Reversible Oxidations in Ditertiary-phosphine Bridged Derivatives of $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$

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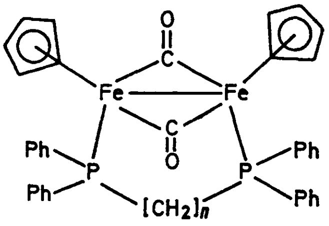
Summary The carbonyl–diphosphine bridged dimer $[(\pi\text{-}C_5H_5)Fe(CO)]_2[Ph_2P(CH_2)_3PPh_2]$ {Fe_2(diphos)} is reversibly oxidized electrochemically to the cation $Fe_2(diphos)^+$ which disproportionates in acetonitrile and is further oxidized to the transient dication $Fe_2(diphos)^{2+}$.

HAINES and DU PREEZ[1] have described the preparations of the ditertiary-phosphine–carbonyl bridged dimers $[(\pi\text{-}C_5H_5)\text{-}Fe(CO)]_2[Ph_2P(CH_2)_nPPh_2]$ (n = 1—3), {Fe_2 diphos}. They had reported earlier[2] that oxidation of the dimers by an equimolar amount of iodine in benzene gave the paramagnetic cations $[(\pi\text{-}C_5H_5)Fe(CO)]_2[Ph_2P(CH_2)_nPPh_2]^+$ in which there is an effective 'one electron metal–metal bond.' They also found that oxidation with excess of iodine gave various products which depended somewhat upon the bridging diphosphine ligand. We have investigated the oxidation–reduction properties of these dimers electrochemically, partly for comparison with the iron carbonyl dimer $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$. No evidence for intermediate oxidation states has been found in its oxidation.[3]



$$[(\pi\text{-}C_5H_5)Fe(CO)_2]_2 + 2S \xrightarrow{-2e} 2(\pi\text{-}C_5H_5)Fe(CO)_2S^+$$
$$(S{=}MeCN,\ Me_2CO)$$

A cyclic voltammogram† (100 V s^{-1}) of $[(\pi\text{-}C_5H_5)Fe(CO)]_2\text{-}[Ph_2P(CH_2)_3PPh_2]$ in acetonitrile is shown in the Figure. We have investigated the reactions which occur at the various waves by spectral and electrochemical methods and by the isolation of products. At wave 2 the dimer loses an electron reversibly to give the cation (reaction 1). The

$$\text{Fe (diphos)} \underset{+e}{\overset{-e}{\rightleftharpoons}} \text{Fe}_2\ \text{(diphos)}^+\ (E_{\frac{1}{2}} = -\ 0{\cdot}09\ \text{V}) \qquad (1)$$

cation is stable in dichloromethane solution for hours but disproportionates rapidly in acetonitrile {$t_{\frac{1}{2}} < 1$ min at

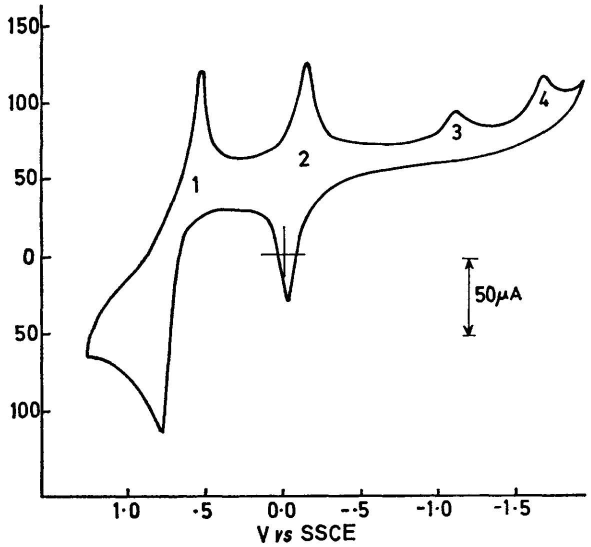


FIGURE. 100 V s^{-1} *cyclic voltammogram of* $[(\pi\text{-}C_5H_5)\ Fe(CO)]_2\ [Ph_2\ P(CH_2)_3\ PPh_2]$ *in* 0·1M-$[Bu^n_4][PF_6]$ *solution in acetonitrile.*

† All electrochemical measurements were made at platinum electrodes *vs.* saturated sodium chloride–calomel electrode. Potential measurements are uncorrected for junction potentials. The supporting electrolyte was $[Bu^n_4N][PF_6]$.

22 ± 2 °C; [Fe_2 (diphos)$^+$] *ca.* $6 \times 10^{-3}\text{M}$} (reaction 2) to

$$2\text{MeCN} + 2[(\pi\text{-C}_5\text{H}_5)\text{Fe(CO)}]_2[\text{Ph}_2\text{P(CH}_2)_3\text{PPh}_2]^+ \rightarrow [(\pi\text{-C}_5\text{H}_5)\text{Fe(CO)}]_2[\text{Ph}_2\text{P(CH}_2)_3\text{PPh}_2] + [(\pi\text{C}_5\text{H}_5)\text{Fe(CO)(NCMe)}]_2[\text{Ph}_2\text{P(CH}_2)_3\text{PPh}_2]^{2+} \quad (2)$$

give the neutral dimer and the ditertiary-phosphine bridged acetonitrile complex. The behaviour of the other two dimers ($n = 1$, 2) at this wave is identical. The $n = 2$ cation, however, disproportionates at a measurable rate {$t_{\frac{1}{2}}$ 30 ± 5 min at 22 ± 2 °C; [Fe_2 (diphos)$^+$ ($n = 2$)] *ca.* $3 \times 10^{-2}\text{M}$}.

At wave 1 the one electron metal-metal bonded cation loses a second electron reversibly to give the dication (reaction 3). The peak height for the cathodic portion of

$$\text{Fe}_2\ \text{diphos}^+ \underset{+e}{\overset{-e}{\rightleftharpoons}} \text{Fe}_2\ (\text{diphos})^{2+}\ (E_{\frac{1}{2}} = 0{\cdot}77\ \text{V}) \quad (3)$$

the wave decreases as the sweep rate is decreased. The cathodic reaction (4) is the recapture of the dication at the electrode (by reduction) which is competitive with decomposition on the time scale of the experiment (100—10 V s^{-1}).

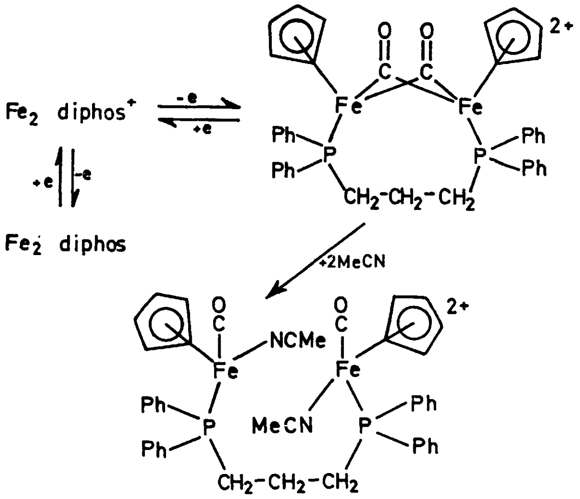
$$\text{Fe}_2\ \text{diphos}^{2+} \xrightarrow{+e} \text{Fe}_2\ (\text{diphos})^+ \quad (4)$$

We estimate the half life for decomposition (giving > 90% of the ditertiary phosphine bridged acetonitrile complex) to be 10—20 ms. The overall oxidation is shown in the Scheme. The oxidation chemistry of the other bridged dimers ($n = 1$ and 2) is similar, but we have not observed the dications even at very fast scan speeds, and both symmetric and asymmetric cleavage paths (5) and (6) are important. In the asymmetric path one iron atom has

$$\text{Fe}_2\ \text{diphos}^{2+} \begin{cases} \rightarrow [(\pi\text{-C}_5\text{H}_5)\text{Fe(CO)(NCMe)}]_2[\text{Ph}_2\text{P(CH}_2)_n\text{PPh}_2]^{2+}\ (n = 1 \text{ or } 2) & (5) \\ \rightarrow (\pi\text{-C}_5\text{H}_5)\text{Fe(CO)}_2[\text{Ph}_2\text{P(CH}_2)_n\text{PPh}_2]^+\ (n = 1 \text{ or } 2) + \text{Fe}^{2+} & (6) \end{cases}$$

captured both bridging carbonyls and the bridging diphosphine ligand. The symmetric path is favoured at higher temperatures.

The appearance of multiple oxidation states in the dimers, but not in $[(\pi\text{-C}_5\text{H}_5)\text{Fe(CO)}_2]_2$, is apparently a consequence of the ditertiary-phosphine bridge. The structural integrity of the dication is clearly dependent on the diphosphine bridge since in it the metal–metal bond has been completely oxidized. We assume that the dicarbonyl bridge remains intact in the dication because of the reversibility of the $\text{Fe}_2(\text{diphos})^+$–$\text{Fe}_2(\text{diphos})^{2+}$ couple. Electrochemical reduction of either $[(\pi\text{-C}_5\text{H}_5)\text{Fe(CO)(NCMe)}]_2[\text{Ph}_2\text{P(CH}_2)_n\text{PPh}]_2^{2+}$ or $(\pi\text{-C}_5\text{H}_5)\text{Fe(CO)}_2[\text{Ph}_2\text{P(CH}_2)_n\text{PPh}_2]^+$ (in both of which the dicarbonyl bridge has been broken) is irreversible and occurs at less than $-1{\cdot}0$ V. The dication may be observable at low temperatures by i.r. spectroscopy.



SCHEME

At the irreversible reduction waves (3 and 4) the electron transfer reactions involve the unidentate diphosphine complex $(\pi\text{-C}_5\text{H}_5)\text{Fe(CO)}_2[\text{Ph}_2\text{P(CH}_2)_3\text{PPh}_2]^+$ formed in small amount when the dication decomposes. The same

$$2(\pi\text{-C}_5\text{H}_5)\text{Fe(CO)}_2[\text{Ph}_2\text{P(CH}_2)_n\text{PPh}_2]^+ \xrightarrow{+2e} [(\pi\text{-C}_5\text{H}_5)\text{Fe(CO)}_2]_2 + \text{Ph}_2\text{P(CH}_2)_n\text{PPh}_2\ (\text{wave } 3)$$

$$[(\pi\text{-C}_5\text{H}_5)\text{Fe(CO)}_2]_2 \xrightarrow{+2e} 2(\pi\text{-C}_5\text{H}_5)\text{Fe(CO)}_2^-\ (\text{wave } 4)$$

pattern toward reduction has been observed for the complexes $(\pi\text{-C}_5\text{H}_5)\text{Fe(CO)}_2\text{L}^+$ {L = PPh_3, CO, or NCMe} in 1,2-dimethoxyethane by Dessy, King, and Waldrop.[4]

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