane solution of **9** at a Pt electrode, scan rate 200 mV s^{-1} .

The electrochemical behavior of the bridged complexes 4–7 is similar to that of the complexes 1–3 in the region studied. The reduction peaks due to the $[\text{Fe}(\text{CO})_4]$ moiety are localized at more cathodic potentials [18].

Substitution of a phosphine ligand for carbon monoxide in $[\text{Fe}_3(\text{CO})_{12}]$ makes the potentials significantly more cathodic for the first reduction peaks in the bridged complexes. The same behavior was observed with increasing phosphine substitution in the chelated complexes, i.e. with increasing charge on the iron atom (Table 3), as has already been observed for phosphine substitution in cobalt clusters [20]. These first reduction potentials are remarkably insensitive to the σ -donor capabilities of the ligands for the bridged and chelated complexes. This is in direct contrast to the large variation in $E_{1/2}$ with ligand basicity, found for the oxidation potentials of a number of mononuclear carbonyl complexes [21–23]. While for mononuclear derivatives the redox orbitals appear to have contributions from both the carbonyl and phosphine ligands [21,24], for the clusters the redox orbitals are largely metal in character, and small variations in charge on the metal atoms are buffered through delocalization over the cluster unit [18].

Acknowledgements

The authors are indebted to FAPESP for financial support.

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