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ORGANOMETALLIC LIGANDS

II*. THE COORDINATION CHEMISTRY OF 1-[(DIMETHYLAMINO)-METHYL]-2-(DIPHENYLPHOSPHINO)FERROCENE

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Summary

Complexes of the organometallic ligand $(h^5\text{-}C_5H_5)Fe[(h^5\text{-}C_5H_3)(1\text{-}CH_2NMe_2)\text{-}(2\text{-}PPh_2)]$ (≡ FcCNP) have been prepared with the carbonyls of chromium, molybdenum, tungsten, iron, and cobalt and with borane. With the Group VIB metals, the ligand forms complexes of the type $(FcCNP)M(CO)_4$ in which the FcCNP ligand is chelating. However, in the case of $(FcCNP)Fe(CO)_4$ and $[(FcCNP)_2Co(CO)_3]BPh_4$ the ligand is monodentate, the phosphorus acting as the donor atom. Infrared and NMR data were used to establish the mode of coordination in each case. The electrochemistry of the Group VIB metal carbonyl complexes has been investigated, the chromium complex being of particular interest. The cyclic voltammogram of $(FcCNP)Cr(CO)_4$ consists of two, reversible, one electron redox waves at $E_{\text{peak, anodic}}$ + 0.54 V and + 0.96 V (vs. SCE in CH_2Cl_2), and a third, irreversible wave at $E_{\text{peak, anodic}}$ + 1.47 V. At + 0.54 V the solution color changed from yellow to orange and the $\nu(CO)$ bands shifted from 2011 w, 1891 s, and 1831 s (cm^{-1}) in the neutral complex to 2080 m, 2000 s, and 1970 s (cm^{-1}) in the singly oxidized species. At + 0.96 V, the color changed further to blue-green, but no additional shift in $\nu(CO)$ was observed. On the basis of this information, it is concluded that the first redox wave represents the process $Cr^0 \rightarrow Cr^+$ and the second wave $Fe^{2+} \rightarrow Fe^{3+}$. Other aspects of the electrochemistry of the Group VIB metal carbonyl complexes are discussed.

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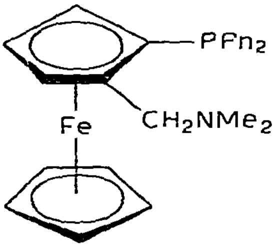
Introduction

Our recent work on the coordination chemistry of ferrocenylphenylphosphines [1] and ferrocenyldichloroborane [2] has demonstrated that, when a ferrocenyl group replaces a phenyl group on a phosphorus or boron atom, there is a definite effect on the coordination chemistry of the molecule. In an effort to examine this effect further and to extend our work on organometallic ligands in general, we have studied a potentially bidentate "mixed" organometallic ligand, 1-[(dimethylamino)methyl]-2-(diphenylphosphino)ferrocene (I) (herein abbreviated as FcCNP) [3].



(I)

The coordination chemistry of FcCNP may be compared with the behavior of similar organic ligands [4, 5] and with our previous studies of the ferrocenylphenylphosphines. In addition, comparison may be made with the reported coordination chemistry of three other nitrogen-containing derivatives of ferrocene: [(dimethylamino)methyl]ferrocene [6], formylferrocene thiosemicarbazones [7] and 1-[(dimethylamino)methyl]-2-(2-pyridyl)ferrocene [8]; the last of these is a bidentate ligand most closely analogous with FcNCP.

Experimental

General techniques and equipment

Syntheses were carried out under nitrogen using normal techniques or in a preparative vacuum line of conventional design. Solvents were routinely dried and distilled before use; other chemicals were used as received from commercial sources.

Proton NMR spectra were obtained at ambient temperature using a Varian A-60, Varian XL-100, or Hitachi—Perkin—Elmer R-10A spectrometer; TMS was used as an internal standard. Infrared spectra were obtained as Nujol mulls on a Perkin—Elmer 337 or 257.

Preparation of the ligand

1-[(Dimethylamino)methyl]-2-(diphenylphosphino)ferrocene (FcCNP) was prepared according to the method of Marr and Hunt [3]. The compound was recrystallized from petroleum ether (30-60°) to give a yellow powder, m.p. 97-99°; NMR data are collected in Table 2.

Preparation of metal carbonyl complexes

A. (FcCNP)M(CO)$_4$ (M = Cr, Mo, W). These complexes were prepared using a procedure similar to that of Dobson, Taylor and Walsh [4]. Equimolar amounts of $M(CO)_6$ and FcCNP were refluxed in an appropriate solvent (Cr, xylene; Mo, toluene; W, mesitylene). [Sublimation of unreacted $M(CO)_6$ into the condenser is a great nuisance in reactions of this type. We have found that the addition of 1-2 ml of 30-60° petroleum ether to the reaction solvent solved this problem entirely. Apparently the petroleum ether refluxes higher in the condenser than does the reaction solvent and washes the sublimed metal hexacarbonyl back into the boiling flask.] Following reflux, the reaction mixture was cooled in an ice bath for about 1 h and then filtered rapidly. The solvent was removed in vacuo. The remaining solid product was recrystallized from acetone/light petroleum ether; yields averaged 60-85%. Analytical, NMR and infrared data are collected in Tables 1-3.

B. $(FcCNP)Fe(CO)_4$. This complex was prepared by refluxing FcCNP (2 mmol) and $Fe(CO)_5$ (7 mmol) for 2.5 h in dry toluene. Following reflux, the reaction mixture was allowed to cool and was then filtered rapidly. The solvent was removed in vacuo. The remaining solid was recrystallized from light petroleum ether; yields averaged 50%. Analytical, NMR and infrared data are collected in Tables 1-3.

C. $[(FcCNP)_2Co(CO)_3]BPh_4$. FcCNP (2.08 mmol) was treated with $Co_2(CO)_8$ (1.04 mmol) by the same procedure used with the previously reported ferrocenylphosphine—cobalt carbonyl reactions [1]. In this case 1.06 mmol of CO was produced, presumably as a result of reaction 1. The infrared spectrum of the red-brown product showed bands at 2061 w, 1981 s, and 1871 vs, a pattern in very good agreement with the spectra of the previously reported triphenylphosphine and ferrocenyldiphenylphosphine analogues. The ultimate product, the BPh_4^- salt, was prepared in the same manner as the previously reported ferrocenylphosphine analogue. Analytical data for $[(FcCNP)_2Co(CO)_3]BPh_4$ are recorded in Table 1 and infrared data in Table 3. The molar conductivity of the salt was found to be 14.1 $ohm^{-1}\ cm^2\ mol^{-1}$ when 1 m*M* in nitrobenzene, a value in excellent agreement with previously reported 1/1 electrolytes of this type [9].

$$2\ FcCNP + Co_2(CO)_8 \rightarrow [(FcCNP)_2Co(CO)_3][Co(CO)_4] + CO \qquad (1)$$

TABLE 1

ANALYTICAL DATA FOR THE FcCNP[a] COMPLEXES

Compound	M.p. (°C) (uncorrected)	Analysis found (calcd.) (%)	
		C	H
$(FcCNP)Cr(CO)_4$	160-164	58.84 (58.89)	4.52 (4.44)
$(FcCNP)Mo(CO)_4$	175-178 (dec.)	54.65 (54.80)	4.21 (4.09)
$(FcCNP)W(CO)_4$	203-206 (dec.)	48.10 (48.16)	3.73 (3.63)
$(FcCNP)Fe(CO)_4$[b]	144-146	58.24 (58.49)	4.53 (4.37)
$[(FcCNP)_2Co(CO)_3]BPh_4$[c]	100-110	69.11 (70.21)	5.41 (5.47)

[a] FcCNP = 1-[(dimethylamino)methyl]-2-(diphenylphosphino)ferrocene. [b] Found: N, 2.20. Calcd.: N, 2.35%. [c] Mol. wt. (in $CHCl_3$): found 1311; calcd., 1316.

Preparation of FcCNP · 2BH$_3$

FcCNP (1.04 mmol) was reacted with B_2H_6 (2.72 mmol) in CH_2Cl_2 in vacuo. The yellow di-adduct formed immediately, and 1.66 mmol of B_2H_6 was recovered to give the reaction ratio of FcCNP/B_2H_6 1.04/1.06. NMR data for

TABLE 2

PROTON NMR DATA FOR FcCNP AND ITS COMPLEXES[a]

Compound	Line Structure (relative area)	Assignment	Chemical shift (τ) (ppm)
FcCNP[b]	3 multiplets (10)	phenyl	2.72, 2.87, 2.92
	multiplet (1) triplet (1)	π-C_5H_3	5.56, 5.77
	singlet and doublet (7)	π-C_5H_3 1 CH_2 proton π-C_5H_5	6.11, 6.47
	doublet (1)	1 CH_2 proton	6.62
	singlet (6)	—NMe_2	8.02
(FcCNP)Cr(CO)$_4$	3 multiplets (10)	phenyl	1.91, 2.47, 2.74
	singlets (3)	π-C_5H_3	5.55, 5.58, 5.68
	singlet (5)	π-C_5H_5	6.31
	doublet (1)	1 CH_2 proton	5.63[c, d]
	doublet (1)	1 CH_2 proton	7.15[d]
	2 singlets (6)	—NMe_2	7.20, 7.96
(FcCNP)Mo(CO)$_4$	3 multiplets (10)	phenyl	1.94, 2.48, 2.78
	2 singlets and multiplet (3)	π-C_5H_3	5.54, 5.57, 5.62
	doublet (1)	1 CH_2 proton	5.48[e]
	doublet (1)	1 CH_2 proton	7.00[e]
	singlet (5)	π-C_5H_5	6.34
	2 singlets (6)	—NMe_2	7.10, 7.81
(FcCNP)W(CO)$_4$	3 multiplets (10)	phenyl	1.96, 2.48, 2.78
	2 singlets and 1 multiplet (3)	π-C_5H_3	5.53, 5.55, 5.60
	singlet (5)	π-C_5H_5	6.33
	doublet (1)	1 CH_2 proton	5.34[f]
	doublet (1)	1 CH_2 proton	6.77[f]
	2 singlets (6)	—NMe_2	6.85, 7.58
(FcCNP)Fe(CO)$_4$	3 multiplets (10)	phenyl	2.46, 2.65, 2.83
	multiplet (1) triplet (1) multiplet (1)	π-C_5H_3	5.48, 5.73, 6.14
	singlet (5)	π-C_5H_5	6.10
	doublet (1)[g]	1 CH_2 proton	6.39[e]
	doublet (1)	1 CH_2 proton	6.64[e]
	singlet (6)	—NMe_2	8.03
FcCNP · 2BH$_3$	3 multiplets (10)	phenyl	2.35, 2.51, 2.61
	quartet triplet doublet	π-C_5H_3	4.96, 5.45,[h] 5.94
	singlet (5)	π-C_5H_5	5.90
	doublet (1)	1 CH_2 proton	5.38[e]
	doublet (1)	1 CH_2 proton	6.09[e]
	2 singlets (6)	—NMe_2	7.67, 8.00

(continued)

TABLE 2 (continued)

Compound	Line Structure (relative area)	Assignment	Chemical shift (τ) (ppm)
$[(FcCNP)_2Co(CO)_3][Co(CO)_4]$[i]	3 multiplets (10)	phenyl	1.99, 2.24, 2.35
	3 multiplets (1 each)	π C_5H_3	5.11, 5.23, 5.63
	singlet (5)	π C_5H_5	5.85
	2 doublets (1 each)	CH_2	6.89, 7.18[d]
	singlet	$-NMe_2$	8.08

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[a] All spectra were run in $CDCl_3$. [b] See also ref. 3. [c] This doublet was partially hidden beneath the π-C_5H_3 lines. The position is an estimate. [d] J_{AB} 14 Hz. [e] J_{AB} 13 Hz. [f] J_{AB} 12 Hz. [g] Each member of this doublet is further split into a doublet with a coupling constant of 2 Hz. [h] Line separation ca 4 Hz [i] Spectrum run in CD_3COCD_3.

the adduct are included in Table 2. The ν(B—H) bands were found at 2410 m, 2370 s, 2330 (sh), 2300 m, and 2250 m.

Electrochemistry

All electrochemical experiments were performed on a multipurpose electroanalytical instrument designed by Woodward and Ridgway [10]. For controlled potential coulometry the instrument was modified with a current-voltage booster amplifier [10]. The working and auxiliary electrodes were a platinum wire and spiral, respectively, and the reference electrode was saturated calomel. The compounds were dissolved in dry, reagent-grade dichloromethane or acetonitrile (1-2 m*M*) which was 0.2 *M* in supporting electrolyte (tetraethylammonium perchlorate in acetonitrile and tetrabutylammonium perchlorate in dichloromethane.) Infrared spectra of solutions were done before and after electrolysis by syringing the solution into a demountable cell with a 0.1 m path length and NaCl windows.

TABLE 3

CO STRETCHING FREQUENCIES FOR METAL CARBONYL COMPLEXES OF FcCNP

Compound	Band frequency (in cm^{-1}) and relative intensity[a]
$(FcCNP)Cr(CO)_4$	2011 w, 1906 (sh), 1891 s, 1837 (sh), 1831 s
$(FcCNP)Mo(CO)_4$	2021 w, 1917 (sh), 1897 s, 1889 (sh), 1843 (sh), 1836 s
$(FcCNP)W(CO)_4$	2018 w, 1910 (sh), 1889 s, 1839 (sh), and 1832 s
$(FcCNP)Fe(CO)_4$	2051 m, 1984 m, 1952 s, and 1940 s
$[(FcCNP)_2Co(CO)_3][Co(CO)_4]$	2061 w, 1981 s, and 1871 vs
$[(FcCNP)_2Co(CO)_3]BPh_4$	2060 w, 1999 s, and 1980 s

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[a] w = weak, m = medium, s = strong, vs = very strong, and (sh) = shoulder.

Results and discussion

Structure and bonding in metal carbonyl derivatives of 1-[(dimethylamino)-methyl]-2-(diphenylphosphino)ferrocene

The ligand was reacted with the carbonyls of chromium, molybdenum, tungsten, iron and cobalt in an attempt to study, among other things, the "mixed ligand" character of this amine—phosphine. The organometallic ligand possesses both soft (phosphorus) and hard (nitrogen) donor sites. With metal softness (for low valent transition metals in their compounds) increasing across the periodic table from left to right, FcCNP would be expected to bond differently depending on the particular metal used; that is, it could be a chelating, bidentate ligand; a bidentate, bridging ligand; or a monodentate ligand with a choice of nitrogen or phosphorus bonding.

In the case of the Group VIB metal carbonyls, the complexes formed were of the type $(FcCNP)M(CO)_4$, the empirical formula suggesting that the ligand was bidentate and chelating. Indeed, the pattern of carbonyl stretching modes (Table 3) agreed favorably with that described for compounds of the type *cis*-$M(CO)_4L_2$(C_{2v}; IR active modes = $2A_1$, B_1, and B_2) [4, 11].

The best evidence that the metal tetracarbonyls had a structure such as II, however, was their NMR spectra (Table 2). (A representative spectrum is shown in Fig. 1.) Whereas the N—CH_3 protons are a singlet in FcCNP (Table 2), they give rise to a pair of lines in the complex. Furthermore, the methylene protons are now seen as a pair of widely separated doublets with a chemical shift difference in the range τ 1.43 to 1.52 ppm. The methylene protons are "diastereomeric" in both FcCNP and the $(FcCNP)M(CO)_4$ complexes, and they are expected to differ in chemical shift as a result [12]. (For example, in a series of *ortho*-substituted *N*, *N*-[(dimethylamino)methyl]ferrocenes, Slocum and co-workers

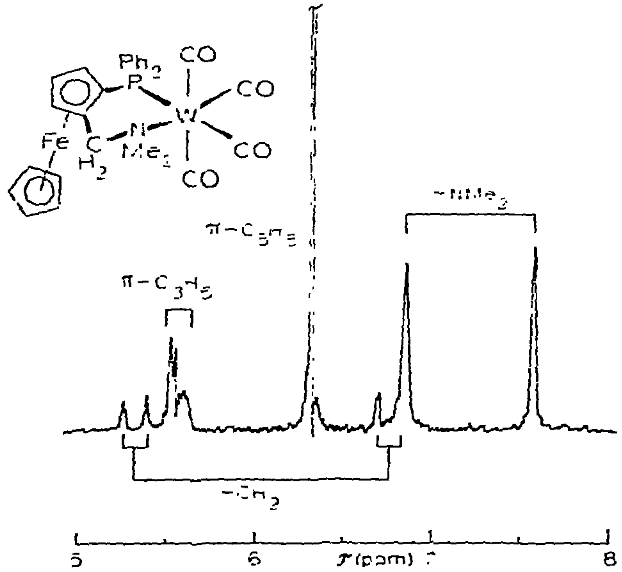
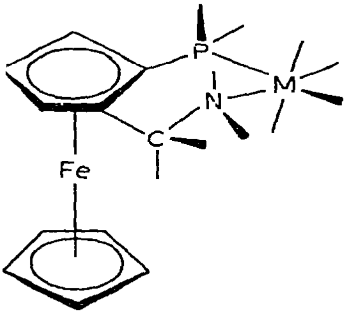


Fig. 1. Proton NMR spectrum of $(FcCNP)W(CO)_4$ in $CDCl_3$ at ambient temperature. Phenyl protons are not shown.

find chemical shift differences of 0.1 to 1.4 ppm for the methylene protons [13].) However, the doublet separation increases drastically when the ligand is complexed to a $M(CO)_4$ moiety, suggesting that II is formed[*].



(II)

The infrared spectrum of $(FcCNP)Fe(CO)_4$ (Table 3) suggests that the complex has a monodentate ligand attached in an axial position. If the local symmetry about the metal were C_{3v}, three infrared active bands of E and A_1 symmetry would be predicted, the E mode having greater intensity. However, if the asymmetry of the ligand lowers the local symmetry about the metal to C_s, the degeneracy of the E mode is lifted and two more bands result; three A' and one A'' modes are now predicted [14], a result closer to that observed for $(FcCNP)Fe(CO)_4$. Such spectra have also been observed for axially substituted metal carbonyls such as $Ph_3GeCo(CO)_4$ (C_{3v}) and $PhCl_2GeCo(CO)_4$ (C_s) [15]. By analogy with these compounds and other complexes of the type $LFe(CO)_4$, we assign the bands in $(FcCNP)Fe(CO)_4$ as follows: 2051 m, $A'^{(2)}$; 1984 m, $A'^{(1)}$; 1952 s, A'; 1940 s, A''. It is worth pointing out that the ratio:

$$\frac{A'^{(1)} - \left(\frac{A' + A''}{2}\right)}{A'^{(2)} - \left(\frac{A' + A''}{2}\right)} = \frac{(1984 - 1946)\ \mathrm{cm}^{-1}}{(2051 - 1946)\ \mathrm{cm}^{-1}}$$

is 0.36, a ratio observed for a large number of $LCo(CO)_4$ and $LFe(CO)_4$ complexes of nominal C_{3v} symmetry [14, 15]. Indeed, this may be a good argument against the possibility that the FcCNP ligand is substituted in an equatorial position to give a complex of C_{2v} symmetry, a geometry which should also give rise to four ν(CO) bands.

The question remaining is the point of attachment of the FcCNP in the iron complex. The NMR spectrum (Table 2) shows only a single line for the N-methyl protons, the line having virtually the same chemical shift as the corresponding protons in the free ligand. This observation suggests, of course, that

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[*] Note that there are four isomers possible for this molecule. There are two ring conformations, each having an enantiomer. Although we have no evidence favoring one conformation over the other, we should note that there was no change in the ^1H NMR spectrum of the compound on warming to 80°. This implies either that the ring is conformationally non-rigid even at room temperature or that it is still locked in one or the other conformation at the higher temperature.

coordination occurs through phosphorus only. Corroborating evidence is found in the infrared spectrum. Venanzi and his co-workers have found that, in *ortho*-(dimethylamino)(diphenylphosphino)benzene, coordination of the *N*-methyl group could be detected by disappearance of a band in the 2750-2800 cm^{-1} region [16]. This band, found at 2770 cm^{-1} in free FcCNP, was in fact observed to disappear upon coordination to the Group VIB metal carbonyls, but it remained in the spectrum of the iron carbonyl complex.

On the basis of NMR and infrared spectral evidence, we conclude that the ligand in $(FcCNP)Fe(CO)_4$ is bound through the phosphorus and occupies an axial position in a trigonal bipyramidal complex. The preferential coordination of phosphorus is of course often observed for metals at the right end of the transition metal series and is readily rationalized. These metals have a greater *d* electron density than those earlier in the series; consequently, replacement of the excellent π acceptor ligand CO must be made by another good π acceptor and nitrogen is notably poor in this regard.

Reaction of FcCNP with $Co_2(CO)_8$ presumably gives an ionic product $[(FcCNP)_2Co(CO)_3][Co(CO)_4]$ according to reaction 1. This is entirely analogous to the product isolated with the simple tertiary phosphines PPh_3 and $FcPh_2P$ [1]. The nature of the final product, $[(FcCNP)_2Co(CO)_3]BPh_4$, is supported by analysis and molecular weight determination (Table 1), conductivity measurements and comparison of the infrared spectrum with that of the triphenyl and ferrocenyldiphenylphosphine analogues. The point of attachment of the ligand is again thought to be the phosphorus atom. This is based on the observation that the band for an uncoordinated $—NMe_2$ group is present in the 2750-2800 cm^{-1} region and that the NMR spectrum for $[(FcCNP)_2Co(CO)_3]$-$[Co(CO)_4]$ shows an unsplit and unshifted *N*-methyl resonance line (at τ 8.04). Th geometry of the $[(FcCNP)_2Co(CO)_3]^+$ ion is probably *trans*, since two closely-spaced strong ν(CO) bands are observed [14]. (Apparently the degeneracy of the predicted *E* mode is removed by ligand asymmetry.)

One of the motivations of this research has been the hope of discovering new organometallic "mixed valence" compounds (vide infra). In the $[(FcCNP)_2Co(CO)_3]^+$ cation there are two metals in different formal oxidation states, so intramolecular electron transfer is feasible. However, such transfer apparently does not occur. The Mossbauer quadrupole splitting and isomer shift parameters for $[(FcCNP)_2Co(CO)_3]BPh_4$ were found to be 2.48 mm/sec and 0.80 mm/sec at 85 K, respectively; both of these values agree very favorably with those for ferrocene itself at 85 K (*QS*, 2.46 mm/sec and *IS*, 0.78 mm/sec)*.

The bis-borane adduct

This complex is of interest because of its NMR spectrum (Table 2). In $FcCNP \cdot 2BH_3$ (III) both the $—CH_2—$ protons and the *N*-methyl groups are diastereomeric [12, 13]. As a result, the methylene protons give rise to an AB pattern, and the *N*-methyl groups result in two separate lines**. (The closest

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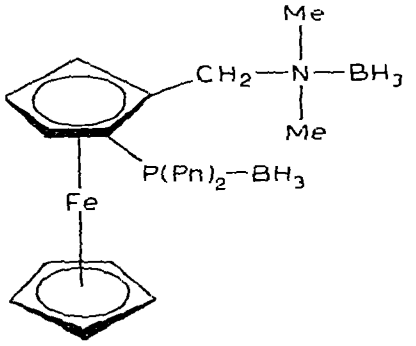
* We especially wish to thank Professor C.U. Pittman, Jr and Mr. Y. Sasaki of the University of Alabama for these measurements.

** In contrast, the $—NMe_2$ group in the BH_3 adduct of [(dimethylamino)methyl]ferrocene gives rise to only a single resonance line (τ 7.62 ppm) as do the $—CH_2—$ protons (τ 6.20 ppm); neither group is diastereomeric in this case analogy is (IV) where the C-methyl groups are nonequivalent [13].) However, neither the methylene A—B separation nor the separation of the *N*-methyl resonance lines is as great in III as in (FcCNP)M(CO)$_4$ where the ligand is chelating.



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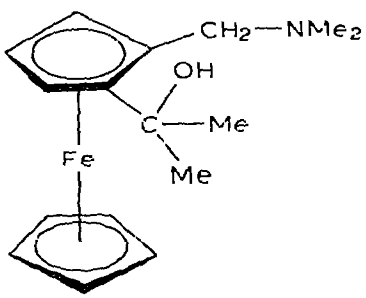

(IV)

Electrochemistry of the metal tetracarbonyl complexes of 1-[(dimethylamino)-methyl]-2-(diphenylphosphino)ferrocene

After Dessy's initial survey [17] of the electrochemical behavior of organometallic compounds there has been an increase in activity in this area, and many interesting new results have been reported [18-20]. For example, McCleverty recently reported that a chromium complex with an organometallic ligand, $Cr(CO)_5[FcC(X)]$ (where X = OEt, OMe, or pyrrolidin-1-yl, and Fc is the monosubstituted ferrocenyl group) did not show the expected two separate oxidations of chromium and ferrocenyl iron [21]. Rather only one wave representing a reversible one-electron oxidation-reduction was observed in the cyclic voltammogram of this complex. McCleverty suggested that this observation indicates that the orbital from which the electron is removed "encompasses both potential redox centers [and] corresponds to the generation of $[A—B]^+$" [21]. Such complexes are worthy of study as they may represent potential "mixed valence" compounds, a class of compounds having unique properties [22]. Consequently we have begun a systematic examination of the electrochemistry of organometallic ligands and their complexes.

The electrochemical behavior of FcCNP is not simple, and the compound continues to be under active investigation in our laboratory; however, some data are included here (Table 4) for comparison with its complexes. Only the third wave in Fig. 2 represents a truly reversible process, and it is therefore assigned tentatively to the normally reversible oxidation-reduction of the ferrocenyl iron*.

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* When the —NMe$_2$ group is uncomplexed, as it is in FcCNP and (FcCNP)Fe(CO)$_4$, significant and as yet unexplained differences in electrochemical behavior are observed when the compound is run in acetonitrile instead of CH_2Cl_2. In the case of FcCNP the first wave is much more reversible in CH_3CN, when the voltage sweep is reversed at + 0.6 V, nearly the same amount of current flows on reduction (at E_{peak} = + 0.44 V) as on oxidation (at E_{peak} = + 0.51 V). The corresponding process in CH_2Cl_2 is not reversible at all. However, when the voltage is swept to + 1.4 V in CH_3CN before reversing, a new electroactive species is produced at the expense of the original FcCNP. Subsequent sweeps of the potential range 0 to + 1.6 V show this new species undergoing nearly reversible oxidation-reduction at E_{peak} = + 0.74 V and an almost total lack of the original compound.

TABLE 4

ELECTROCHEMICAL DATA FOR FcCNP AND ITS COMPLEXES[a]

Compound	E_{peak} (V vs. SCE)[b] Anodic portion	Cathodic portion	Remarks
FcCNP[c]	0.66		Irreversible
	0.86	0 76	Quasi-reversible
	1.03	0.86	Reversible
(FcCNP)Cr(CO)$_4$	0.54	0.43	Reversible[d]
	0.96	0.84	Reversible[e]
	1.47		Irreversible
(FcCNP)Mo(CO)$_4$	0.76		Irreversible
	0.99	0.86	Reversible
(FcCNP)W(CO)$_4$	0.78		Irreversible
	0.99	0.85	Reversible
FcCNP · 2BH$_3$	0.96	0.78	Reversible
	1.2		Irreversible

[a] All data were obtained by cyclic voltammetry; solutions were 2 mmolar in CH_2Cl_2 with 0 2 *M* tetrabutylammonium perchlorate as supporting electrolyte. [b] One criterion of reversibility is that the anodic and cathodic waves are separated by 59 mV. However, under our experimental conditions, clearly reversible waves had peak separations of 110-180 mV; for example, the $E_{p, a}$-$E_{p, c}$ separation for ferrocene under the conditions in *a* above was 130 mV Separations of 170 to 230 mV have been reported for similar complexes under similar conditions. (See ref 21). [c] Severe electrode coating observed. [d] Solution color changed from yellow to orange on oxidation. [e] Solution color changed from orange to blue-green on oxidation.

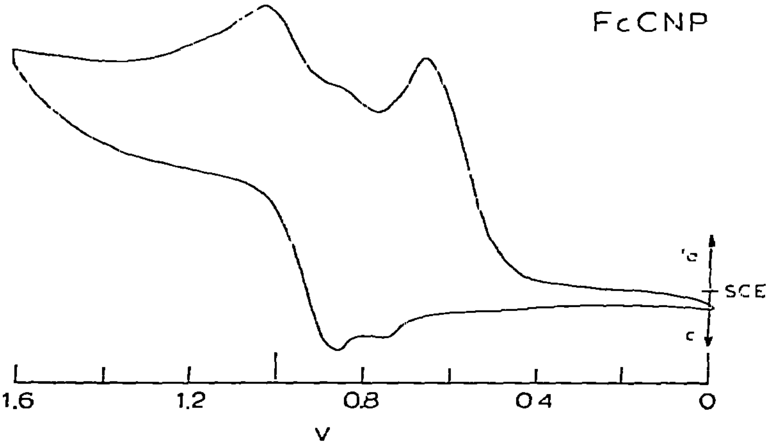

Fig. 2. Cyclic voltammogram of FcCNP (2 mmolar) in CH_2Cl_2 with 0.2 *M* tetrabutylammonium perchlorate as supporting electrolyte. Anodic voltage sweep at the start. Electrode coating reduced current in subsequent sweeps.

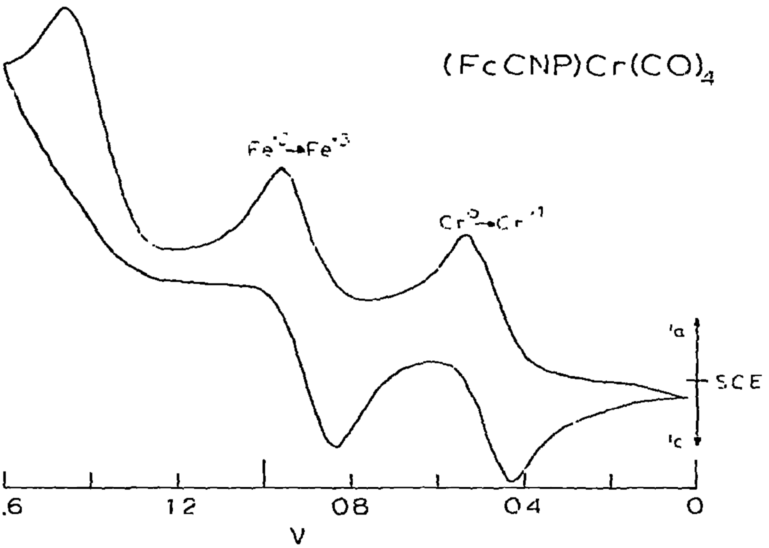

Fig. 3. Cyclic voltammogram of $(FcCNP)Cr(CO)_4$ (2 mmolar) in CH_2Cl_2 with 0.2 M tetrabutylammonium perchlorate as supporting electrolyte. Anodic voltage sweep at the start.

When both the nitrogen and phosphorus are complexed*, the electrochemical behavior of FcCNP changes considerably. The complex $(FcCNP)Cr(CO)_4$ is of particular interest in this regard. Two reversible one-electron redox waves are now observed along with an irreversible wave at very anodic potentials (Table 4 and Fig. 3). The following pieces of experimental evidence support the assignment of the first of these waves to chromium oxidation [$Cr^0 \rightarrow Cr^+$], the second to ferrocenyl iron oxidation [$Fe^{2+} \rightarrow Fe^{3+}$], and the third to further chromium oxidation [$Cr^+ \rightarrow Cr^{n+}$] with concomitant destruction of the complex:

a. On complete electrolysis the solution color changed from the normal yellow to orange at + 0.54 V and finally to blue-green at + 0.96 V. The latter is the color often observed for the ferrocenium ion in solution [23].

b. The infrared spectrum of the solution after partial oxidation at + 0.7 V showed the three bands for the complex shifted to 2080 cm^{-1} (shift = + 65 cm^{-1}), 2000 cm^{-1} (shift = + 109 cm^{-1}), and 1970 cm^{-1} (shift = + 139 cm^{-1}); however, no additional shift was observed after oxidation at + 1.1 V. The spectrum returned to that of the neutral complex, $(FcCNP)Cr(CO)_4$, after reduction at + 0.2 V.

c. The ligand in the bis-borane adduct, FcCNP · $2BH_3$, is also bidentate. Its cyclic voltammogram consisted of a reversible one-electron redox wave followed closely by an irreversible wave (Table 4). The first wave most probably represents oxidation of the ferrocenyl iron, and the second is assigned tentatively to oxidation of the amine group which has been freed by loss of BH_3 after oxidation of the ferrocenyl group**. The important observations here, however,

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* The electrochemical behavior of such complexes is the same in both CH_3CN and CH_2Cl_2.

** It is possible that this is due to BH_3 oxidation. However, there is no evidence of such a process in the cyclic voltammograms of a variety of ferrocenylphosphine—borane complexes which are reported in Part III of this series [25] is that the ferrocenyl group oxidation occurs at E_{peak} = + 0.94 V, a potential very close to that assigned to the same process in (FcCNP)Cr(CO)$_4$. It seems likely that only oxidation of the metal directly bearing the carbonyl groups cou lead to such a large change in ν(CO) as that observed [24]. Indeed, this observat coupled with the observed color changes and determination of the ferrocenyl group oxidation potential in a fully complexed ligand, leaves little doubt as to the correctness of the interpretation of the cyclic voltammagram of (FcCNP)-Cr(CO)$_4$.

When the electrochemical behavior series of Group VIB metal tetracarbony complexes is compared, there are several additional points of interest. Just as the chemistry of chromium compounds is frequently different from that of molybdenum and tungsten compounds, the oxidation potential of chromium in (FcCNP)Cr(CO)$_4$ is different from molybdenum and tungsten oxidation potentials[*]. Moreover, the latter oxidations [$M^0 \rightarrow M^+$] are completely irreversible as compared to the completely reversible $Cr^0 \rightarrow Cr^+$ oxidation. We also observe that there is little or no change in the oxidation potential of the ferrocenyl iron in the series, and, when the ferrocenyl group is oxidized, there is little or no change in ν(CO) for the chromium attached carbonyl groups. Both of these observations suggest that there is no significant interaction between the metal centers in (FcCNP)M(CO)$_4$.

Finally, it is significant that the Group VIB metal in (FcCNP)M(CO)$_4$ is oxidized at a lower potential than the ferrocenyl group, the latter usually oxidizing at relatively low potentials. In contrast, the Group VIB metal in complexes of the type $[Fc_xPh_{3-x}P]_{1,2}M(CO)_{5,4}$ (Fc = monosubstituted ferrocene) oxidize at potentials higher than the ferrocenyl group [25]. This is undoubtedly due to the fact that, in the FcCNP complexes, a carbonyl group has been replaced by a donor group, $-NMe_2$, that cannot function as a π acceptor. The electron density at the metal is therefore higher in the FcCNP complexes, and oxidation occurs at lower potentials[**]. Furthermore, because the oxidation of the Group VIB metal occurs at such a low potential, the ferrocenyl iron oxidation is observed at higher than normal potentials, since the latter is oxidized only after the complex has acquired a + 1 charge.

These observations on the electrochemistry of the FcCNP complexes are compared with the results for some complexes of simple, tertiary ferrocenylphenylphosphine complexes of a variety of Lewis acids in Part III of this series [25].

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[*] McCleverty and his co-workers have recently made the same observation on a series of complexes of the type $M(CO)_4L_2$ and $M(CO)_4(L-L)$ where M is Cr, Mo, or W and L or L—L are various nitrogen and phosphorus donor ligands [21].

[**] McCleverty and his co-workers have also observed that the oxidation potential of the metal drops dramatically as carbonyl groups are replaced by poorer π acceptors; for example: $(PPh_3)Cr(CO)_5$, $E_{1/2}$ = + 1.15 V vs. SCE; $(NH_3)Cr(CO)_5$, $E_{1/2}$ = + 0.71 V; and $[H_2N(Me)CH-CH(Me)NH_2]Cr(CO)_5$, $E_{1/2}$ = + 0.14 V [21, 26].

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References

1 J C Kotz and C.L. Nivert, J. Organometal. Chem., 52 (1973) 387.
2 J.C. Kotz and E.W. Post, Inorg. Chem., 9 (1970) 1661.
3 G. Marr and T. Hunt, J. Chem. Soc. C, (1969) 1070.
4 G.R. Dobson, R.C. Taylor and T.D. Walsh, Inorg. Chem., 6 (1967) 1929
5 H.P. Fritz, I.R. Gordon, K.E. Schwarzhans and L M. Venanzi, J. Chem. Soc., (1965) 5210.
6 E.B. Moyhanan, F.D. Popp and M.F. Wernke, J. Organometal. Chem., 19 (1969) 229.
7 D.M. Wiles and T. Suprunchuk, Can. J. Chem., 46 (1968) 1865.
8 D.J. Booth and B.W. Rockett, Inorg. Nucl. Chem. Lett., 6 (1970) 121.
9 W.J. Geary, Coord. Chem. Rev., 7 (1971) 81.
10 W.S. Woodward, T.H. Ridgway, and C.N. Reilley, Anal. Chem., 45 (1973) 435 and private communication to RCR.
11 M.Y. Darensbourg and D.J. Darensbourg, J. Chem. Ed , 47 (1970) 33.
12 A.H. Lewin, J. Kipowitz and T. Cohen, Tetrahedron Lett., (1965) 1241; P.L. Southwick, J.A. Fitzgerald and G.E. Milliman, Tetrahedron Lett., (1965) 1247
13 P. Smith, J.J. McLeskey, III and D.W. Slocum, J. Org. Chem., 30 (1965) 4356. D W Slocum and T.R. Engelmann, J. Org. Chem., 34 (1969) 4101.
14 F.A. Cotton and R.V. Parish, J. Chem. Soc., (1960) 1440.
15 D.J Patmore and W.A.G. Graham, Inorg Chem., 6 (1967) 981.
16 R.E. Christopher, I.R. Gordon and L.M. Venanzi, J. Chem. Soc. A, (1968) 205.
17 R.E. Dessy and L.A. Bares, Accounts Chem. Res., 5 (1972) 415.
18 J.A. Ferguson and T.J. Meyer, Inorg. Chem., 11 (1972) 631.
19 P. Hydes, J.A. McCleverty and D.G. Orchard, J. Chem. Soc. A, (1971) 3660.
20 L.I. Denisovich and S.P. Gubin, J. Organometal. Chem., 57 (1973) 87 and refs. therein.
21 M.K. Lloyd, J.A McCleverty, D.G. Orchard, J.A Connor, M.B. Hall, I.H. Hillier, E M. Jones and G.K. McEwen, J. Chem. Soc., Dalton Trans., (1973) 1743.
22 For example, D.O Cowan, C. LeVanda, R L Collins, G A. Candela, U.T. Mueller-Westerhoff and P. Eilbracht, Chem. Commun., (1973) 329.
23 M. Rosenblum, Chemistry of the Iron Group Metallocenes, Interscience, New York, 1965, p. 49.
24 R.E. Dessy and L. Wieczorek, J. Amer. Chem. Soc., 91 (1969) 4963.
25 J.C. Kotz, C.L. Nivert, J.M. Lieber and R.C. Reed, J. Organometal. Chem., submitted
26 J.A. McCleverty, D.G. Orchard, J.A. Connor, E.M. Jones, J.P. Lloyd and P D. Rose, J. Organometal. Chem., 30 (1971) C75.