ORGANOMETALLIC LIGANDS

THE PREPARATION AND PROPERTIES OF COMPLEXES OF THE FERROCENYLPHOSPHINES*

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SUMMARY

Coordination complexes of ferrocenyldiphenylphosphine, diferrocenylphenylphosphine, and triferrocenylphosphine have been prepared. An examination of the C–O stretching frequencies of the eight possible compounds of the series $(Fc_xPh_{3-x}P)$ $M(CO)_5$ (M = Mo, W) showed that the A_1^1 and E modes decreased in frequency as the number of ferrocenyl groups increased. This has been interpreted as resulting from a concomitant increase in the σ donor ability of the ferrocenylphosphine. ^1H NMR studies of $(Fc_xPh_{3-x}P)Me^+I^-$ and methylbis(dimethylglyoximato)(ferrocenylphosphine)cobalt(III) demonstrate the same trend, that is, the P–Me or Co–Me groups are increasingly shielded with increasing ferrocenyl group substitution. Although the σ donor ability of the phosphine increases with increasing ferrocenyl substitution, the steric requirements of the ligand also increase greatly. As evidence, no ligand exchange is observed in solutions of Fc_3P and methylbis(dimethylglyoximato)(pyridine)cobalt(III), nor is complexation observed between this same phosphine and bis(acetylacetonato)nickel(II); however, ligand exchange or complexation is observed for the other phosphines of the series. The contact shifted NMR spectra of $FcPh_2P$ and Fc_2PhP show that spin may not be delocalized from the substituted π-C_5H_4 ring through the iron atom into the π-C_5H_5 ring and that more spin density may be delocalized into the phenyl groups than into the ferrocenyl groups; this latter result may be a manifestation of the fact that the phenyl group is less electron releasing than the ferrocenyl group. In a preliminary survey of the electrochemistry of these phosphines and their complexes, it was found that the ferrocenyl group of $FcPh_2P$ and $(FcPh_2P)Mo(CO)_5$ underwent reversible, one-electron

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oxidation at +0.48 and +0.62 V $vs.$ S.C.E., respectively. At more oxidizing potentials, more complex, irreversible processes occur.

INTRODUCTION

Over the past several years, we have been engaged in a study of the synthesis and properties of organometallic ligands, molecules which may function as Lewis acids or bases and which have a metal–carbon bond or bonds as an integral and important part of the molecular framework[1−5]. In the course of a study of the synthesis and chemical properties of ferrocenyldichloroborane[2], we found that the ferrocenyl group had a definite influence on the properties of the attached boron-containing group. Therefore, this work has been extended to an examination of other inorganically substituted ferrocenes, in particular the series of phosphines generated by successively replacing phenyl groups with ferrocenyl groups on triphenylphosphine: ferrocenyldiphenylphosphine (FcPh$_2$P), diferrocenylphenylphosphine (Fc$_2$-PhP), and triferrocenylphosphine (Fc$_3$P)[6,7].

Only two papers have appeared describing systematic studies of the properties of the ferrocenylphosphines. On the basis of a study of the rate of hydrolysis of benzyl iodide salts of the ferrocenylphosphines [Fc$_x$Ph$_{3−x}$PBz$^+$ I$^−$], McEwen and his co-workers concluded that "there is a strong interaction between the ferrocenyl group and the cationoid phosphorus which decreases the electrophilic reactivity of the latter"[8]. In addition, they deduced that the steric bulk of the ferrocenyl group had no influence on the rate of the hydrolysis reactions. Although the work described below indicates that the ferrocenyl group does indeed have an electronic effect on the attached phosphorus, the steric bulk of the ferrocenyl group has been found to have a decided effect under certain circumstances.

Very recently Pittman and Evans prepared and characterized monosubstituted triferrocenylphosphine derivatives of M(CO)$_6$ (M=Cr, Mo, W), Fe(CO)$_5$, and Mn$_2$(CO)$_{10}$[9]. A comparison of the v(CO) force constants for Ph$_3$PM(CO)$_5$ and Fc$_3$PM(CO)$_5$ reveals that triferrocenylphosphine is generally a better σ donor than triphenylphosphine.

The coordination chemistry of organic phosphines and arsines has of course been extensively explored[10], and that of organometallic phosphines based on non-transition metals has also been actively studied by Schumann and his co-workers[11]. The use of organometallic transition metal compounds as ligands, however, has been reported only infrequently. In addition to the triferrocenylphosphine complexes reported by Pittman and Evans[9], there appear to be only three other very brief reports of ferrocenylphosphine complexes[12−14]. Metal complexes have also been reported for ferrocene-1,1′-bis(dimethylarsine)[15], acetylferrocene and 1,1′-diacetylferrocene[16], formylferrocene thiosemicarbazones[17], the β-diketones FcCOCH$_2$COR (R=Me, Ph)[18,19], [(dimethylamino)methyl]ferrocene[20], 1-(2-pyridyl)-2-[(dimethylamino)-methyl]ferrocene[21], and, most recently, ferrocenylcarbene[22].

In general, our work with organometallic ligands has taken several directions: (i) the synthesis and study of a wide range of such materials; (ii) the synthesis and examination of coordination complexes of these ligands with transition metals, particularly those complexes having unusual magnetic or electrochemical properties;

and (iii) the influence of such ligands on reactions at the coordinated metal, especially those catalyzed by the metal. This paper takes up the second of these topics for the series of ferrocenylphosphines noted above. A preliminary communication has appeared regarding the contact shifted proton NMR spectrum of $FcPh_2P$[23], and a subsequent paper in this series will deal with our current work on 1-[(dimethyl-amino)methyl]-2-(diphenylphosphino)ferrocene.

EXPERIMENTAL

Equipment and general techniques

Reactions were carried out under dry nitrogen using normal techniques or in a preparative vacuum line. Non-volatile air-sensitive substances were handled in a drybox equipped with a drying and deoxygenating system.

Elemental analyses of most compounds prepared were done by Galbraith Laboratories, Inc.; the results are listed in Table 1.

TABLE 1

ANALYTICAL DATA FOR THE FERROCENYLPHOSPHINES AND THEIR COMPLEXES

Compound	M.p. (°C) (uncorrected)	Analyses found (calcd.) (%)	
		C	H
$FcPh_2P$	122–123	71.58 (71.37)	5.12 (5.17)
Fc_2PhP	193–195 (dec.)	65.14 (65.31)	5.00 (4.85)
Fc_3P	270–280 (dec.)	61.25 (61.47)	4.87 (4.64)
$Ph_3PMo(CO)_5$	130–131	55.22 (55.43)	2.97 (3.01)
$FcPh_2PMo(CO)_5$	168–170	53.26 (53.50)	3.19 (3.16)
$Fc_2PhPMo(CO)_5$	180–185 (dec.)	52.27 (52.13)	3.41 (3.25)
$Fc_3PMo(CO)_5$	260 (dec.)	51.30 (51.09)	3.44 (3.28)
$Ph_3PW(CO)_5$	146–147	47.29 (47.10)	2.67 (2.56)
$FcPh_2PW(CO)_5$	183–184	48.07 (46.67)	3.03 (3.88)
$Fc_2PhPW(CO)_5$	213–216 (dec.)	46.30 (46.38)	3.01 (2.87)
$Fc_3PW(CO)_5$	260 (dec.)	46.03 (46.15)	3.10 (2.96)
$CH_3Co(DH)_2(Ph_3P)$[a]	212–213	57.29 (57.25)	5.84 (5.69)
$CH_3Co(DH)_2(FcPh_2)P$	218–220 (dec.)	55.41 (55.21)	5.55 (5.38)
$CH_3Co(DH)_2(Fc_2Ph)P$	218–220 (dec.)	54.37 (53.73)	5.40 (5.15)
$(Ph_3P)_2Co(CO)_3^+ BPh_4^-$	145–150 (dec.)	76.45 (76.67)	5.18 (5.07)
$(FcPh_2P)_2Co(CO)_3^+ BPh_4^-$	120–125	69.76 (70.88)	4.96 (4.83)

[a] $CH_3Co(DH)_2(R_3P)$ = methylbis(dimethylglyoximato) (phosphine)cobalt(III).

Proton NMR spectra were obtained using a Varian A-60 or Perkin–Elmer R-10 spectrometer; TMS was used as an internal standard. Proton NMR data for most compounds prepared are listed in Table 2. Except as noted, IR spectra were run as Nujol mulls on a Perkin–Elmer 337 or 457.

Cyclic voltammetry experiments were done using a three-electrode potentiostat-galvanostat system previously described[24]. The experiments were performed in a nitrogen-filled glove bag. The acetonitrile solutions were usually about 2 mM in phosphine or phosphine complex and 0.1 M in tetraethylammonium perchlorate.

TABLE 2

PROTON NMR DATA FOR THE FERROCENYLPHOSPHINES AND THEIR COMPLEXES

Compound	Line structure[a] (relative area)	Assignment	Chemical shift[b] (τ)	Spin coupling constants (Hz)[c]
$FcPh_2P$	m(10)	Phenyl	2.70	
	t(2)	π-C_5H_4	5.65	4
	t(2)	π-C_5H_4	5.92	4
	s(5)	π-C_5H_5	5.95	
Fc_2PhP	m(5)	Phenyl	2.77	
	m(4)	π-C_5H_4	5.72	
	m(2)	π-C_5H_4	5.80	
	m(2)	π-C_5H_4	6.00	
	s(10)	π-C_5H_5	5.92	
Fc_3P	t(2)	π-C_5H_4	5.72	2
	t(2)	π-C_5H_4	5.82	2
	s(5)	π-C_5H_5	5.93	
$FcPh_2PMo(CO)_5$[d]	m(10)	Phenyl	2.55	
	m(2)	3,4 H's of π-C_5H_4	5.52	i
	m(2)	2,5 H's of π-C_5H_4	5.75	i
	s(5)	π-C_5H_5	6.05	
$Fc_2PhPMo(CO)_5$	m(5)	Phenyl	2.70	
	m(4)	π-C_5H_4	5.56	
	m(4)	π-C_5H_4	5.76	
	s(10)	π-C_5H_5	5.80	
$Fc_3PMo(CO)_5$	m(2)	π-C_5H_4	5.47	2
	m(2)	π-C_5H_4	5.55	2
	s(5)	π-C_5H_5	6.00	
$CH_3Co(DH)_2(py)$[e]	s(2)	O–H...O	−9.0	
	d(2)	Pyridine	1.38	5
	m($\sim$1)	Pyridine	2.32	
	m($\sim$2)	Pyridine	2.69	
	s(12)	Gly-CH_3[f]	7.88	
	s(3)	Co–CH_3	9.31	
$CH_3Co(DH)_2(Ph_3P)$	s(2)	O–H...O	−8.1	
	d(15)	Phenyl	2.69	5
	d(12)	Gly-CH_3	8.16	3
	d(3)	Co–CH_3	8.82	4
$CH_3Co(DH)_2(FcPh_2P)$	s(2)	O–H...O	−7.7	
	m(10)	Phenyl	2.61	
	q(2)	π-C_5H_4	5.70	1.5
	q(2)	π-C_5H_4	6.03	1.5
	s(5)	π-C_5H_5	6.12	
	d(12)	Gly-CH_3	8.15	3
	d(3)	Co–CH_3	8.92	4
$CH_3Co(DH)_2(Fc_2PhP)$[g]	m(5)	Phenyl	2.66	
	m(2)	π-C_5H_4	5.40	1.5
	m(2)	π-C_5H_4	5.55	1.5
	m(2)	π-C_5H_4	5.70	1.5

TABLE 2 (*continued*)

Compound	Line structure (relative area)	Assignment	Chemical shift (τ)	Spin coupling constants (Hz)
	s(10)	π-C_5H_5	5.90	
	m(2)	π-C_5H_4	6.21	1.5
	d(12)	Gly-CH_3	8.16	3
	d(3)	Co–CH_3	8.98	4
$Ph_3PMe^+I^-$ [b]	m(15)	Phenyl	2.2	
	d(3)	CH_3	6.85	14.5
$FcPh_2PMe^+I^-$ [b]	m(10)	Phenyl	2.2	
	q(2)	π-C_5H_4	5.05(5.13)[h]	2
	q(2)	π-C_5H_4	5.23(5.30)	2
	s(5)	π-C_5H_5	5.72(5.78)	
	d(3)	CH_3	6.98(6.86)	14.5
$Fc_2PhPMe^+I^-$	m(5)	Phenyl	2.2	
	m(4)	π-C_5H_4	5.17	2
	m(4)	π-C_5H_4	5.28	2
	s(10)	π-C_5H_5	5.75	
	d(3)	CH_3	7.03	14.0
$Fc_3PMe^+I^-$	s(12)	π-C_5H_4	5.20	
	s(15)	π-C_5H_5	5.83	
	d(3)	CH_3	7.20	13.5

[a] s = Singlet, d = doublet, t = triplet, q = quartet, m = multiplet. [b] Chemical shifts are measured against TMS as an internal standard. All data obtained in $CDCl_3$ *except* the methyl phosphonium iodides; the latter were run in DMSO-d_6. [c] In most cases, the values given are not true coupling constants, but are multiplet line separations. [d] The spectrum of the π-C_5H_4 protons of this complex is given in Fig. 1. [e] $CH_3Co(DH)_2(Ph_3P)$ = methylbis(di-methylglyoximato) (triphenylphosphine)cobalt(III). [f] Gly-CH_3 = methyl groups of the dimethylglyoximato ligand. [g] The O–H...O proton was not located in this spectrum. [h] Shift values listed in parentheses were obtained in $CDCl_3$. [i] See Fig. 1.

Preparation of the ferrocenylphosphines

Ferrocenyldiphenylphosphine and diferrocenylphenylphosphine were prepared according to the procedures outlined by Sollott, *et al.*[6,7], with one change. Following the hydrolysis of the reaction mixture, the solid was extracted with benzene as directed; instead of evaporating this benzene solution to dryness and then extracting with heptane, the benzene extract was reduced in volume on a rotating evaporator and then chromatographed with benzene on a 20×5 cm alumina column; $CHCl_3$ was used to remove the phosphine oxide from the column. Literature yields were equalled or exceeded with this more convenient procedure. The compounds were recrystallized from chloroform/ethanol; melting points and analytical data appear in Table 1; NMR are collected in Table 2.

Triferrocenylphosphine was prepared according to the procedure of Sollott and Peterson[7] with the exception that diethylaminophosphorus chloride was used instead of the dimethylamino derivative, and the benzene extraction was carried out in a Soxhlet extractor. The compound was also recrystallized from chloroform/ethanol; analytical results appear in Table 1.

Preparation of metal carbonyl derivatives

Complexes of the type $R_3PM(CO)_5$ (M = Mo, W) were prepared by the follow-

ing procedure: The phosphine (2 mmoles) and appropriate metal hexacarbonyl (5 mmoles) were refluxed in dry diglyme. [Monoglyme was found to be more suitable for the preparation of $Ph_3PMo(CO)_5$.] In the case of the tungsten complexes reflux time was 4 h, and for the molybdenum complexes it was 2–3 h. Any metal carbonyl which sublimed from the reaction mixture during reflux was returned by shaking the flask and condenser assembly. After the appropriate length of time, the reaction mixture was allowed to cool for about 1 h and then filtered rapidly. Solvent and excess metal hexacarbonyl were removed *in vacuo*. The remaining solid product was recrystallized 3–4 times from chloroform/ethanol; yields averaged 30–50%. Melting points and analytical data are collected in Table 1; NMR data are presented in Table 2.

The phosphine cobalt carbonyl complexes were prepared in a three-neck flask attached to the vacuum line. Dry CH_2Cl_2 was first condensed into the flask containing the phosphine. After warming to $0°$, $Co_2(CO)_8$ was added from a solids-addition tube[25] which had been placed in one of the flask necks. Evolution of CO began immediately and was complete in a matter of minutes. After measuring the quantity of CO evolved with a Toepler pump, the solvent was distilled off to leave the desired product. The product was stored *in vacuo* until needed.

The literature indicates that reaction (1) should occur at low temperatures[26,27]

$$2\ L + Co_2(CO)_8 \rightleftharpoons L_2Co(CO)_3^+ Co(CO)_4^- + CO \tag{1}$$

That this is indeed the case is seen from the quantity of CO evolved, IR spectra, and conductivity studies (*vide infra*). When 2.32 mmoles of Ph_3P were used with 1.16 mmoles of $Co_2(CO)_8$, 1.17 mmoles of CO were isolated. With 3.77 mmoles of $FcPh_2P$, the addition of 1.88 mmoles of $Co_2(CO)_8$ resulted in the evolution of 1.44 mmoles of CO. Vohler has reported carbonyl stretching frequencies of 2072 vw, 2002 s, 1927 w, and 1883 vs cm^{-1} for $(Ph_3P)_2Co(CO)_3^+ Co(CO)_4^-$ [28]. These compare favorably with those found in this study for the Ph_3P complex (2062 w, 1988 s, 1937 w, 1865 vs cm^{-1}) and the $FcPh_2P$ complex (2064 w, 1987 s, 1870 vs cm^{-1}).

The first product of the phosphine cobalt carbonyl reaction, $L_2Co(CO)_3^+ Co(CO)_4^-$, is unstable to loss of CO [26,27]. In order to examine the properties of the cation, the $Co(CO)_4^-$ ion was exchanged for BPh_4^-. An acetone solution of $NaBPh_4$ (5 mmoles) was added to 5 mmoles of the $Co(CO)_4^-$ salt in acetone. After stirring for 10 min, 50 ml of N_2-saturated water was added dropwise. The resulting precipitate was filtered and washed with water and 30–60° petroleum ether. Samples for conductivity measurements and analysis were recrystallized five times from acetone/water. Analytical data are collected in Table 1. A single carbonyl stretching band was found at 1999 cm^{-1} for the PPh_3 complex (lit.[28]: 2006 cm^{-1}). However, the slightly lower local symmetry of the cobalt atom in the $FcPh_2P$ complex is indicated by the fact that the main band was split (2006, 1982 cm^{-1}) and a very weak band appeared at 2059 cm^{-1}.

Infrared studies of the Group VIB phosphine metal pentacarbonyls

Spectra of solutions of $LM(CO)_5$ ($M = Mo$, W) were obtained on a Perkin–Elmer 337 equipped with an auxiliary Honeywell Electronik 16 recorder. The recorder was calibrated using HCl and DCl gas. Hexane was used as a solvent for all complexes except those of Fc_3P which required a hexane/chloroform mixture to

TABLE 3

CO STRETCHING FREQUENCIES FOR PHOSPHINE METAL PENTACARBONYLS[a,b]

Compound	Band frequency (cm^{-1})			
	A_1^2	B_1	A_1^1	E
$Ph_3PMo(CO)_5$	2075.0	1989.5		1952.0[c]
$FcPh_2PMo(CO)_5$	2075.0	1988.0	1952.0	1947.0
$Fc_2PhPMo(CO)_5$	2073.0	1982.5	1948.0	1943.0
$Fc_3PMo(CO)_5$	2077.0	1988.0		1947.0[c]
$Ph_3PW(CO)_5$	2074.0	1980.5		1942.0[c]
$FcPh_2PW(CO)_5$	2074.0	1980.0	1946.0	1938.0
$Fc_2PhPW(CO)_5$	2071.0	1974.5	1943.0	1936.0
$Fc_3PW(CO)_5$	2076.0	1981.0		1939.0[c]

[a] All spectra run as solutions in hexane with the exception of Fc_3P derivatives which were run in 1/1 hexane/CHCl$_3$. [b] The frequencies of all bands were measured from either $Mo(CO)_6$ (1989 cm^{-1}) or W-(CO)$_6$ (1983 cm^{-1}); the appropriate metal hexacarbonyl was present in solution as an internal standard. [c] The A_1^1 band was obscured by the E band in the case of the Ph_3P and Fc_3P derivatives.

TABLE 4

MOLAR CONDUCTIVITIES OF NaBPh$_4$ AND $(R_3P)_2Co(CO)_3^+ BPh_4^-$ IN NITROMETHANE AND NITROBENZENE

Compound	Molar conductivities at specified concentrations in nitromethane (nitrobenzene) (ohm^{-1}·cm^2·mole^{-1})			
	6 mM	3 mM	1.5 mM	1 mM
NaBPh$_4$	44.2	50.5	60.4	62[a] (25.4)
$(Ph_3P)_2Co(CO)_3^+ BPh_4^-$	22.7	29.0	37.9	40[a] (15.1)
$(FcPh_2P)_2Co(CO)_3^+ BPh_4^-$	20.8	27.8	33.3	37[a,b] (14.2)

[a] Extrapolated value. [b] Molar conductivities of 31.5 (at 2.4 mM) and 37.9 (at 1.2 mM) were also found in nitromethane.

reach a usable concentration; 0.1 mm cells were used. Spectra were run at several chart speeds, with and without the appropriate metal hexacarbonyl as an internal standard. Results are summarized in Table 3.

Conductivity studies of phosphine cobalt carbonyl complexes

Conductivities of the phosphine cobalt carbonyl complexes and NaBPh$_4$ at several concentrations in nitrobenzene and nitromethane were measured using a small volume cell having shiny platinum electrodes (3 ml volume; cell constant 0.0757) and a Beckman Model RC-16B or Model RC-18A bridge. Experimental data are collected in Table 4.

Preparation of methylbis(dimethylglyoximato)(phosphine)cobalt(III) complexes[*]

A slight excess of phosphine (2.2 mmoles) in 25 ml of CS$_2$ was added to 2 mmoles

[*] The methylbis(dimethylglyoximato)cobalt(III) portion of the molecule is often called methyl-cobaloxime[29] and is abbreviated CH$_3$Co(DH)$_2$. These abbreviations will be used in this paper.

of methylbis(dimethylglyoximato)(dimethylsulfide)cobalt(III) (prepared by the method of Schrauzer and Windgassen[29]) in 25 ml of 95% ethanol. The mixture was warmed gently for 30 min, during which time approximately half of the CS_2 boiled off. After cooling, 20–25 ml of ethanol was added; the precipitated product was filtered and then recrystallized from chloroform/ethanol. Analytical data are presented in Table 1 and NMR data in Table 2.

Ligand exchange with methylbis(dimethylglyoximato)(pyridine)cobalt(III)

A study of the exchange of phosphine for pyridine in pyridinemethylcobaloxime was carried out by an NMR method. Appropriate amounts of a phosphine and pyridinemethylcobaloxime were weighed out in an NMR tube and then dissolved in 1 ml $CDCl_3$. Immediately upon complete dissolution of the solids (about 1 min), the NMR spectrum was observed at 35°. Equilibrium had apparently been achieved in the first minute, since no change was observed in spectra obtained 30 min later. The relative amounts of phosphinemethylcobaloxime and pyridinemethylcobaloxime at equilibrium were obtained by measuring the relative areas of the glyoxime–methyl proton resonances for the two complexes. These resonance lines were readily distinguishable, since the glyoxime– or cobalt–methyl protons gave rise to doublets for the phosphine complexes; further, the signals were well-separated as seen from the data in Table 2. From the relative areas of the glyoxime–methyl signals and the absolute concentrations of phosphine- and pyridinemethylcobaloxime at the start, the K_{eq} of the reaction could be calculated. The necessary data are presented in Table 5.

TABLE 5

DETERMINATION OF THE EQUILIBRIUM CONSTANT FOR THE EXCHANGE OF PHOSPHINE FOR PYRIDINE ON METHYLBIS(DIMETHYLGLYOXIMATO)(PYRIDINE)COBALT-(III)[a]

Phosphine	Initial concentrations (molar)		Ratio of equilibrium concentrations $[Co-R_3P]/[Co-Py]^b$	K_{eq}
	Phosphine	$CH_3Co(DH)_2(Py)$		
Ph_3P	0.200	0.098	0.293	0.0375
$FcPh_2P$	0.200	0.103	0.304	0.0405
Fc_2PhP	0.200	0.103	0.166	0.0126
Fc_3P	0.400	0.126	[c]	

[a] Reaction done in $CDCl_3$. [b] Equal to the ratio of areas of the glyoxime–methyl proton resonance lines in the NMR spectrum of the equilibrium mixture at 35°. [c] No exchange observed.

Methyl iodide salts of the phosphines

Excess MeI was added to a benzene solution of 0.5 mmoles of phosphine. Immediate precipitation of orange, crystalline phosphonium salt occurred. The formulation of the compounds as phosphonium iodides was verified by their integrated proton NMR spectra in dimethylsulfoxide-d_6. Appropriate data are given in Table 2. Excellent agreement was obtained with the literature in the case of $Ph_3PMe^+I^-$ [30].

NMR contact shift studies

These studies were done according to well-documented procedures[23,31,32]. One ml of a CDCl$_3$ solution of the phosphine (of known concentration) was added to an NMR tube containing a weighed amount of NiAcac$_2$. The phosphine concentration used in these studies was usually 0.149 M and the NiAcac$_2$ concentrations varied from 0 to 0.15 M. Experimental data for NiAcac$_2$-containing solutions of PPh$_3$, FcPh$_2$P and Fc$_2$PhP are given in Table 6; the data for FcPh$_2$P and Fc$_2$PhP are plotted in Fig. 6.

TABLE 6

PROTON ISOTROPIC SHIFT DATA FOR Ph$_3$P, FcPh$_2$P, AND Fc$_2$PhP

Compound	Proton type	Isotropic shifts in Hz at specified concentrations of NiAcac$_2$ in CDCl$_3$						
		0.02 M	0.04 M	0.06 M	0.08 M	0.10 M	0.12 M	0.14 M
Ph$_3$P[a]	Ortho	+19	+45	+79	+93	+116	+138	+138
	Para	+26	+56	+96	+116	+145	+170	+182
	Meta	−18	−37	−69	−79	−100	−115	−124
FcPh$_2$P[a]	Ortho	+21	+37	+48	+67	+88	+101	+114
	Para	+31	+49	+64	+87	+115	+132	+146
	2,5[b]	+15	+25	+33	+45	+60	+70	+77
	C$_5$H$_5$[c]	−1	−1	−2	−2	−2	−3	−5
	Meta	−21	−33	−43	−60	−78	−89	−100
	3,4[d]	−24	−39	−50	−68	−88	−100	−111
Fc$_2$PhP[a]	Ortho	e	e	+15	+23	+25	+31	+34
	Para	e	e	+21	+30	+32	+39	+43
	2,5[b]	+2	+6	+9	+13	+14	+18	+20
		+5	+8	+12	+17	+19	+23	+27
	C$_5$H$_5$[c]	0	0	0	−1	−1	−1	−1
	Meta	e	e	−11	−16	−17	−20	−22
	3,4[d]	−4	−8	−12	−16	−18	−22	−24

[a] Absolute shifts for diamagnetic compounds in Hz from TMS all shifts downfield from TMS: Ph$_3$P· 439. FcPh$_2$P: phenyl, 437; C$_5$H$_5$, 244, 2,5 H's 245; 3,4 H's, 261. FcPhP: o-phenyl, 453; m-, p-phenyl, 441; C$_5$H$_5$, 245; 2,5 H's, 239, 253; 3,4 H's, 257. + =upfield from absolute position; − =downfield from absolute position. [b] Ortho position of substituted cyclopentadienyl ring. [c] Unsubstituted cyclopentadienyl ring. [d] Meta position of substituted cyclopentadienyl ring. [e] At these concentrations the phenyl protons were a complex multiplet; individual line assignments could not be made with confidence.

It must be mentioned that, if one is to obtain reproducible results, it is especially important that the NiAcac$_2$ be thoroughly dry[31]. The NiAcac$_2$ used in these studies was dried *in vacuo* for two days at 50–80° before each experiment.
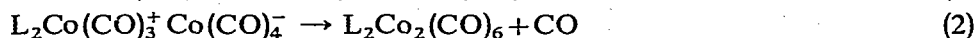
RESULTS AND DISCUSSION

Metal carbonyl derivatives

(a). *Preparation.* Complexes of metal carbonyls of the type LM(CO)$_5$ (where L=amine or phosphine, and M=Cr, Mo, or W) have been extensively used as a probe of the electronic properties of L[33−35]. It was for this reason that we synthesized

complexes of PPh$_3$ and the ferrocenylphosphines with the carbonyls of molybdenum and tungsten. Pittman and Evans have been engaged in a similar project and have also synthesized monosubstituted triferrocenylphosphine complexes with the carbonyls of the Group VIB metals as well as with those of iron and manganese[9].

The crystalline molybdenum and tungsten complexes of each phosphine could be prepared in good yield by the reaction of M(CO)$_6$ with the ligand in refluxing diglyme. The reaction of FcPh$_2$P with Co$_2$(CO)$_8$, however, occurs very readily at 0°; therefore, it was carried out on a vacuum line so that the evolution of CO could be followed. The literature indicated that two reactions [(1) and (2)] are possible[26,27]. However, as very nearly one mole of CO was evolved per mole of Co$_2$(CO)$_8$, it is apparent that only reaction(1)

$$2\,L + Co_2(CO)_8 \rightarrow L_2Co(CO)_3^+\,Co(CO)_4^- + CO \tag{1}$$

$$L_2Co(CO)_3^+\,Co(CO)_4^- \rightarrow L_2Co_2(CO)_6 + CO \tag{2}$$

occurs at 0° for both PPh$_3$ and FcPh$_2$P. The IR spectra of both L$_2$Co(CO)$_3^+$ Co(CO)$_4^-$ salts were nearly identical in the CO stretching region, and both compared favorably with the literature spectrum of (Ph$_3$P)$_2$Co(CO)$_3^+$ Co(CO)$_4^-$ [28].

The phosphine-containing cation, L$_2$Co(CO)$_3^+$, was isolated as the more stable tetraphenylborate salt, in which form it could be more highly purified. The molar conductivities of (Ph$_3$P)$_2$Co(CO)$_3^+$ BPh$_4^-$ and (FcPh$_2$P)$_2$Co(CO)$_3^+$ BPh$_4^-$ are compared with that of NaBPh$_4$ at several concentrations in nitromethane and in nitrobenzene in Table 4. The conductivity of NaBPh$_4$ in both solvents is in the range expected for a 1/1 electrolyte containing the BPh$_4^-$ anion[36]. The conductivities of the phosphine complexes are appropriately lower, since the mobility of the L$_2$Co(CO)$_3^+$ ion would be expected to be lower than Na$^+$.

(b). *Infrared spectra.* The principal reason for synthesizing the molybdenum and tungsten LM(CO)$_5$ complexes was to examine the carbonyl stretching frequencies as a function of the number of ferrocenyl groups. IR data for these complexes are given in Table 3; band assignments were made with the aid of previously published spectra[37-38] and the "method of local oscillating dipoles"[39,40].

The A_1^1 and E modes could be clearly resolved when the phosphine was FcPh$_2$P or Fc$_2$PhP, but only one band was seen in the case of the Ph$_3$P or Fc$_3$P derivatives[9]. Although Brown and Darensbourg were able to resolve these bands for Ph$_3$PMo(CO)$_5$[41], neither Angelici and Malone[35] nor Cotton and Kraihanzel[37] were able to resolve them in the case of the chromium or tungsten derivatives of Ph$_3$P. However, force constant calculations by Angelici and Malone indicated that the proper frequencies for Ph$_3$PW(CO)$_5$ were $A_1^1 = 1949.5$ cm^{-1} and $E = 1944$ cm^{-1} [35]. We observed that the unresolved band for this tungsten compound was asymmetric to the high frequency side in agreement with the frequency ordering $A_1^1 > E$. A similar asymmetry was also observed for Ph$_3$PMo(CO)$_5$. Therefore, we conclude that the A_1^1 band is no less than 1952 cm^{-1} for Ph$_3$PMo(CO)$_5$. In the case of the triferrocenylphosphine complexes, the $A_1^1 - E$ band was asymmetric to the low frequency side, indicating that $v(E) > v(A_1^1)$. Therefore, the A_1^1 mode for Fc$_3$PMo(CO)$_5$ is no greater than 1947 cm^{-1}, and no greater than 1939 cm^{-1} for Fc$_3$PW(CO)$_5$*. In summary,

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* In the case of the Fc$_3$P complexes, the exact frequency is not strictly comparable to the other compounds as the solvent system differed slightly. As the Fc$_3$P complexes were much less soluble than the others in hexane, the spectra of the former were run in 1/1 hexane/chloroform.

our experimental results suggest that the A_1^1 and E modes drop in frequency on going from L=Ph$_3$P to L=Fc$_3$P in the LM(CO)$_5$ complexes.

Very recently Pittman and Evans reported similar results for chromium, molybdenum, and tungsten complexes of the two phosphines at the extremes of the series, i.e., Ph$_3$P and Fc$_3$P[9]. On substituting Fc$_3$P for Ph$_3$P, an average drop of about 9 cm^{-1} was observed in the $A_1^1 - E$ band. More importantly, a decrease in the force constants k_1 and k_2 was observed.

(c). *Proton NMR spectra.* In the proton NMR spectra of monosubstituted ferrocene derivatives, the unsubstituted ring gives rise to a single line, and the four protons of the substituted ring result in patterns ranging from a single line to complex multiplets. Most often, however, these protons give rise to two apparent triplets, each of which is due to a pair of equivalent (or nearly equivalent) 2,5 or 3,4 protons. The triplet structure must be due to nearly equal adjacent and cross-ring coupling constants[42]. In any event, an unknown factor in the analysis of such spectra is the assignment of a given triplet (or multiplet) to a given set of protons. The spectrum of FcPh$_2$PMo(CO)$_5$ (Fig. 1 and Table 2) is of special interest as it has permitted us to make an assignment of triplets to particular protons of the π-C$_5$H$_4$ ring. Making the reasonable assumption that $J_{2,3}=J_{4,5}\approx J_{2,4}=J_{3,5}$[42], and that $J(P-H_2)=J(P-H_5)$ $>J(P-H_3)=J(P-H_4)$[43], the higher field multiplet must be assigned to the 2,5 protons and the lower field multiplet to the 3,4 protons. This same assignment was confirmed by our work on the contact shifted NMR spectrum of FcPh$_2$P[23].

Further discussion of this assignment, and a comparison of the phosphine metal carbonyl spectra with the NMR spectra of the phosphines themselves and with other complexes, is deferred to a later section.

(d). *Electrochemical behavior.* One of the most interesting long-range aspects of this work is the study of the electrochemical behaviour of ferrocenyl phosphines and their metal complexes. A preliminary survey has been made and a few results should be introduced here.
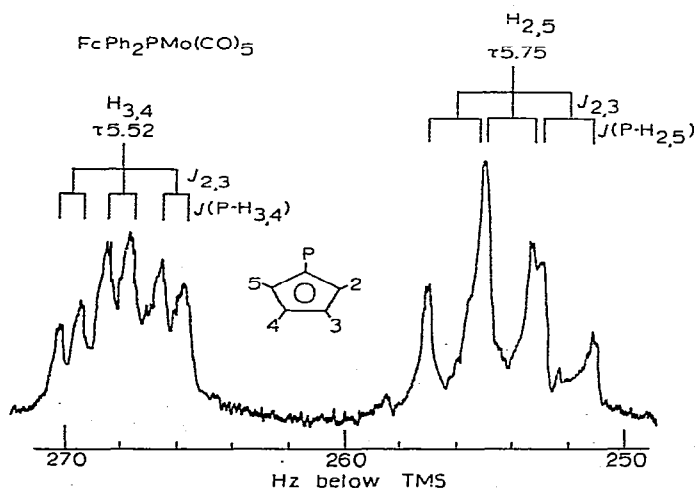

Fig. 1. Proton NMR spectrum of the substituted cyclopentadienyl ring protons of FcPh$_2$PMo(CO)$_5$ in CDCl$_3$ at ambient temperature.
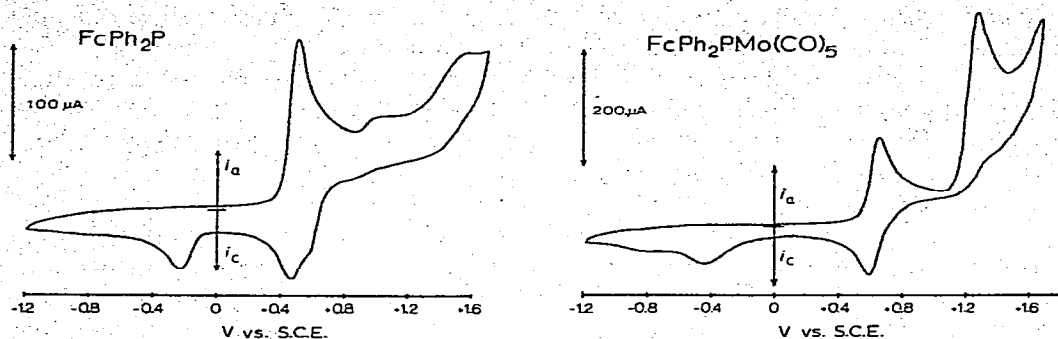
Fig. 2a, b. Cyclic voltammograms of 10^{-3} M FcPh$_2$P and FcPh$_2$PMo(CO)$_5$ in CH$_3$CN, with 0.1 M tetraethylammonium perchlorate as the supporting electrolyte. Anodic voltage sweep at start.

Cyclic voltammograms of FcPh$_2$P and FcPh$_2$PMo(CO)$_5$ are shown in Fig. 2. The one-electron oxidation of FcPh$_2$P at $E_{\frac{1}{2}}=0.48$ V ($vs.$ S.C.E.) is reversible if the potential is taken only to +0.8 V before being reversed; irreversible oxidation occurs near +1.5 V to generate a new species which undergoes reversible oxidation at about +0.6 V. The second step is presumably oxidation at the phosphorus atom, since ferrocene and its simple organic derivatives do not undergo oxidation at higher potentials.

When the phosphine ligand is bound to molybdenum in FcPh$_2$PMo(CO)$_5$, $E_{\frac{1}{2}}$ for the reversible oxidation of the ferrocenyl group increases, as expected, to +0.62 V. The process occurring near +1.3 V is a kinetically-controlled, irreversible process with a minimum of three electrons removed. The products of this step have not been examined as yet. However, it would appear that FcPh$_2$P$^+$ has not been released into the solution, since the new species seen in the cyclic voltammogram of the phosphine itself does not appear in that of the metal complex.

The oxidation of FcPh$_2$PMo(CO)$_5$ is in direct contrast with the oxidation of Ph$_3$PCr(CO)$_5$ and similar compounds reported by McCleverty and co-workers[44]. The (triphenylphosphine)chromium complex, for example, undergoes only a one-electron, reversible oxidation at +1.15 V. The explanation for the difference with the ferrocenylphosphine complex must await further exploration of the electrochemistry of these complexes.

Methylbis(dimethylglyoximato)cobalt(III) adducts

Ferrocenylphosphine adducts of the type CH$_3$Co(DH)$_2$L[29] were synthesized and their NMR spectra studied for two reasons: (*i*) to examine the spectra for any trends in chemical shifts as a function of the number of ferrocenyl groups; and (*ii*) to study the equilibrium system given in reaction (3).

$$CH_3Co(DH)_2(\text{pyridine}) + Fc_xPh_{3-x}P \rightleftharpoons CH_3Co(DH)_2(Fc_xPh_{3-x}P) + \text{pyridine} \quad (3)$$
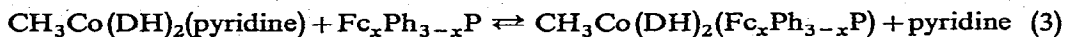
Data pertaining to the NMR spectra of the adducts are given in Tables 2 and 7. Although it would seem that, in general, there is a poor correlation between τ(Co–Me) and the nature of the ligand, within a series of closely related compounds it is more likely that a valid trend can be observed. Note that, although the shift of the glyoxime methyl groups is not affected by the nature of the phosphine (Table 2),

TABLE 7

CHEMICAL SHIFTS OF THE COBALT–METHYL GROUP IN METHYLBIS(DIMETHYL-GLYOXIMATO)COBALT(III) ADDUCTS

Ligand	Cobalt–methyl chemical shift (τ)
Me_2S	9.09^a
Me_2SO	9.59^a
C_5H_5N	9.35^a
Me_3N	9.43^a
MeCN	9.33^a
Ph_3P	8.82^b
$FcPh_2P$	8.92^b
Fc_2PhP	8.98^b
$(MeO)_3P$	9.08^a
$(EtO)_3P$	9.18^a

^{a} Values from ref. 45b; shifts determined in CH_2Cl_2. ^{b} Values determined in this work; all shifts obtained in $CDCl_3$.

the axial cobalt–methyl group shifts to higher fields as the number of ferrocenyl groups is increased (Table 7).

The triferrocenylphosphine adduct does not appear in Tables 2 or 7 for the reason that it could not be synthesized. We are forced to conclude that steric hindrance prevents its formation.

The steric requirement of the ferrocenyl group was also made quite apparent in the study of reaction (3). Not only is the equilibrium constant quite small, but there is a dramatic shift to still lower constants after the addition of two or more ferrocenyl groups; no exchange was observed in the case of Fc_3P (Table 5).

Another important observation with regard to reaction (3) is that equilibrium was established in the time of mixing of the solutions. We presume that ligand exchange
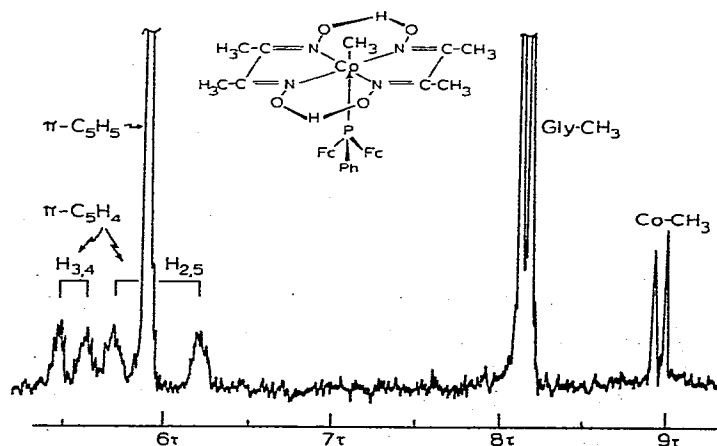

Fig. 3. Proton NMR spectrum of $CH_3Co(DH)_2(Fc_2PhP)$ in $CDCl_3$ at ambient temperature; phenyl protons not shown.

occurs according to the mechanism proposed by Brown and co-workers [reactions (4a) and (4b)][45].

$$CH_3Co(DH)_2(pyridine) \rightleftharpoons CH_3Co(DH)_2 + pyridine \tag{4a}$$

$$CH_3Co(DH)_2 + Fc_xPh_{3-x}P \rightleftharpoons CH_3Co(DH)_2(Fc_xPh_{3-x}P) \tag{4b}$$

The NMR spectrum of $CH_3Co(DH)_2(Fc_2PhP)$ is of interest since it clearly indicates the stereochemistry of the phosphine in this complex. As seen in Fig. 3 the protons of the ferrocenyl C_5H_4 rings apparently give rise to four separate lines of equal intensity; additional, incompletely resolved fine structure is also seen. We presume that this arises from a restriction of rotation of the ferrocenyl groups by the bis(dimethylglyoximato)cobalt(III) plane. Therefore, as shown in Fig. 4, four sets of two equivalent protons each should arise; that is, $2=5'$, $2'=5$, $3=4'$, $4=3'$. The non-equivalency is also illustrated very well by the spectra of solutions of $NiAcac_2$ and Fc_2PhP (*vide infra*), and there is evidence that the rotation of the ferrocenyl groups is sufficiently restricted even in the free phosphine that the C_5H_4 protons are nonequivalent.
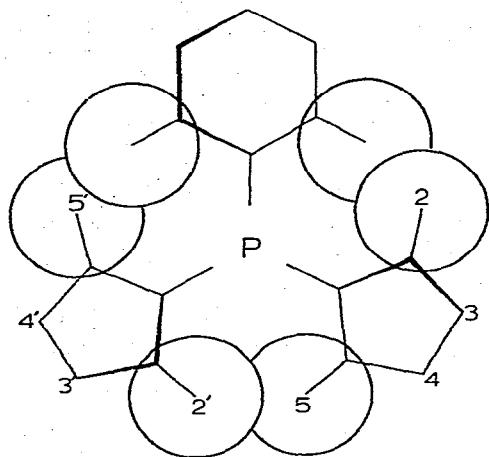

Fig. 4. Illustration of the non-equivalence of adjacent π-C_5H_4 hydrogen atoms resulting from restricted rotation of ferrocenyl groups in complexes of Fc_2PhP. Circles represent Van der Waal's radii of adjacent hydrogen.

Phosphonium salts

It has been suggested that a correlation should exist between the sums of the substituent Taft σ_I parameters and the chemical shift of the P–Me group in methyl phosphonium salts of the type $R_3PCH_3^+I^-$ [43]. We have verified this for the series of phosphines Bu_3P, Bu_2PhP, $BuPh_2P$ and Ph_3P[30] and have also found an excellent correlation with $\Sigma\sigma^*$. In an effort to deduce the σ_I and σ^* values for the ferrocenyl group, we synthesized the series of salts $Fc_xPh_{3-x}PMe^+I^-$ and examined the P–Me chemical shifts (Table 2). It was immediately apparent, however, that these shifts were strongly influenced by anisotropic effects arising from the ferrocenyl group. Methyltributylphosphonium iodide, where $\Sigma\sigma^* = -0.39$, has a P–Me shift of τ 7.93, and the triphenyl analog, where $\Sigma\sigma^* = +0.30$, has a P–Me shift of τ 6.85. On the basis

of these values, and those for the other members of the series, we would predict σ^* for the ferrocenyl group to be $+0.35$, a value far from the literature value of $-0.33^{42,46}$: similar disagreement occurs with σ_I. The extent of the anisotropy effect is seen from the fact that, by using the literature value for σ^*, the chemical shift of the P–Me group in $Fc_3PMe^+I^-$ would be predicted to be τ 8.2.

Contact shifted proton NMR spectra

The phenomenon of NMR isotropic shifts in paramagnetic transition metal complexes has been studied more and more extensively over the past ten years[47,48]. Nonetheless, it remains a less-than-completely understood phenomenon, and one that must be interpreted with great care. For example, Drago and his co-workers in particular have recently argued that it is extremely difficult to define precisely the mechanism of spin delocalization as well as the orbitals in which spin is found[49]. To circumvent some of these difficulties, we have chosen to examine a series of compounds and observe changes which may occur as progressively greater amounts of a paramagnetic complex are formed in solution.

In these experiments, progressively greater amounts of bis(acetylacetonato)-nickel(II) $[NiAcac_2]_3$ were added to a constant amount of ligand. The equilibrium reaction which exists in solution is given in eqn. (5). Therefore, the observed contact shift depends on the fraction of complexed ligand in the solution. Exploiting this fact,

$$2 \, L + \tfrac{1}{3} [NiAcac_2]_3 \rightleftharpoons L_2NiAcac_2 \tag{5}$$
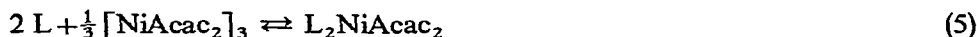
we found that the extent of interaction of the phosphine with $NiAcac_2$ falls off precipitously in the order $Ph_3P > FcPh_2P > Fc_2PhP > Fc_3P$. This may be seen by comparing the contact shifts of the *ortho* protons of the phenyl groups at the same ratio of phosphine/$NiAcac_2$. When the phosphine concentration was $0.149 \, M$ and the $NiAcac_2$ concentration was $0.1 \, M$, the *ortho* phenyl proton shifts were (see Table 6): Ph_3P, 116 Hz; $FcPh_2P$, 88 Hz: Fc_2PhP, 25 Hz; and Fc_3P, ca. 0 Hz. It is evident that the equilibrium constant for eqn. (5) decreases with increasing ferrocenyl substitution. *We contend that this is the result of steric hindrance and not due to a decrease in the intrinsic basicity of the phosphine.* Very much the same result was found in the experiment involving methylcobaloxime ligand exchange (*vide supra*).

A contact shifted spectrum of Fc_2PhP is shown in Fig. 5, and Figs. 6a and 6b are plots of the isotropic proton resonance shifts (at 60 MHz) *vs.* $[NiAcac_2]$ for $FcPh_2P$ and Fc_2PhP (see also Table 6). Line assignments given in Fig. 5 are based, as they were for $FcPh_2P^{23}$, on relative intensities and the variation in shifts, line widths, and spin coupling patterns as the $NiAcac_2$ concentration was increased. The most striking feature of this spectrum is the observation of two lines for the 2,5 or *ortho* protons of the ferrocenyl group. The fact that these protons give rise to separate lines must be due to the sterically restricted configuration of Fc_2PhP (Fig. 4) and its complexes as noted previously in connection with the Fc_2PhP–methylcobaloxime complex.

As is usually done in the case of octahedral nickel(II) complexes, we shall assume that the observed isotropic shifts in the phosphines arise only as a result of a contact interaction; that is, pseudo-contact interactions are assumed to be negligible[49]. We may then conclude that the lack of attenuation and the alternation in direction of the shifts of the *ortho*, *meta* and *para* phenyl protons, as well as those of
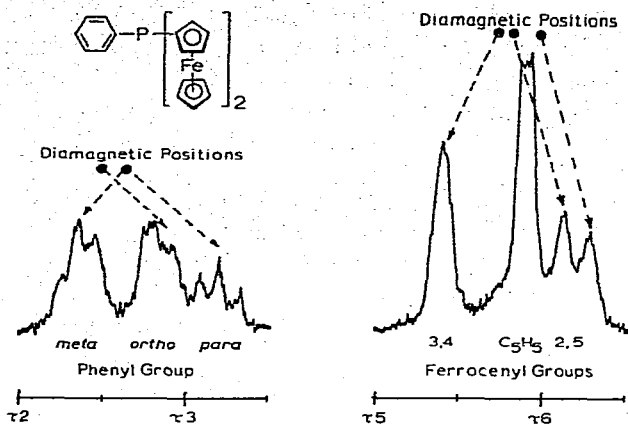
CONTACT SHIFTED NMR SPECTRUM

Fig. 5. Contact shifted proton NMR spectrum of the phenyl and ferrocenyl-protons of Fc_2PhP in $CDCl_3$ at ambient temperature. Solution contained 0.149 M Fc_2PhP and 0.1 M $NiAcac_2$ in $CDCl_3$. Diamagnetic positions of individual protons are marked as solid dots.

the C_5H_4 ring, indicate that spin has been delocalized primarily into π orbitals of these groups[*,23,49]. Note that we cannot legitimately also conclude that spin reaches these orbitals via metal–phosphorus d_π–d_π bonding. On the contrary, the results suggest that such π bonding is probably not the predominant mechanism for Ni—P—R spin transfer. Overlap of filled nickel t_{2g} orbitals with phosphorus d_π orbitals would place "spin down" in the d_π orbitals[49]. π Delocalization from phosphorus to the aromatic group would lead to a reversal of the observed contact shifts.

As was the case with $FcPh_2P$[23], a greater amount of spin is delocalized into the phenyl group than into the ferrocenyl groups of Fc_2PhP. Similar observations were made in the ESR spectra of electrochemically generated radical anions of benzoylferrocene and (p-nitrophenyl)ferrocene[51]. It is extremely tempting to infer that this is a manifestation of the greater releasing tendency of the ferrocenyl group. Indeed, such a conclusion is well supported by, inter alia, the stability of α-ferrocenyl-carbonium ions[52] and the enhanced reactivity of the ferrocene system in electrophilic aromatic substitution[42]. However, in drawing this conclusion from these experiments, we would be equating charge delocalization with spin delocalization. As Dessy and his co-workers have clearly shown, they are not necessarily related[53]. This point may in fact be illustrated by the ferrocenylphosphines. In these compounds, little if any spin is delocalized from the $P–C_5H_4$ ring into the unsubstituted C_5H_5 ring. On the contrary, substitution of one ring clearly affects the chemistry of the other ring. Since substituent effects are "charge delocalization" effects, it is clear that, in this case, charge and spin delocalization may not be parallel phenomena.

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* Spin may also have been delocalized into the ligand σ framework, but proton NMR experiments can give no information on this point. Instead, ^{13}C NMR spectroscopy must be employed. Using this method, Doddrell and Roberts have found that σ delocalization of spin does indeed occur in triphenyl-phosphine in addition to π delocalization[50].
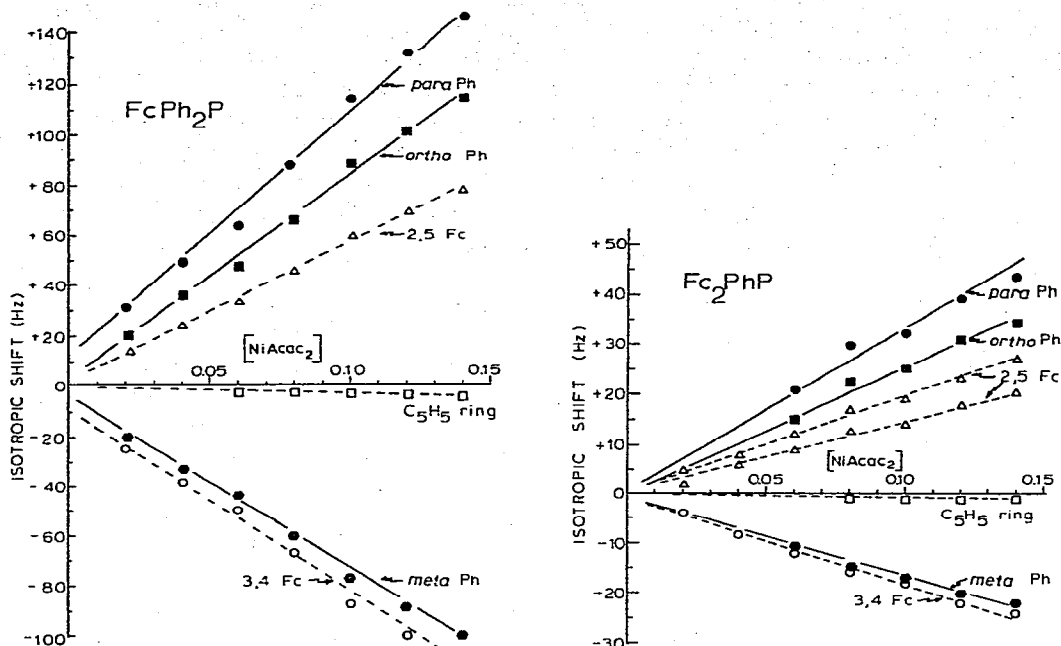
Fig. 6 a,b. Plots of isotropic proton resonance shifts at 60 MHz *vs.* [NiAcac$_2$] for FcPh$_2$P and Fc$_2$PhP. Solid lines: phenyl protons; dotted lines: ferrocenyl protons.

General comments on NMR spectra

Two general observations may be made with regard to the proton NMR spectra of the ferrocenylphosphines and their complexes. Firstly, there is evidence [contact shift experiments and spectrum of FcPh$_2$PMo(CO)$_5$] that, at least for the ferrocenyl groups of FcPh$_2$P, Fc$_2$PhP, and FcPh$_2$PMo(CO)$_5$, the 3,4 protons of the π-C$_5$H$_4$ ring lie downfield of the 2,5 protons, both sets of protons being deshielded relative to the π-C$_5$H$_5$ ring. There are apparently *no other examples* of such behavior. In fact, the only compound whose behavior approaches that of the ferrocenylphosphines is FcSiMe$_3$; the 2,5 protons are found at τ 6.02, the 3,4 protons at τ 5.79, and the π-C$_5$H$_5$ at τ 5.98[42a]. Slocum and Ernst have argued that "electron withdrawal via d orbitals on silicon should deshield H$_{3,4}$..."[42]. Similar arguments could be advanced in the case of the ferrocenylphosphines and their complexes.

The second observation is that, as expected, the resonance lines for the ferrocenyl group move downfield upon formation of a coordination complex (see Table 2)[9]. It might be noted, however, that a greater downfield shift is experienced for the phosphonium salts than for the metal carbonyl or cobaloxime adducts. It is possible that in the latter, σ electron withdrawal upon complex formation is tempered by d_π–d_π backbonding between the phosphine and the complexed metal. Such bonding cannot occur in the case of the methylphosphonium salts.

CONCLUSIONS

The two main conclusions that may be derived from the experiments described

above are: (1) as the number of ferrocenyl groups is increased, the σ donor ability of the phosphine increases; and (2) in certain instances, the increased donor ability of diferrocenylphenylphosphine and triferrocenylphosphine, relative to triphenylphosphine, is negated by the steric requirements of several ferrocenyl groups.

For Group VIB phosphine metal carbonyl complexes, $LM(CO)_5$, Pittman and Evans[9] have found that the force constants for CO stretching decrease on exchange of Fc_3P for Ph_3P. From these force constants, they have calculated values for Graham's $\Delta\sigma$ parameter[33]. At least in the case of the chromium and molybdenum complexes the $\Delta\sigma$ parameters are more negative for the Fc_3P complexes than for the Ph_3P complexes, indicating an increase in σ donor ability on increasing the number of ferrocenyl groups; only small changes in Graham's $\Delta\pi$ parameter were found. An increase in the σ donor ability upon increasing the number of ferrocenyl groups was similarly manifested in a number of experiments described herein. (i). We observed a progressive lowering of the A_1^1 and E carbonyl stretching modes as the number of ferrocenyl groups increased in the complexes $(Fc_xPh_{3-x}P)M(CO)_5$ ($M=Mo$, W), a decrease presumably accompanied by a decrease in CO force constants. Such a lowering of force constants is usually taken as an indication of an increase in ligand σ donor ability or decrease in ligand π acceptor ability, or both. (ii). The chemical shift of a methyl group was followed as a function of the number of ferrocenyl groups for ferrocenylphosphinemethylcobaloxime adducts and methyl iodide salts of the phosphines. In both cases, the methyl group became more highly shielded as the number of ferrocenyl groups increased. Such a trend can be most easily rationalized in terms of increased electron donation on the part of the ferrocenylphosphine.

The steric requirement of the ferrocenyl group is most clearly illustrated by the contact shift experiments, which depend on the formation of phosphine–$NiAcac_2$ complexes, and by the exchange of phosphine for pyridine on methylcobaloxime. For complexation to occur in both instances, it is necessary for the phosphine to bind to a metal which forms the center of a large, planar system. This requirement seriously affected the complexing ability of diferrocenylphenylphosphine and made it impossible for triferrocenylphosphine to form a stable complex, even though the σ donor ability of the latter ligand is apparently the largest of the four compounds of the series.

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