chloroform solution containing the above-mentioned complexes invariably leads to the decomposition of the azide and to the formation of the following complexes: $Cu_2L_3Cl_2$, $[AgLCl]_4$, and AuLCl. It should be noted that $CHCl_3$ itself does not undergo photochemical decomposition under the same conditions.[30] Mass spectral analysis of the gaseous products obtained from the photolysis of CuL_2N_3 indicates the products to consist of over 98% N_2. Small amounts of CO_2, O_2, and H_2 are also present and their source is currently being studied.[31] Quantitative nitrogen analysis showed that the decomposition produced nitrogen in 85% yield based on 100% yield for the complete conversion of azide to nitrogen. The remaining nitrogen was accounted for as hydrazoic acid which was obtained in the forerun of the distillation of the photolyzed solution.

The decomposition of transition metal azides to produce nitrogen has been interpreted to proceed either by homolytic cleavage of the metal–nitrogen bond[32] or by cleavage of the N–N bond of the azide resulting in the formation of a metal–nitrene intermediate.[3] From the evidence available to us to date it appears that the photolysis leads to homolytic cleavage of the copper–nitrogen bond resulting in the formation of azide radicals and a Cu(0) complex which then react with the solvent.[30] However, we cannot rule out the second possibility since we have failed to detect any volatile compounds other than $CHCl_3$, C_2H_5OH, and HN_3. This interesting reaction is currently being investigated in detail.

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[30] During the reaction we note the buildup of an intense purple color in solution. Spectral measurements indicate the maximum to be centered at 5400 Å with a shoulder at around 4600 Å. The solution also appears to be paramagnetic and this will be reported at a later date.

[31] One possible source for these gases is the ethanol which is present as an inhibitor in chloroform.

[32] V. Balzani, L. Maggi, F. Scandola, and V. Carassiti, *Inorg. Chim. Acta Rev.*, **1**, 7 (1967).

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The Electrochemical Oxidation of 1,2-Bis(diphenylphosphino)ethanebis(π-cyclopentadienylcarbonyliron)

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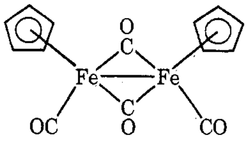
The electrochemical oxidation of the metal–metal bond in the carbonyl-diphosphine bridged dimer $[(\pi\text{-}C_5H_5)Fe(CO)]_2(Ph_2PCH_2CH_2PPh_2)$ (Ph = C_6H_5) (I) in a variety of solvents occurs by two one-electron steps. The removal of the first electron to give the cation $\{[(\pi\text{-}C_5H_5)Fe(CO)]_2(Ph_2PCH_2CH_2PPh_2)\}^+$ (II) is electrochemically reversible in all media studied. Compound II is apparently isostructural with I and contains a "one-electron" metal–metal bond. Removal of a further electron from II in acetonitrile gives two kinds of reaction products by separate reaction paths. The product from one path is the diphosphine-bridged acetonitrile complex $\{[(\pi\text{-}C_5H_5)Fe(CO)(NCCH_3)]_2(Ph_2PCH_2CH_2PPh_2)\}^{2+}$ (IV) which arises from symmetrical cleavage of the molecule after complete oxidation of the metal–metal bond, and in the other, unsymmetrical cleavage gives the unidentate diphos complex $[(\pi\text{-}C_5H_5)Fe(CO)_2(Ph_2PCH_2CH_2PPh_2)]^+$ (III) and Fe^{2+}. The relative importance of the two paths depends upon the solvent and the temperature. In acetonitrile, II disproportionates with a half-time of 30 ± 5 min at 22 ± 2° to give $[(\pi\text{-}C_5H_5)Fe(CO)]_2(Ph_2PCH_2CH_2PPh_2)$ (I) and $\{[(\pi\text{-}C_5H_5)Fe(CO)(NCCH_3)]_2(Ph_2PCH_2CH_2PPh_2)\}^{2+}$ (IV).

Introduction

Haines and Du Preez have reported the preparations of the bridged diphosphine complexes $[(\pi\text{-}C_5H_5)Fe(CO)]_2[Ph_2P(CH_2)_nPPh_2]$ (n = 1, 2, 3).[1] From infrared and nmr data the structures of the complexes are as shown in Figure 1 where 1,2-bis(diphenylphosphino)ethane (n = 2) is the bridging ligand.

The complexes are oxidized by iodine in benzene solution.[2] Equimolar iodine gives the cations $\{[(\pi\text{-}C_5H_5)Fe(CO)]_2[Ph_2P(CH_2)_nPPh_2]\}^+$ in which a single electron has been lost giving a "one-electron metal–metal bond" and the bridging carbonyls and diphosphine remain intact. Oxidation of either $[(\pi\text{-}C_5H_5)Fe(CO)]_2(Ph_2CH_2CH_2PPh_2)$ or $\{[(\pi\text{-}C_5H_5)Fe(CO)]_2(Ph_2PCH_2CH_2PPh_2)\}^+$ by excess iodine gives the unidentate diphos complex $[(\pi\text{-}C_5H_5)Fe(CO)_2(Ph_2PCH_2CH_2PPh_2)]^+$ as the major product.

We recently reported that electrochemical oxidation of the metal–metal bond in the related iron carbonyl dimer



occurs by a two electron transfer step and that oxidation proceeds with symmetric cleavage of the molecule[3]

$$2S + [(\pi\text{-}C_5H_5)Fe(CO)_2]_2 \xrightarrow{-2e^-} 2[(\pi\text{-}C_5H_5)Fe(CO)_2S]^+ \quad (S = CH_3CN, (CH_3)_2CO)$$

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[1] R. J. Haines and A. L. Du Preez, *J. Organometal. Chem.*, **21**, 181 (1970).

[2] R. J. Haines, A. L. Du Preez, and G. T. W. Wittmann, *Chem. Commun.*, 611 (1968).

[3] J. A. Ferguson and T. J. Meyer, *Inorg. Chem.*, **10**, 1025 (1971).

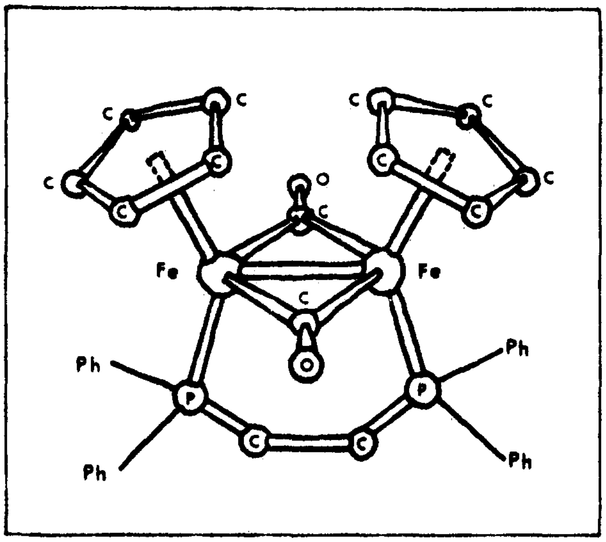

Figure 1.

Oxidations with ferric ion are similar[4]

$$2CH_3CN + 2Fe^{3+} + [(\pi\text{-}C_5H_5)Fe(CO)_2]_2 \longrightarrow 2Fe^{2+} + 2[(\pi\text{-}C_5H_5)Fe(CO)_2(NCCH_3)]^+$$

In neither case is there evidence for an initial one-electron oxidation product, $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2^+$, analogous to $\{[(\pi\text{-}C_5H_5)Fe(CO)]_2(Ph_2PCH_2CH_2PPh_2)\}^+$.

This study extends our earlier work on the oxidation–reduction properties of compounds containing metal–metal bonds.[3–5] It was undertaken in order to make comparisons with the iron carbonyl dimer, to verify the existence of multiple oxidation states in the diphos system $[(\pi\text{-}C_5H_5)Fe(CO)]_2(Ph_2PCH_2CH_2PPh_2)^{+,0}$, and to understand the oxidation–reduction chemistry of the diphos dimer and of the dimer cation.

Experimental Section[6]

Measurements.—Ultraviolet–visible spectra were recorded on a Cary Model 14 spectrophotometer and infrared spectra on a Perkin-Elmer Model 421 spectrophotometer. Infrared extinction coefficients for carbonyl bands were determined by measuring the total area under the peaks in question. The extinction coefficients for a given compound were determined for a series of concentrations. The values so obtained were used to measure unknown concentrations of the compound in the same medium. Nmr measurements were made on a Jeolco 60-MHz high-resolution spectrometer. All electrical measurements were made *vs.* the saturated sodium chloride calomel electrode (ssce) using standard three-electrode operational amplifier circuitry as previously described.[3] *n* determinations, where *n* is the total number of electrons transferred in an exhaustive electrolysis at constant potential, were obtained by measuring the total area under a current *vs.* time curve with a planimeter and represent the averaged value of at least three separate experiments. All cyclic voltammetric measurements were carried out at a platinum bead electrode at a scan rate of 200 mV/sec. Epr measurements were made on a Varian Model E-3 spectrometer.

Materials.—Tetra-*n*-butylammonium hexafluorophosphate (TBAH) was prepared by standard techniques,[7] recrystallized three times from hot ethanol–water mixtures, and dried in a vacuum oven for 10 hr at 70°. $[(\pi\text{-}C_5H_5)Fe(CO)]_2(Ph_2PCH_2CH_2PPh_2)$ was prepared as described by Haines and Du Preez.[2] Spectrograde acetonitrile was dried over activated alumina and reagent grade acetone over anhydrous magnesium sulfate before use. *n*-Butyronitrile was purified by vacuum distillation from sodium carbonate–potassium permanganate and dried over activated alumina. All other chemicals were spectrograde, reagent grade, or polarographic grade and used without further purification.

Preparations and Reactions.—All manipulations were carried out under nitrogen in deaerated solvents.

1. Solutions of $\{[(\pi\text{-}C_5H_5)Fe(CO)]_2(Ph_2PCH_2CH_2PPh_2)\}^+$ (II). (i) **In Dichloromethane.**—In a typical experiment, 100 mg of $[(\pi\text{-}C_5H_5)Fe(CO)]_2(Ph_2PCH_2CH_2PPh_2)$ was dissolved in 20 ml of a 0.1 *M* solution of TBAH in dichloromethane. The resulting green solution was oxidized at a platinum electrode at a potential difference of +0.5 V *vs.* the ssce for 1.5 hr. The reaction was monitored by following the current *vs.* time curve on a linear recorder. After complete oxidation, the infrared spectrum of the resulting deep brown solution had a single very broad band in the carbonyl region centered at 1775 cm^{-1}. An epr spectrum of the dichloromethane solution at room temperature gave no signal. Attempts to isolate pure samples of complex II as its hexafluorophosphate salt were unsuccessful (see section A in Results) and it was therefore characterized *in situ* as described in the Results.

(ii) **In Acetonitrile.**—$[(\pi\text{-}C_5H_5)Fe(CO)]_2(Ph_2PCH_2CH_2PPh_2)$ (I) is only slightly soluble in acetonitrile. Solutions containing the cation II in 0.1 *M* TBAH–acetonitrile can be prepared by the one-electron suspension oxidation of I at a platinum electrode at +0.50 V *vs.* the ssce. However, the solutions are unstable since II disproportionates in acetonitrile (see section A in Results).

2. The Oxidation of $\{[(\pi\text{-}C_5H_5)Fe(CO)]_2(Ph_2PCH_2CH_2PPh_2)\}^+$ (II). (i) **In Dichloromethane.**—A dark brown solution of II in dichloromethane, prepared as described above, was oxidized at a platinum electrode at +1.2 V *vs.* the ssce until the current–time curve indicated the oxidation was complete. The infrared spectrum of the pale yellow solution in the carbonyl region had bands at 2057 and 2013 cm^{-1} indicating the presence of $[(\pi\text{-}C_5H_5)Fe(CO)_2(Ph_2PCH_2CH_2PPh_2)]^+$ (III).[8] Attempts to isolate III as its hexafluorophosphate salt were unsuccessful. For example, it cannot be separated from TBAH on a Florisil column. Because of the problems encountered in trying to purify III it was determined *in situ* using the area under the carbonyl bands and its cyclic voltammetric properties as described in the Results. In a separate experiment, the oxidation was repeated in dichloromethane which was 0.1 *M* in TBAH and 0.1 *M* in 1,10-phenanthroline. The oxidation was carried out at a platinum electrode at a potential difference of +0.95 V *vs.* the ssce. The amount of III was determined by infrared in the carbonyl region. A known volume of the solution was evaporated to dryness, dissolved in a few milliliters of acetonitrile, and diluted with water to a known volume. The ferrous ion in the solution was determined spectrophotometrically as the tris(1,10-phenanthroline) complex $Fe(phen)_3^{2+}$ (ϵ 11,100 at 510 nm).[9] Ferric ion was shown to be absent by adding a few drops of the solution to an aqueous solution of ferrocyanide. The deep color of the Prussian blue complex was not observed.

(ii) **In Acetonitrile.**—A 30-mg sample of $[(\pi\text{-}C_5H_5)Fe(CO)]_2(Ph_2PCH_2CH_2PPh_2)$ was suspended in 20 ml of a 0.1 *M* TBAH–acetonitrile solution and oxidized at +0.50 V *vs.* the ssce. When the current had reached about 50% of its initial value, the solution was clear [nearly complete formation of $[(\pi\text{-}C_5H_5)Fe(CO)]_2(Ph_2PCH_2CH_2PPh_2)^+$ (II)]. The potential was then increased to +1.20 V [to oxidize (II)] and electrolysis continued until the reaction was complete (2 hr). Two carbonyl-containing products were observed: $[(\pi\text{-}C_5H_5)Fe(CO)_2(Ph_2PCH_2CH_2PPh_2)]^+$ (III) (ν_{CO} 2057 and 2013 cm^{-1}) and $\{[(\pi\text{-}C_5H_5)Fe(CO)(NCCH_3)]_2(Ph_2PCH_2CH_2PPh_2)\}^{2+}$ (IV) (ν_{CO} 1982 cm^{-1}). They were determined quantitatively from infrared measurements in the carbonyl region. Compounds III and IV cannot be separated by chromatography on Florisil.

3. Two-Electron Oxidation of $[(\pi\text{-}C_5H_5)Fe(CO)]_2(Ph_2PCH_2CH_2PPh_2)$ (I).—(i) **In Dichloromethane.**—A 27-mg sample of I was dissolved in 25 ml of a 0.1 *M* TBAH–dichloromethane solution and oxidized at +1.30 V *vs.* the ssce for 1 hr at a platinum electrode. The solution was quantitatively transferred to a volumetric flask and diluted to the mark. An infrared spectrum

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[4] E. C. Johnson, T. J. Meyer, and N. Winterton, *Chem. Commun.*, 934 (1970); E. C. Johnson, T. J. Meyer, and N. Winterton, *Inorg. Chem.*, **10**, 1673 (1971).

[5] J. A. Ferguson and T. J. Meyer, *Chem. Commun.*, 623 (1971).

[6] Abbreviations used here include TBAH for tetra-*n*-butylammonium hexafluorophosphate and ssce for saturated sodium chloride calomel electrode.

[7] L. Lange and B. Müller, *Ber. Deut. Chem. Ges. B*, **63**, 1058 (1930).

[8] M. L. Brown, T. J. Meyer, and N. Winterton, *Chem. Commun.*, 309 (1971).

[9] W. B. Fortune and M. G. Mellor, *Ind. Eng. Chem., Anal. Ed.*, **10**, 60 (1938).

TABLE I

SPECTRAL PROPERTIES OF THE COMPOUNDS[a]

Compound	Medium[b]	ν_{CO}, cm^{-1}	λ_{max}, nm	$\tau(\pi\text{-}C_5H_5)$
$[(\pi\text{-}C_5H_5)Fe(CO)]_2(Ph_2PCH_2CH_2PPh_2)$ (I)	CH_2Cl_2	1715 w, 1670 s	650 (ϵ ~497) 370 (sh, ϵ ~4950)	5.82[c]
$\{[(\pi\text{-}C_5H_5)Fe(CO)]_2(Ph_2PCH_2CH_2PPh_2)\}^+$ (II)	0.1 *M* TBAH–CH_2Cl_2	~1840 sh, 1775 br, s	645 (ϵ ~1680) 512 (ϵ ~3250) 440 (sh, ϵ ~8080) 265 (sh, ϵ ~39,600)	. . .
$[(\pi\text{-}C_5H_5)Fe(CO)_2(Ph_2PCH_2CH_2PPh_2)]^+$ (III)	CH_2Cl_2	2054 s, 2013 s	350 (sh, ϵ ~1450)	4.50[d]
$\{[(\pi\text{-}C_5H_5)Fe(CO)(NCCH_3)]_2(Ph_2PCH_2CH_2PPh_2)\}^{2+}$ (IV)	0.1 *M* TBAH–CH_3CN	1982 s[e]	510 (ϵ ~460)[f] 398 (ϵ ~1700) 328 (sh, ϵ ~1672)	5.17[d]

[a] ϵ values are molar extinction coefficients. Key: br, broad; sh, shoulder; s, strong. Ultraviolet–visible spectra were recorded from 800 to 220 nm. [b] TBAH is tetra-*n*-butylammonium hexafluorophosphate. [c] In $DCCl_3$ *vs.* TMS. [d] In acetone-d_6 *vs.* acetone at τ 7.93. [e] ν_{CN} at 2189 cm^{-1} in a KBr pellet. [f] In CH_2Cl_2.

showed that $[(\pi\text{-}C_5H_5)Fe(CO)_2(Ph_2PCH_2CH_2PPh_2)]^+$ (III) was the only carbonyl-containing species present. Compound III was determined quantitatively by infrared and ferrous ion spectrophotometrically as $Fe(phen)_3^{2+}$.

(ii) **In Acetonitrile.**—In a typical experiment 40 mg of I was suspended in a 0.1 *M* TBAH–acetonitrile solution and exhaustively electrolyzed at +1.20 V *vs.* the ssce at a platinum electrode. The oxidations were carried out at four different temperatures. Temperature control was maintained by immersing the electrochemical cell in a large crystallizing dish filled with water at the appropriate temperature. When the solution inside the cell came to thermal equilibrium, $[(\pi\text{-}C_5H_5)Fe(CO)]_2(Ph_2PCH_2CH_2PPh_2)$ was added and electrolysis begun. When the electrolysis was complete (approximately 2.5 hr at 22 ± 2°), the solution was quantitatively transferred to a volumetric flask and diluted to the mark. At 0, 22, and 51° two carbonyl-containing products were observed, $[(\pi\text{-}C_5H_5)Fe(CO)_2(Ph_2PCH_2CH_2PPh_2)]^+$ (III) and $\{[(\pi\text{-}C_5H_5)Fe(CO)(NCCH_3)]_2(Ph_2PCH_2CH_2PPh_2)\}^{2+}$ (IV). They were determined quantitatively in the infrared and ferrous ion spectrophotometrically as $Fe(phen)_3^{2+}$.

(iii) **In Acetone.**—A 50-mg sample of I was suspended in a 0.1 *M* TBAH–acetone solution at 22° and exhaustively electrolyzed at a platinum electrode at +1.2 V *vs.* the ssce for 3 hr. When the oxidation was complete, the solution was quantitatively transferred to a volumetric flask and diluted to the mark. The infrared spectrum of the pale yellow solution had carbonyl bands characteristic of $[(\pi\text{-}C_5H_5)Fe(CO)_2(Ph_2PCH_2CH_2PPh_2)]^+$ and a new, relatively weak band (less than 5% of the total reaction product) at 1946 cm^{-1}.

4. **Preparation of $\{[(\pi\text{-}C_5H_5)Fe(CO)(NCCH_3)]_2(Ph_2PCH_2CH_2PPh_2)\}(PF_6)_2$.**—A 270-mg sample of $[(\pi\text{-}C_5H_5)Fe(CO)]_2(Ph_2PCH_2CH_2PPh_2)$ was suspended in 200 ml of 0.1 *M* ammonium hexafluorophosphate–acetonitrile solution at 75°. The solution was oxidized at +1.2 V *vs.* the ssce for 80 min to give a deep red-orange solution. Integration of the total current *vs.* time curve for the oxidation gave n = 2.05. Infrared analysis indicated that the oxidation of I to $\{[(\pi\text{-}C_5H_5)Fe(CO)(NCCH_3)]_2(Ph_2PCH_2CH_2PPh_2)\}^{2+}$ was quantitative. The solution was filtered, evaporated to dryness, and washed with water to remove the ammonium hexafluorophosphate. The crude product was washed several times with benzene, recrystallized from dichloromethane–pentane, and then air dried to give 320 mg (85% yield) of the orange solid $\{[(\pi\text{-}C_5H_5)Fe(CO)(NCCH_3)]_2(Ph_2PCH_2CH_2PPh_2)\}(PF_6)_2$. *Anal.* Calcd for $C_{42}H_{40}P_4N_2O_2Fe_2F_{12}$: C, 46.90; H, 3.78; N, 2.52. Found: C, 46.82; H, 3.98; N, 2.44. τ values in acetone-d_6 *vs.* acetone at τ 7.93: $-C_6H_5$, 2.52; $\pi\text{-}C_5H_5$, 5.17; $NCCH_3$, 7.14; $-CH_2-$, 7.51. The calculated followed by observed ratios of proton peak intensities are as follows: $-C_6H_5$, 20, 20; $\pi\text{-}C_5H_5$, 10, 9; $NCCH_3$, 6, 6; $-CH_2-$, 4, 4.

5. **Disproportionation of $\{[(\pi\text{-}C_5H_5)Fe(CO)]_2(Ph_2PCH_2CH_2PPh_2)\}^+$ (II).**—Solutions of II in 0.1 *M* TBAH–dichloromethane were generated electrochemically. The TBAH was separated using column chromatography on a 50 cm × 1 cm 60–100 mesh Florisil column by eluting with a 1:1 mixture (by volume) of chloroform–dichloromethane. The eluent was carefully evaporated to dryness under a stream of nitrogen. Acetonitrile was added and the solution diluted to a known volume. The infrared spectrum of the solution from 2200 to 1500 cm^{-1} was scanned at 3-min intervals until reaction was complete. The only products observed (by infrared and ultraviolet–visible spectra) were $[(\pi\text{-}C_5H_5)Fe(CO)]_2(Ph_2PCH_2CH_2PPh_2)$ (I) and $\{[(\pi\text{-}C_5H_5)Fe(CO)(NCCH_3)]_2(Ph_2PCH_2CH_2PPh_2)\}^{2+}$ (IV). Compounds I and IV were analyzed quantitatively by infrared.

Results

The important features of the infrared, ultraviolet–visible, and nmr spectra of the diphos bridged dimer $[(\pi\text{-}C_5H_5)Fe(CO)]_2(Ph_2PCH_2CH_2PPh_2)$ (I), its one-electron oxidation product $\{[(\pi\text{-}C_5H_5)Fe(CO)]_2(Ph_2PCH_2CH_2PPh_2)\}^+$ (II), the unidentate diphosphine complex $[(\pi\text{-}C_5H_5)Fe(CO)_2(Ph_2PCH_2CH_2PPh_2)]^+$ (III), and the diphos-bridged acetonitrile complex $\{[(\pi\text{-}C_5H_5)Fe(CO)(NCCH_3)]_2(Ph_2PCH_2CH_2PPh_2)\}^{2+}$ (IV) are summarized in Table I. For the spectral studies, solid samples of IV were prepared as described in the Experimental Section and samples of III as described in a recent communication.[8] It was not possible to prepare analytically pure salts of II. Such samples invariably contained small amounts of $[(\pi\text{-}C_5H_5)Fe(CO)_2(Ph_2PCH_2CH_2PPh_2)]^+$ and $[(\pi\text{-}C_5H_5)Fe(CO)]_2(Ph_2PCH_2CH_2PPh_2)$ (I). The data for II in Table I were obtained for solutions of II prepared by electrochemical oxidation of I as described in the Experimental Section.

A. Characterization and Disproportionation of $\{[(\pi\text{-}C_5H_5)Fe(CO)]_2(Ph_2PCH_2CH_2PPh_2)\}^+$ (II).—As mentioned above, analytically pure salts of II could not be obtained. Consequently it was characterized in solution by the following experiments.

A 40-mg sample of $[(\pi\text{-}C_5H_5)Fe(CO)]_2(Ph_2PCH_2CH_2PPh_2)$ (I) was dissolved in 30 ml of a 0.1 *M* TBAH–dichloromethane solution and exhaustively oxidized at a platinum electrode at +0.5 V *vs.* the ssce. The n value was 0.97 (1.0 calculated for the conversion I → II). The ultraviolet–visible and infrared spectra of the oxidized solution were as given for II in Table I.

A portion of the oxidized solution was exhaustively reduced at a platinum electrode at −0.5 V *vs.* the ssce. The n value was 0.98 (1.0 calculated). The infrared and ultraviolet–visible spectra of the reduced solution were identical with those obtained for a pure sample of I. Reduction of a further portion of the oxidized solution using a few drops of hydrazine also gave quantitative conversion to I.

The tetraphenylboron salt of II, $\{[(\pi\text{-}C_5H_5)Fe(CO)]_2(Ph_2PCH_2CH_2PPh_2)\}^+BPh_4^-$, has been reported to have a magnetic moment corresponding to the expected one unpaired electron.[2] We have been unable to obtain either an epr signal for II in dichloromethane at room temperature or a pure sample of the tetraphenylborate salt of II. Compound II is apparently isostructural with I. From its infrared spectrum it has only bridging carbonyls and it is readily reconverted into I by either chemical or electrochemical reduction.

$\{[(\pi\text{-}C_5H_5)Fe(CO)]_2(Ph_2PCH_2CH_2PPh_2)\}^+$ (II) disproportionates in acetonitrile. From infrared studies, the products of the reaction $[(\pi\text{-}C_5H_5)Fe(CO)]_2(Ph_2PCH_2CH_2PPh_2)$ (I) and $\{[(\pi\text{-}C_5H_5)Fe(CO)(NCCH_3)]_2(Ph_2PCH_2CH_2PPh_2)\}^{2+}$ (IV) are formed in 46 ± 4 and 53 ± 10% yields, respectively, indicating the stoichiometry

$$2CH_3CN + 2\{[(\pi\text{-}C_5H_5)Fe(CO)]_2(Ph_2PCH_2CH_2PPh_2)\}^+ \longrightarrow [(\pi\text{-}C_6H_5)Fe(CO)]_2(Ph_2PCH_2CH_2PPh_2) + \{[(\pi\text{-}C_5H_5)Fe(CO)(NCCH_3)]_2(Ph_2PCH_2CH_2PPh_2)\}^{2+} \quad (1)$$

The half-time for this reaction at 22 ± 2° is $t_{1/2} = 30 \pm 5$ min for (II) $\sim 3 \times 10^{-2}$ *M*.

Disproportionation is considerably slower in acetone where the dominant products are I and $[(\pi\text{-}C_5H_5)Fe(CO)_2(Ph_2PCH_2CH_2PPh_2)]^+$ (III). In dichloromethane disproportionation has not been observed. Disproportionation also occurs thermally in solid samples (to give I and III) which accounts for our inability to obtain satisfactory analytical data for salts of II.

The preparation of the bis-acetonitrile complex (IV) by the high-temperature two-electron oxidation of I (at +1.2 V) in acetonitrile was described in the Experimental Section. It can also be prepared quantitatively at 22 ± 2° and +0.50 V by utilizing the disproportionation reaction followed by electrochemical oxidation of I.

$$\begin{tikzcd}
{[(\pi\text{-}C_5H_5)Fe(CO)]_2(Ph_2PCH_2CH_2PPh_2)} \arrow[r, "-e^-"] & {} \\
{} \arrow[u] \arrow[d, "CH_3CN"] & {\{[(\pi\text{-}C_5H_5)Fe(CO)]_2(Ph_2PCH_2CH_2PPh_2)\}^+} \arrow[l, dash] \\
{\{[(\pi\text{-}C_5H_5)Fe(CO)(NCCH_3)]_2(Ph_2PCH_2CH_2PPh_2)\}^{2+}} &
\end{tikzcd}$$

B. Oxidation of $\{[(\pi\text{-}C_5H_5)Fe(CO)]_2(Ph_2PCH_2CH_2PPh_2)\}^+$ (II).—Further oxidation of the one-electron metal–metal bonded cation $\{[(\pi\text{-}C_5H_5)Fe(CO)]_2(Ph_2PCH_2CH_2PPh_2)\}^+$ (II) in dichloromethane (at a platinum electrode at 0.9 V *vs.* the ssce) gives as products the unidentate diphos complex $[(\pi\text{-}C_5H_5)Fe(CO)_2(Ph_2PCH_2CH_2PPh_2)]^+$ (III) and ferrous ion. The results are summarized in Table II (experiments 2, 3, 4). Fe(II) was determined quantitatively by carrying out the oxidation in the presence of 1,10-phenanthroline (or by adding the phenanthroline after oxidation was complete) and then measuring the tris(1,10-phenanthroline)iron(II) complex spectrophotometrically as described in the Experimental Section. Compound III was determined by infrared frequencies in the carbonyl region. Failure to obtain mass balance may reflect limitations in the analyses for III and Fe(II) or the presence of other iron-containing products which were undetected. Two electron oxidation of I (experiment 1) gives the same product distribution within experimental error as the stepwise oxidation (through II).

The oxidation of II in acetonitrile at 22 ± 2° also gives as products III and Fe(II) and in addition the diphosphine-bridged acetonitrile complex $\{[(\pi\text{-}C_5H_5)Fe(CO)(NCCH_3)]_2(Ph_2PCH_2CH_2PPh_2)\}^{2+}$ (IV). The quantitative determination of the products of oxidation of II in acetonitrile is complicated by its disproportionation (see reaction 1 in section A). To avoid this complication, suspensions of $[(\pi\text{-}C_5H_5)Fe(CO)]_2(Ph_2PCH_2CH_2PPh_2)$ (I) (I is only slightly soluble in acetonitrile) were exhaustively electrolyzed at +1.2 V *vs.* the ssce. At +1.2 V any II formed is immediately oxidized and disproportionation is not competitive. The absence of any substantial buildup of II during the course of the oxidation was verified by infrared and cyclic voltammetry measurements. The products of the oxidations were determined quantitatively as described above. The results are summarized in Table II.

TABLE II

PRODUCTS OF THE ELECTROCHEMICAL OXIDATIONS OF I AND II[a]

Expt	Medium	Temp,[b] °C	Starting material	% III[c]	% IV[c]	% Fe^{2+} [d]
1	0.1 *M* TBAH–CH_2Cl_2	22	I	45	. . .	43
2	0.1 *M* $TBAClO_4$[e]–CH_2Cl_2	22	II	41	. . .	
3	0.1 *M* TBAH–CH_2Cl_2	22	II	40	. . .	
4	0.1 *M* $TBAClO_4$–0.1 *M* 1,10 phenanthroline–CH_2Cl_2	22	II	37	. . .	44
5	0.1 *M* TBAH–$(CH_3)_2CO$	22	I	39	. . .	
6	0.1 *M* TBAH–CH_3CN	0	I	22	10	
7	0.1 *M* TBAH–CH_3CN	22	I	22	44	12
8	0.1 *M* TBAH–CH_3CN	51	I	10	86	10.5
9	0.1 *M* TBAH–CH_3CN	75	I	. . .	100	. . .

[a] At a platinum electrode at >0.90 V *vs.* the ssce; I = $[(\pi\text{-}C_5H_5)Fe(CO)]_2(Ph_2PCH_2CH_2PPh_2)$, II = $\{[(\pi\text{-}C_5H_5)Fe(CO)]_2(Ph_2PCH_2CH_2PPh_2)\}^+$, III = $[(\pi\text{-}C_5H_5)Fe(CO)_2(Ph_2PCH_2CH_2PPh_2)]^+$, IV = $\{[(\pi\text{-}C_5H_5)Fe(CO)(NCCH_3)]_2(Ph_2PCH_2CH_2PPh_2)]\}^{2+}$. [b] Deviation ±2°. [c] As determined by infrared frequencies in the carbonyl region; values are ±10%. [d] Determined spectrophotometrically as the tris(1,10-phenanthroline) complex $Fe(phen)_3{}^{2+}$. [e] $TBAClO_4$ is $[CH_3(CH_2)_3]_4NClO_4$.

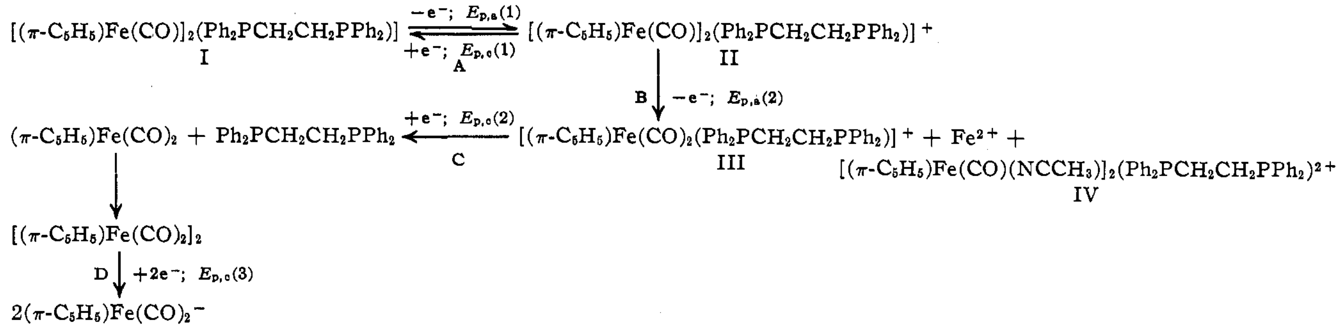
The products of the electrochemical oxidation of II are clearly dependent upon the solvent and the temperature. In experiments where the acetonitrile complex $\{[(\pi\text{-}C_5H_5)Fe(CO)(NCCH_3)]_2(Ph_2PCH_2CH_2PPh_2)\}^{2+}$ (IV) is formed quantitatively from I, *n* values are essentially 2 (1.85–2.05), as expected. However, in all three solvents when $(\pi\text{-}C_5H_5)Fe(CO)_2(Ph_2PCH_2CH_2PPh_2)^+$ (III) is a major product, *n* values from 3 to >5 are observed.

At room temperature or below (experiments 6 and 7) the times for electrolysis in acetonitrile become appreciably longer and further complications appear. Mass balance is not obtained and *n* values are large ($n > 5$). It appears that for long electrolysis times considerable diffusion out of the working electrode compartment occurs which would explain our inability to obtain mass balance.

The Fe^{3+}–Fe^{2+} couple is electrochemically irreversible in 0.1 *M* TBAH–acetonitrile. A well-defined $Fe^{2+} \rightarrow Fe^{3+}$ wave is not observed out to +2.0 V *vs.* the ssce which explains why Fe^{2+} once formed stays as Fe^{2+} and is not further oxidized to Fe^{3+} even at +1.2 V. Blank experiments indicate that Fe^{2+} is very slowly oxidized to Fe^{3+} at this potential.

C. Cyclic Voltammetry.—A cyclic voltammogram of $\{[(\pi\text{-}C_5H_5)Fe(CO)]_2(Ph_2PCH_2CH_2PPh_2)\}^+$ (II) in 0.1 *M* TBAH–acetonitrile solution at a platinum bead electrode is given in Figure 2. The electron-transfer reactions which occur at the various E_p (cyclic peak potential) values are as written in Scheme I.

SCHEME I



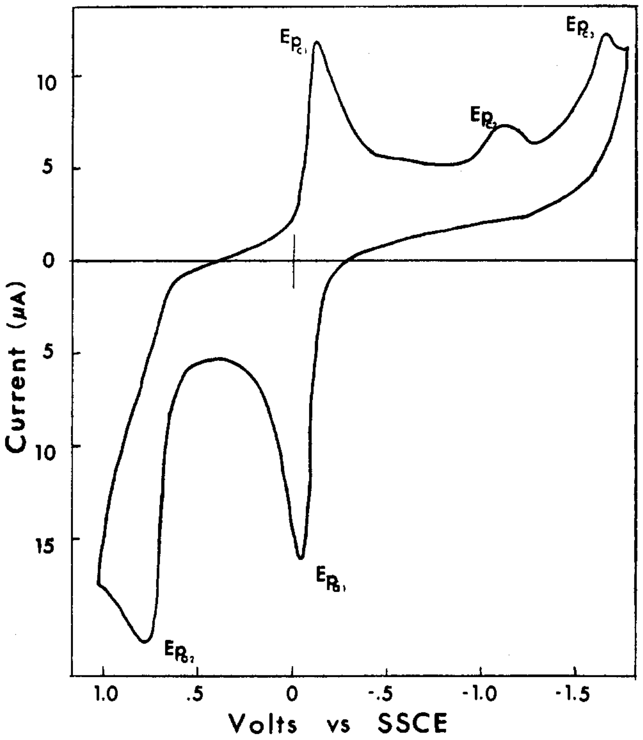
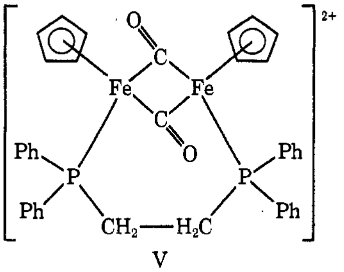


Figure 2.

The quantitative determinations of the products of reactions A and B were discussed in sections A and B, respectively. Reaction A [$E_{p,a}(1)$ and $E_{p,c}(1)$] involves the reversible loss of an electron from I to give II and reaction B the loss of a second electron from II to give symmetric (IV) and asymmetric (III) cleavage products. In reaction B, attempts to observe an initially formed intermediate having no metal–metal bond but retaining the carbonyl and diphosphine bridges as in V using fast-scan cyclic voltammetry (100 V/sec) were unsuccessful.[10]



V

The origins of $E_{p,c}(2)$ (reaction C) and $E_{p,c}(3)$ (reaction D) were determined by the following experiments. Cyclic voltammograms of [(π-C_5H_5)Fe$(CO)_2$($Ph_2PCH_2CH_2PPh_2$)]$^+$ (III) in acetonitrile have only two cathodic peaks, corresponding exactly to $E_{p,c}(2)$ and $E_{p,c}(3)$. Exhaustive electrolysis of solutions of III at a platinum electrode at −1.5 V *vs.* the ssce (n = 1.1) yielded [(π-C_5H_5)Fe$(CO)_2$]$_2$ which was identified by infrared and ultraviolet–visible spectral comparisons with a known sample. Cyclic voltammograms of the iron dimer in the same medium have a peak identical with $E_{p,c}(3)$. The same pattern toward reduction of the series of complexes [(π-C_5H_5)Fe$(CO)_2$L]$^+$ (L = PPh_3, CO, $NCCH_3$) in 1,2-dimethyoxyethane has been observed.[11]

The data for $E_{p,a}(1)$ and $E_{p,a}(2)$ in a variety of solvents are summarized in Table III. Both oxidations are somewhat solvent dependent. For $E_{p,a}(2)$ an apparent correlation does exist between the ease of oxidation (shift to less positive or more cathodic values) and the solvating or coordinating ability of the solvent.

TABLE III

ANODIC E_p VALUES FOR THE OXIDATION OF [(π-C_5H_5)Fe(CO)]$_2$($Ph_2CH_2CH_2PPh_2$) AND {[(π-C_5H_5)Fe(CO)]$_2$($Ph_2PCH_2CH_2PPh_2$)}$^+$ IN VARIOUS SOLVENTS[a]

Solvent	$E_{p,a}(1)$	$E_{p,a}(2)$	Solvent	$E_{p,a}(1)$	$E_{p,a}(2)$
CH_2Cl_2	0.10	0.95	$CH_3(CH_2)_2CN$	0.00	0.82
CH_2Cl_2[b]	0.02	0.86	$(CH_3)_2SO$	0.10	0.80
$(CH_3)_2CO$	0.08	0.88	CH_3CN	−0.05	0.75

[a] At a platinum bead electrode at 22 ± 2° at a 200-mV/sec sweep rate in 0.1 M tetra-n-butylammonium hexafluorophosphate. [b] In the presence of 0.1 M 1,10-phenanthroline.

Discussion

The electrochemical oxidation of [(π-C_5H_5)Fe(CO)]$_2$($Ph_2PCH_2CH_2PPh_2$) (I) in dichloromethane, acetone, dimethyl sulfoxide, butyronitrile, or acetonitrile occurs in two successive one-electron steps. Detailed studies in acetone, dichloromethane, and acetonitrile indicate that a common mechanism exists for all three (see Scheme II). The products of the two reactions indicate that the metal–metal bond between iron atoms is the source of electrons in the oxidation–reduction reactions.

The loss of the first electron from I to give the one-electron metal–metal bonded cation II is both chemically and electrochemically reversible. The subsequent loss of an electron from II is electrochemically irreversible. This reaction is written here as an electrical–chemical (EC) step in which the initial product of oxida-

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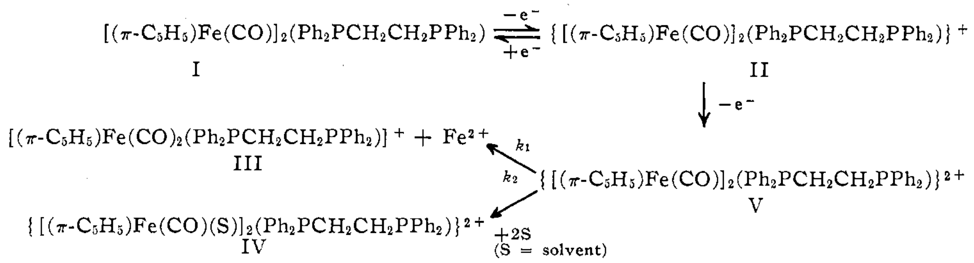
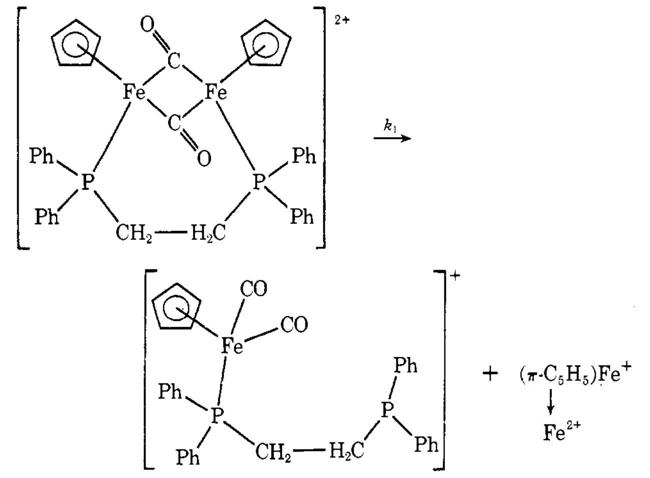
[10] Initial experiments on the propane-bridged diphos dimer [(π-C_5H_5)Fe(CO)]$_2$($Ph_2PCH_2CH_2CH_2PPh_2$) clearly indicate the existence of an intermediate like V. Fast-scan cyclic voltammograms show *two* reversible oxidation waves.

[11] R. E. Dessy, R. B. King, and M. Waldrop, *J. Amer. Chem. Soc.*, **88**, 5115 (1966).

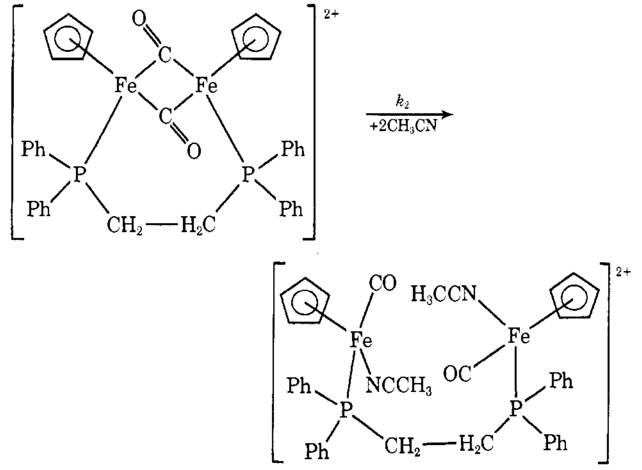
SCHEME II



tion (V) containing no metal–metal bond reacts further by either asymmetric (k_1 path)



or symmetric (k_2 path)



cleavage of the diphosphine and carbonyl bridges.

Attempts to observe V using fast-scan cyclic voltammetry were unsuccessful, and a mechanism in which a discrete intermediate like V is not formed cannot be ruled out (however, see footnote 10).

In either case it is clear that the ultimate products of oxidation of II arise from two separate reaction paths. In the k_1 path, the loss of an electron from II to give V is followed by an internal rearrangement in which the previously bridging carbonyl and diphosphine ligands become attached to a single iron giving $[(\pi\text{-}C_5H_5)Fe(CO)_2(Ph_2PCH_2CH_2PPh_2)]^+$ (III) and $(\pi\text{-}C_5H_5)Fe^+$. The latter apparently rapidly decomposes to give Fe^{2+}. In dichloromethane, only the k_1 path is important and conversion to III and Fe^{2+} is quantitative. When the k_1 path is important, the overall n values for oxidation of II are significantly greater than 1 apparently because of the oxidation of fragments released upon the decomposition of $(\pi\text{-}C_5H_5)Fe^+$.

In the better coordinating solvent acetonitrile, the k_2 path is important. It may arise by the attack of solvent on the initial product of the oxidation of II (V?) before it can undergo internal ligand rearrangement. In acetonitrile at 22° (experiment 7 in Table II) k_2 is clearly competitive with k_1. At higher temperatures, the k_2 path dominates and at 75° the symmetrical cleavage product $\{[(\pi\text{-}C_5H_5)Fe(CO)(NCCH_3)]_2(Ph_2PCH_2CH_2PPh_2)\}^{2+}$ is formed quantitatively and can be isolated as its hexafluorophosphate salt.

In contrast, in the Fe^{3+} and electrochemical oxidations of $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ in acetone and acetonitrile only symmetrical cleavage products $\{[(\pi\text{-}C_5H_5)Fe(CO)_2S]^+$; $S = CH_3CN$ or $(CH_3)_2CO\}$ are observed.[3,4] Symmetrical cleavage also occurs in the disproportionation of II since there the products are $[(\pi\text{-}C_5H_5)Fe(CO)]_2(Ph_2PCH_2CH_2PPh_2)$ and $\{[(\pi\text{-}C_5H_5)Fe(CO)(NCCH_3)]_2(Ph_2PCH_2CH_2PPh_2)\}^{2+}$. The latter reaction represents an example of the outer-sphere oxidation of II (by itself). The difference in product distributions between the electrochemical oxidation of II and the disproportionation of II may result from the difference in medium for the two experiments (0.1 M TBAH–acetonitrile *vs.* acetonitrile) or perhaps in the electrochemical experiment the doubly oxidized intermediate V decomposes within the electrode double layer.

Loss of an electron from $[(\pi\text{-}C_5H_5)Fe(CO)]_2(Ph_2PCH_2CH_2PPh_2)$ (I) to give the cation $\{[(\pi\text{-}C_5H_5)Fe(CO)]_2(Ph_2PCH_2CH_2PPh_2)\}^+$ (II) leaves the molecular framework intact. The system is probably best regarded as having two accessible molecular oxidation states 0 and 1+ with the iron atoms in the latter in the formal oxidation state $Fe^{1.5+}$. However, no evidence is presented here which rules out distinctly different iron atoms $\{Fe^I, Fe^{II}\}$ in the cation.

The iron diphosphine dimer is then an example of a compound which contains a strong metal–metal bond and which also remains structurally intact in more than one *molecular* oxidation state. The existence of multiple oxidation states probably arises from stabilization of the one electron metal–metal bond in the cation (II) by the diphos bridge.

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