1.70. In **10a** and **10b**, the Mo–S distances were kept equal to 2.54 Å and the S–S separations were 2.95 and 2.00 Å, respectively; the geometry of the $CpMo(CO)_2$ fragments is the same as in **9**, and their respective orientations with respect to the rest of the molecule have been optimized, as well as the Mo–S–Mo angles.

Acknowledgment. We thank Professor A. Darchen for helpful discussions.

Registry No. **4a**, 122190-30-1; **5**, 122190-31-2; **7a**, 98606-16-7; **7b**, 122190-32-3; **8**, 122190-33-4; **10a**, 122190-35-6; **10b**, 122190-36-7; $[Cp_2W_2(CO)_4(\mu\text{-}Te_2H_2)]^{2+}$, 122190-34-5.

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Steric Effects Associated with Monosubstituted Cyclopentadienyl Transition-Metal Complexes. Synthesis and NMR Spectroscopic and Molecular Mechanics Study of $[(\eta^5\text{-}C_5H_4Bu^t)Fe(CO)(L)I]$ Complexes and Crystal Structure Determination of $[(\eta^5\text{-}C_5H_4Bu^t)Fe(CO)(PPh_3)I]$

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Received July 12, 1988

The influence of the bulky cyclopentadienyl substituent *tert*-butyl (Bu^t) on the conformational preferences of complexes of the type $[(\eta^5\text{-}C_5H_4Bu^t)Fe(CO)(L)I]$, where L = group 15 donor ligand, was investigated. ^1H NMR spectra show that the four protons, H_2–H_5, on the cyclopentadienyl ligand give rise to four separate resonance groups. The distance between the two outer resonances, corresponding to the two ortho ring protons, increases with increasing size of L and ring substituent (Me, Bu^t). NMR coupling and nOe spectroscopy unambiguously indicate a conformational preference where H_4 (the "meta" cyclopentadienyl ring proton) and the group 15 donor ligand are close to being eclipsed. Molecular mechanics methods were applied to $[(\eta^5\text{-}C_5H_4Bu^t)Fe(CO)P(OMe)_3I]$ to obtain a preferential conformation and energy profile for rotation about the iron–cyclopentadienyl bond axis. The lowest energy conformation obtained corresponded to that deduced from NMR spectroscopy. The crystal and molecular structure of $[(\eta^5\text{-}C_5H_4Bu^t)Fe(CO)(PPh_3)I]$ was obtained. ($FeC_{28}H_{28}OIP$: space group $P\bar{1}$; $Z = 2$; $a = 9.231$ (2), $b = 10.484$ (2), $c = 14.082$ (2) Å; $\alpha = 111.47$ (2), $\beta = 79.02$ (1), $\gamma = 93.17$ (2)°; $R = 0.049$.) The conformation of this compound when viewed along the iron–cyclopentadienyl axis corresponds to the most favorable conformer obtained from NMR and molecular mechanics studies, with H_4 close to the PPh_3 ligand.

Introduction

The η^5-bonded cyclopentadienyl ring occupies three coordination sites when bonded to transition metals and relative to three monosubstituted ligands is regarded as a small ligand.[1,2] Consequently, in most discussions involving the cyclopentadienyl ligand emphasis has been placed on the electronic rather than the steric effects of the ligand.[3]

In a recent investigation of the synthesis and NMR spectra of $[(\eta^5\text{-}C_5H_4Me)Fe(CO)(L)I)]$ (L = group 15 donor ligand) we observed a correlation between the cone angle of L and the NMR parameter $\Delta(H_2\text{–}H_5)$,[4] where H_2 and H_5 are the chemical shifts of the resonances associated with the two cyclopentadienyl ring protons *ortho* to the ring methyl group.[4] It was thus apparent that NMR spectroscopy could be used to assess steric properties of the ligands L associated with $[(\eta^5\text{-}C_5H_4Me)Fe(CO)(L)I]$. In the above complexes ambiguity existed as to whether the methyl group was sufficiently bulky to influence the conformational preferences of the ligand set and be detected by NMR spectroscopy. The use of bulky substituents on cyclopentadienyl[5–8] (and arene[9]) rings to influence ring rotational effects has been described, and we now wish to report on the use of the bulky Bu^t group to enhance the difference in conformer populations in our iron complexes. By a combination of NMR spectroscopy, an X-ray structure determination, and molecular mechanics calculations, on a series of $[(\eta^5\text{-}C_5H_4Bu^t)Fe(CO)(L)I]$ complexes, we have now *unambiguously* shown that preferential ring conformations can be observed by NMR spectroscopy for all the complexes containing a Bu^t ring substituent. From extrapolation of the data it is now apparent that even the methyl cyclopentadienyl ring substituent can influence the conformation of the cyclopentadienyl ring in the related $[(\eta^5\text{-}C_5H_4Me)Fe(CO)(L)I]$ complexes.

Experimental Section

General Procedures. All reactions and chromatographic separations and recrystallizations were carried out under a N_2 atmosphere, using degassed solvents. The solvents used were dried and distilled by standard procedures.

Infrared spectra were recorded on either a Perkin-Elmer 580B or Pye Unicam SP300 spectrometer using NaCl solution cells. NMR spectra were recorded on a Bruker AC 200 NMR spectrometer. Mass spectra were recorded on a Finnegan Mat 8200 spectrometer operating at 70 eV. Microanalyses were performed by the Micro Analytical Laboratories, CSIR, Pretoria, South Africa. Melting points were determined on a Kofler micro hot-stage apparatus and are uncorrected.

$[Fe_2(CO)_9]$ and $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ were obtained from Strem chemicals, and the ligands were obtained from various sources.

Preparation of $[(\eta^5\text{-}C_5H_4Bu^t)Fe(CO)_2]_2$. $[Fe_2(CO)_9]$ (100 mmol) and $C_5H_5Bu^t$[10] (50 mmol) in benzene (150 mL) were stirred under nitrogen for 48 h. The disappearance of the golden-colored $[Fe_2(CO)_9]$ could be followed visually, and the solution became brown due to the formation of the new complex as the reaction progressed. After disappearance of the $[Fe_2(CO)_9]$ the solution was filtered through Celite to remove decomposed and pyrophoric residues and the solvent was removed on a rotary evaporator. Column chromatography could not be used, due to product instability; hence, purification was done by recrystallization from CH_2Cl_2/hexane (8.2% yield): mp 150 °C dec; IR (CH_2Cl_2) ν(CO) 1988

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(1) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.
(2) Maitlis, P. M. *Chem. Soc. Rev.* **1981**, *10*, 1.
(3) For example: Bönnemann, H. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 248. However, for a recent discussion of the role of cyclopentadienyl steric effects in $[(\eta^5\text{-}C_5H_5)_3UL]$ complexes, see: Xing-Fu, L; Au-Ling, G. *Inorg. Chim. Acta* **1987**, *134*, 143.
(4) Johnston, P.; Loonat, M. S.; Ingham, W. L.; Carlton, L.; Coville, N. J. *Organometallics* **1987**, *6*, 2121.
(5) For example: Werner, H.; Hofmann, W. *Chem. Ber.* **1981**, *114*, 2681.
(6) Luke, W. D.; Streitweiser, A., Jr. *J. Am. Chem. Soc.* **1981**, *103*, 3241.
(7) Adams, H.; Bailey, N. A.; Mann, B. E.; Taylor, B. F.; White, C.; Yavari, P. *J. Chem. Soc., Dalton Trans.* **1987**, 1947 and references cited therein.
(8) Benn, R.; Grondey, H.; Notte, R.; Erker, G. *Organometallics* **1988**, *7*, 777 and references cited therein.
(9) Hy, X.; Duchowski, J.; Pomeroy, R. K. *J. Chem. Soc., Chem. Commun.* **1988**, 362.
(10) Reimschneider, R.; Reisch, A.; Horak, H. *Monatsh. Chem.* **1960**, *91*, 805.

(s), 1948 (m), 1770 (s) $\mathrm{cm^{-1}}$; MS m/z (% abundance) 466 (80), 438 (41), 410 (59), 382 (100), 354 (24); ^{1}H NMR (C_6D_6) δ 4.52 (t, 2 H, $J_{\mathrm{H-H}}$ = 2.2 Hz, Cp), 3.88 (t, 2 H, $J_{\mathrm{H-H}}$ = 2.2 Hz, Cp), 1.24 (s, 9 H, $\mathrm{Bu^t}$).

Preparation of $[(\eta^5\text{-}C_5H_4Bu^t)Fe(CO)_2I]$. I_2 in $CHCl_3$ was added gradually to $[(\eta^5\text{-}C_5H_4Bu^t)Fe(CO)_2]_2$ (2.15 mmol) in $CHCl_3$ (25 mL) at room temperature until all of the dimer had been converted to the iodo derivative. The reaction was followed by IR spectroscopy and thin-layer chromatography. The solution was neutralized with sodium thiosulphate and dried, and the solvent was then removed. The crude product was then purified by column chromatography (alumina, activity III; CH_2Cl_2/hexane mixtures as eluant) and yielded the pure product (36% yield): mp 59–63 °C; IR (CH_2Cl_2) ν(CO) 2030, 1988 $\mathrm{cm^{-1}}$; ^{1}H NMR (C_6D_6) δ 4.22 (s, 2 H, Cp), 4.13 (s, 2 H, Cp), 0.87 (s, 9 H, $\mathrm{Bu^t}$).

Preparation of $[(\eta^5\text{-}C_5H_4Bu^t)Fe(CO)(L)I]$ (L = $P(OCH_2)_3CCH_3$, $P(OMe)_3$, $P(O\text{-}o\text{-}CH_3C_6H_4)_3$, PPh_3, $P[OCH_2C(CH_3)_3]_3$, $P[OCH(CH_3)_2]_3$). $[(\eta^5\text{-}C_5H_4Bu^t)Fe(CO)_2I]$ (1 mmol), L (1.1 mmol), and the catalyst $[(\eta^5\text{-}C_5H_4Bu^t)Fe(CO)_2]_2$ (50 mg) were refluxed together in benzene (15 mL) until IR spectroscopy and thin-layer chromatography indicated completion of the reaction (2–8 h). The products were purified by column chromatography (alumina, activity III), with either CH_2Cl_2/hexane or benzene/hexane mixtures as eluants. Recrystallization was done at 0 °C from toluene/hexane or CH_2Cl_2/hexane mixtures. Yields obtained were 36–80%. L = $P(OCH_2)_3CCH_3$: mp 205 °C dec; IR (CH_2Cl_2) ν(CO) 1967 $\mathrm{cm^{-1}}$; MS m/z (% abundance) 480 (20), 452 (82), 325 (14), 304 (100). L = $P(OMe)_3$: mp 69.5–71.0 °C; IR (CH_2Cl_2) ν(CO) 1958 $\mathrm{cm^{-1}}$. Anal. Calcd for $FeC_{13}H_{22}O_4IP$: C, 34.24; H, 4.86. Found: C, 34.40; H, 4.81. L = $P[OCH(CH_3)_2]_3$: IR (CH_2Cl_2) ν(CO) 1949 $\mathrm{cm^{-1}}$; MS m/z (% abundance) 540 (18), 513 (100), 386 (56), 304 (64). L = $P[OCH_2C(CH_3)_3]_3$: mp 109–111.5 °C; IR (CH_2Cl_2) ν(CO) 1956 $\mathrm{cm^{-1}}$; MS m/z (% abundance) 624 (12), 596 (100), 526 (41), 469 (4), 304 (19). L = PPh_3: mp 142.0–143.0 °C; IR (CH_2Cl_2) ν(CO) 1943 $\mathrm{cm^{-1}}$; MS m/z (% abundance) 594 (3), 566 (9), 439 (7), 304 (8), 262 (100). Anal. Calcd for $FeC_{28}H_{28}OIP$: C, 56.59; H, 4.75. Found: C, 56.11; H, 5.15. L = $P(O\text{-}o\text{-}CH_3C_6H_4)_3$: mp 89–94 °C; IR ($CH_2Cl_2$) ν(CO) 1972 $\mathrm{cm^{-1}}$. Anal. Calcd for $FeC_{31}H_{34}O_4IP$: C, 54.41; H, 5.01. Found: C, 54.94; H, 4.44.

Preparation of $[(\eta^5\text{-}C_5H_4D)Fe(CO)(PMePh_2)I]$. $[(\eta^5\text{-}C_5H_4D)Fe(CO)_4Fe(\eta^5C_5H_5)]$ was prepared according to a literature method.[11] This dimer was cleaved by using I_2 as described above to give a mixture of $[(\eta^5\text{-}C_5H_4D)Fe(CO)_2I]$ and $[(\eta^5C_5H_5)Fe(CO)_2I]$. The mixture was reacted with $PMePh_2$ in the presence of catalyst, $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$, as described above to give the product $[(\eta^5\text{-}C_5H_4D)Fe(CO)(PMePh_2)I]$ together with the nondeuterated product. A mixture of the deuterated and nondeuterated products was obtained after purification by column chromatography (alumina, activity III; hexane/CH_2Cl_2 mixtures as eluant). $[(\eta^5\text{-}C_5H_4D)Fe(CO)_4Fe(\eta^5\text{-}C_5H_5)]$: MS m/z (% abundance) 355 (29), 327 (24), 299 (32), 271 (17), 243 (100). $[(\eta^5\text{-}C_5H_4D)Fe(CO)(PPh_2Me)I]$: IR ($CH_2Cl_2$) ν(CO) 1949 $\mathrm{cm^{-1}}$; MS m/z (% abundance) 477 (18), 449 (100), 369 (40), 322 (46), 297 (43); ^{1}H NMR (C_6D_6) δ 1.96 (d, $J_{\mathrm{P-H}}$ = 9.1 Hz, $P(CH_3)Ph_2$), 4.5 (d, $J_{\mathrm{P-H}}$ = 1.4 Hz, Cp), 6.98 and 7.08 (m, $PMePh_2$, $H_{m,p}$), 7.30 and 7.66 (m, $PMePh_2$, H_o).

Crystallography. $[(\eta^5\text{-}C_5H_4Bu^t)Fe(CO)(PPh_3)I]$. Suitable crystals of $[(\eta^5\text{-}C_5H_4Bu^t)Fe(CO)(PPh_3)I]$ were grown from CH_2Cl_2/hexane at 0 °C, and a single crystal was mounted in a Lindemann tube. Data collection was carried out at room temperature on a Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo Kα (0.7107 Å) radiation. The space group was found to be $P\bar{1}$ from intensity statistics and confirmed by structure refinement, with a = 9.231 (2) Å, b = 10.484 (2) Å, c = 14.082 (2) Å, α = 111.47 (2)°, β = 79.02 (1)°, γ = 93.17 (2)°, U = 1244.81 Å^3, Z = 2, μ = 19.1 $\mathrm{cm^{-1}}$, and D_{calcd} = 1.585 g $\mathrm{cm^{-3}}$. A total number of 7485 reflections were collected with an ω–2θ scan mode in the range 3° ≤ θ ≤ 30°, where the octants collected were $-13 \le h \le 13$, $-14 \le k \le 14$, and $0 \le l \le 19$. There were 6233 unique reflections with R_{int} = 0.0232, and 4648 reflections $F > 3\sigma(F)$ were used for structure solution. The structure was solved by using the program SHELXS-82.[12] The heavy atoms were placed by a Patterson synthesis, and the positions of the other atoms were found by difference Fourier synthesis except for H(22)–H(26), which were placed in calculated positions. Data were corrected for absorption[13] with a transmission factor range of 80.9–99.9%. Refinement of positional parameters of all atoms and anisotropic temperature factors for the non-phenyl atoms was done by full-matrix least-squares analysis, and refinement converged to R = 0.049 and R_w = 0.049. After refinement small electron density peaks were observed in the vicinity of C(21)–C(26) (phenyl ring), and this suggested disorder in this ring. Final atomic coordinates for the non-hydrogen atoms are given in Table I, and bond length and bond angle data are collected in Table III.

Table I. Fractional Coordinates (×10^4, Except for Fe, I, and P (×10^5)) and Equivalent Isotropic Temperature Factors (Å^2 × 10^3, Except for Fe, I, and P (Å^2 × 10^4)) for Non-Hydrogen Atoms

	x/a	y/b	z/c	U_{eq}[a]
Fe	15236 (7)	15465 (7)	27610 (6)	376 (1)
I	42937 (4)	12926 (5)	28530 (4)	639 (1)
P	17668 (12)	34431 (12)	23761 (9)	333 (2)
O	2136 (5)	−178 (4)	613 (3)	62 (1)
C(10)	1892 (6)	495 (6)	1430 (5)	50 (1)
C(12)	2993 (6)	4964 (5)	4124 (4)	40 (1)*
C(13)	3649 (7)	6118 (6)	4750 (5)	49 (1)*
C(14)	3857 (6)	7252 (6)	4509 (5)	50 (1)*
C(15)	3422 (7)	7302 (6)	3639 (5)	52 (1)*
C(16)	2770 (6)	6158 (6)	3010 (4)	44 (1)*
C(11)	2549 (5)	4983 (5)	3243 (4)	35 (1)*
C(22)	2323 (6)	4148 (6)	595 (4)	50 (1)*
C(23)	3137 (7)	4135 (7)	−338 (5)	65 (2)*
C(24)	4392 (8)	3336 (7)	−774 (6)	69 (2)*
C(25)	4843 (8)	2564 (7)	−303 (5)	66 (2)*
C(26)	4049 (6)	2571 (6)	645 (4)	50 (1)*
C(21)	2772 (5)	3372 (5)	1110 (4)	41 (1)*
C(32)	−821 (5)	5079 (5)	3166 (4)	40 (1)*
C(33)	−2312 (6)	5320 (6)	3209 (5)	48 (1)*
C(34)	−3023 (7)	4480 (6)	2444 (5)	53 (1)*
C(35)	−2274 (7)	3420 (6)	1638 (5)	52 (1)*
C(36)	−803 (6)	3156 (6)	1588 (4)	45 (1)*
C(31)	−74 (5)	3993 (5)	2367 (3)	34 (1)*
C(1)	−306 (6)	355 (6)	3082 (4)	46 (1)
C(2)	771 (7)	358 (7)	3671 (5)	54 (1)
C(3)	942 (7)	1722 (7)	4326 (5)	59 (2)
C(4)	33 (7)	2574 (7)	4136 (5)	52 (1)
C(5)	−743 (6)	1733 (5)	3351 (4)	43 (1)
C(6)	−1050 (6)	−884 (6)	2402 (5)	54 (1)
C(7)	−2388 (9)	−1153 (9)	3108 (8)	76 (2)
C(8)	−1551 (8)	−596 (7)	1526 (6)	62 (2)
C(9)	−19 (9)	−2138 (7)	1928 (8)	79 (2)

[a] Asterisk indicates an isotropic temperature factor. $U_{\mathrm{eq}} = {}^1/_3\sum_i\sum_j U_{ij}a_i^*a_j^*(a_ia_j)$.

Molecular Mechanics Calculations for $[(\eta^5\text{-}C_5H_4Bu^t)Fe(CO)(P(OMe)_3)I]$. A procedure similar to that outlined previously[14] was employed in which bond length and bond angle parameters (supplementary material) were obtained from the harmonic approximation, with strain energy contributions defined by $V = kr(r - r_0)^2$ and $V = k_\theta(\theta - \theta_0)^2$, respectively ($r_0$ and θ_0 are strain-free values of bond length and bond angles with the force constants, kr and k_θ given in mdyn/Å and mdyn Å). van der Waals interactions were described by Buckingham potential functions of the form $V = A\exp(-Br) - Cr^{-6}$, where r is the distance between two nonbonded atoms. The constants B and C needed for each atom pair were estimated by the method of Scott and Scheraga.[15] The constant A was used to balance the attractive and repulsive parts of the potential function so as to produce a minimum energy at the sum of the van der Waals radii. Energy, U, was measured in units of 10^{-11} erg/molecule.

Torsional contributions to steric strain were calculated from the expression commonly used for 3-fold rotational barriers, i.e. $V = 0.5A(1 + 3\cos\theta)$, but this term was considered to be zero for all torsion angles θ greater than 60°. Torsional interactions except those involving the cyclopentadienyl ring (where A = 0.05) were set at $A = 0.014U$. Constraints were placed on the angular movement (δ) of the atoms bound to cyclopentadienyl carbons out of the plane of the cyclopentadiene ring. This potential function has the form $V = 0.5k\delta^2$. The program used[16] employed a full-matrix Newton–Raphson minimization algorithm and offered the option of "driving" angles about a specified torsion, while refining the structure of each step. In order to model the ring rotation, the necessary torsion was obtained by specifying a bond between Fe and an interactionless "pseudoatom" (Cen) at the centroid of the five-membered ring. This method also allows simplification of the model by manipulation of Fe–Cen–C angles, which were restricted to 90° by

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(11) Orlova, T. Yu; Setkina, V. N.; Sizoi, V. F.; Kursarov, N. *J. Organomet. Chem.* **1983**, *252*, 201.

(12) SHELXS-82: Sheldrick, G. M. In *Crystallographic Computing 3*, Sheldrick, G. M., Krüger, C., Goddard, R., Eds.; Oxford University Press: Oxford, England, 1985.

(13) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A* **1983**, *39*, 158.

(14) Johnston, P.; Denner, L.; Marais, C. F.; Boeyens, J. C. A.; Coville, N. J. *J. Crystallogr. Spectrosc. Res.*, in press.

(15) Scott, R. A.; Scheraga, H. A. *J. Chem. Phys.* **1965**, *42*, 2209.

(16) Boyd, R. H. *J. Chem. Phys.* **1968**, *49*, 2574.

Table II. ^1H and ^{13}C NMR Spectral Data for [(η^5-$C_5H_4Bu^t$)Fe(CO)(L)(I)]

^1H NMR Data[a,b]

L	$\delta(Bu^t)$/ppm	$\delta(H_2)$/ppm	$\delta(H_3)$/ppm	$\delta(H_4)$/ppm	$\delta(H_5)$/ppm	$\Delta(H_2–H_5)$/ppm	θ/deg[c]	J_{P-H_4}/Hz	J_{P-H_2}/Hz
$P(OCH_2)_3CCH_3$[d]	1.56	5.36	5.33	4.70	4.15	1.21	101	4.4	1.4
$P(OMe)_3$[e]	1.22	5.00	4.89	4.13	3.50	1.50	107	4.5	1.5
$P(OPr^i)_3$[f]	1.23	5.11	4.93	4.36	3.62	1.49	130	*k*	*k*
$P(O$-*o*-$CH_3C_6H_4)_3$[g]	1.10	4.98	4.85	4.10	2.60	2.38	141	5.6	2.5
PPh_3[h]	1.31	5.30	4.64	3.69	3.03	2.27	145	6.2	1.5
$P[OCH_2C(CH_3)_3]_3$[i]	1.27	5.06	5.13	4.39	3.60	1.46	*j*	4.5	1.5

^{13}C NMR Data[a,l,m]

	$\delta(C_5H_4C(CH_3)_3)$	$\delta(C_5H_4C(CH_3)_3)$	$\delta(C_1)$	$\delta(C_2)$	$\delta(C_3)$	$\delta(C_4)$	$\delta(C_5)$	$\delta(CO)$
$P(OMe)_3$[n]	31.66	32.22	112.97	89.29 (4.7)	84.79 (4.6)	79.51	73.83 (1.5)	221.69 (46.1)
$P[O$-*o*-$C_6H_4CH_3]_3$[o]	31.58	31.72	117.03	88.64 (5.5)	84.54 (6.0)	80.23 (2.2)	69.38	220.93 (44.1)
PPh_3[p]	31.74	32.21	112.84 (3.5)	91.96 (3.6)	85.77	82.85	71.08	*k*
$P[OCH_2C(CH_3)_3]_3$[q]	31.70	32.28	114.08 (4.9)	88.94 (4.5)	84.96	79.33	72.59	221.82 (46.8)

[a] Recorded in C_6D_6. [b] Relative to Me_4Si. [c] θ = cone angle. Data taken from ref 1. [d] $P(OCH_2)_3CCH_3$: δ 1.90 (s, 3 H, $P(OCH_2)_3CCH_3$), 3.85 (d, 6 H, $J_{P-H} = 4.8$ Hz, $P(OCH_2)_3CCH_3$). [e] $P(OMe)_3$: δ 3.45 (d, 9 H, $J_{P-H} = 11.0$ Hz, $P(OCH_3)_3$). [f] $P(OPr^i)_3$: δ 1.19 (d, 9 H, $J_{H-H} = 6.2$ Hz, $P[OCH(CH_3)_2]_3$), 1.23 (d, 9 H, $J_{H-H} = 6.2$ Hz, $P[OCH(CH_3)_2]_3$), 4.90 (d of septets, 3 H, $J_{H-H} = 6.2$ Hz, $J_{P-H} = 8.7$ Hz, $P[OCH(CH_3)_2]_3$). [g] $P(O$-*o*-$CH_3C_6H_4)_3$: δ 2.27 (s, 9 H, $C_6H_4CH_3$), 6.87 (m, 9 H, Ph $H_{m,p}$), 7.74 (d, 3 H, Ph H_o). [h] PPh_3: δ 6.99 (m, 9 H, Ph $H_{m,p}$), 7.75 (m, 6 H, Ph H_o). [i] $P[OCH_2C(CH_3)_3]_3$: δ 0.95 (s, 27 H, $P[OCH_2C(CH_3)_3]_3$), 3.86 (d of doublets, 3 H, $J_{P-H_b} = 4.4$ Hz, $J_{H_a-H_b} = 9.2$ Hz, $P[OCH_aH_bC(CH_3)_3]_3$), 3.99 (d of doublets, 3 H, $J_{P-H_a} = 3.8$ Hz, $J_{H_a-H_b} = 9.2$ Hz, $P[OCH_aH_bC(CH_3)_3]_3$). [j] Estimate at 110°. [k] Values were not obtained. [l] Figures indicated in parentheses are J_{P-C} values in Hz. [m] Relative to C_6D_6; chemical shift δ given in ppm. [n] $P(OMe)_3$: δ 54.22 (d, $J_{P-C} = 5.8$ Hz, $P(OCH_3)_3$). [o] $P(O$-*o*-$C_6H_4CH_3)_3$: δ 17.98 (s, $P[OC_6H_4CH_3]_3$), 131.04 (d, $J_{P-C} = 4.7$ Hz, Ph substituted C_o), 121.95 (d, $J_{P-C} = 3.7$ Hz, Ph unsubstituted 125.62, 127.62, 132.58 (s, Ph $C_{m,p}$), 151.63 (d, $J_{P-C} = 10.0$ Hz, Ph C_{ipso}). [p] PPh_3: δ 128.93 (d, $J_{P-C} = 9.5$ Hz, Ph C_m), 130.76 (d, $J_{P-C} = 1.7$ Hz, Ph C_p), 134.74 (d, $J_{P-C} = 9.2$ Hz, Ph C_o), 137.58 (d, $J_{P-C} = 42.7$ Hz, Ph C_{ipso}). [q] $P[OCH_2C(CH_3)_3]_3$: δ 27.28 (s, $P[OCH_2C(CH_3)_3]_3$), 33.30 (d, $J_{P-C} = 6.5$ Hz, $P[OCH_2C(CH_3)_3]_3$), 77.03 (d, $J_{P-C} = 7.3$ Hz, $P[OCH_2C(CH_3)_3]_3$).

specifying large force constants. Rigidity of the ring was ensured by fixing bond lengths in the same way. Interactions between Fe and carbons of the cyclopentadienyl ring were therefore ignored. Lone pairs (Lp) on the oxygen atoms of the $P(OMe)_3$ ligand were treated as hydrogen atoms in nonbonded interactions.

In our experience, this force field method produces correct structural features over a surprisingly wide range of force field constants (this is probably due to the fact that the model is over parametrized). While energy differences calculated with such an approximate set of constants are not very accurate, it becomes a relatively straightforward task to obtain useful structural information. The energy profile obtained for rotation of the ring (driving the torsion defined by P–Fe–Cen–C_4) is shown in Figure 1.

Results and Discussion

$C_5H_5Bu^t$ was synthesized from cracked dicyclopentadiene, EtMgBr, and Bu^tCl via a literature procedure.[10] Reaction of the ligand with $[Fe_2(CO)_9]$ in benzene gave [(η^5-$C_5H_4Bu^t$)$Fe(CO)_2$]$_2$ (I), which was subsequently reacted with I_2 to give [(η^5-$C_5H_4Bu^t$)$Fe(CO)_2I$] (II). Both the above new complexes were fully characterized by IR, NMR, and mass spectroscopy.

An attempt to synthesize I from $[Fe(CO)_5]$ and the substituted cyclopentadiene synthesized from the reaction of $Na[C_5H_5]$ and Bu^tCl/THF in refluxing THF was also made. This procedure yielded a ca. 1:1 mixture of [(η^5-$C_5H_4Bu^t$)$Fe(CO)_2$]$_2$ and [(η^5-$C_5H_4Pr^i$)$Fe(CO)_2$]$_2$ (approximate ratios determined by ^1H NMR spectroscopy). Attempts to separate the mixture, their iodo complexes [(η^5-C_5H_4R)$Fe(CO)_2I$], or their substituted derivatives [(η^5-C_5H_4R)Fe(CO)(L)I] (R = Bu^t, Pr^i; L = PPh_3, $P(OMe)_3$) were unsuccessful. The Pr^i complex [(η^5-$C_5H_4Pr^i$)$Fe(CO)_2$]$_2$ was independently synthesized from dimethylfulvene[17] and provided confirmation of the presence of the Pr^i derivative in the reaction mixture. The mechanism for conversion of the *tert*-butyl derivative to the isopropyl derivative is unclear at this stage but may involve a radical pathway.

Reaction of II with L (L = $P(OCH_2)_3CCH_3$, $P(OMe)_3$, $P(O$-*o*-$CH_3C_6H_4)_3$, PPh_3, $P[OCH_2C(CH_3)_3]_3$, $P[OCH(CH_3)_2]_3$) in the presence of I as catalyst[18] readily gave the required products [(η^5-$C_5H_4Bu^t$)Fe(CO)(L)I] in high yield. All the new complexes were fully characterized by IR and NMR spectroscopy, elemental analysis, and mass spectroscopy. The above information unambiguously confirmed the formation of the new complexes.

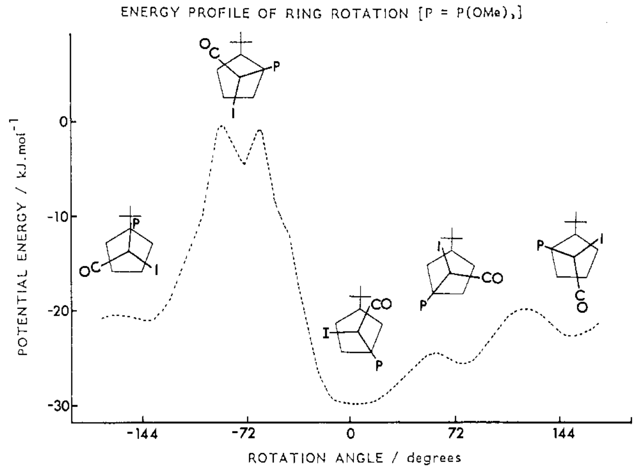

Figure 1. Energy profile for the rotation around the Fe–ring centroid axis. The rotation angle refers to the dihedral angle, ϕ, between P and C_4 of P–Fe–ring centroid–C_4.

^1H and ^{13}C NMR Spectroscopy. ^1H and ^{13}C NMR spectra of the [(η^5-$C_5H_4Bu^t$)Fe(CO)(L)I] complexes are reported in Table II. The ^1H NMR spectra showed four complex multiplets for the four ring protons,[4] and the system was assumed to be first order (AGNX). NOe[19] spectra were used to correlate the ring resonances with the ring protons. For example, irradiation of the Bu^t protons of the $C_5H_4Bu^t$ ligand where L = PPh_3 resulted in the growth of the resonances associated only with the two ring protons adjacent (ortho) to the Bu^t group (Figure 2g). The ring

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(17) Ziegler, K.; Gellert, H.-G.; Martin, A.; Nagel, G.; Schneider, J. *Liebigs Ann. Chem.* **1954**, *589*, 7.

(18) Coville, N. J.; Albers, M. O.; Singleton, E. *J. Chem. Soc., Dalton Trans.* **1982**, 1389.

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

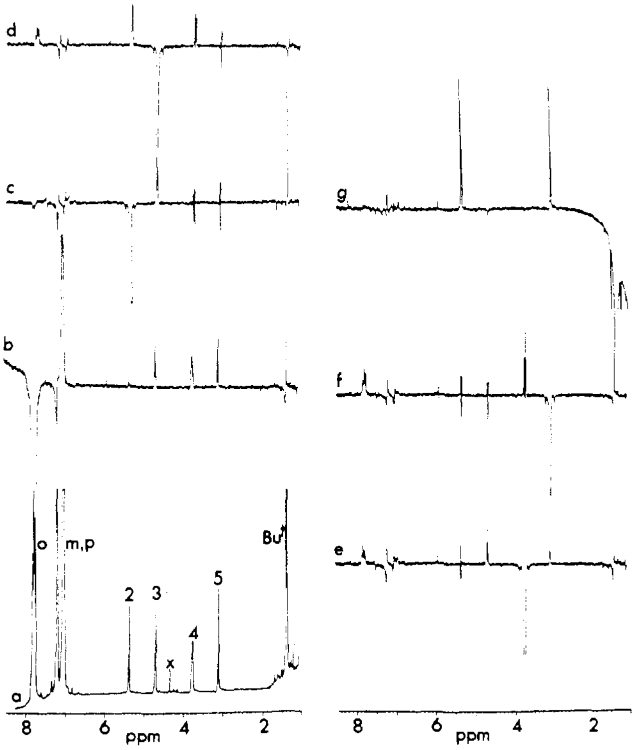
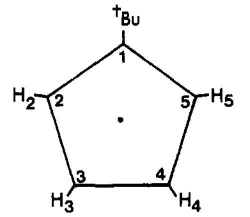


Figure 2. NOe spectra for [(η^5-$C_5H_4Bu^t$)Fe(CO)(PPh_3)I]: (a) nonirradiated, where o, m, and p represent signals corresponding to the ortho, meta, and para protons on the PPh_3 phenyl rings, 2–5 represent signals for the protons H_2–H_5 on the Cp ring, and Bu^t represents the signal for the protons on Bu^t; (b) irradiated ortho phenyl ring proton (H_o); (c) irradiated ring proton H_2; (d) irradiated ring proton H_3; (e) irradiated ring proton H_4; (f) irradiated ring proton H_5; (g) irradiated C_5H_4*Bu^t*. Absorption marked X is an impurity peak.

numbering system was arbitrarily chosen to be anticlockwise, with the protons closest to the Bu^t group being labeled H_2 and H_5.



Ring coupling constants for protons were determined by decoupling experiments. In *all* complexes studied a large P–H_4 coupling constant relative to other P–H couplings was observed (Table II). The larger coupling can readily be detected visually without recourse to decoupling experiments (e.g. Figure 2a; resonance H_4). The nOe spectra (L = $P(OMe)_3$, $P(O$-o-$CH_3C_6H_4)_3$, PPh_3) were consistent with a conformational preference where the group 15 donor ligand is situated in the vicinity of H_4 and far removed from H_1; cf. Figure 2b–f, where irradiation of the ortho phenyl proton of the PPh_3 ligand resulted a growth of the resonances associated with H_3, H_4, and H_5 but not H_2. This information implies that there is a preferred conformation in all the complexes studied. ^{13}C NMR spectra further confirmed this proposal. Assignment of the ^{13}C spectra with the ring carbon atoms was made by using CH-correlated (XHCORR) spectra, since the proton spectra had been assigned from nOe difference spectra (above).[20] Significantly, the carbon atoms C_1 and C_2 showed large coupling to the P atom (relative to C_3–C_5). Thus, both the C–P and H–P coupling constants are consistent with a conformation in which the P atom is in the vicinity of C_4 and H_4.

A variable-temperature NMR study was carried out on [(η^5-$C_5H_4Bu^t$)Fe(CO)(L)I] (L = $P(OMe)_3$, PPh_3) in toluene-d_8

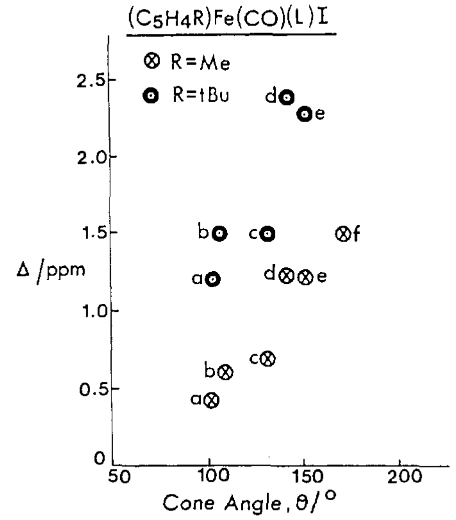


Figure 3. Plot of cone angle (θ/deg) against Δ(H_2–H_5)/ppm for the complexes [(C_5H_4R)Fe(CO)(L)(I)] (R = Me, Bu^t): (a) L = $P(OCH_2)_3CCH_3$; (b) L = $P(OMe)_3$; (c) L = $P(OPr^i)_3$; (d) L = $P(O$-o-$Tol)_3$; (e) L = PPh_3; (f) L = $P(C_6H_{11})_3$.

(−80 to +90 °C). Over this temperature range the values of Δ(H_2–H_5) changed from 2.31 to 2.09 ppm (10%) for L = PPh_3 and from 1.70 to 1.34 ppm (21%) for L = $P(OMe)_3$. The trend is in the correct direction, suggesting that H_2 and H_5 become more similar with increasing temperature and that alternative conformers are now becoming more populated.

Molecular Mechanics Calculations. The molecular mechanical analysis was done to investigate the steric energy as the three groups, I, CO, and $P(OMe_3)$, attached to the central Fe are rotated relative to the substituted cyclopentadienyl ring. The energy profile, reproduced in Figure 1, is counterintuitive but consistent with observation and the simulation procedure that allows full optimization at each rotational step. This permits gearing and accounts for the unexpected local energy minima at the phosphite-eclipsing positions of 0, ±72, and ±144°, respectively. The most favorable situation occurs when the bulky Bu^t and $P(OMe)_3$ groups are separated by two projected bonds. The CO and Bu^t groups mesh together somewhat more conveniently, and therefore this grouping is stabilized relative to the Bu^t–I encounter. Least favorable is the one projected-bond separation between *tert*-butyl and phosphine. In this case however, the Bu^t orientation that meshes best with $P(OMe)_3$ clashes more drastically with CO than I. This qualitative account is in detailed accord with the nonbonded interatomic distances, calculated for each rotameric arrangement.

The significant features are therefore the prediction of an energy minimum with the $P(OMe)_3$ ligand under C_4 and a high-energy barrier corresponding to the approach of the $P(OMe)_3$ ligand to the ring Bu^t group. These general features of the calculations are consistent with the NMR data (see above). Deviations of the ring from planarity and complete bond delocalization, effects that might increase the energy barriers, have not been included in the calculations. However, the observed low-energy barrier is indicative of free rotation around the Fe–Cp centroid axis in solution. This is consistent with the results obtained by other authors.[21]

Steric Effects. From the above data a clear picture has emerged of the steric influences of ring substituents on the ring rotation in complexes of the type [(η^5-C_5H_4R)Fe(CO)(L)I]. That this effect can be quantified is highlighted by comparing the plots of the Tolman cone angle of the ligands L for the complexes [(η^5-C_5H_4R)Fe(CO)(L)I] (R = Me, Bu^t) against Δ(H_2–H_5), the chemical shift difference of the *ortho* ring protons (Table II), as shown in Figure 3. It is also clear that even the ring methyl group is sufficiently large to be "sensed" by the ligands in the ligand set. This is further highlighted by the NMR spectra of [(η^5-

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(20) Carlton, L.; Johnston, P.; Coville, N. J. *J. Organomet. Chem.* **1988**, *339*, 339.

(21) Campi, E. M.; Gatehouse, B. M. K.; Jackson, W. R.; Rae, I. D.; Wang, M. G. *J. Chem. Soc., Chem. Commun.* **1984**, 175.

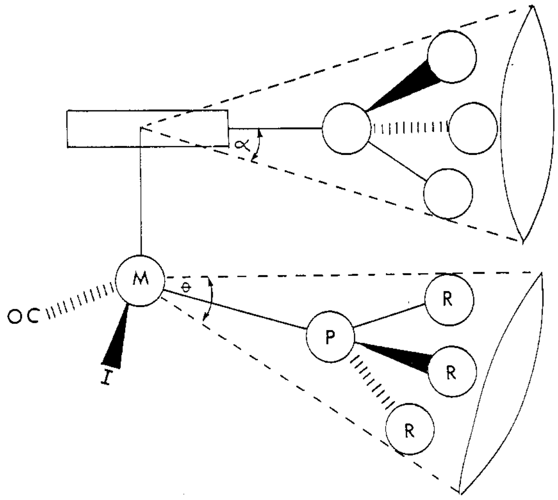

Figure 4. Cone angle interactions for $[(\eta^5\text{-}C_5H_4R)Fe(CO)(PR_3)I]$ (R = H, Me). θ is the Tolman cone angle,[1] and α is a steric measure of the cyclopentadienyl ring substituent.

Table III. Selected Bond Lengths (Å), Bond Angles (deg), and Torsional Angles (deg) with Esd's in Parentheses for $[(\eta^5\text{-}C_5H_4Bu^t)Fe(CO)(PPh_3)(I)]$

Fe–I	2.618 (1)	P–Fe–Cen	123.10
Fe–P	2.234 (1)	C(10)–Fe–Cen	127.20
Fe–C(10)	1.769 (6)	I–Fe–C(10)	89.4 (2)
Fe–C(1)	2.123 (5)	I–Fe–P	97.0 (0)
Fe–C(2)	2.100 (6)	P–Fe–C(10)	91.4 (2)
Fe–C(3)	2.108 (6)	C(10)–Fe–C(1)	92.5 (2)
Fe–C(4)	2.103 (6)	I–Fe–C(2)	93.4 (2)
Fe–C(5)	2.091 (5)	I–Fe–C(3)	89.0 (2)
Fe–Cen[a]	1.731	P–Fe–C(4)	90.6 (2)
O–C(10)	1.095 (6)	Fe–C(10)–O	178.3 (5)
P–C(11)	1.839 (5)	C(1)–C(2)–C(3)	108.0 (5)
C(1)–C(2)	1.409 (7)	C(2)–C(3)–C(4)	109.1 (5)
C(2)–C(3)	1.409 (9)	C(3)–C(4)–C(5)	107.5 (5)
C(3)–C(4)	1.385 (8)	C(1)–C(5)–C(4)	108.1 (5)
C(4)–C(5)	1.425 (8)	C(5)–C(1)–C(6)	124.7 (5)
C(1)–C(5)	1.415 (7)	C(10)–Fe–Cen–C(1)	−1.1
C(1)–C(6)	1.522 (7)	P–Fe–Cen–C(1)	120.9
I–Fe–Cen	120.0	I–Fe–Cen–C(1)	−116.2

[a] Distances to centroid calculated from XANADU; hence, no esd's given.

$C_5H_4D)Fe(CO)(PMePh_2)I]$, which reveals *only one* proton cyclopentadienyl ring resonance (see Experimental Section). This result indicates that the inherent chirality in the molecule is insufficient to account for the separation of the ortho ring protons H_2 and H_5 (i.e. $\Delta(H_2\text{–}H_5)$) and that this separation must be influenced by the steric size of the ring substituent.

Remarkably, even though the cyclopentadienyl ligand and its substituted analogues are one of the most common ligand types encountered in transition-metal chemistry, there has been little attempt to quantify the steric size of these ligands. In a forthcoming publication we will report on our attempts to quantify this steric property by methods similar to those used to measure phosphine cone angles.[22,23]

The new data for the $C_5H_4Bu^t$ complexes have now permitted us to correlate the ^1H and ^{13}C NMR data of the $[(\eta^5\text{-}C_5H_4Me)Fe(CO)(L)I]$ complexes with orientational effects of the ligand set. It is now apparent that for those complexes in *solution* the L group (if bulky) is preferentially situated away from the Me group (C–P and H–P coupling constant data are similar to the data for the $C_5H_4Bu^t$ complexes)[4] even though the molecular structures obtained from X-ray crystallography indicate that the L group occupies a position as close to the ring methyl group as possible. Presumably, the small energy barrier to ring rotation for a methyl-substituted ring allows for packing effects to become dominant and to determine the final solid-state conformation.

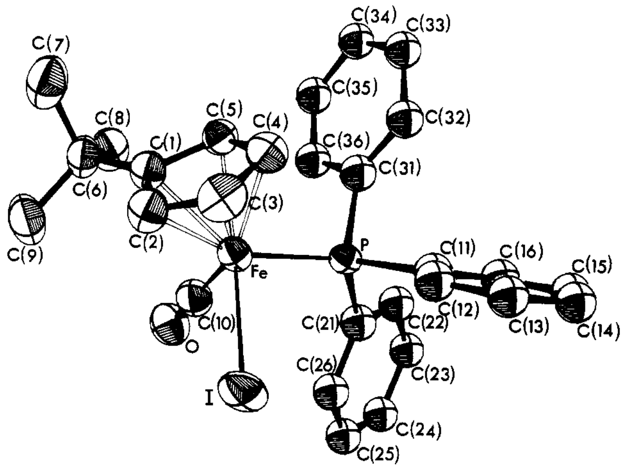

Figure 5. ORTEP drawing of the molecular structure of $[(\eta^5\text{-}C_5H_4Bu^t)Fe(CO)(PPh_3)I]$.

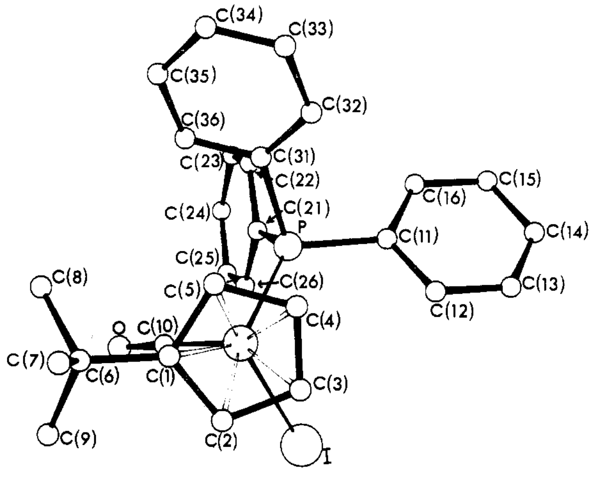

Figure 6. ORTEP drawing of $[(\eta^5\text{-}C_5H_4Bu^t)Fe(CO)(PPh_3)I]$, viewed down the Fe–ring centroid axis.

Table IV. Deviations (Å) from the Least-Squares Mean Plane Defined by the Ring Atoms[a]

C(1)	−0.0135	C(3)	0.0074	C(5)	0.0090	Fe	1.7305
C(2)	0.0129	C(4)	−0.0010	C(6)	−0.2340		

[a] Equation of plane: $(0.7288)x_0 + (0.1179)y_0 + (-0.6750)z_0 = 2.9494$ $[(5.4281)x + (3.7411)y + (-9.5058)z = -2.9494]$.

Crystal Structure of $[(\eta^5\text{-}C_5H_4Bu^t)Fe(CO)(PPh_3)I]$. Bond length and bond angle data are given in Table III, and an ORTEP[24] diagram of the molecule is given in Figure 5. Figure 6 shows a projection of the molecule down the Fe–Cen (Cen = ring centroid) axis and indicates the ligand orientation relative to the ring. As can be seen, the PPh_3 ligand is found close to C_4, indicating that the solution and solid-state structures are equivalent. Furthermore, the CO ligand is close to the Bu^t group, as also predicted by the molecular mechanics calculations ($L = P(OMe)_3$).

Other points to note are as follows. (1) The Fe–I bond length (2.618 (1) Å) is similar to other Fe–I bond lengths in related structures.[25] (2) Least-squares planes indicate only minor shifts of the ring C atoms from planarity (Table IV). (3) The Bu^t group is shifted away from the plane of the ring (8.8°), but this value

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(22) Hunter, G.; Weakley, T. J. R.; Weissensteiner, W. *J. Chem. Soc., Dalton Trans.* **1987**, 1545.

(23) Ferguson, G.; Roberts, P. J.; Alyea, E. C.; Kahn, M. *Inorg. Chem.* **1978**, *17*, 2695.

(24) Johnson, C. K. "ORTEP"; Report ORNL-3794; Oak Ridge National Laboratory: Oak Ridge, TN, 1965.

(25) (a) Balavoine, G.; Brunie, S.; Kagan, H. B. *J. Organomet. Chem.* **1980**, *187*, 125. (b) Andrianov, V. G.; Chapovskii, Yu. A.; Semion, V. A.; Struchkov, Yu. T. *Chem. Commun.* **1968**, 282. (c) Attig, T. G.; Teller, R. G.; Wu, S. M.; Ben, R.; Wojcicki, A. *J. Am. Chem. Soc.* **1979**, *101*, 619. (d) Reference 14.

is similar (9–11°) to values observed in other related complexes containing the $C_5H_4Bu^t$ ring.[26] (4) Fe–C(ring) distances are all close to 2.10 Å and do not reveal that the Fe has been displaced from the ring center. The C(ring)–C(ring) distances are all close to 1.41 Å, where significance cannot be attached to the differences in length as they lie in the range of standard deviations. (5) If the cyclopentadienyl ring is regarded as occupying 3 coordination sites, a near-octahedral arrangement of ligands is observed with P–Fe–I (97.0 (1)°), P–Fe–CO (91.4 (2)°), and I–Fe–CO (89.4 (2)°) angles being close to 90°.

Conclusion. The use of the bulkier substituent on the cyclopentadienyl ligand has resulted in the detection of preferred conformers for all of the new complexes $[(\eta^5\text{-}C_5H_4Bu^t)Fe(CO)(L)I]$. The preferred conformation with L near trans to the ring substituent is readily confirmed by NMR spectroscopy (P–H and P–C coupling constants, nOe spectra), molecular mechanics calculations, and an X-ray crystal structure determination (L = PPh_3). The effect is clearly related to steric effects associated with both the ligand set and the ring substituent.

Acknowledgment. We wish to thank the University of the Witwatersrand and the FRD for financial support, Dr. S. Dobson and C. Allen for assistance with the crystal structure determination, and S. Heiss for running NMR spectra. We also thank a reviewer and Prof. J. W. Faller for helpful comments.

Registry No. $[Fe_2(CO)_9]$, 15321-51-4; $C_5H_5Bu^+$, 41539-65-5; $[(\eta^5\text{-}C_5H_4Bu^t)Fe(CO)_2]_2$, 95765-96-1; $[(\eta^5\text{-}C_5H_4Bu^t)Fe(CO)_2I]$, 122189-23-5; $P(OCH_2)_3CCH_3$, 1449-91-8; $P(OMe)_3$, 121-45-9; $P(O\text{-}o\text{-}CH_3C_6H_4)_3$, 2622-08-4; $P[OCH_2C(CH_3)_3]_3$, 14540-52-4; $P[OCH(CH_3)_2]_3$, 116-17-6; $[(\eta^5\text{-}C_5H_4Bu^t)Fe(CO)(P(OCH_2)_3CCH_3)I]$, 122189-24-6; $[(\eta^5\text{-}C_5H_4Bu^t)Fe(CO)(P(OMe)_3)I]$, 122189-25-7; $[(\eta^5\text{-}C_5H_4Bu^t)Fe(CO)(P[OCH(CH_3)_2]_3)I]$, 122189-26-8; $[(\eta^5\text{-}C_5H_4Bu^t)Fe(CO)(P[OCH_2C(CH_3)_3]_3)I]$, 122189-27-9; $[(\eta^5\text{-}C_5H_4Bu^t)Fe(CO)(PPh_3)]$, 122189-28-0; $[(\eta^5\text{-}C_5H_4Bu^t)Fe(CO)(P(O\text{-}o\text{-}CH_3C_6H_4)_3)I]$, 122212-53-7; $[(\eta^5\text{-}C_5H_4D)Fe(CO)(PMePh_2)I]$, 122189-29-1; $PMePh_2$, 1486-28-8; $[(\eta^5\text{-}C_5H_4D)Fe(CO)_2I]$, 122189-30-4; $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$, 12154-95-9.

Supplementary Material Available: Tables listing details of the force field in the molecular mechanics calculations, parameters of nonbonded interactions (Buckingham potential), and fractional coordinates (×10^4) and common isotropic temperature factors (Å^2 × 10^3) for hydrogen atoms, anisotropic temperature factors (Å^2 × 10^3) for non-hydrogen atoms, and bond lengths (Å) and angles (deg) for $[(\eta^5\text{-}C_5H_4Bu^t)Fe(CO)(PPh_3)I]$ (6 pages); a structure factor table for $[(\eta^5\text{-}C_5H_4Bu^t)Fe(CO)(PPh_3)I]$ (28 pages). Ordering information is given on any current masthead page.

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[26] (a) Howie, R. A.; McQuillan, G. P.; Thompson, D. W.; Lock, G. A. *J. Organomet. Chem.* **1986**, *303*, 213. (b) Howie, R. A.; McQuillan, G. P.; Thompson, D. W. *J. Organomet. Chem.* **1984**, *268*, 149. (c) Erker, G.; Muhlenberndt, T.; Benn, R.; Rubinska, A.; Tsay, Y.-H.; Krüger, C. *Angew Chem., Int. Ed. Engl.* **1985**, *24*, 321.

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Preparation and Properties of Tantalum Imido Complexes and Their Reactions with Alkynes. Coordination Control through Multiple Metal–Ligand Bonding

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Received April 5, 1989

The reaction of $TaCl_5$ with $Me_3SiNHAr$ (NAr = $N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2$), in the presence of donor solvents, provides the imido complexes $Ta(NAr)Cl_3L_2$ (L = tetrahydrofuran (THF, **1**), $^1/_2$ dimethoxyethane (dme, **2**), pyridine (py, **3**), tetrahydrothiophene (THT, **4**)) in high yield. These adducts are shown to exhibit a *cis,mer* geometry. The reaction of these compounds with 1 equiv of lithium alkoxides produces the imido alkoxide metathesis products $Ta(NAr)(OR)Cl_2L_2$ (**5**, OR = $O\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2$ (DIPP), L = THF; 6, OR = DIPP, L = $^1/_2$ dme; **7**, OR = DIPP, L = py; **8**, OR = $O\text{-}2,6\text{-}C_6H_3Me_2$ (DMP), L = py). The reaction of Me_3SiNEt_2 with $TaCl_5$ in toluene/diethyl ether gives a high yield of dimeric $[Ta(NEt_2)_2Cl_3]_2$ (**9**), from which the imido amide $Ta(NAr)(NEt_2)Cl_2(py)_2$ (**11**) can be prepared by the reaction of **9** with LiNHAr. Dimeric **9** can be converted easily to the monomeric adduct $Ta(NEt_2)_2Cl_3(py)$ (**10**) upon reaction with pyridine. When these tantalum imides are reduced in the presence of alkynes, either alkyne adducts or metallacyclopentadienes are isolated. Thus, the compounds $(EtC{\equiv}CEt)Ta(NAr)Cl(py)_2$ (**12**), $(PhC{\equiv}CPh)Ta(NAr)Cl(py)_2$ (**13**), $(Me_3SiC{\equiv}CMe)Ta(NAr)Cl(py)_2$ (**14**), $(\overline{C(CMe_3){=}CHCH{=}C(CMe_3))Ta}(NAr)Cl(py)_2$ (**15**), $(EtC{\equiv}CEt)Ta(NAr)(DIPP)(py)_2$ (**16**), and $(PrC{\equiv}CPr)Ta(NAr)(DIPP)(py)_2$ (**17**) are prepared from the two-electron reduction of either $Ta(NAr)Cl_3(py)_2$ (**3**) or $Ta(NAr)(DIPP)Cl_2(py)_2$ (**7**) in the presence of the appropriate alkyne. Crystals of the imido alkoxide $Ta(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)(O\text{-}2,6\text{-}C_6H_3Me_2)Cl_2(C_5H_5N)_2$ (**8**) belong to the monoclinic space group $P2_1/c$ with a = 9.547 (2) Å, b = 17.089 (3) Å, c = 19.135 (3) Å, β = 91.86 (1)°, and V = 3120.4 Å^3 for Z = 4 with ρ(calcd) = 1.50 g/cm^3. The X-ray structural study on **8** reveals a six-coordinate structure with cis-phenylimide and alkoxide ligands and mutually trans-chloride ligands. The imido linkage features a Ta–N bond of 1.769 (5) Å and Ta–N–C_{ipso} angle of 179.1 (5)°, suggesting a Ta–N bond order between 2 and 3 and emphasizing the additional π donation of the nitrogen lone pair to an empty metal orbital. The phenoxide ligand is characterized by a Ta–O distance of 1.905 (5) Å and Ta–O–C_{ipso} angle of 145.1 (5)°.

Introduction

The control of reactivity at a transition-metal center by steric manipulations is effected typically by varying the size of its anionic ligands[1] or controlling the "cone angle" of its neutral ligands,[2] which often promote coordinative unsaturation by ligand dissociation.[3] A more extreme method of steric control uses a formal dianionic ligand—occupying a single coordination site—in the place of two monoanions. Therefore, by the introduction of metal–ligand multiple bonding at this site,[4] the coordination number of the metal is decreased while its oxidation state is sustained. This approach has been used in designing olefin metathesis catalysts,[5] in developing reactive compounds for alkane

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[1] See, for example: (a) Kruse, W. *J. Organomet. Chem.* **1972**, *42*, C39. (b) Giering, W. P.; Rosenblum, M. *J. Organomet. Chem.* **1970**, *25*, C71. (c) Listemann, M. L.; Schrock, R. R.; Dewan, J. C.; Kolodziej, R. M. *Inorg. Chem.* **1988**, *27*, 264. (d) Akiyama, M.; Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Haitko, D. A.; Little, D.; Fanwick, P. E. *Inorg. Chem.* **1979**, *18*, 2266.

[2] See, for example: (a) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313. (b) Bartik, T.; Himmler, T.; Schulte, H.-G.; Seevogel, K. *J. Organomet. Chem.* **1984**, *272*, 29. (c) Tolman, C. A.; Seidel, W. C.; Gosser, L. W. *Organometallics* **1983**, *2*, 1391.

[3] Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.

[4] Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; Wiley-Interscience: New York, 1988.

[5] (a) Schrock, R. R.; DePue, R. T.; Feldman, J.; Schaverien, C. J.; Dewan, J. C.; Liu, A. H. *J. Am. Chem. Soc.* **1988**, *110*, 1423. (b) Schaverien, C. J.; Dewan, J. C.; Schrock, R. R. *J. Am. Chem. Soc.* **1986**, *108*, 2771. (c) Murdzek, J. S.; Schrock, R. R. *Organometallics* **1987**, *6*, 1373.