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Substituted Cyclopentadienyl Complexes. 1. The Proton Nuclear Magnetic Resonance Spectra of $[(\eta^5\text{-}C_5H_4Me)Fe(CO)(L)I]$ and $[(\eta^5\text{-}C_9H_7)Fe(CO)(L)I]$

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The synthesis of a range of $[(\eta^5\text{-}C_5H_4Me)Fe(CO)(L)I]$, $[(\eta^5\text{-}C_5H_4Me)Fe(CO)_2L]I$, and $[(\eta^5\text{-}C_9H_7)Fe(CO)(L)I]$ complexes (L = phosphine, phosphite) is reported. The ^1H NMR spectra of the non-salt methylcyclopentadienyl complexes give up to four separated ring proton absorptions, and NOE difference spectra (L = $P(OMe)_3$, $PMePh_2$, PMe_2Ph, $P(CH_2C_6H_5)_3$) reveal that the two outer resonances are associated with the protons (H1 and H4) ortho to the ring methyl group. Simulated spectra (L = $P(OMe)_3$) and decoupling experiments give the following coupling constants: adjacent ring protons, J = 1.5–2.6 Hz; cross ring protons, J = 0–1.7 Hz and J(P–H) = 0–2.4 Hz for the complexes studied. The shape of the proton absorptions are strongly influenced by the J(H1–H4) (<0.7 Hz) and J(H2–H3) (2.0–2.6 Hz) coupling constants which allows for facile assignment of the ring proton absorptions. For the $[(\eta^5\text{-}C_5H_4Me)Fe(CO)(L)I]$ complexes the difference in the chemical shifts between the two outer absorptions, Δ(H1–H4), varies with L, and a correlation between Δ(H1–H4) and the Tolman cone angle, θ, is observed. The NOE difference spectra of $[(\eta^5\text{-}C_5H_4Me)Fe(CO)(PMePh_2)I]$ also reveals ring rotation relative to the ligand set and nonequal conformational populations in solution. The cyclopentadienyl ring proton NMR spectra of the indenyl complexes are also discussed.

Introduction

The cyclopentadiene ligand is an ubiquitous ligand and is found coordinated to transition-metal complexes in both high and low oxidation states. The many synthetic strategies available for synthesizing *substituted* cyclopentadiene ligands have also made accessible a wide range of substituted cyclopentadienyl transition-metal complexes which have consequently been well-studied.[1]

Recently while investigating the role of catalysts[2] in the synthesis of a range of cyclopentadienyl metal complexes,[3,4] viz.

$$[(\eta^5\text{-}C_5H_4R)Fe(CO)_2I] + L \xrightarrow{\text{cat.}} [(\eta^5\text{-}C_5H_4R)Fe(CO)(L)I] + CO$$

R = H, Me, t-Bu, CPh_3, etc.; L = PR_3, $P(OR)_3$, RNC

we noted that the *positions* of the proton resonances in the ^1H NMR spectrum corresponding to the cyclopentadienyl hydrogen atoms varied extensively as L was varied. The iron atom in the above complexes is chiral, and up to four magnetically nonequivalent protons could be detected in the NMR spectrum.

A survey of the literature has revealed that in the NMR spectra of related monosubstituted cyclopentadienyl metal complexes from one to four "multiplet" resonances are generally observed.[5] An analysis of the NMR spectrum of monosubstituted ferrocene complexes which had been appropriately deuteriated has suggested that the downfield resonance(s) should correlate with the protons closest to the ring substituent if the ring substituent is an electron-donating group.[6] This rule has been used to assign ring proton resonances of other cyclopentadienyl metal complexes,[5] but exceptions to the rule have been observed.[7] Meta coupling constants for the cyclopentadienyl protons have also been used to assign proton resonances in substituted ferrocene complexes.[8] Although ring rotation should be rapid in cyclopentadiene metal complexes,[7,9] conformational preferences of the ligand set with respect to the ring[10] could also influence the proton NMR spectra of the cyclopentadiene ring, but this possibility has not been explicitly considered.[5]

It is thus apparent that *simple* definitive methods for correlating cyclopentadienyl ring protons with NMR spectra are still required. In this publication we wish to report on the reaction between $[(\eta^5\text{-}C_5H_4Me)Fe(CO)_2I]$ (1) or $[(\eta^5\text{-}C_9H_7)Fe(CO)_2I]$ (2) and L in the presence of catalysts and on a ^1H NMR spectral analysis of the substituted products $[(\eta^5\text{-}C_5H_4Me)Fe(CO)(L)I]$[11,12] (3) and $[(\eta^5\text{-}C_9H_7)Fe(CO)(L)I]$[13] (4). An attempt to establish the factors responsible for the relative positions of the proton resonances in the above complexes is reported.

Experimental Section

$[(\eta^5\text{-}C_5H_4Me)Fe(CO)_2I]$ and $[(\eta^5\text{-}C_9H_7)Fe(CO)_2I]$ were prepared by the literature methods.[14,15] The ligands were obtained from

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[1] For example: (a) Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds. *Comprehensive Organometallic Chemistry*; Pergamon: Oxford, 1982. (b) Rausch, M. D.; Hart, W. P.; Macomber, D. W. *J. Macromol. Sci., Chem.* **1981**, *A16*, 243. (c) Macomber, D. W.; Hart, W. P.; Rausch, M. D. *Adv. Organomet. Chem.* **1982**, *21*, 1.

[2] Albers, M. O.; Coville, N. J. *Coord. Chem. Rev.* **1984**, *53*, 227.

[3] (a) Coville, N. J.; Darling, E. A.; Hearn, A. W.; Johnston, P. *J. Organomet. Chem.*, in press. (b) Coville, N. J.; Albers, M. O.; Singleton, E. *J. Chem. Soc., Dalton Trans.* **1983**, 947.

[4] Albers, M. O.; Singleton, E.; Coville, N. J. *J. Organomet. Chem.* **1987**, *326*, 229. (b) Loonat, M. S., unpublished results.

[5] For example: (a) Ross, D. A.; Wojcicki, A. *Inorg. Chim. Acta* **1978**, *28*, 59. (b) Macomber, D. W.; Hart, W. P.; Rausch, M. D. *Adv. Organomet. Chem.* **1982**, *21*, 1. (c) Herrmann, W. A.; Huber, M. *Chem. Ber.* **1978**, *111*, 3124. (d) Conway, B. G.; Rausch, M. D. *Organometallics* **1985**, *4*, 688. (e) Gassman, P. G.; Winter, C. H. *J. Am. Chem. Soc.* **1986**, *108*, 4228. (f) Cesarotti, E.; Angoletta, M.; Walker, N. P. C.; Hursthouse, M. B.; Vefghi, R.; Schofield, P. A.; White, C. *J. Organomet. Chem.* **1985**, *286*, 343.

[6] Slocum, D. W.; Jones, W. E.; Ernst, C. E. *J. Org. Chem.* **1972**, *37*, 4278.

[7] Arthurs, M.; Nelson, S. M.; Drew, M. G. B. *J. Chem. Soc., Dalton Trans.* **1977**, 779.

[8] Kamezawa, N. *J. Magn. Reson.* **1973**, *11*, 88.

[9] (a) Werner, H.; Hofmann, W. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 794. (b) Werner, H.; Hoffman, W. *Chem. Ber.* **1981**, *114*, 2681. (c) Eisenberg, A.; Shaver, A.; Tsutsui, T. *J. Am. Chem. Soc.* **1980**, *102*, 1416.

[10] (a) Albright, T. A.; Hofmann, P.; Hoffmann, R. *J. Am. Chem. Soc.* **1977**, *99*, 7546. (b) Albright, T. A.; Hoffmann, R. *Chem. Ber.* **1978**, *111*, 1578.

[11] Brown, D. A.; Lyons, H. J.; Manning, A. R.; Rowley, J. M. *Inorg. Chim. Acta* **1969**, *3*, 346.

[12] Brown, D. A.; Lyons, H. J.; Manning, A. R. *Inorg. Chim. Acta* **1970**, *4*, 428.

[13] Hammud, H. H.; Moran, G. M. *J. Organomet. Chem.* **1986**, *307*, 255.

[14] King, R. B. *Organometallic Syntheses*; Academic: New York, 1965; Vol. I.

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Table I. Analytical and Spectroscopic Data for $[(\eta^5\text{-}C_5H_4Me)Fe(CO)(L)I]$

L	mp, °C	elemental anal.[a] C	elemental anal.[a] H	IR ν(CO),[b] cm^{-1}	MS,[c] *m/z* (%)
t-BuNC[d]	32–34	38.7 (38.6)	4.35 (4.32)	1975	
2,6-$Me_2C_6H_3NC$[e]	98–99	45.2 (45.6)	3.75 (3.83)	1987	
PMe_3	61–63			1954	366 (13), 338 (100), 262 (30), 211 (92)
PMe_2Ph	52–53	42.3 (42.1)	4.15 (4.23)	1953	428 (9), 400 (45), 273 (26), 138 (100)
$PMePh_2$	76–78	48.6 (49.0)	4.00 (4.11)	1952	
PPh_3	150–152	54.2 (54.4)	3.85 (4.02)	1960, 1950	
$P(OMe)_3$	45–46	28.8 (29.0)	3.84 (3.90)	1975, 1965	414 (25), 386 (95), 262 (88), 142 (100)
P(O-*i*-Pr)$_3$	45–47			1974, 1956	498 (30), 470 (100), 386 (30), 343 (40)
$P(OMe)_2Ph$	96–98	39.4 (39.2)	3.86 (3.94)	1972, 1961	460 (21), 432 (100), 170 (46), 139 (47)
$P(C_6H_{11})_3$	154–156			1945	570 (1), 280 (21), 214 (86), 198 (100)
$P(CH_2C_6H_5)_3$	144–146	56.4 (56.6)	4.67 (4.75)	1950	

[a] Found (calculated values in parentheses). [b] Recorded in hexane. [c] Only parent ion and three largest peaks *m/z* >100 are listed. [d] N, 3.87 (3.86); γ(NC) 2140 cm^{-1}. [e] N, 3.17 (3.33); γ(NC) 2112 cm^{-1}.

Table II. Proton NMR Spectral Data for $[(\eta^5\text{-}C_5H_4Me)Fe(CO)(L)I]$[a,b]

L	Me	H1	H2	H3	H4	(H1 + H4)/2	(H2 + H3)/2	(H1 + H4)/2 – (H2 + H3)/2	Δ(H1–H4)	Δ(H2–H3)	(H1 + H2 + H3 + H4)/4		C_5H_5[c] ($CDCl_3$)	(C_5H_5 – C_5H_4Me)[d]
											C_6D_6	$CDCl_3$		
t-BuNC[e]	1.74	4.24	4.10	3.95	4.24	4.24	4.02	0.22	0	0.15	4.13	4.55	4.72	0.17
2,6-$Me_2C_6H_3NC$[f]	1.78	4.22	4.15	4.14	4.22	4.22	4.15	0.07	0	0	4.19	4.62	4.88	0.26
PMe_3[g]	1.90	4.30	3.75	3.66	3.63	3.99	3.72	0.28	0.64	0.12	3.86	4.34		
PMe_2Ph[h]	1.73	4.25	3.69	3.52	3.52	3.89	3.61	0.28	0.73	0.17	3.70	4.14	4.38	0.24
$PMePh_2$[i]	1.77	4.50	3.98	3.50	3.47	3.99	3.74	0.25	1.03	0.48	3.87	4.20	4.45	0.25
PPh_3[j]	1.93	4.63	4.12	3.49	3.41	4.02	3.81	0.21	1.22	0.63	3.92	4.19	4.47	0.28
$P(OMe)_3$[k]	1.84	4.48	4.28	4.00	3.87	4.14	4.15	–0.01	0.61	0.28	4.15	4.46	4.71	0.25
P(O-*i*-Pr)$_3$[l]	1.83	4.59	4.53	4.13	3.89	4.24	4.33	–0.09	0.70	0.40	4.29	4.50	4.64	0.14
$P(OMe)_2Ph$[m]	1.74	4.38	4.01	3.78	3.78	4.08	3.90	0.18	0.60	0.23	3.99	4.64		
$P(C_6H_{11})_3$[n]	1.96	4.88	4.81	4.04	3.39	4.43	4.14	0.29	1.49	0.77	4.29	4.53		
$P(CH_2C_6H_5)_3$[o]	1.76	4.51	4.13	2.78	2.72	3.63	3.46	0.17	1.81	1.35	3.54	3.63	3.76	0.13
CO	1.49	3.85	3.84	3.84	3.85	3.85	3.85	0	0	0	3.85	4.88[p]	5.05	0.17

[a] Recorded in C_6D_6. [b] δ relative to Me_4Si. [c] C_5H_5 for $[(\eta^5\text{-}C_5H_5)Fe(CO)(L)I]$; data taken from ref 2 and 3. [d] Difference in proton ring resonance between $[(\eta^5\text{-}C_5H_5)Fe(CO)(L)I]$ and average value of ring resonance for $[(\eta^5\text{-}C_5H_4Me)Fe(CO)(L)I]$ ($CDCl_3$). [e] *t-Bu*NC, δ 0.96; H1 and H4 appear as a triplet and H2 and H3 as quartets; coupling constants are given in Figure 3a. [f] 2,6-$Me_2C_6H_3NC$, δ 2.19; aromatic, δ 6.6–6.7. [g] PMe_3, δ 1.12 (d, J_{P-H} = 9.5 Hz). [h] PMe_2Ph, δ 1.72 (d, J_{P-H} = 9.8 Hz), 1.44 (d, J_{P-H} = 9.9 Hz); PMe_2Ph, δ 7.0 and 7.3 (2:3 ratio); H2, apparent quintet with $J \approx 2.2$ Hz. [i] $PMePh_2$, δ 1.97 (d, J_{P-H} = 9.0 Hz); $PMePh_2$, four complex resonances at approximately 7.7, 7.3, 7.0, 6.9 (2:2:3:3 ratio), see Figure 2; H2 and H3, apparent quintets. [j] PPh_3, δ 6.9 and 7.7 (2:3 ratio); coupling constants are given in Figure 3c. [k] $P(OMe)_3$, δ 3.43 (d, J_{P-H} = 11.1 Hz); coupling constants are given in Figure 3b. [l] $P[OCH(CH_3)_2]_3$, δ 4.88 (d of septets, J_{H-H} = 6.2 Hz, J_{P-H} = 8.9 Hz); CH_3, δ 1.17 (d, J_{H-H} = 6.2 Hz) and 1.22 (d, J_{H-H} = 6.2 Hz); coupling constants are given in Figure 3d. [m] $P(OMe)_2Ph$, δ 3.23 (d, J_{P-H} = 11.8 Hz), 3.38 (d, J_{P-H} = 11.4 Hz); *Ph*, δ 7.0, 7.8 (ratio 2:3); H2, apparent quintet with $J \approx 2.2$ Hz. [n] $P(C_6H_{11})_3$, δ ~1.01–2.2 (CH_2 br). [o] $P(CH_2C_6H_5)_3$, δ 3.26 (d of quartets, J_{H-H} = 14.4 Hz, J_{P-H} = 10.8 Hz) and 3.53 (J_{H-H} = 14.4 Hz, J_{P-H} = 6.8 Hz); *Ph*, δ 7.01–7.11; coupling constants are given in Figure 3e. [p] Complex doublet.

available sources and were used without further purification. $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ was purchased from Strem Chemicals and $NMe_3O\cdot 2H_2O$ from Aldrich Chemicals.

Infrared spectra were recorded on either a Perkin-Elmer 580B or Pye Unicam SP300 spectrometer and NMR spectra on either a Bruker WP80 FTNMR or Bruker AC 200 NMR spectrometer. Mass spectra were recorded on a Varian MAT CH5 or Finnegan-Mat 8200 spectrometer operating at 70 eV. Melting points were determined on a Kofler micro hot-stage apparatus and are uncorrected. Micro analyses were performed by the Micro Analytical Laboratories, CSIR, Pretoria. All reactions were routinely carried out under nitrogen by using dry, degassed solvents.

NMR. Experimental Details. NOE Difference Spectra.[16–18] The NMR spectra were recorded on a Bruker AC 200 spectrometer equipped with an Aspect 3000 data system. Spectra were obtained from ca. 20 mM solutions in deoxygenated C_6D_6. The NOE difference spectra were generated by first subtracting the reference FID, with the decoupler off-resonance, from a similar FID of the same sample in which the desired resonance was saturated with a decoupler pulse at 40-dB attenuation of a nominal 0.2 W. A total of 816 transients were accumulated for the $PMePh_2$ complex. Resonance lines of multiplets were irradiated sequentially.[19,20]

Simulation Study. The cyclopentadienyl signals in the ^1H spectrum of $[(\eta^5\text{-}C_5H_4Me)Fe(CO)[P(OMe)_3]I]$, with decoupling of the C_5H_4Me methyl proton resonances and using resolution enhancement, were simulated by using the simulation program "PANIC" (Parameter Adjustment in NMR by Iteration Calculation). The nuclei were assumed to be weakly coupled, and line shape was taken to be Lorentzian (line width = 0.4 Hz).

The Catalyzed Synthesis of $[(\eta^5\text{-}C_5H_4Me)Fe(CO)(L)I]$ (L = *t*-BuNC, 2,6-$Me_2C_6H_3NC$, $P(OMe)_3$, P(O-*i*-Pr)$_3$, $P(OMe)_2Ph$). $[(\eta^5\text{-}C_5H_4Me)Fe(CO)_2I]$ (1 mmol) and L (1.1 mmol) were added to benzene (10 mL). The solution was brought to reflux, and $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ (10 mg) was then added to the reaction mixture. The progress of the reaction was monitored by IR spectroscopy or TLC (silica gel; benzene as eluent). Upon completion of the reaction the solution was cooled to room temperature, solvent removed on a rotary evaporator, and the desired product purified by column chromatography (silica gel; benzene/hexane mixtures as eluent). The product was crystallized from either hexane or toluene/hexane mixtures (60–80% yield). Analytical and spectroscopic data are recorded in Tables I and II.

The Catalyzed Synthesis of $[(\eta^5\text{-}C_5H_4Me)Fe(CO)(L)I]$ and $[(\eta^5\text{-}C_5H_4Me)Fe(CO)_2L]I$ (L = PMe_3, PMe_2Ph, $PMePh_2$, PPh_3, $P(C_6H_{11})_3$, $P(CH_2C_6H_5)_3$). $[(\eta^5\text{-}C_5H_4Me)Fe(CO)_2I]$ (1 mmol) and L (1.1 mmol) were added to benzene (10 mL). The solution was

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(15) (a) Hallam, B. F.; Pauson, P. L. *J. Chem. Soc.* **1958**, 646. (b) Forscher, T. C.; Cutler, A. R. *Inorg. Chim. Acta* **1985**, *102*, 113.

(16) Bell, R. A.; Saunders, J. K. *Top. Stereochem.* **1973**, *7*, 1.

(17) Sanders, J. K. M.; Mersh, J. D. *Prog. Nucl. Magn. Reson. Spectrosc.* **1983**, *15*, 353.

(18) Noggle, J. H.; Schirmer, R. E. *The Nuclear Overhauser Effect*; Academic: New York, 1971.

(19) Neuhaus, D. *J. Magn. Reson.* **1983**, *53*, 109.

(20) Kinns, K.; Saunders, J. M. *J. Magn. Reson.* 1984, *56*, 518.

Table III. IR and NMR Spectra for some $[(\eta^5\text{-}C_5H_4Me)Fe(A)_2B]$ Complexes

	NMR δ^a					
	cyclopentadiene					
complex	H2, H3(B)	H1, H4(A)	Δ(A–B)	CH_3	other^c	IR ν(CO),^{b} cm^{-1}
$[(\eta^5\text{-}C_5H_4Me)Fe(CO)_2I]$	4.86	4.88	0.02	2.18		2032, 1989
$[(\eta^5\text{-}C_5H_4Me)Fe(CNR)_2Br]^{d,e}$	4.39	4.16	0.23	1.94	CH_3, 1.18	
$[(\eta^5\text{-}C_5H_4Me)Fe(CO)_2PMe_3]I$	5.51^f	5.61^f	0.10	2.16	CH_3, 1.99 (d, J_{P-H} = 11.1 Hz)	2042, 1999
$[(\eta^5\text{-}C_5H_4Me)Fe(CO)_2PMe_2Ph]I$	5.39	5.44	0.05	1.97	CH_3, 2.29 (d, J_{P-H} = 10.7 Hz)	2042, 1997
$[(\eta^5\text{-}C_5H_4Me)Fe(CO)_2PMePh_2]I^g$	5.42	5.43	0.01	2.07	CH_3, 2.63 (d, J_{P-H} = 10.2 Hz)	2046, 2000
$[(\eta^5\text{-}C_5H_4Me)Fe(CO)_2PPh_3]I$	5.28	5.42	0.14	2.16		2046, 2002
$[(\eta^5\text{-}C_5H_4Me)Fe(CO)_2P(C_6H_{11})_3]I$	5.43	5.63	0.20	2.18	CH_2, 2.0 (br)	2035, 1994

^{a} Recorded in $CDCl_3$ relative to Me_4Si (200 MHz) unless otherwise stated. All cyclopentadiene resonances occur as two complex resonances, A and B. ^{b} Recorded in CH_2Cl_2. ^{c} Phenyl absorptions not listed. ^{d} R = *t*-BuNC; recorded in C_6D_6. ^{e} Reference 3. ^{f} Apparent quintet. ^{g} An NOE experiment confirmed that the H_1 and H_4 protons, as expected, corresponded to the downfield multiplet. It is assumed that this holds true for the other complexes listed in this table. See also the discussion of the ring assignments of complex 3 discussed in the text.

Table IV. IR and Proton NMR Spectral Data for $[(\eta^5\text{-}C_9H_7)Fe(CO)(L)I]^a$

		NMR^c (cyclopentadienyl ring)								
L	IR ν(CO),^{b} cm^{-1}	H1	H2	H3	(H1 + H3)/2	Δ(H1–H3)	*J*(H1–H2)^d	*J*(P–H2)^d	θ,^{d} deg	NMR^c (other)^f
PMe_2Ph	1941	4.49	4.20 (q)	3.84	4.17	0.65	2.6	2.6	122	CH_3, 1.41 (d, *J* = 10.8); 1.35 (d, *J* = 10.8)
$PMePh_2$	1946	4.41	4.29 (dt)	4.07	4.24	0.34		3.4	136	CH_3, 1.80 (d, *J* = 9.4)
PPh_3	1950	4.47	4.43 (q)	4.14	4.28	0.33	2.6	2.6	145	
$P(OMe)_3$	1959	5.01	4.59 (q)	4.20	4.61	0.81	2.8	2.8	107	CH_3, 3.37 (d, *J* = 11.2)
$P(OEt)_3$	1957	5.08	4.70 (q)	4.22	4.65	0.86	2.9	2.9	109	
$P(O\text{-}i\text{-}Pr)_3$	1952	5.64	4.85^g	3.77	4.71	1.87	2.6	*g*	130	CH_3, 1.16 (d, *J* = 5.6), 1.19 (d, *J* = 5.6) CH, 4.8^g (m, J_{P-H} = 8.9)
$P(O\text{-}o\text{-}CH_3C_6H_4)_3$	1976	5.48	4.57 (dt)	3.22	4.34	2.26	2.4	5.8	145	CH_3, 2.14
$P(OPh)_3$	1978	5.07^h	4.69 (dt)	2.94^i	4.00	2.13	2.5	6.0	128	
$P(OMe)_2Ph$	1959	4.57	4.37	4.11	4.34	0.46			115	CH_3, 3.14 (d, *J* = 11.7), 3.28 (d, *J* = 11.7)
$P(OMe)Ph_2$	1948	4.87	4.42 (dt)	3.85	4.36	1.02	2.5	4.4	132	CH_3, 3.23 (d, *J* = 12.2)
$P(CH_2C_6H_5)_3$	1949	5.58	3.83 (dt)	2.46	4.02	3.12	2.6	5.8	165	CH_2, 3.18 (q, J_{H-H} = 14.2, J_{P-H} = 10.9), 3.43 (q, J_{H-H} = 14.2, J_{P-H} = 7.3)
CO	2033, 1990	4.43 (d)	4.08 (t)	(4.43)	4.43	0	2.6		95	

^{a} See Figure 1 for definition of H1, H2, and H3. ^{b} IR spectra recorded in $CHCl_3$ and NMR spectra in C_6D_6. ^{c} δ relative to Me_4Si. Abbreviations: d, doublet; t, triplet; q, apparent quartet; dt, doublet of triplets. ^{d} In Hz. ^{e} θ = cone angle. Data taken from ref 29. ^{f} The indenyl and phenyl ligand resonances overlap and give complex patterns, δ 6–8. ^{g} Overlap of the methine proton with the H2 proton. ^{h} J_{P-H} = 1.6 Hz. ^{i} $J_{P-H} \approx 0$ Hz.

brought to reflux, and $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ (10 mg) was then added to the reaction mixture. The solution turned green, and a yellow precipitate formed. The progress of the reaction was monitored by IR spectroscopy. Upon disappearance of ν(CO) absorptions corresponding to the starting materials, the reaction was allowed to proceed for a further 15 min. After cooling the reaction mixture was filtered through a cellulose column (benzene). The filtrate was then pumped to dryness. The desired $[(\eta^5\text{-}C_5H_4Me)Fe(CO)(L)I]$ was purified by column chromatography (silica gel; benzene as eluent) and crystallized from either hexane or toluene/hexane mixtures (20–70% yield). The yellow precipitate that collected on the cellulose column was washed through the column with CH_2Cl_2 and the product $[(\eta^5\text{-}C_5H_4Me)Fe(CO)_2L]I$ crystallized from CH_2Cl_2/ether/hexane (30–60% yield). Analytical and spectroscopic properties for the iron complexes are given in Tables I–III.

The Synthesis of $[(\eta^5\text{-}C_9H_7)Fe(CO)(L)I]$ (L = $P(OMe)_3$, $P(OEt)_3$, $P(O\text{-}i\text{-}Pr)_3$, $P(OPh)_3$, $P(O\text{-}o\text{-}CH_3C_6H_4)_3$, $P(OMe)Ph_2$).[11] $[(\eta^5\text{-}C_9H_7)Fe(CO)_2I]$ (1 mmol) and L (1.1 mmol) were added to hexane (20 mL), and the solution was brought to reflux. The reaction was monitored by IR spectroscopy, and at the end of the reaction (60–90 min) the reaction mixture was cooled and filtered through alumina (2-cm column, activity 4). Recrystallization from hexane or hexane/toluene mixtures gave the required products (40–55% yield), and spectroscopic data on these complexes are given in Table IV.

The Synthesis of $[(\eta^5\text{-}C_9H_7)Fe(CO)(L)I]$ (L = PMe_2Ph, $PMePh_2$, PPh_3, $P(CH_2C_6H_5)_3$, $P(OMe)_2Ph$). $[(\eta^5\text{-}C_9H_7)Fe(CO)_2I]$ (1 mmol) and L (1.1 mmol) were refluxed in hexane (20 mL) and yielded insoluble salt products $[(\eta^5\text{-}C_9H_7)Fe(CO)_2L]I$.[13] The salts were filtered off and redissolved in degassed CH_2Cl_2. Excess $NMe_3O\cdot2H_2O$ was added to the CH_2Cl_2 solution. The yellow solutions turned red, and the IR spectra indicated formation of a new complex. Water was added to the reaction mixture, and the solution was then dried by passage through a $MgSO_4$ column (2 cm). The required product was purified by crystallization from a pentane/CH_2Cl_2 mixture (20–40% yield), and spectroscopic data for a range of these complexes are given in Table IV. $[(\eta^5\text{-}C_9H_7)Fe(CO)[P(CH_2C_6H_5)_3]I]$: mp 120–121 °C; light green. Anal. Calcd for $C_{31}H_{28}OIPFe$: C, 59.1; H, 4.44. Found: C, 58.3; H, 4.22. $[(\eta^5\text{-}C_9H_7)Fe(CO)(PPh_3)I]$: mp 122–123 °C; purple-red. Anal. Calcd for $C_{28}H_{22}OIPFe$: C, 57.1; H, 3.74. Found: C, 56.5; H, 3.78. $[(\eta^5\text{-}C_9H_7)Fe(CO)(PMePh_2)I]$: mp 55–60 °C; red-brown; MS, *m/z* 527 (1), 399 (4), 215 (100), 201 (54).

Results and Discussion

Synthesis. The thermal reaction between $[(\eta^5\text{-}C_5H_4Me)Fe(CO)_2I]$ (1) and various ligands, L, have been reported to yield $[(\eta^5\text{-}C_5H_4Me)Fe(CO)(L)I]$ (3).[11,12] We have repeated some of these reactions and have observed formation of 3 as well as the salts $[(\eta^5\text{-}C_5H_4Me)Fe(CO)_2(L)]I$ (5) (for L = phosphines). Addition of the dimer $[(\eta^5\text{-}C_5H_4R)Fe(CO)_2]$ (R = H, Me) to the reaction mixture resulted in more rapid formation of *both* the products; however the catalyst with R = H was found to give more rapid reactions than the catalyst with R = Me. Similar results have been observed previously for the reaction between $[(\eta^5\text{-}C_5H_5)Fe(CO)_2I]$ and L in the presence of catalysts, and hence synthetic and mechanistic details will not be discussed further.[1-4]

The thermal reaction between $[(\eta^5\text{-}C_9H_7)Fe(CO)_2I]$ (2) and L gave either $[(\eta^5\text{-}C_9H_7)Fe(CO)(L)I]$ (4) (L = phos-

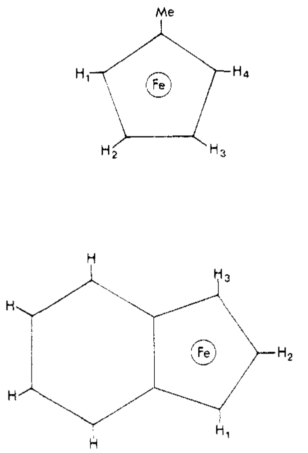

Figure 1. Numbering system used for the $[(\eta^5\text{-}C_9H_7)Fe(CO)(L)I]$ and $[(\eta^5\text{-}C_5H_4Me)Fe(CO)(L)I]$ complexes.

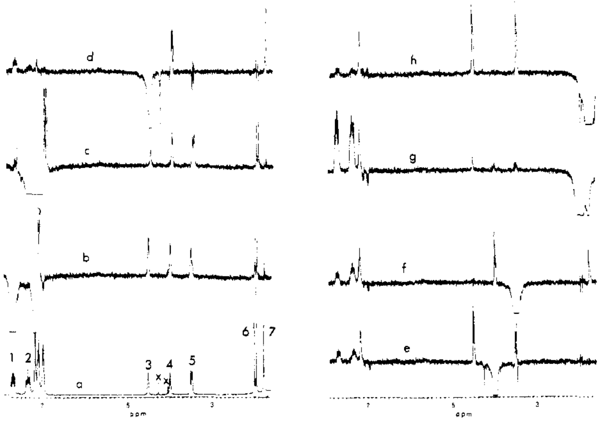

Figure 2. NOE experimental data for $[(\eta^5\text{-}C_5H_4Me)Fe(CO)(PMePh_2)I]$: (a) non-irradiated spectrum; irradiation of (b) ortho proton (1); (c) ortho proton (2); (d) ring proton H1 (3); (e) ring proton H2 (4); (f) ring protons H3 and H4 (5); (g) P*Me*Ph_2 (6); (h) C_5H_4*Me* (7). Absorptions marked X are impurity peaks. Scale: 32× nonirradiated spectrum.

phite, phosphonite, phosphinite) or the salt products $[(\eta^5\text{-}C_9H_7)Fe(CO)_2(L)]I$ (**6**) (L = phosphine). While this work was in progress, Hammud and Moran[13] reported similar observations for the reaction between **2** and phosphines, and this reaction will thus not be discussed further. Conversion of the salt **6** to the desired non-salt product **4** was achieved via one of two methods. In the first method NMe_3O was used which has been shown to readily convert coordinated CO to CO_2 when the ν(CO) stretching frequency of the reactant is >2000 cm^{-1}.[21] This method thus provides a general procedure[22] for carrying out reactions of the type

$$[M(CO)_n]^+X^- \rightarrow [M(CO)_{n-1}X] + CO$$

and was successfully applied in this work (see Experimental Section). In the second method addition of small amounts of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ to **6**, L = $P(C_6H_5)_3$, in benzene gave a rapid conversion of **6** to **4**. Thus, replacement of CO by I^- is catalyzed by $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ (in the absence of catalyst no conversion occurs) and provides another example of the use of iron dimer catalysts in CO substitution reactions.[2]

Product Characterization. Product characterization was achieved by IR and NMR spectroscopy and by elemental analyses and mass spectroscopy. The IR spectrum, when recorded in hexane, gave the expected two ν(CO) vibrations for certain of the derivatives.[11,12] The NMR spectra are discussed more fully below. In every instance correct intensity ratios as well as the requisite number of absorptions (cyclopentadienyl ring and ligands) were observed in the NMR spectra. Mass spectra were also recorded on some of the new products, and data are given in Table I and in the Experimental Section.

NMR Spectra. Methylcyclopentadiene Complexes. Introduction of a substituent onto a cyclopentadienyl ring reduces the fivefold symmetry of the ring and results in all four of the remaining protons becoming magnetically nonequivalent (AA′XX′ or AA′BB′). Thus in monosubstituted cyclopentadienyl metal complexes the four ring protons, labeled H1 through H4 (Figure 1a), could give rise to a maximum of four separated proton absorption envelopes in the NMR spectrum. If, however, the H1 and H4 as well as the H2 and H3 protons experience the same chemical environment, which can occur in complexes of the type $[(\eta^5\text{-}C_5H_4Me)Fe(A)_2(B)]$, through either symmetry (fast ring rotation[23]) or a preferential ligand conformation (slow ring rotation), two separated envelopes can be expected. Indeed the salts $[(\eta^5\text{-}C_5H_4Me)Fe(CO)_2L]I$ (L = PMe_3, PMe_2Ph, $PMePh_2$, PPh_3, $P(C_6H_{11})_3$) all give two closely spaced sets of resonances (Table III).

Complexes of the type $[(\eta^5\text{-}C_5H_4Me)Fe(A)(B)(C)]$ contain a chiral iron atom and should give rise to a more complex NMR spectrum. All four ring protons are magnetically and chemically nonequivalent, and the NMR spectra of the complexes $[(\eta^5\text{-}C_5H_4Me)Fe(CO)(L)(I)]$ do generally give four distinct, and complex, ring proton resonance sets (Table II).

To establish a correlation between the ring hydrogen atoms and the proton resonances NOE experiments were carried out.[16-18] The NOE allows for the correlation of proximal protons, and difference spectra should readily indicate which protons are in ortho positions relative to the ring methyl group. Irradiation of the ring methyl group clearly established that the resonances corresponding to H1 and H4 were the outer proton resonances (**3**, L = $P(OMe)_3$, $PMePh_2$, PMe_2Ph, $P(CH_2C_6H_5)_3$).[24] Irradiation of the various ring resonances also established H2 as the second downfield ring resonance;[25] e.g. irradiation of H1 resulted in a growth of the H2 resonance (see Figure 2). The NOE experiment *is unambiguous and provides a definitive assignment of the ring protons*.[6,7] Further, an NOE experiment performed on $[(\eta^5\text{-}C_5H_4Me)Fe(CO)_2(PMePh_2)]I$ indicated that the technique could differentiate between ring protons separated by 0.01 ppm (Table III, footnote g).

Decoupling experiments were also carried out on the complex ring proton spectra to establish the respective coupling constants. From this analysis the following coupling constants were determined: (i) *J*(H1–H4), 0–0.7 Hz; (ii) *J*(H1–H2), *J*(H2–H3), and *J*(H3–H4), 1.5–2.6 Hz; (iii) *J*(P–H2) and *J*(P–H3), 2.0–2.6 Hz; (iv) *J*(P–H1) and *J*(P–H4), 0–2.5 Hz; (v) *J*(H1–H3) and *J*(H2–H4), 1.3–1.7 Hz; (vi) *J*(CH_3–H), 0–0.2 Hz.[26] Some specific examples

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[21] Koëlle, U. *J. Organomet. Chem.* **1977**, *133*, 53.

[22] For other examples see: (a) Pourreau, D. B.; Geoffroy, G. L.; Rheingold, A. L.; Geib, S. J. *Organometallics* **1986**, *5*, 1337. (b) Davies, S. G. *J. Organomet. Chem.* **1979**, *179*, C5.

[23] Theoretical[10] and experimental[9] data support fast ring rotation.

[24] The only exception to this rule was found for L = PMe_3. Here the H4 resonance was found downfield of the H3 resonance and could readily be detected from the *shape* of the resonance envelope (see text).

[25] The choice of an anti-clockwise arrangement of H1 to H4 rather than a clockwise arrangement is an arbitrary choice.

[26] This is the coupling constant of the Me group to the ring protons H1–H4. The value was determined from decoupling experiments performed on $[(\eta^5\text{-}C_5H_5)Fe(CO)(P(OMe)_3)]I$. See Figure 3.

Table V. Effect of Solvent on the Proton NMR Spectra of [(η^5-C_5H_4Me)Fe(CO)(L)I] (L = PPh_3, $PMePh_2$)[a]

	cyclopentadienyl ring[b]						
L	Me	H1	H2	H3	H4	Δ(H1–H4)	Δ(H2–H3)
PPh_3							
$CDCl_3$	2.14	4.80	4.42	3.86	3.67	1.13	0.56
$(CD_3)_2CO$	2.05	4.82	4.39	3.95	3.95	0.87	0.44
C_6D_6	1.93	4.63	4.12	3.49	3.41	1.22	0.63
CCl_4[c]	2.16	4.74	4.24	3.70	3.68	1.06	0.54
$PMePh_2$							
$CDCl_3$	1.97	4.76	4.36	3.95	3.73	1.03	0.41
$(CD_3)_2CO$	1.98	4.83	4.35	4.08	4.02	0.81	0.27
C_6D_6	1.79	4.50	3.98	3.50	3.47	1.03	0.48
CCl_4[c]	2.00	4.71	4.21	3.80	3.77	0.94	0.41

[a] See Figure 1 for definition of H1, H2, H3 and H4. [b] δ relative to Me_4Si. [c] Recorded at 60 Mz on a Varian EM 60 spectrometer.

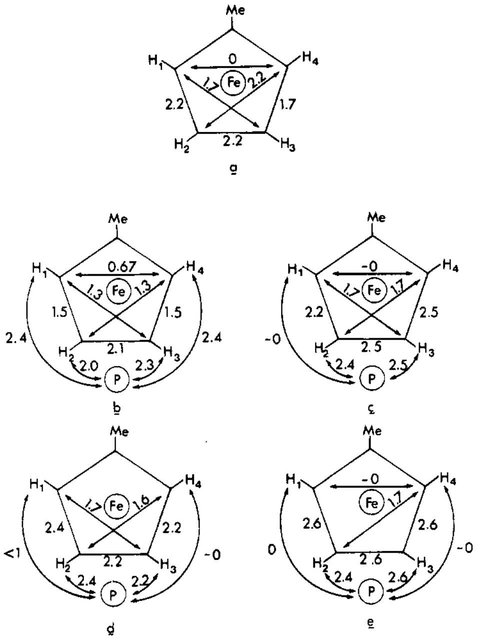

Figure 3. Coupling constant data for selected [(η^5-C_5H_4Me)-Fe(CO)(L)I] complexes (J ±0.2 Hz). Data for **b** (L = $P(OMe)_3$) were taken from the simulated spectrum (J = ±0.05 Hz): (a) t-BuNC; (b) $P(OMe)_3$; (c) PPh_3; (d) $P(O\text{-}i\text{-}Pr)_3$, (e) $P(CH_2C_6H_5)_3$.

are given in Figure 3 and are in agreement with values determined for substituted ferrocene complexes.[27] The *shapes* of the absorptions are dominated by the J(H1–H4) vs. J(H2–H3) coupling constants. The small value of J-(H1–H4) results in the absorption envelopes for H1 and H4 being broad and unresolved whereas the H2 and H3 resonances often appear as resolved "apparent" quintets. Removal of the ring Me coupling results in complex but resolved envelopes for *all* the ring protons, but even here the effect of J(H1–H4) vs. J(H2–H3) coupling constants determines the different envelope shapes (Figure 4). The large variation in J(P–H1) and J(P–H4) with L could relate to different conformer populations, i.e., rotation of the cyclopentadiene ligand relative to the ligand set. Simulation of the NMR spectrum of 3, L = $P(OMe)_3$, confirms the proposed assignments from the decoupling experiments (see Figure 4). The NMR spectrum of 3, L = t-BuNC, in which no P–H coupling occurs, shows a simpler apparent triplet and quartet arrangement for the H1, H4 and H2, H3 resonances, respectively, and confirms the size of the P–H coupling constants when L = a group 15 donor ligand (Figure 3). It is to be noted that H1 and H4 are coincident in this spectrum.

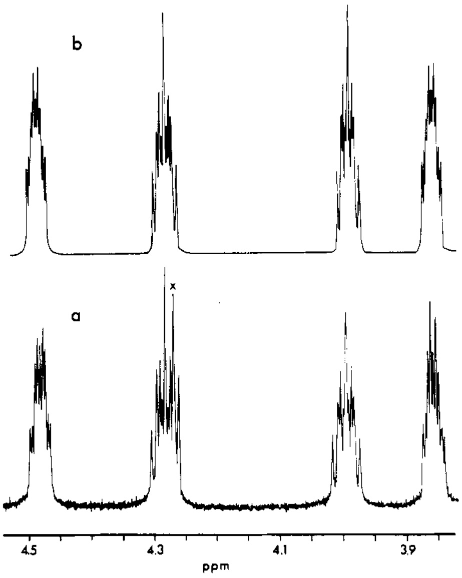

Figure 4. NMR spectrum of [(η^5-C_5H_4Me)Fe(CO)[$P(OMe)_3$]I]. The ring methyl–ring proton coupling has been removed from both the experimental (a) and the simulated spectra (b).

Table VI. Variable-Temperature NMR Spectra of [(η^5-C_5H_4Me)Fe(CO)(L)I][a] (L = PPh_3, $PMePh_2$)

	PPh_3			$PMePh_2$[b]		
T, K	Δ(H1–H4)[c]	Δ(H2–H3)[c]	Me[d]	Δ(H1–H4)[c]	Δ(H2–H3)[c]	Me[d]
213	1.28	0.63	0.00	1.02	0.48	0.00
253	1.18	0.61	–0.01	1.01	0.44	0.04
363	1.07	0.56	–0.02	0.93	0.41	0.19

[a] NMR spectra were recorded in toluene-d_8 relative to Me_4Si. [b] The difference between the two resonances corresponding to the ortho protons on the phenyl ring was reduced with increase in temperature (0.45 → 0.28 ppm). [c] Difference between the chemical shifts of H1 and H4 or H2 and H3 in ppm. [d] Me resonance of the cyclopentadiene ring. Difference values relative to resonance at 213 K in ppm.

Thus, for the complexes under consideration *visual inspection* of the proton absorption shape allows for assignment of the ring proton resonances H1 through H4, a result supported by the definitive NOE experiments. This result is independent of the size of Δ(H1–H4) and is not affected by variation of the solvent. The solvent does however affect the *position* of the proton resonances in the spectrum (Tables II and V).

An explanation for the separation of the four ring resonances with variation of L in 3 is provided by viewing the protons as existing in two distinct sets: H1, H4 and H2, H3. The *averaged* values for these sets of resonances appear with chemical shifts expected for complexes of the type [(η^5-C_5H_4Me)Fe$(A)_2$B] and are only separated by between 0 and 0.22 ppm (Table II), a separation similar

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[27] Crecely, R. W.; Crecely, K. M.; Goldstein, J. H. *Inorg. Chem.* **1969**, *8*, 252.

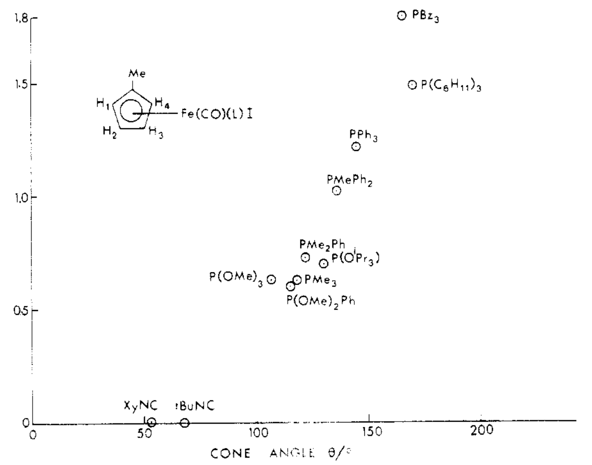

Figure 5. Plot of cone angle (θ, deg) against Δ(H1–H4) (ppm) for [(η^5-C_5H_4Me)Fe(CO)(L)I] (PBz_3 = $P(CH_2C_6H_5)_3$, XyNC = 2,6-$Me_2C_6H_3NC$). Cone angle[29] and fan angle data[41] were taken from the literature.

to that found for the [(η^5-C_5H_4Me)Fe$(A)_2$B] complexes listed in Table III. The averaged values for all four resonances appear ±0.2 ppm downfield from the corresponding [(η^5-C_5H_5)Fe(CO)(L)I] complexes, a result which is in keeping with the introduction of the electron-donating methyl group on the ring.

From the above it appears that the H1 and H4 (as well as the H2 and H3) resonances move upfield and downfield by the same amounts, as L is varied. Since similar shifts have been found for the separation of resonances (H or Me) in *geminal* arrangements, the *gem* arrangement provides a model for rationalizing the separation of the ring protons.[28] Thus, factors responsible for the size of the resonance separation for *gem* groups should also be responsible for the size of the resonance separation for the methycyclopentadienyl ring protons. The two major factors responsible are the ligand size (cone angle, θ)[29] and anisotropic effects.[30] A plot of cone angle, θ, against Δ(H1–H4) is shown in Figure 5 and indicates that Δ(H1–H4) increases with θ. It is apparent, however, that other factors (e.g. anisotropic effects) also influence Δ(H1–H4). No correlation was observed between electronic factors (e.g., ν(CO)[29] or pKa[31]) and the proton resonances.

The NOE experiments also provide information on the rotation of the ring relative to the ligand set. Irradiation of the ligand methyl or phenyl groups in **3** (L = $P(OMe)_3$, $PMePh_2$, PMe_2Ph) resulted in an *increase in the intensity of all four* ring resonances, although the increase in intensity was *not always the same* for all four cyclopentadienyl resonances (e.g., see Figure 2b, c, and g). This strongly suggests that the ring is rotating and that there is an unequal distribution of conformers in solution.[32] Variable-temperature NMR spectra recorded on **3** (L = PPh_3, $PMePh_2$; Table VI) indicated that only small (downfield) shifts in Δ(H1–H4) and Δ(H2–H3) occurred with increasing temperature (213–363 K), indicating only small changes in conformer populations with temperature.

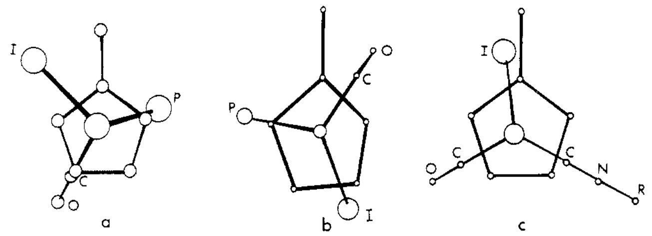

Figure 6. Newman projection of the crystal structures of [(η^5-C_5H_4Me)Fe(CO)(L)I] (**a**, L = $P(C_6H_{11})_3$; **b**, L = $P(OMe)_3$; **c**, L = 2,6-$Me_2C_6H_3NC$) viewed down the Fe–ring axis. The figures do not indicate details of the L ligands but rather highlight the orientation of the ligand set relative to the cyclopentadiene ring.

Crystal structure determinations were performed on **3** (L = $P(C_6H_{11})_3$, $P(OMe)_3$, 2,6-$Me_2C_6H_3NC$)[33] to obtain information on the conformational preferences. For both L = $P(OMe)_3$ and $P(C_6H_{11})_3$ the L group was found close to H1 or H4 (Figure 6a,b), whereas for the *small* ligand 2,6-$Me_2C_6H_3NC$ I is observed close to H1 or H4 (Figure 6c). The observation of the large L group appearing close to the ring Me group seems counter-intuitive; e.g., the $P(C_6H_{11})_3$ ligand that has a larger cone angle than I and CO[29] might have been predicted to have gone *trans* to the methyl group on steric grounds. Many examples of a large L group situated trans to a ring substituent are to be found in the literature.[34]

The observation that Δ(H1–H4) ≈ 2Δ(H2–H3) is consistent with similar conformations being dominant in solution since it has been noted that the resonance separation for *gem* groups falls off with distance from the source of asymmetry.[35] This would suggest that H1 and H4 are closer on average to L than H2 and H3 (L = PR_3).

Molecular mechanics calculations on **3** (L = $P(OMe)_3$) have indicated that although the energy barrier to ring rotation is small (< 6 kJ mol^{-1}), the conformations predicted are those observed in the crystal structure.[33] As L becomes larger, this conformational energy barrier will become larger. The calculations presently do not allow us to precisely delineate the factors responsible for the minimum energy conformations observed. However, it is to be noted that in related indenyl complexes similar observations on conformers have been rationalized by trans effects.[36]

Information on the *preferred conformations of the groups on the L ligands* (e.g., L = $PMePh_2$) is also given by our NMR results. For instance the remarkable *upfield* shift of the ring Me group in **3** (L = $PMePh_2$) with temperature (313–363 K, Table VI) suggests that at low temperatures the preferred orientation of groups on P has the Me group pointing *away* from the ring. As the temperature is increased, all conformations now become more accessible resulting in a change in the magnetic environment of the ring Me group. For **3** (L = PPh_3), as expected, the ring methyl resonance is invariant with temperature. The conformational preferences suggested are entirely consistent with earlier work reported by Faller and coworkers[37] on related systems using lanthanide shift reag-

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(28) This analogy is based on the fixed arrangement of protons in space and not on the coupling patterns. The *gem* arrangement has an AB coupling pattern whereas the H1 and H4 protons are best viewed as AX coupled (Δ(H1–H4) variable but ≫ *J*(H1–H4) ± 0.5 Hz; all other couplings ignored).

(29) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

(30) Jennings, B. J. *Chem. Rev.* **1975**, *75*, 307.

(31) (a) Allman, T.; Goel, R. G. *Can. J. Chem.* **1982**, *60*, 716. (b) Streuli, C. A. *Anal. Chem.* **1960**, *32*, 985. (c) Jackson, R. A.; Kanluen, L.; Poe, A. *Inorg. Chem.* **1984**, *23*, 523.

(32) For a recent example of the use of NOE difference spectroscopy in organometallic chemistry see: Hunter, B. K.; Baird, M. C. *Organometallics* **1985**, *4*, 1481.

(33) Johnston, P.; Denner, L.; Boeyens, J. C. A.; Marais, C. F.; Coville, N. J., to be submitted for publication.

(34) For example: (a) Zaworotko, M. J.; Shakir, R.; Atwood, J. L.; Sriyunyongwat, V.; Reynolds, S. D.; Albright, T. A. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1982**, *B38*, 1572. (b) Cesaroti, E.; Ciani, G.; Sironi, A. *J. Organomet. Chem.* **1981**, *216*, 87.

(35) Whitesides, G. M.; Holtz, D.; Roberts, J. D. *J. Am. Chem. Soc.* **1964**, *86*, 2628.

(36) Faller, J. W.; Crabtree, R. H.; Habib, A. *Organometallics* **1985**, *4*, 929.

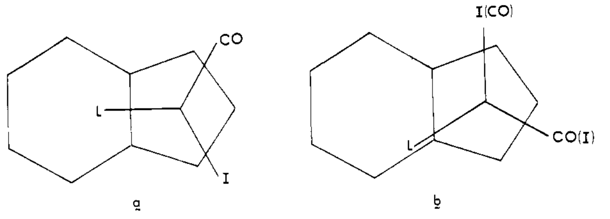

Figure 7. Newman projections of [(η^5-C_9H_7)Fe(CO)(L)I] viewed down the Fe–ring axis: (a) idealized arrangement of the ligand set relative to the indenyl ring; (b) conformation where L = $P(OPh)_3$ as suggested from *J*(P–H) data (see text).

ents. These conformational preferences are thus independent of the presence of the ring Me group.

The observation that in the NOE difference spectrum of **3** (L = $PMePh_2$, Figure 2) irradiation of the ortho ring protons gives rise to different intensity increases for the four ring resonances is to be noted. Irradiation of the cyclopentadienyl ring protons results in a similar increase in the corresponding ortho proton resonances (Figure 2d, resonance (% increase) 1 (1.5), 2 (0.5); Figure 2e, 1 (2.4), 2 (2.4); Figure 2f, 1 (1.5), 2 (2.0)). The phenyl groups in the ligand $PMePh_2$ are diastereotopic.[37,38] If the assumption of free rotation of the phenyl group around the P–C bond is made,[38] then the two separated ortho absorptions arise from the two diastereotopic phenyl groups. The NOE data would then suggest preferential conformational arrangements of the phenyl groups relative to the cyclopentadiene ring. However, further work, e.g., to establish the orientation of the phenyl groups (rotor sense) and their mechanism of interchange,[38,39] is still required before firmer conclusions can be drawn from the data.

NMR Spectra. Indenyl Complexes. The indenyl complexes provide information on the NMR spectra of ortho-disubstituted cyclopentadienyl complexes. For complexes of the type [(η^5-C_9H_7)Fe(A)$_2$B], e.g., as found in [(η^5-C_9H_7)Fe(CO)$_2$I], only two ring proton resonances are observed in a 2:1 ratio and correspond to H1, H3, and H2, respectively (Figure 1b). Replacement of one of the CO groups to give [(η^5-C_5H_7)Fe(CO)(L)I] results in the iron atom becoming chiral, a reduction in the molecular symmetry, and three proton resonances now being detected in the NMR spectrum. Data in Table V indicate that Δ(H1 – H2) varies with L. Decoupling experiments provided information on the coupling constants, and it was found that (i) *J*(H1–H3) ≈ 0 Hz, (ii) *J*(H1–H2) or *J*(H2–H3) ± 2.5 Hz, and (iii) *J*(P–H2) = 2–6 Hz and *J*(P–H1) or *J*(P–H3) = 0–1.6 Hz. There is thus strong coupling from the ligand to the central ring proton H2.

A conformational analysis of indenyl metal complexes has suggested that the ligand sets arrange themselves with respect to the ring according to trans directing influences.[36] This would suggest that the L ligands orientate themselves to be under the indenyl phenyl ring (Figure 7a). Our data are consistent with this view providing trans coupling of P to H2 is larger than cis coupling to H1 or H3.[40] There is a correlation between Δ(H1 – H3) and *J*(P–H2), i.e., the larger the separation, Δ, the larger the interaction of P with H2. No correlation between cone angle and Δ(H1–H3) is observed for these molecules. Anisotropic effects from the ligands L as *well as the indenyl ring* do not necessarily reinforce the steric effects, and consequently Δ does not vary smoothly with θ.

The coupling constant data for L = $P(OPh)_3$ indicate P coupling to H2 (6.0 Hz) and H1 (1.6 Hz) but not H3 (< 0.2 Hz) occurs. This suggests that conformation b (Figure 7) is the most probable conformation.

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Registry No. **1**, 32628-97-0; **2**, 36561-93-0; **3** (L = *t*-BuNC), 86957-95-1; **3** (L = 2,6-$Me_2C_6H_3NC$), 109527-73-3; **3** (L = PMe_3), 109527-74-4; **3** (L = PMe_2Ph), 109527-75-5; **3** (L = $PMePh_2$), 109527-76-6; **3** (L = PPh_3), 32054-66-3; **3** (L = $P(OMe)_3$), 31811-44-6; **3** (L = P(O-*i*-Pr)$_3$), 31798-37-5; **3** (L = $P(OMe)_2Ph$), 109527-77-7; **3** (L = $P(C_6H_{11})_3$), 109527-78-8; **3** (L = $P(CH_2C_6H_5)_3$), 109527-79-9; **4** (L = PMe_2Ph), 109552-16-1; **4** (L = $PMePh_2$), 109527-85-7; **4** (L = PPh_3), 109527-86-8; **4** (L = $P(OMe)_3$, 109527-87-9; **4** (L = $P(OEt)_3$), 109552-17-2; **4** (L = P(O-*i*-Pr)$_3$), 109527-88-0; **4** (L = P(*o*-$CH_3OC_6H_5)_3$), 109527-89-1; **4** (L = P-$(OPh)_3$), 36561-94-1; **4** (L = $P(OMe)_2Ph$), 109527-90-4; **4** (L = $P(OMe)Ph_2$), 109527-91-5; **4** (L = $P(CH_2C_6H_5)_3$), 109527-92-6; **5** (L = PMe_3), 109527-80-2; **5** (L = PMe_2Ph), 109527-81-3; **5** (L = $PMePh_2$), 109527-82-4; **5** (L = PPh_3), 109527-83-5; **5** (L = P-$(L_6H_{11})_3$), 109527-84-6; *t*-BuNC, 7188-38-7; 2,6-$Me_2C_6H_3NC$, 2769-71-3; PMe_3, 594-09-2; PMe_2Ph, 672-66-2; $PMePh_2$, 1486-28-8; PPh_3, 603-35-0; $P(OMe)_3$, 121-45-9; P(O-*i*-Pr)$_3$, 116-17-6; P-$(OMe)_2Ph$, 2946-61-4; $P(C_6H_11)_3$, 2622-14-2; $P(CH_2C_6H_5)_3$, 7650-89-7; [(η^5-C_5H_5)Fe(CO)$_2$]$_2$, 12154-95-9; $P(OEt)_3$, 122-52-1; P(*o*-$CH_3OC_6H_5)_3$, 4731-65-1; $P(OPh)_3$, 101-02-0; $P(OMe)Ph_2$, 4020-99-9.

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[37] Faller, J. W.; Anderson, A. S.; Jakubowski, A. *J. Organomet. Chem.* **1971**, *27*, C47.

[38] Faller, J. W.; Johnson, B. V. *J. Organomet. Chem.* **1975**, *96*, 99.

[39] Brunner, H.; Hammer, B.; Krüger, C.; Angermund, K. Bernal, I. *Organometallics* **1985**, *4*, 1063.

[40] Powell, J.; Shaw, B. L. *J. Chem. Soc. A* **1967**, 1839.

[41] Yamamoto, Y.; Aoki, K.; Yamazaki, H. *Inorg. Chem.* **1979**, *18*, 1681.