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Steric Measurement of Substituted Cyclopentadiene Ligands and the Synthesis and ^1H NMR Spectral Analysis of $[(\eta^5\text{-}C_5H_4R)Fe(CO)(L)I]$ Complexes with Variable R

Neil J. Coville,[*] Mohammed S. Loonat,[†] David White, and Laurence Carlton

Centre for Applied Chemistry and Chemical Technology, Department of Chemistry, University of the Witwatersrand, P.O. Wits 2050, Johannesburg, Republic of South Africa

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The synthesis of a range of complexes, $[(\eta^5\text{-}C_5H_4R)Fe(CO)(L)I]$ (R = COOMe, I, $CHPh_2$, iPr, $SiMe_3$, Ph, CPh_3; L = $P(OMe)_3$, $P(OCH_2CMe_3)_3$, $P(O\text{-}o\text{-}Tol)_3$, $P(OiPr)_3$, $P(OPh)_3$, PPh_3, $P(CH_2Ph)_3$, PPh_2Me, $P(NMe_2)_3$) is reported. Complexes were characterized by NMR and IR spectroscopy, mass spectrometry, and elemental analysis. Four separate cyclopentadienyl ring proton resonances are observed in the NMR spectra of the iron complexes, and their assignments were determined by NOE experiments. NOE data obtained on $[(\eta^5\text{-}C_5H_4R)Fe(CO)(L)I]$ in which the ortho phenyl ring protons (L = PPh_3) or O*Me* protons (L = $P(OMe)_3$) were irradiated revealed preferred solution conformations of the ligand set relative to the ring substituent. For instance, for R = iPr, CPh_3, tBu, and $SiMe_3$, the PPh_3 oriented itself close to the ring C atoms meta to the cyclopentadienyl ring substituent. For R = Me and I, near equal probability of all possible solution conformers was observed. The steric size of the substituted cyclopentadienyl ring was determined using the cone angle concept with either the metal (θ_1) or the ring centroid (θ_2) as the apex of the cone. Cone angles for a range of substituted C_5H_4R ligands were determined. A correlation between the cone angles (θ_2, ring centroid as apex) and $\Delta(H2 - H5)$ (H2, H5 ortho cyclopentadienyl ring protons resonances) of the $[(\eta^5\text{-}C_5H_4R)Fe(CO)(L)I]$ complexes was observed ($R^2 = 0.96$, adjusted for degrees of freedom). This correlation was improved upon inclusion of an electronic paramter (i.e. $\Delta(H2 - H5) = a\theta_2 + bE$; E = Hammett function, a, b = constants), e.g. $E = \sigma_{R^-}$: $R^2 = 0.99$.

Introduction

The cyclopentadienyl and substituted cyclopentadienyl ligands are commonly found associated with many organometallic complexes. Although as common a ligand type as the group 15 donor ligands, very few *systematic* studies on the effect of varying the ring substituent, R, on the chemical or physical properties of organometallic complexes containing the cyclopentadienyl ring have been reported.[1,2] Thus, some years ago, we initiated a study to systematically examine the influence of a ring substituent on the properties of a series of cyclopentadienyl-containing organometallic complexes.

Early studies in our laboratories on $[(\eta^5\text{-}C_5H_4Me)Fe(CO)(L)I]$ complexes (L = phosphine, phosphite) showed that the piano-stool, chiral iron species were ideally suited to NMR characterization.[3] Indeed, our study revealed that NMR parameters associated with the ring protons could be correlated with the size of the L group. These studies were extended to $[(\eta^5\text{-}C_5H_4tBu)Fe(CO)(L)I]$ complexes,[4] where it was suggested that the *size* of the ring substituent appeared to influence the ^1H NMR parameters. We now wish to report an extension of this early work to a systematic investigation of the variation of ring substituent on the chemical and physical properties of a series of $[(\eta^5\text{-}C_5H_4R)Fe(CO)(L)I]$ complexes in which *L is kept constant*.

In this publication, we also describe the synthesis of a range of substituted cyclopentadienyl complexes of the type $[(\eta^5\text{-}C_5H_4R)Fe(CO)_2I]$ (R = COOMe, I, $CHPh_2$, iPr, $SiMe_3$, Ph, CPh_3) and their reactions with ligands L (L = phosphine, phosphite) to yield the required $[(\eta^5\text{-}C_5H_4R)Fe(CO)(L)I]$ complexes. These products have been completely characterized, and their detailed ^1H NMR properties are described.

It has been ascertained, from a recent literature survey,[2] that little is known about the *steric* component of substituents on a cyclopentadienyl ring. Indeed, the only *quantitative* measurements of a cone angle associated with a cyclopentadienyl ligand, are those of Tolman (C_5H_5)[5] and Maitlis (C_5H_5 and C_5Me_5).[6] Reports on cone angle measurements of some di-[7] and tricyclopentadienyl[8]-containing complexes have also been published. In all the above reports, the cyclopentadienyl size has been measured with the *metal as the apex* of the cone (Figure 1a). However, no quantitative measure of the substituent size *relative to the ring centroid as the apex* (Figure 1b) has been reported, although we did propose, earlier, that this would be a viable measure of the ligand size.[4] Herein, we report on the measurement of the size of a range of substituted cyclopentadienyl ligands using both the above methods. We also report on our attempts to correlate the NMR parameters of a series of $[(\eta^5\text{-}C_5H_4R)Fe(CO)(L)I]$ (L = PPh_3, $P(OMe)_3$) complexes with the cyclopentadienyl cone angles, as well as their preferred solution conformers.

Experimental Section

All ligands were obtained from available sources. The complexes $[(\eta^5\text{-}C_5H_4iPr)Fe(CO)_2]_2$, $[(\eta^5\text{-}C_5H_4CHPh_2)Fe(CO)_2]_2$,

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[*] To whom correspondence should be addressed.

[†] Present address: Department of Chemistry, University of South Africa, P.O. Box 392, Pretoria 0001, Republic of South Africa.

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Table I. ^{1}H NMR Data for [(η^5-C_5H_4R)Fe(CO)(L)I]^a

R	L	Me(ring)	H2	H3	H4	H5	(H2 – H5)
COOMe	P(OMe)$_3$	3.47	5.41	4.26	4.08	5.04	0.37
	P(OCH$_2$CMe$_3$)$_3$	3.51	5.57	4.42	4.17	5.10	0.47
	PPh$_2$Me	3.56	5.42	3.93	3.63	4.98	0.54
	P(O-*o*-Tol)$_3$	3.51	5.48	4.26	3.48	4.79	0.69
	PPh$_3$	3.51	5.65	4.05	3.37	4.76	0.89
	CO	3.32	4.98	3.73	3.73	4.98	
	dimer	3.60	4.90	4.35	4.35	4.90	
CPh$_3$	P(OMe)$_3$		4.94	4.97	4.53	3.59	1.38
	P(OiPr)$_3$		5.42	4.78	4.65	3.49	1.93
	P(OPh)$_3$		4.72	4.41	4.14	2.34	2.38
	P(O-*o*-Tol)$_3$		4.85	4.72	4.56	2.64	2.21
	PPh$_2$Me		4.98	4.41	3.94	2.68	2.30
	PPh$_3$		5.01	5.11	4.00	2.76	2.35
SiMe$_3$	P(OMe)$_3$	0.34	5.15	4.98	4.21	3.81	1.34
	P(OCH$_2$CMe$_3$)$_3$	0.42	5.35	5.28	4.28	3.82	1.53
	PPh$_3$	0.45	5.56	4.61	3.52	3.56	2.00
	P(NMe$_2$)$_3$	0.49	5.55	5.49	3.94	3.33	2.22
	P(CH$_2$Ph)$_3$	0.38	5.17	4.24	2.94	2.91	2.26
	CO	0.34	4.54	4.19	4.19	4.54	
	dimer	0.34	4.53	4.19	4.19	4.53	
I	P(OMe)$_3$		4.97	4.21	3.93	4.15	0.86
	PPh$_3$		4.91	4.14	3.43	3.77	1.14
	P(NMe)$_3$		5.09	4.83	3.66	3.92	1.43
	CO		5.25	5.09	5.09	5.25	
iPr	P(OMe)$_3$	1.06	4.77	4.67	3.95	3.75	1.02
	PPh$_2$Me	1.10	4.91	4.52	3.33	3.25	1.66
	PPh$_3$	1.17	5.04	4.56	3.38	3.27	1.77
	P(NMe$_2$)$_3$	0.78	5.22	4.02	3.91	3.50	1.72
	P(CH$_2$Ph)$_3$	1.05	4.81	4.17	2.74	2.64	2.07
	CO	0.86	4.04	4.02	4.02	4.04	
	dimer	1.10	4.36	3.99	3.99	4.36	
CHPh$_2$	P(OMe)$_3$	5.83^b	4.80	4.59	3.44	4.04	0.76
	PPh$_3$	6.13	5.15	4.33	2.40	3.82	1.33
	CO		3.72	4.29	4.29	3.72	
	dimer	5.88	4.05	4.05	4.05	4.05	

^{a} δ/ppm, recorded in C_6D_6, relative to TMS. ^{b} C*H*Ph$_2$ resonance.

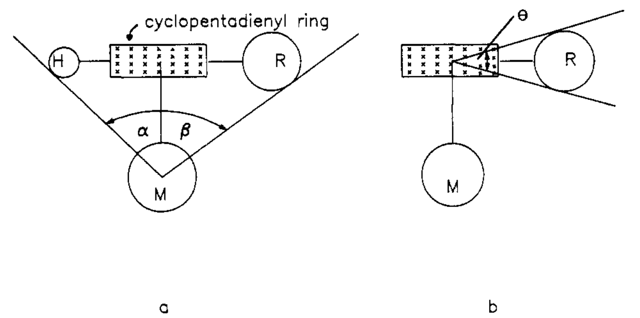

Figure 1. Measurement of cyclopentadienyl ring cone angle (a) with metal as apex (θ_1) and (b) with the ring centroid as apex (θ_2).

[(η^5-C_5H_4iPr)Fe(CO)$_2$I], and [(η^5-$C_5H_4CHPh_2$)Fe(CO)$_2$I] were prepared by a literature method.[9] All organometallic preparations were carried out under nitrogen using deoxygenated, dry, distilled solvents. Melting points were recorded on a Kofler hot stage melting point apparatus, IR spectra on a Perkin-Elmer 580B IR spectrometer and NMR spectra on a Bruker AC200 NMR spectrometer. All analyses were carried out at the CSIR, Pretoria, South Africa. NOE data were recorded as described previously.[3]

Synthesis of C_5H_5R/(C_5H_5R)$_2$ (R = SiMe$_3$, CPh$_3$, COOMe, Ph). The cyclopentadiene ligands were prepared by literature procedures: $C_5H_5SiMe_3$ (bp 47 °C, 20 mmHg, 69% yield),[10] $C_5H_5CPh_3$ (mp 53 °C, 58% yield),[11] C_5H_5COOMe (mp 48 °C, 60% yield).[12] C_5H_5Ph was not obtained in pure form and contained 3-phenylcyclopent-1-one as an impurity.[13]

Synthesis of Diazocyclopentadiene. Diazocyclopentadiene was prepared by a modification of the Wiel–Cais method.[14] A mixture of *p*-toluenesulfonyl azide, cyclopentadiene, and acetonitrile–diethylamine was kept at −20 °C for 3 days. After the addition of water, the thick brown mass was extracted exhaustively with ether and purified at low temperature by column chromatography. The pure diazocyclopentadiene gave a bright red solid when treated with triphenylphosphine (mp 121 °C). The yield in this reaction was used to calculate the concentration of the diazocyclopentadiene solution used in subsequent reactions.

Synthesis of Isopropyl- and Benzhydrylcyclopentadiene. 6,6-Diphenylfulvene was prepared by Thiele's method[15] by reacting diphenylketone with cyclopentadiene in the presence of equimolar amounts of sodium alkoxide in an alcohol medium. 6,6-Dimethylfulvene was prepared by a literature procedure[16] using primary amines as catalysts in an alcohol medium. The disubstituted fulvenes were reduced, with $LiAlH_4$, to the corresponding substituted cyclopentadienyl anions and converted to the substituted cyclopentadiene by literature procedures.[17]

Synthesis of [(η^5-$C_5H_4SiMe_3$)Fe(CO)$_2$]$_2$.[18] Dry, filtered $Fe(CO)_5$ (1.96 g, 0.01 mol) was heated to 110 °C together with (trimethylsilyl)cyclopentadiene (10 mL, 0.02 mol) and stirred overnight. Solvent was removed from the dark solution in vacuo and the residue recrystallized from CH_2Cl_2/hexane under nitrogen (−18 °C) and yielded a black solid (2.00 g, 80%), mp 96–97 °C (lit. 107 °C).[18] The product was characterized by IR and NMR spectroscopy (Table I) and mass spectrometry (Table II).

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Table II. Analytical and Mass Spectral Data for Selected $[(\eta^5\text{-}C_5H_4R)Fe(CO)(L)I]$ Complexes

R	L	mp/°C	analysis[a]		mass spectrum
			C	H	
COOMe	PPh_3	173–174	51.68 (52.38)	3.81 (3.72)	
	CO	75–76	30.39 (29.87)	2.05 (1.95)	
	dimer[b]		46.38 (46.00)	2.94 (3.00)	
CPh_3	PPh_3	172–173	65.41 (66.18)	4.48 (4.49)	
$SiMe_3$	PPh_3	146–147	52.17 (53.19)	4.39 (4.62)	
	dimer[c]				M^+ (4%), $M^+ - 4CO$ (100%)
$CHPh_2$	PPh_3	170–171	62.87 (63.09)	4.13 (4.29)	
I	PPh_3	156–157	44.40 (43.43)	3.07 (2.90)	M^+ (36%)
iPr	PPh_3	129–131	65.41 (66.18)	3.79 (4.39)	

[a] Found, calculated in parentheses. [b] $[(\eta^5\text{-}C_5H_4COOMe)Fe(CO)_2]_2$. [c] $[(\eta^5\text{-}C_5H_4SiMe_3)Fe(CO)_2]_2$. Other fragments observed: $M^+ - CO$ (7%), $M^+ - 2CO$ (3%), $M^+ - 3CO$ (12%) plus numerous monomer fragments.

Synthesis of $[(\eta^5\text{-}C_5H_4CPh_3)Fe(CO)_2]_2$. Dry, filtered $Fe(CO)_5$ (8.00 mL, 0.06 mol) and tritylcyclopentadiene (7.37 g, 0.024 mol) were added to a mixture of diglyme/heptane (100 mL, 1:10). After deoxygenating the solution, the mixture was heated to 120 °C under nitrogen for 24 h. The black solution was cooled in ice and filtered, yielding a black solid (10.3 g). Refrigeration of the mother liquor yielded a further 4.8 g of solid (total yield 75%). Characterization of the product was achieved by IR and NMR spectroscopy (Table I).

Synthesis of $[(\eta^5\text{-}C_5H_4COOMe)Fe(CO)_2]_2$.[19] A mixture of dry, filtered $Fe(CO)_5$ (16 mL, 0.12 mol), diglyme/heptane (200 mL, 1:10), and (methoxycarbonyl)cyclopentadiene (6.0 g, 0.048 mol) was deoxygenated and the reaction mixture heated under reflux for 24 h. The mixture was cooled in ice and filtered, yielding a deep purple solid (2.66 g). Storage of the mother liquor at −18 °C for 24 h yielded a further 360 mg (total yield 57%). Characterization of the product was achieved by IR and NMR spectroscopy (Table I).

Synthesis of $[(\eta^5\text{-}C_5H_4SiMe_3)Fe(CO)_2I]$. An iodine solution in CH_2Cl_2 (1.2 g, 4.8 mmol in 150 mL) was slowly added to $[(\eta^5\text{-}C_5H_4SiMe_3)Fe(CO)_2]_2$ (2.04 g, 4.10 mmol) dissolved in CH_2Cl_2 (70 mL) at room temperature, with stirring under nitrogen. The progress of the reaction was followed by IR spectroscopy at regular intervals. Upon completion of the reaction (20 min), the excess iodine was removed by adding an aqueous sodium thiosulfate solution (1.0 g in 25 mL water). The organic layer was separated and dried ($MgSO_4$) and solvent removed in vacuo, yielding a dark oil (1.21 g, 80%), which was characterized by IR and NMR spectroscopy (Table I).

Synthesis of $[(\eta^5\text{-}C_5H_4CPh_3)Fe(CO)_2I]$. $[(\eta^5\text{-}C_5H_4CPh_3)Fe(CO)_2]_2$ (870 mg, 1 mmol) was dissolved in CH_2Cl_2 (50 mL), and iodine (0.26 g, 1.0 mmol), dissolved in CH_2Cl_2 (40 mL), was added dropwise to the stirred solution, under nitrogen, at room temperature. The progress of the reaction was monitored by IR spectroscopy. Upon completion (2 h) excess iodine was removed by addition of an aqueous solution of sodium thiosulfate (500 mg in 10 mL of water). The organic layer was separated and dried ($MgSO_4$) and solvent removed in vacuo to yield a black solid (690 mg). After purification by column chromatography (silica gel/hexane slurry, eluted with benzene) black crystals were obtained (540 mg, 70%). The product was characterized by IR and NMR spectroscopy (Table I).

Synthesis of $[(\eta^5\text{-}C_5H_4COOMe)Fe(CO)_2I]$. $[(\eta^5\text{-}C_5H_4COOMe)Fe(CO)_2]_2$ (0.45 g, 0.94 mmol) was dissolved in CH_2Cl_2 (25 mL), and iodine (0.26 g, 1.0 mmol), dissolved in CH_2Cl_8 (40 mL), was added dropwise to the stirred solution, under nitrogen, at room temperature. The progress of the reaction was monitored by IR spectroscopy, and complete conversion was noted after 15 min. Excess iodine was removed by addition of an aqueous solution of sodium thiosulfate (500 mg in 10 mL of water). The organic layer was separated and dried ($MgSO_4$) and solvent removed in vacuo to yield a black solid (0.55 g, 80%). The product was characterized by IR and NMR spectroscopy (Table I).

Synthesis of $[(\eta^5\text{-}C_5H_4I)Fe(CO)_2I]$.[20a] $Fe(CO)_4I_2$ (33.7 g, 80 mmol) was added to diazocyclopentadiene (10.4 g, 100 mmol) in benzene (100 mL). The stirred solution was heated under nitrogen and gradually (over a period of 1 h) brought to reflux. At 45 °C vigorous bubbling was observed. The mixture was heated under reflux for 2 h, after which the black reaction mixture was allowed to cool to room temperature and silica gel added (50 g). The mixture was filtered and the silica gel washed with benzene (100 mL). The filtrate was evaporated to yield a black oil which was recrystallized from CH_2Cl_2/petroleum ether, giving black microcrystals. The mother liquor also gave diiodoferrocene (characterized by NMR spectroscopy and melting point analysis[20]). Further recrystallization from ether at 18 °C gave black needles of the desired product (2.2 g, 49%).

Synthesis of $[(\eta^5\text{-}C_5H_4SiMe_3)Fe(CO)(L)I]$ (L = $P(OMe)_3$, $P(OCH_2CMe_3)_3$, $P(NMe_2)_3$, PPh_3, $P(CH_2Ph)_3$). $[(\eta^5\text{-}C_5H_4SiMe_3)Fe(CO)_2I]$ (400 mg, 1 mmol) and the ligand, L (1.1 mmol), were dissolved in benzene (10 mL), and the solution was heated under reflux with $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ (10 mg) as catalyst. The reaction, monitored by IR spectroscopy, was complete within 1 h. Passage of the crude material through a silica column (benzene eluent) gave bright green or brown bands, from which the product was obtained and characterized by IR and NMR (Table I) spectroscopy.

Synthesis of $[(\eta^5\text{-}C_5H_4CPh_3)Fe(CO)(L)I]$ (L = $P(OMe)_3$, $P(OiPr)_3$, $P(OPh_3)_3$, $P(O\text{-}o\text{-}Tol)_3$, PPh_2Me, PPh_3). The iodo complex, $[(\eta^5\text{-}C_5H_4CPh_3)Fe(CO)_2I]$ (326 mg, 1 mmol) and the ligand, L, were dissolved in benzene (10 mL), and the solution was heated under reflux with $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ (10 mg) as catalyst. The reaction, monitored by IR spectroscopy, was complete within 15 min. New products were characterized by IR and NMR spectroscopy (Table I).

Synthesis of $[(\eta^5\text{-}C_5H_4COOMe)Fe(CO)(L)I]$ (L = $P(OMe)_3$, PPh_3, $P(CH_2Ph)_3$, $P(OCH_2CMe_3)_3$, $P(OCH_3CMe_3)_3$). $[(\eta^5\text{-}C_5H_4COOMe)Fe(CO)_2I]$ (362 mg, 1 mmol) and the ligand, L (1.1 mmol), were dissolved in benzene (10 mL), and the solution was heated under reflux with $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]$ (10 mg) as catalyst. The IR spectrum showed a carbonyl stretching vibration in the region 1712–1745 cm^{-1} assigned to the ring substituent carbonyl, in addition to the coordinated carbonyl group vibration at ~1950 cm^{-1}. Passage of the crude material through a silica column (benzene eluent) gave bright green or brown bands, from which the product was obtained and characterized by IR and NMR spectroscopy (Table I).

Synthesis of $[(\eta^5\text{-}C_5H_4iPr)Fe(CO)(L)I]$ (L = $P(OMe)_3$, PPh_3, $P(CH_2Ph)_3$). $[(\eta^5\text{-}C_5H_4iPr)Fe(CO)_2I]$ (346 mg, 1 mmol) and the ligand, L (1.1 mmol), were dissolved in benzene (10 mL), and the solution was heated under reflux with $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ (10 mg) as catalyst. The reaction, monitored by IR spectroscopy, was complete within 2.5 h. The solution was pumped to dryness, and the crude product was dissolved in benzene and passed through an alumina column (benzene eluent). The second brightly coloured band was collected and characterized by IR and NMR spectroscopy (Table I), as the desired complex.

Synthesis of $[(\eta^5\text{-}C_5H_4CHPh_2)Fe(CO)(L)I]$ (L = $P(OMe)_3$, PPh_3, $P(CH_2Ph)_3$). $[(\eta^5\text{-}C_5H_4CHPh_2)Fe(CO)_2I]$ (175 mg, 0.37 mmol) and the ligand, L (0.4 mmol), were dissolved in benzene

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(5 mL), and the solution was heated under reflux with $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ (10 mg) as catalyst. The reaction, monitored by IR spectroscopy, was complete in less than 3 h. The crude material was passed through a silica column (benzene eluent) and revealed a small, lightly coloured and a large, slower moving, brightly coloured band. The slower moving band was collected, and the solvent was removed in vacuo to yield a complex which was characterized as the product by IR and NMR spectroscopy (Table I).

Synthesis of $[(\eta^5\text{-}C_5H_4I)Fe(CO)(L)I]$ (L = $P(OMe)_3$, PPh_3, $P(CH_2Ph)_3$). $[(\eta^5\text{-}C_5H_4I)Fe(CO)_2I]$ (233 mg, 0.5 mmol) and the ligand, L (0.55 mmol), were dissolved in benzene (7 mL), and the solution was heated under reflux with $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ (10 mg) as catalyst. The reaction, monitored by IR spectroscopy, was complete within 1 h. Passage of the crude material through a silica column (benzene eluent) gave bright green or brown bands, from which the product was obtained and characterized by IR and NMR spectroscopy (Table I).

Synthesis of $[(\eta^5\text{-}C_5H_4Ph)Fe(CO)P(OMe)_3I]$. The iodo complex, $[(\eta^5\text{-}C_5H_4Ph)Fe(CO)_2I]$[21] (380 mg, 1 mmol), and trimethyl phosphite (1.1 mmol) were dissolved in benzene (10 mL), and the solution was heated under reflux with $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ (10 mg) as catalyst. The reaction, monitored by IR spectroscopy, was complete within 2 h. The complete disappearance of the bands in the ν(CO) region at 2046 and 1986 cm^{-1} was taken as the point of reaction completion. Passage of the crude material through a silica column (benzene eluent) gave a bright brown band, yielding a red product (340 mg, 70%) characterized by IR and NMR spectroscopy (Table I).

Results and Discussion

Synthesis of the Cyclopentadiene Ligands. A survey of the literature[2] has revealed that there are two *major* strategies toward the synthesis of monosubstituted cyclopentadienyl organometallic complexes: the substituent, R, is attached to the cyclopentadiene ring, followed by reaction of the substituted cyclopentadiene with a metal complex; or the metal is first coordinated to the cyclopentadiene ring, and then the ring is modified chemically. Our work utilized the first of these strategies, since, in general, the synthetic procedures to generate the substituted cyclopentadienes have been well documented, and use readily available starting materials (see Experimental Section).

Reaction of Substituted Cyclopentadienes with $Fe_2(CO)_9$ or $Fe(CO)_5$. The substituted cyclopentadiene (R = $SiMe_3$, CPh_3, COOMe) was treated, at high temperatures, with $Fe(CO)_5$ over a long period (24 h) and yielded dark precipitates which were readily crystallized to give the dimers $[(\eta^5\text{-}C_5H_4R)Fe(CO)_2]_2$ in 60–90% yields (characterized by NMR spectroscopy; see Table I). An alternative method, required when the ligand was thermally sensitive (R = Ph, iPr, $CHPh_2$), was to react the ligand with $Fe_2(CO)_9$ at room temperature.

Synthesis of $[(\eta^5\text{-}C_5H_4R)Fe(CO)_2I]$ (R = $SiMe_3$, COOMe, CPh_3, $CHPh_2$, iPr, Ph). The $[(\eta^5\text{-}C_5H_4R)Fe(CO)_2]_2$ complexes were readily cleaved by the addition of elemental iodine in CH_2Cl_2 solution to give the monomeric iodo complexes.[22] The procedure involved addition of the iodine solution, dropwise, to a solution of the dimer in CH_2Cl_2 and monitoring by IR spectroscopy (50–80% yield). The synthesis of $[(\eta^5\text{-}C_5H_4I)Fe(CO)_2I]$ was achieved by reacting diazocyclopentadiene directly with the dihalogen complex $Fe(CO)_4I_2$. The reaction yielded not only the desired product but also 1,1′-diiodoferrocene.

Synthesis of $[(\eta^5\text{-}C_5H_4R)Fe(CO)(L)I]$. A variety of procedures are available for the substitution of carbonyls in metal carbonyl complexes, encompassing both the traditional (thermal, photochemical) as well as more recent approaches using chemical reagents and catalysts.[23] In previous studies, emanating from our laboratory, the use of metal dimer catalysts to bring about single carbonyl substitution has been explored in some detail,[24] and this approach was used in this study to synthesize the required complexes. The preparations were carried out by heating $[(\eta^5\text{-}C_5H_4R)Fe(CO)_2I]$ with the ligand, L, in the presence of small amounts of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ as catalyst, in refluxing benzene. The mechanism of this reaction is still not known with certainty;[23,24] one possibility is shown as follows:

$$[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2 \rightleftharpoons 2[(\eta^5\text{-}C_5H_5)Fe(CO)_2]^\bullet$$

$$[(\eta^5\text{-}C_5H_5)Fe(CO)_2]^\bullet + L \rightleftharpoons [(\eta^5\text{-}C_5H_5)Fe(CO)(L)]^\bullet + CO$$

$$[(\eta^5\text{-}C_5H_5)Fe(CO)(L)]^\bullet + [(\eta^5\text{-}C_5H_4R)Fe(CO)_2I] \rightleftharpoons [(\eta^5\text{-}C_5H_5)Fe(CO)(L)I] + [(\eta^5\text{-}C_5H_5R)Fe(CO)_2]^\bullet$$

etc.

The free radical reaction suggests that $[(\eta^5\text{-}C_5H_5)Fe(CO)(L)I]$, as well as the expected $[(\eta^5\text{-}C_5H_4R)Fe(CO)(L)I]$ should be formed, and both these products can readily be *detected* in the NMR spectra of the crude products, for most of the reactions studied. The unsubstituted dimer catalyst could be replaced by the substituted dimer catalyst, if pure products are required. The reaction was also found to proceed rapidly (for R = I, iPr) when the reactants were allowed to stand in bright sunlight.

In the case of strongly nucleophilic ligands (L = $P(NMe_2)_3$, $P(C_6H_{11})_3$, PPh_2Me, $P(CH_2Ph)_3$), the iodine ligand was displaced from the metal in preference to the carbonyl group, yielding salts, $[(\eta^5\text{-}C_5H_4R)Fe(CO)_2(L)]I$. These were readily identified by NMR and IR spectroscopy and by their insolubility in benzene and ready solubility in chloroform. The effect of cyclopentadienyl ring substituents on the nature of the products can be anticipated.[2] Electron-donating R groups slow the reaction down by increasing the strength of the metal–carbonyl bond. The combined effect of the electron-donating R group and high nucleophilicity of the ligand, L, thus results in preferential metal–iodine bond cleavage under thermal conditions. Conversion of the salts to the desired neutral complexes was achieved by reaction with trimethylamine *N*-oxide (Me_3NO) if the IR carbonyl absorption was greater than 2000 cm^{-1}.[23,25] In many of the reactions, salts were produced in small quantities and did not warrant isolation. In such cases the presence of small amounts of catalyst and increased time periods gave conversion of the salt to the desired neutral complex. Replacement of the carbonyl group with iodine in the salt is *catalyzed* by the iron dimer, $[(\eta^5\text{-}C_5H_4R)Fe(CO)_2]_2$, since no conversion occurred in the absence of the catalyst.[26]

Characterization of the New Products. The IR spectra of all the iron cyclopentadienyl complexes, $[(\eta^5\text{-}C_5H_4R)Fe(CO)_2]_2$, $[(\eta^5\text{-}C_5H_4R)Fe(CO)_2I]$, and $[(\eta^5\text{-}C_5H_4R)Fe(CO)(L)I]$, studied in this work revealed the appropriate number of ν(CO) absorption bands, the positions of which were influenced by both L and R groups. Selected $[(\eta^5\text{-}C_5H_4R)Fe(CO)(L)I]$ complexes were also

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Table III. Reported Cone Angles (θ) for $(C_nR_n)M$

ligand	θ/deg	ligand	θ/deg
Rh^{III}–C_5Me_5	188[a]	Rh^I–C_5H_5	150[a]
Rh^I–C_5Me_5	182[a]	C_5H_5	136[b]
Rh^{III}–C_5H_5	148[a]		

[a] Reference 5. [b] Reference 6.

characterized using mass spectrometry (Table II). The spectra, on occasion, showed parent ions, but generally, the first significant ion was that due to CO loss. The NMR spectra confirmed the composition of the new complexes. Up to four magnetically nonequivalent *ring* protons can be detected in the ^1H NMR spectra of $[(\eta^5\text{-}C_5H_4R)Fe(CO)(L)I]$. As predicted, the dimers $[(\eta^5\text{-}C_5H_4R)Fe(CO)_2]_2$ and the unsubstituted iodo derivatives $[(\eta^5\text{-}C_5H_4R)Fe(CO)_2I]$ revealed only two closely spaced *ring* resonances in the ^1H NMR spectrum. The NMR spectra of all complexes showed the characteristic number of peaks for the ligand, the ring, and the ring substituent with correct intensities, and the resonances were in the correct region of the spectrum. NOE spectra were used to assign the ring protons to the specific NMR resonances.[3]

Steric Size Measurements in Organometallic Chemistry. Prior to a discussion of the measurement of the steric size of a cyclopentadiene ring, it is worth commenting on the methods used to measure the steric size of ligands, in particular group 15 donor ligands, commonly used in organometallic chemistry.[2] The general approach used is based on the Tolman cone angle[5] in which θ (Figure 1a) is a measure of the size of a ligand. Some of the assumptions that were used by Tolman in establishing a *relative* set of ligand sizes are: (i) the cone is regarded as a hollow, right circular cone, (ii) the M–P distance is set at 2.28 Å, and (iii) average values are chosen for unsymmetrical ligands. The measurements assume (i) no meshing of ligands, (ii) no conformations other than the minimum chosen, and (iii) no distortion of the ligand in different complexes, which could modify metal–ligand bond distances, etc.[27a] Attempts to address these types of limitations have been made by using (i) computer analyses of different conformer energies,[27b] (ii) solid angle measurements,[28] and (iii) ligand profiles, sometimes presented in spherical coordinates.[29]

The original cone angle measurements were correlated with results from equilibrium studies in which the equilibrium concentrations of NiL_4 and NiL_3, in the equilibrium $NiL_4 \rightleftharpoons NiL_3 + L$, were shown to correlate with the size of L.[5] Numerous other physical parameters have been correlated with the cone angle of group 15 donor ligands, e.g. (i) methanol bonding in $[Co(dimethylglyoximato)_2L(MeOH)]$ as L is varied,[30] and (ii) cis/trans isomerization for $W(CO)_4(L)(L')$ complexes.[31] Later studies on ligand sizes have indicated that steric factors can be correlated with a reaction steric profile.[32,33] These studies have shown that only when a ligand reaches a critical size for a specific system will steric effects be detected.

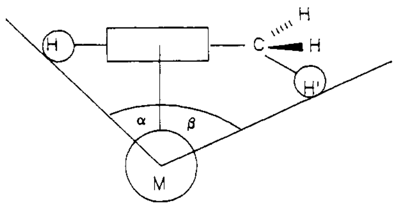

Figure 2. Measurement of θ_1 for R = CH_3, with the C_2–C_1–C–H′ (see Figure 6 for ring numbering) torsion angle = 90°. This geometry gives a maximum cone angle value. Values for θ_2 for a range of substituents, measured by a similar procedure, are given in Table IV.

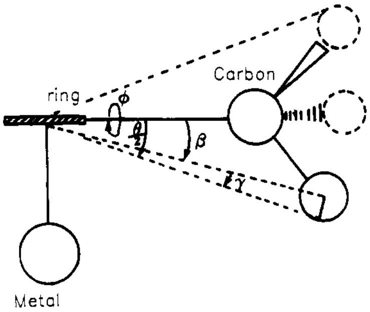

Figure 3. Measurement of θ_2 by procedure 1, showing details of the labeling system used in the text.

Although Tolman, in his review,[5] did measure the cone angles of ligands other than Group 15 donor ligands, little use has been made of these other measurements. Yamazaki and co-workers[34a] have also reported on the cone and fan angles of some isonitrile ligands. Otherwise little *quantitative* information is available on other commonly used ligands in organometallic chemistry.[34b]

Steric Size of the Substituted Cyclopentadienyl Ligand. As mentioned in the Introduction, only Tolman[5] and Maitlis[6] have reported *quantitative* measurements for the cyclopentadienyl ligand cone angles (see Table III). It is also to be noted that Mingos[35] has reported "cluster cone angles" for $(C_5H_5)M$ fragments in which the M–M bond in a metal cluster was varied. Values for the unsubstituted ring cone angle ranged between 82 and 97°. Values were determined assuming symmetrical $(\eta^5\text{-}C_5R_5)M$ (R = H, Me) structures using the metal, M, as the apex (Figure 1a).

Cone Angle: Metal as the Apex (θ_1). We have extended the procedure used by Tolman to generate the cone angles of a wide range of commonly used C_5H_4R ligands. The cone angles were generated using ALCHEMY[36] with the following assumptions: (i) The cone angle is defined as $\theta_1 = 2[(4/5)\alpha + (1/5)\beta]$ (Figure 1a). (ii) An M–ring centroid distance of 1.73 Å was used. This value corresponds to the Fe–ring centroid distances obtained for a range of $[(\eta^5\text{-}C_5H_4R)Fe(CO)(L)I]$ complexes.[2,37] (iii) The C_5H_4R ligand was considered to have equivalent C–C (ring centroid–C_{ring} = 1.20 Å) and C–M bond distances. (iv) The atom of the R group directly attached to the ring C atom was assumed to lie in the plane of the ring. (v) For symmetrical substituents (e.g. tBu), the *maximum* cone angle was measured (i.e. with the C–H bond of the CH_3 group perpendicular to the ring plane (Figure 2)). (vi) For unsymmetrical substituents, an *average* cone angle was

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Table IV. Maximum Cone Angles, θ_1 and θ_2, for C_5H_4R

R	θ_1/deg[a]	θ_2/deg
H	128	55
CH_3	141	64[b]
CH_2CH_3[c]	146	85
$CH(CH_3)_2$[d]	150	107
$C(CH_3)_3$	154	128
$Si(CH_3)_3$	158	138
$CH_2CH_2CH_3$	178	172
CH_2Ph[e]	150	102
$CHPh_2$[f]	158	140
$C(CH_3)Ph_2$[a]	163	161
$C(CH_3)_2Ph$[h]	158	144
CPh_3	167	178
Ph[i]	133	71
$CH{=}CH_2$[j]	151	39
CO_2CH_3[j]	132	47
$COCH_3$[j]	142	47
OCH_3	155	132
SCH_3	154	122
$P(CH_3)_3$	159	143
PPh_3	170	149
NH_2	141	64
$N(CH_3)_2$	154	131
$N(CH_2CH_3)_2$	176	174
NO_2	142	60
I	131	62

[a] Calculated from {0.8(C_5H_5) + 0.2(C_5R_5)}. [b] The cone angle for Fe–C_5Me_5 (Fe–centroid distance – 1.73 Å) is 194°. [c] Calculated from {$^1/_3$(tBu) + $^2/_3$(CH_3)}. [d] Calculated from {$^1/_3$(CH_3) + $^2/_3$(tBu)}. [e] Calculated from {$^1/_3$(CPh_3) + $^2/_3$(CH_3)}. [f] Calculated from {$^1/_3$(CH_3) + $^2/_3$(CPh_3)}. [g] Calculated from {$^1/_3$(tBu) + $^2/_3$(CPh_3)}. [h] Calculated from {$^1/_3$(CPh_3) + $^2/_3$(tBu)}. [i] Assuming the aryl and cyclopentadienyl rings are mutually at 45°. [j] Calculated by assuming the substituent and cyclopentadienyl rings are coplanar.

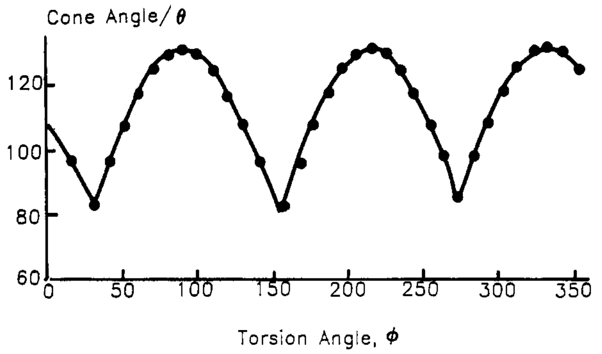

Figure 4. Ligand profile for η^5-C_5H_4tBu as generated by CONEEX.

calculated using the maxima measured in (iv). (vii) Free rotation of C_5H_4R is assumed, and a hollow, right circular cone is thus implied.

Values of θ_1 calculated by this procedure are given in Table IV.

Cone Angle: Cyclopentadienyl Ring Centroid as the Apex (θ_2). We have also measured the cyclopentadienyl size from the perspective of the C_5H_4R ring centroid as the apex atom (Figure 1b). This has been accomplished by two different methods.

Procedure 1. The method used is similar to that used to generate "ligand profiles" for PR_3 ligands.[28,29] A computer program, CONEEX, was developed for this purpose, and details of the method and the program are given in the supplementary material. In brief, a half cone angle, α, is defined as the angle between the vector joining the centers of the ring centroid, C1, and the X atom (X = substituent atom coordinated to C1) and the vector joining the ring centroid to the van der Waals radius of the outermost atom on X (Figure 3). As the ring substituent is rotated about the centroid–C1–X axis, the outermost atom on X moves and α varies, generating a ligand profile.

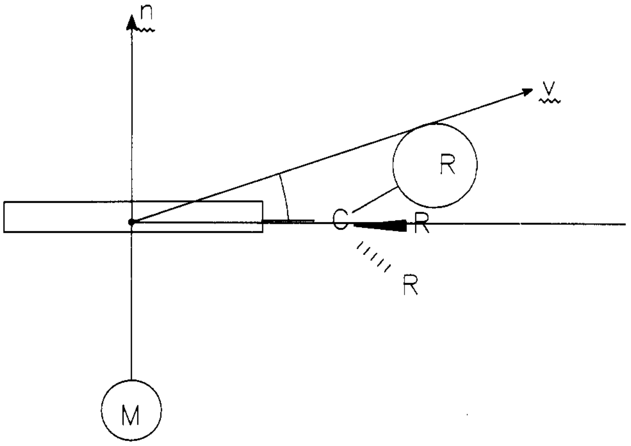

Figure 5. Measurement of θ_2 by procedure 2, showing details of the labeling system used in the text.

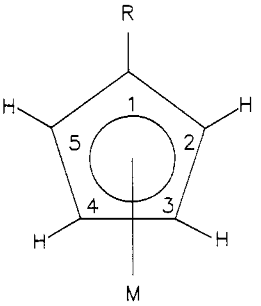

Figure 6. Cyclopentadienyl ring numbering system used in the text.

Figure 4 shows an example for a tBu substituent. The program permits for bending of the X atom from the cyclopentadienyl plane, as observed in nearly all crystallographic studies,[2] but this has a small effect on α (α vaires by 1 for every 2° bend of X out of the cyclopentadienyl ring plane).

Procedure 2. A plane is defined through the five cyclopentadienyl ring carbon atoms. The angle, α, between the vector from the centroid of the ring, tangential to the van der Waals radius of the outermost substituent atom, and its projection in the plane is calculated. The ring substituent is then allowed to rotate, and α varies with variation in torsion angle (Figure 5). Details of the method are given in the supplementary material. ALCHEMY[36] was used to build the molecules for study.

Data generated from the above two procedures are similar, and the averaged values of θ_{max} determined by procedure 2 are given in Table IV.

Conformational Studies. In previous publications,[34] we have reported that it is possible to obtain information on the preferred orientation of the ligand set (CO, L, I) relative to the ring substituent (R) in [(η^5-C_5H_4R)Fe(CO)(L)I] complexes. The NMR data revealed that as the *size* of L increased, a preference was shown for L to occupy the site as close to H3 as possible. Molecular mechanics calculations further confirmed the low energy barrier (<20 kJ·mol^{-1}) to ring rotation (L = $P(OMe)_3$; R = Me,[38] tBu[4]) and that the preferred ligand arrangement was similar to that predicted by the NMR study.

The range of new complexes synthesized in this study, permits us to *assess the effect of varying R on the ligand conformation while keeping L constant.* NOE difference spectra were thus recorded on the complexes [(η^5-

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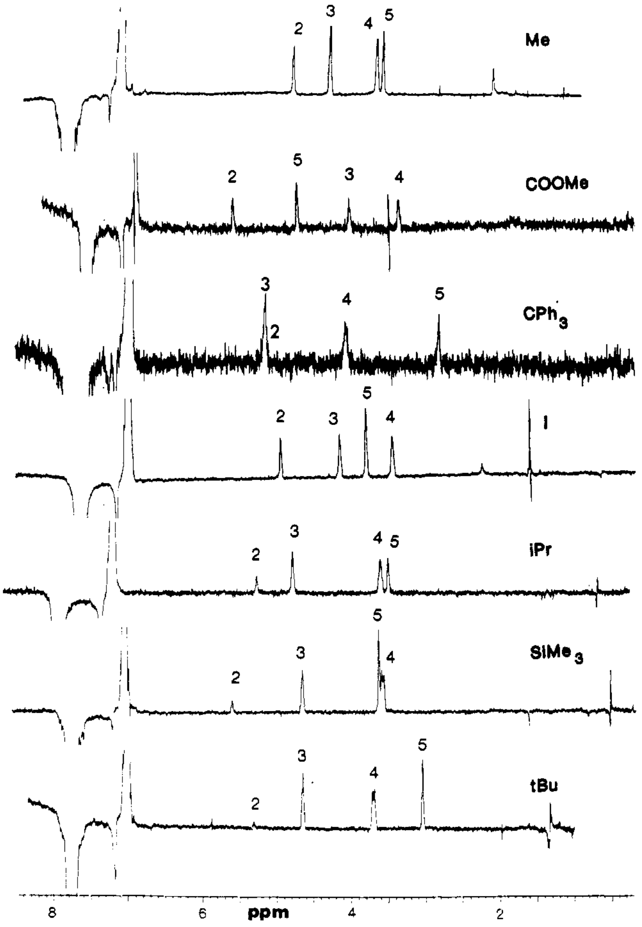

Figure 7. NOE difference spectra recorded on a series of $[(\eta^5\text{-}C_5H_4R)Fe(CO)PPh_3I]$ complexes. The data shown are those in which the ortho protons of the PPh_3 have been irradiated.

$C_5H_4R)Fe(CO)(L)I]$ (R = $SiMe_3$, $CHPh_2$, I, CPh_3, iPr, COOMe; L = PPh_3, $P(OMe)_3$). Consecutive irradiation of the cyclopentadienyl resonances observed in the ^1H NMR spectrum permitted correlation of the resonances with the ring protons H2–H5 (Figure 6). The data are shown in Table I.

Identification of the conformational preferences of the ring relative to the ligand set was achieved by irradiation of the ligand resonances (ortho phenyl proton in PPh_3 and methyl protons of $P(OMe)_3$) which resulted in varying increases in the integral intensities associated with ring protons H2–H5.

Selected NOE spectra for $[(\eta^5\text{-}C_5H_4R)Fe(CO)PPh_3I]$ complexes are shown in Figure 7. For R = I, COOMe, and Me, almost, equal growth of all four resonances associated with protons H2–H5 occurred, suggesting near equal occupancy of all possible conformations. The NOE spectra of complexes with R = $SiMe_3$, tBu, iPr, and CPh_3 indicate varying increases in intensity (Figure 7) for the resonances associated with the ring protons. For example, for R = iPr, H2 is 30% the size of H3, H4, or H5. This result is consistent with a dominant conformation in which the PPh_3 ligand is closer to H3–H5 than it is to H2. Coupling constant data ($J_{P\text{-}H4} > J_{P\text{-}H2}$)[9] also suggest that the PPh_3 ligand is closest to H4 in the dominant conformer. Visual inspection of the spectra also reveals that H3 and H4 are associated with broader resonances that H2 and H5, a feature which arises from a larger coupling of the phosphine with these protons.[3,4] It was not possible to apply this technique to the complex with R = $CHPh_2$ owing to the overlap of ortho ring protons in the substituent and ligand. Instead, consecutive irradiation of protons H2–H5 was performed and the data revealed that only H3, H4, and H5 caused a growth in the ortho phenyl resonances in the ligand. NMR data were, again, consistent with the ligand being preferentially close to H4. Similar results were obtained for $[(\eta^5\text{-}C_5H_4R)Fe(CO)P(OMe)_3I]$, where irradiation of the methyl group resonances of the ligand caused unequal growth of ring proton resonances. For the bulky R groups, ring protons H4 and H5 show far less growth than H2 and H3, suggesting that $P(OMe)_3$ is closer to H2 and H3 than H4 or H5 (Table I).

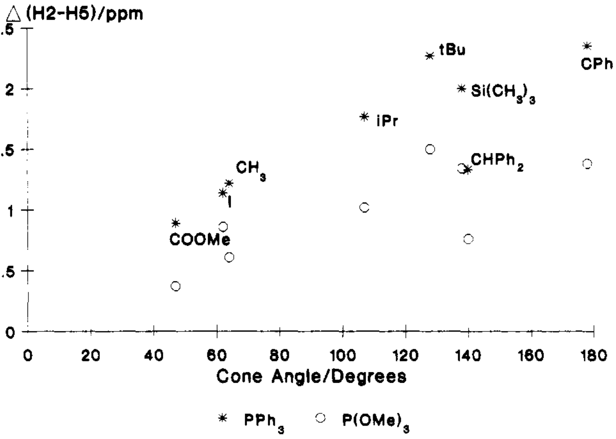

Figure 8. Plot of $\Delta(H2 - H5)$ versus θ_2 max (by procedure 2) for $[(\eta^5\text{-}C_5H_4R)Fe(CO)(L)I]$ complexes, L = (★) $P(OMe)_3$, (O) PPh_3 (R = COOMe, Me, I, Ph, iPr, $CHPh_2$, $SiMe_3$, tBu, and CPh_3).

Correlation of Cyclopentadienyl Steric Size with NMR Parameters of $[(\eta^5\text{-}C_5H_4R)Fe(CO)(L)I]$ Complexes. It has long been recognized that both steric and electronic effects associated with a cyclopentadienyl ligand, in a half-sandwich complex, can be measured. For instance, recent studies on $[(\eta^5\text{-}C_5H_4R)Rh(CO)_2]$ (R = NO_2, CF_3, etc.) revealed that σ and π electronic ring substituent effects could be correlated with CO substitution kinetic data.[39] Numerous other studies have also been reported in which the ring substituent electronic effects have also been correlated with other physical parameters associated with $[(\eta^5\text{-}C_5H_4R)ML_n]$ complexes.[40]

Steric effects have also been measured by NMR spectral parameters. Typically, the size of R influences its interaction with the rest of the ligands below the ring plane in $[(\eta^5\text{-}C_5H_4R)ML_n]$ complexes. VTNMR studies have, consequently, led to the measurement of ring rotational barriers through this interaction.[3,4,41,42] However, no *systematic* attempt to quantify the role of the steric effect on physical parameters associated with the complex type has been reported to date.

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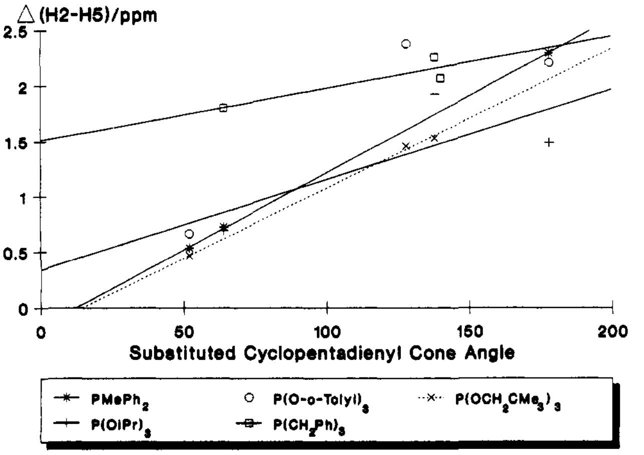

Figure 9. Plot of Δ(H2 - H5) versus θ_2 max (by procedure 2) for $[(\eta^5\text{-}C_5H_4R)Fe(CO)(L)I]$ complexes. L = PPh_2Me, $P(O\text{-}o\text{-}tolyl)_3$, $P(OCH_2CMe_3)_3$, $P(OiPr)_3$, $P(CH_2Ph)$ (R = COOMe, Me, iPr, $SiMe_3$, tBu, and CPh_3).

As mentioned in the introduction, we have previously reported that, for the complexes $[(\eta^5\text{-}C_5H_4R)Fe(CO)(L)I]$ (R = Me[3], tBu[4]), the steric size of L correlates with the parameter Δ(H2 -H5) (H2, H5; NMR resonances associated with ring protons 2 and 5, respectively). Since the relationship should be reciprocal, it can be anticipated that for a given L, Δ(H2 - H5) should be influenced by the size of R. We have found that a correlation exists between Δ(H2 - H5) and the steric effect measured by θ_2 (ring centroid as apex) for a range of R groups in which L (L = $P(OMe)_3$ or PPh_3) is kept constant (Figure 8). This is also shown in Figure 9 for a larger, but less complete, range of L and R groups. (Further, as the steric size of L increases the value of Δ(H2 - H5) also increases, thus providing a measure of the interaction of the substituted ring with groups below the ring plane.) From the scatter of the data points it is also apparent that factors other than steric effects influence the value of Δ(H2 - H5). These effects could be due to both electronic factors associated with R, and anisotropic factors associated with the ligand, L. Further consideration of the data in Figure 8 reveals that the deviation for a particular R group is similar for both the PPh_3 and $P(OMe)_3$ ligands. A plot of Δ(H2 - H5) for the PPh_3-containing complexes against Δ(H2 - H5) for the $P(OMe)_3$-containing complexes reveals a linear relationship (slope = 0.76, intercept = -0.28, R^2 = 0.99 at 95% confidence), confirming this suggestion (Figure 10). Plots for the data contained in Figure 9 also reveal similar relationships. This finding suggests that anisotropic effects associated with the L group do not significantly influence Δ(H2 - H5) and that the value is determined only by steric and electronic effects; this conclusion being supported by a thorough statistical analysis of the data.

Electronic effects associated with the substituted cyclopentadienyl rings have been used to rationalize the catalytic behavior of a series of $[(\eta^5\text{-}C_5H_4R)Co(CO)_2]$ complexes in which steric effects are expected to be small.[43] Perturbation of the Δ(H2 - H5) value due to the electronic effects associated with the R group can thus be anticipated. In all cases, except σ_a,[44] the adjusted correlation coefficient, R^2, was less than 0.71, with most R^2 values less than 0.30. (It is to be noted that Hammett and other parameters are not available for all the substituents used in this study.[44]) We have also attempted to interpret Δ(H2 - H5) as a *linear* combination of steric and electronic effects;[45] i.e. Δ(H2 - H5) = $a\theta_2 + bE$ (E = electronic parameter; a, b = constants). Good correlations were observed between Δ(H2 - H5), the inductive R Hammett parameter, and θ_2 (e.g. R^2 = 0.97, t = -1.56 with 98.3% significance, F = 100.1 with >99.99% significance, mean square error = 0.11 for PPh_3). The best correlations were observed between Δ(H2 - H5), the σ_{R+} and σ_{R-} Hammett functions, and θ_2 (e.g. R^2 = 0.99, t = -1.37 with 74% significance, F = 221.2 with 99.4% signficance, mean square error = 0.013 for σ_{R-} and $P(OMe)_3$).

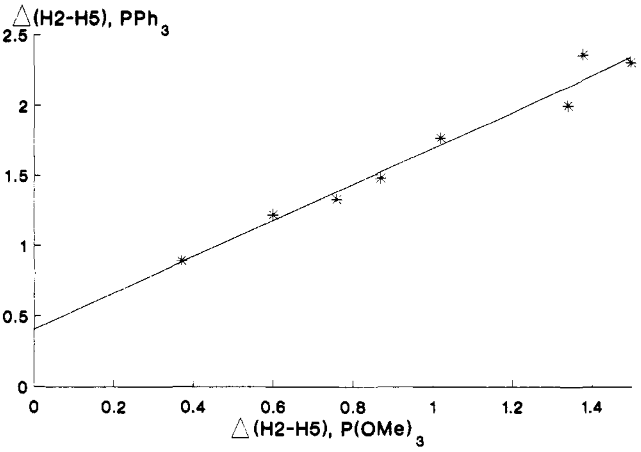

Figure 10. Plot of Δ(H2 - H5) for the PPh_3-containing complexes against Δ(H2 - H5) for the $P(OMe)_3$-containing complexes.

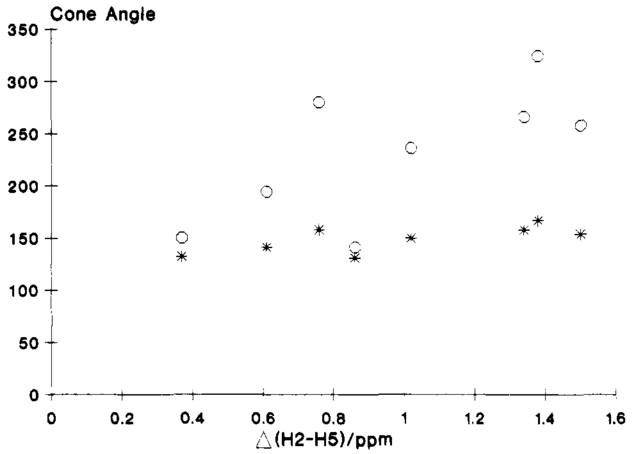

Figure 11. Plot of Δ(H2 - H5) versus θ_1 (cone angle with metal as apex atom) for a series of $[(\eta^5\text{-}C_5H_4R)Fe(CO)P(OMe)_3I]$ complexes: (★) $\theta_1 = 2[(4/5)\alpha + (1/5)\beta]$, (○) $\theta_1 = 2\beta$.

A poor correlation is also observed between Δ(H2 - H5), σ_{R+} or σ_{R-}, and θ_1 (metal as the apex) (e.g. R^2 = 0.92, t = 1.67 with 80.6% significance, F = 22.47 with 98.4% significance and a mean square error of 0.12 for σ_{R-} and $P(OMe)_3$). Figure 11 shows our results for the variation of Δ(H2 - H5) with θ_1 (L = $P(OMe)_3$) as determined by two different procedures. When $\theta_1 = 2[(4/5)\alpha + (1/5)\beta]$ (Figure 1a), little variation of Δ(H2 - H5) with θ is observed. A modification of the method which enhances the steric influences is to measure a "symmetrical" cone angle ($\theta_1 = 2\beta$, Figure 1a). Although a better correlation is observed, difficulties in assessing the cone angles of pentasubstituted versus monosubstituted cyclopentadienyl rings can be predicted.

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The correlation between Δ(H2 – H5) and θ can be anticipated from earlier work on NMR studies on RCH$_2$R′ complexes of geminal nonequivalence.[46] For instance, the larger the groups, R and R′, associated with the geminal protons in RCH$_2$R′, the larger the *difference* between the ^{1}H NMR resonances associated with the two protons. It is to be noted that the separation should be dependent on both R and R′. In our complexes the R and R′ groups correspond to the ring substituent and the ML$_x$ fragment in [(η^5-C$_5$H$_4$R)ML$_x$] complexes. The separation, Δ(H2 – H5), is thus expected to be dependent on R as well as *both M and L$_x$*. This has, indeed, been observed. Thus, for R = Me, M = Ru, and L = phosphine and phosphite, Δ(H2 – H5) is very small (0.1 ppm),[47] while for M = Fe, Δ(H2 – H5) values between 0.6 and 1.81 ppm[3] have been measured. Thus the NMR parameter, Δ(H2 – H5), can give a measure of *both* the size of R and the interaction of R with the rest of the molecule.

Conclusion

The [(η^5-C$_5$H$_4$R)Fe(CO)(L)I] complexes were successfully prepared and characterized by NMR and IR spectroscopy, mass spectrometry, or elemental analysis.

The presence of a stereogenic iron atom in these complexes, gives rise to up to four cyclopentadienyl ring proton resonances in the NMR spectra. The intensities and separation of the resonances has been shown to provide information on (i) the orientation of the ligands in the ligand set relative to the cyclopentadienyl ring and (ii) the steric size of both L and R.

The separation between the ortho cyclopentadienyl ring proton resonances, Δ(H2 – H5), is not influenced by anisotropic effects associated with the L group. For a given L, Δ(H2 – H5) is determined by steric (and electronic) effects associated with the R group. The H2 and H5 protons in [(η^5-C$_5$H$_4$R)Fe(CO)(L)I] can be regarded as equivalent to the geminal protons in RCH$_2$R′. Hence, factors responsible for the *separation* of the geminal proton resonances in RCH$_2$R′ will be the same as those responsible for the separation of the H2 and H5 resonances in the cyclopentadienyl ring.

It is possible that the Tolman cone angle may not be the most appropriate measure of the steric size of the R group, or of ligands in general. We are presently exploring the use of solid angles as a measure of the steric size of substituted cyclopentadienyl ligands,[21] and this work will be reported in a later publication.

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Registry No. [(η^5-C$_5$H$_4$COOMe)Fe(CO)(P(OMe)$_2$)I], 138697-64-0; [(η^5-C$_5$H$_4$COOMe)Fe(CO)(P(OCH$_2$CMe$_3$)$_3$)I], 138697-65-1; [(η^5-C$_5$H$_4$COOMe)Fe(CO)(PPh$_2$Me)I], 138697-66-2; [(η^5-C$_5$H$_4$COOMe)Fe(CO)(P(O-*o*-Tol)$_3$)I], 138697-67-3; [(η^5-C$_5$H$_4$COOMe)Fe(CO)(PPh$_3$)I], 138697-68-4; [(η^5-C$_5$H$_4$COOMe)-Fe(CO)$_2$I], 138697-69-5; [(η^5-C$_5$H$_4$COOMe)Fe(CO)$_2$]$_2$, 84394-02-5; [(η^5-C$_5$H$_4$CPh$_3$)Fe(CO)(P(OMe)$_3$)I], 138697-70-8; [(η^5-C$_5$H$_4$CPh$_3$)Fe(CO)(P(O-*i*-Pr)$_3$)I], 138697-71-9; [(η^5-C$_5$H$_4$CPh$_3$)-Fe(CO)(P(OPh)$_3$)I], 138697-72-0; [(η^5-C$_5$H$_4$CPh$_3$)Fe(CO)(O-*o*-Tol)$_3$I], 138697-73-1; [(η^5-C$_5$H$_4$CPh$_3$)Fe(CO)(PPh$_2$Me)$_3$I], 138697-74-2; [(η^5-C$_5$H$_4$CPh$_3$)Fe(CO)(PPh$_3$)I], 138697-75-3; [(η^5-C$_5$H$_4$SiMe$_3$)Fe(CO)(P(OMe)$_3$)I], 138697-76-4; [(η^5-C$_5$H$_4$SiMe$_3$)-Fe(CO)(P(OCH$_2$CMe$_3$)$_3$I], 138697-77-5; [(η^5-C$_5$H$_4$SiMe$_3$)Fe-(CO)(PPh$_3$)I], 138697-78-6; [(η^5-C$_5$H$_4$SiMe$_3$)Fe(CO)(P(NMe$_2$)$_3$)I], 138697-79-7; [(η^5-C$_5$H$_4$SiMe$_3$)Fe(CO)(P(CH$_2$Ph)$_3$)I], 138697-80-0; [(η^5-C$_5$H$_4$SiMe$_3$)Fe(CO)$_2$I], 138697-81-1; [(η^5-C$_5$H$_4$SiMe$_3$)Fe(CO)$_2$]$_2$, 12570-83-1; [(η^5–C$_5$H$_4$I)Fe(CO)(P(OMe)$_3$)I], 138697-82-2; [(η^5–C$_5$H$_4$I)Fe(CO)(PPh$_3$)I], 125900-04-1; [(η^5–C$_5$H$_4$I)Fe(CO)(P-(NMe$_2$)$_3$)I, 138697-83-3; [(η^5–C$_5$H$_4$I)Fe(CO)$_2$I], 68148-23-2; [(η^5–C$_5$H$_4$iPr)Fe(CO)(P(OMe)$_3$I], 138697-84-4; [(η^5–C$_5$H$_4$iPr)Fe-(CO)(PPh$_2$Me)I], 138697-85-5; [(η^5–C$_5$H$_4$iPr)Fe(CO)(PPh$_3$)I], 125900-05-2; [(η^5–C$_5$H$_4$iPr)Fe(CO)(P(NMe$_2$)$_3$)I], 138722-06-2; [(η^5–C$_5$H$_4$iPr)Fe(CO)(P(CH$_2$Ph)$_3$)I], 138697-86-6; [(η^5–C$_5$H$_4$iPr)Fe(CO)$_2$I], 125900-07-4; [(η^5–C$_5$H$_4$iPr)Fe(CO)$_2$]$_2$, 107891-50-9; [(η^5–C$_5$H$_4$CHPh$_2$)Fe(CO)(P(OMe)$_3$)I], 138697-87-7; [(η^5–C$_5$H$_4$CHPh$_2$)Fe(CO)(PPh$_3$)I], 125900-06-3; [(η^5–C$_5$H$_4$CHPh$_2$)Fe(CO)$_2$I], 105792-27-6; [(η^5–C$_5$H$_4$CHPh$_2$)Fe-(CO)$_2$]$_2$, 107983-49-3; Fe(CO)$_5$, 13463-40-6; [η^5–C$_5$H$_4$CPh$_3$)Fe-(CO)$_2$]$_2$, 138697-88-8; [η^5–C$_5$H$_4$CPh$_3$)Fe(CO)$_2$I], 138697-89-9; Fe-(CO)$_4$I$_2$, 14878-30-9; [(η^5–C$_5$H$_4$Ph)Fe(CO)P(OMe)$_3$I], 138697-91-3; [(η^5–C$_5$H$_4$Ph)Fe(CO)$_2$I], 138697-90-2; [(η^5–C$_5$H$_5$)Fe(CO)$_2$]$_2$, 12154-95-9; diazocyclopentadiene, 1192-27-4; *p*-toluenesulfonyl azide, 941-55-9; cyclopentadiene, 542-92-7; (trimethylsilyl)cyclopentadiene, 25134-15-0; tritylcyclopentadiene, 69468-72-0; (methoxycarbonyl)cyclopentadiene, 35730-27-9.

Supplementary Material Available: Textual presentation of the two procedures for measuring the cyclopentadienyl size and a diagram showing the measurement of θ_2 by procedure 2, with full details of the nomenclature used (6 pages). Ordering information is given on any current masthead page.

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