

η^5 -Cyclopentadienyl and η^5 -Methylcyclopentadienyl 1,2-Bis(dimethylphosphino)ethane Complexes of Titanium(II). The Crystal Structure of $\text{Ti}(\text{C}_5\text{H}_4\text{Me})_2(\text{dmpe})^\dagger$

Gregory S. Girolami and Geoffrey Wilkinson*

Chemistry Department, Imperial College of Science and Technology, London SW7 2AY

Mark Thornton-Pett and Michael B. Hursthouse*

Chemistry Department, Queen Mary College, London E1 4NS

The interaction of the titanium(II) complex $\text{trans-TiCl}_2(\text{dmpe})_2$ with 2 equivalents of $\text{Na}(\text{C}_5\text{H}_5)$ or $\text{Na}(\text{C}_5\text{H}_4\text{Me})$ in diethyl ether gives the dark orange cyclopentadienyl compounds $\text{Ti}(\text{C}_5\text{H}_4\text{R})_2(\text{dmpe})$ ($\text{R} = \text{H}$ or Me , $\text{dmpe} = \text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2$). These diamagnetic 18-electron species give n.m.r. spectra consistent with a bent metallocene structure, confirmed by the X-ray structure analysis of $\text{Ti}(\text{C}_5\text{H}_4\text{Me})_2(\text{dmpe})$ for which Ti-P 2.533(6) Å (mean), Ti-C 2.310(5)—2.441(6) Å, P-Ti-P 76.9(2)°, and centroid-Ti-centroid = 135.3(2)°. The cyclopentadienyl rings are very slightly tilted towards the dmpe ligand due to non-bonding contacts between the ring-bound methyl groups.

In view of the substantial tilting of the cyclopentadienyl (cp) rings in the bis(tertiary phosphine) and chelate 1,2-bis(dimethylphosphino)ethane (dmpe) adducts of manganese(II) cyclopentadienide¹ which are formally 21-electron systems, it was of interest to study a comparable system with formally an 18-electron configuration. Accordingly we have prepared the adducts $\text{Ti}(\eta^5\text{-C}_5\text{H}_5)_2(\text{dmpe})$ and $\text{Ti}(\eta^5\text{-C}_5\text{H}_4\text{Me})_2(\text{dmpe})$ and determined the structure of the latter by X-ray diffraction. There are no bis(tertiary phosphine) adducts of the $(\text{cp})_2\text{Ti}$ unit although adducts with CO, PF_3 , and $\text{P}(\text{OMe})_3$ are known as well as the mixed species $\text{Ti}(\text{C}_5\text{H}_5)_2(\text{CO})(\text{PR}_3)$ ($\text{R} = \text{Et}$ or Ph).²

Results and Discussion

The reduction of TiCl_4 with magnesium in the presence of dmpe gives the octahedral titanium(II) complex, $\text{trans-TiCl}_2(\text{dmpe})_2$.³ Interaction of this compound with 2 equivalents of $\text{Na}(\text{C}_5\text{H}_5)$ or $\text{Na}(\text{C}_5\text{H}_4\text{Me})$ in diethyl ether gives the orange-black complexes $\text{Ti}(\text{C}_5\text{H}_4\text{R})_2(\text{dmpe})$ ($\text{R} = \text{H}$ or Me). An alternative synthesis, reduction of $\text{Ti}(\text{C}_5\text{H}_5)_2\text{Cl}_2$ with sodium amalgam in the presence of dmpe, also yields $\text{Ti}(\text{C}_5\text{H}_5)_2(\text{dmpe})$, although in lower yield.

Both of these titanium(II) species are diamagnetic. The n.m.r. parameters are similar to those of the zirconium complex, $\text{Zr}(\text{C}_5\text{H}_5)_2(\text{dmpe})$, which, along with PMePh_2 , PMe_2Ph , and $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ analogues, was made by ligand-induced reductive elimination of methylcyclohexane from $\text{Zr}(\text{C}_5\text{H}_5)_2\text{H}(\text{CH}_2\text{C}_6\text{H}_{11})$; ⁴ the low oxidation state is reflected by the up-field chemical shifts of the ring protons (δ 4.60) relative to tetravalent analogues. Both compounds are air and moisture sensitive and decompose upon attempted sublimation, and do not give titanium-containing ions in the electron-impact mass spectra.

The crystal structure of $\text{Ti}(\text{C}_5\text{H}_4\text{Me})_2(\text{dmpe})$ has been de-

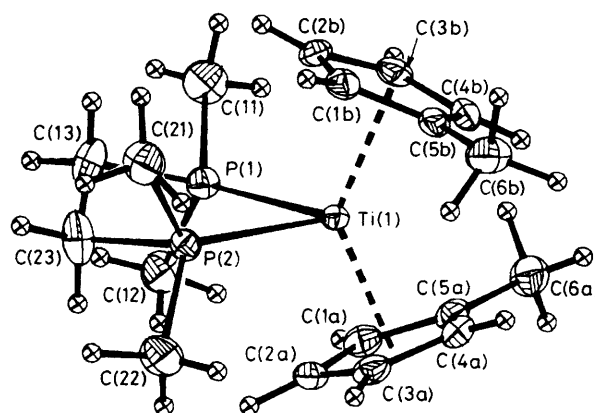


Figure 1. The molecule of $\text{Ti}(\text{C}_5\text{H}_4\text{Me})_2(\text{dmpe})$ showing the atom numbering scheme

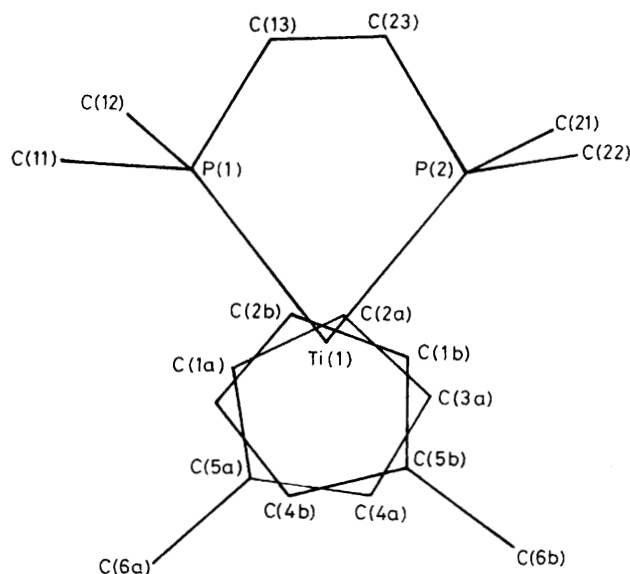
termined by X-ray analysis, Figure 1; important bond lengths and angles are included in Table 1. The molecule has the classical, bent $\text{Ti}(\text{C}_5\text{H}_5)_2\text{X}_2$ structure, with a centroid-Ti-centroid angle of 135.3(2)°. Although one of the cp rings is completely fixed, orientationally, the other shows a small amount of disorder, with two orientations, having occupancies of 0.85 and 0.15. The relative orientation of the fixed and major occupancy $\text{C}_5\text{H}_4\text{Me}$ rings is staggered with respect to the cp rings and the two methyl groups, which are distal to the dmpe ligand, are separated by a projected twist angle of ca. 102° (see Figure 2). The $\text{C}_5\text{H}_4\text{Me}$ group at the minor occupancy site is rotated by a further 40° giving the C_5 ring an approximately eclipsed orientation relative to the fixed $\text{C}_5\text{H}_4\text{Me}$ ring. The geometries of the rings themselves are normal with only small, and barely significant variations in C-C distances [range 1.384(6)—1.428(6) Å], and the rings are accurately planar, with the methyl groups showing only very small out-of-plane deviations [C(6a), -0.04; C(6b), -0.09 Å]. The Ti-C distances show a small and consistent spread of values, from 2.310(5) to 2.441(5) Å, and this corresponds to a small tilt of each ring from perfect η^5 -bonding, with τ values of 3.8 and 4.7°.

[†] [1,2-Bis(dimethylphosphino)ethane]bis(η -methylcyclopentadienyl)titanium.

Supplementary data available (No. SUP 56005, 5 pp.): thermal parameters, H-atom co-ordinates, complete bond lengths and angles. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

Table 1. Selected bond lengths (Å) and angles (°) for $\text{Ti}(\text{C}_5\text{H}_4\text{Me})_2(\text{dmpe})^*$

| | | | | | | | |
|------------------|-----------------|-------------------|------------|------------------|----------|------------------|----------|
| Ti(1)–P(1) | 2.527(4) | Ti(1)–P(2) | 2.540(4) | C(1a)–C(2a) | 1.423(6) | C(1b)–C(2b) | 1.415(7) |
| Ti(1)–C(1a) | 2.395(5) | Ti(1)–C(16) | 2.434(6) | C(2a)–C(3a) | 1.428(6) | C(2b)–C(3b) | 1.438(6) |
| Ti(1)–C(2a) | 2.314(5) | Ti(1)–C(2b) | 2.354(5) | C(3a)–C(4a) | 1.397(6) | C(3b)–C(4b) | 1.403(6) |
| Ti(1)–C(3a) | 2.314(5) | Ti(1)–C(3b) | 2.310(5) | C(4a)–C(5a) | 1.404(6) | C(4b)–C(5b) | 1.420(6) |
| Ti(1)–C(4a) | 2.367(5) | Ti(1)–C(4b) | 2.348(6) | C(5a)–C(1a) | 1.384(6) | C(5b)–C(1b) | 1.391(6) |
| Ti(1)–C(5a) | 2.430(5) | Ti(1)–C(5b) | 2.441(6) | C(5a)–C(6a) | 1.511(7) | C(5b)–C(6b) | 1.477(7) |
| P(1)–C(Me) | 1.826, 1.831(6) | | P(2)–C(Me) | 1.840, 1.825(6) | | C(13)–C(23) | 1.501(8) |
| P(1)–C(13) | 1.847(6) | | P(2)–C(23) | 1.857(6) | | | |
| P(1)–Ti(1)–P(2) | 76.9(2) | Cp(1)–Ti(1)–Cp(2) | 135.3(2) | Ti(1)–P(1)–C(11) | 123.1(2) | Ti(1)–P(2)–C(21) | 123.4(2) |
| P(1)–Ti(1)–Cp(1) | 107.8(2) | P(1)–Ti(1)–Cp(1) | 107.8(2) | Ti(1)–P(1)–C(12) | 121.5(2) | Ti(1)–P(2)–C(22) | 122.3(2) |
| P(1)–Ti(1)–Cp(2) | 106.2(2) | P(2)–Ti(1)–Cp(2) | 107.6(2) | Ti(1)–P(1)–C(13) | 110.3(2) | Ti(1)–P(2)–C(23) | 110.3(2) |
| | | | | P(1)–C(13)–C(23) | 108.4(4) | C(13)–C(23)–P(2) | 110.6(4) |

* Cp is the centroid of the C_5 ring.**Figure 2.** View of the molecule $\text{Ti}(\text{C}_5\text{H}_4\text{Me})_2(\text{dmpe})$ perpendicular to the plane $\text{Ti}(1)$, $\text{P}(1)$, $\text{P}(2)$, showing relative orientations of the fixed, and major occupancy disordered $\text{C}_5\text{H}_4\text{Me}$ rings

The slight tilting of the $\text{C}_5\text{H}_4\text{Me}$ groups towards the dmpe ligand is consistent with structural studies of other bent metallocenes. Thus, all $\text{M}(\text{C}_5\text{H}_4\text{Me})_2\text{L}_n$ compounds show a similar tilt of *ca.* 2° that can be attributed to $\text{H} \cdots \text{H}$ contacts involving the ring-bound methyl groups.⁵ Many $\text{M}(\text{C}_5\text{Me}_5)_2\text{L}_n$ complexes also show a small tilt for presumably similar reasons.⁶ In general, a tilt angle of *ca.* 3° or less can be interpreted to indicate simple η^5 -bonding for a C_5R_5 ring.

In contrast the rings in the manganese complex $\text{Mn}(\text{C}_5\text{H}_5)_2(\text{dmpe})$ show a tilt angle, τ , of 7.5° , with $\text{Mn}-\text{C}$ distances varying from 2.492(6) to 2.742(8) Å.¹ In this case, the cyclopentadienyl rings are tilted in the direction opposite to that in the titanium complex, that is, *away* from the dmpe ligand, and it was presumed that steric interactions between the dmpe and cp groups were responsible for this tilting, even though the formal 21-electron nature of the complex suggests that electronic factors may have to be considered. Obviously a better assessment of the situation would be possible from a comparison of the structures of $\text{Mn}(\text{C}_5\text{H}_5)_2(\text{dmpe})$ and $\text{Ti}(\text{C}_5\text{H}_5)_2(\text{dmpe})$, but unfortunately, the latter complex does not crystallize well enough for X-ray studies. Nevertheless, the structure of $\text{Ti}(\text{C}_5\text{H}_4\text{Me})_2(\text{dmpe})$ clearly implies symmetrical η^5 -bonding in $\text{Ti}(\text{C}_5\text{H}_5)_2(\text{dmpe})$ also.

The existence of $\text{Ti}(\text{C}_5\text{H}_5)_2(\text{dmpe})$ and $\text{Mn}(\text{C}_5\text{H}_5)_2(\text{dmpe})$ prompted attempts to prepare analogous vanadium(II) and chromium(II) species. However, reaction of $\text{VCl}_2(\text{dmpe})_2$ or $\text{CrCl}_2(\text{dmpe})_2$ ³ with 2 equivalents of $\text{Na}(\text{C}_5\text{H}_5)$ gave only the metallocenes $\text{V}(\text{C}_5\text{H}_5)_2$ and $\text{Cr}(\text{C}_5\text{H}_5)_2$. Adduct formation between $\text{V}(\text{C}_5\text{H}_5)_2$ and excess of dmpe does not even occur reversibly in solution, as shown by an e.s.r. study in toluene (see Experimental section). These results are consistent with an earlier study indicating no reaction between vanadocene and triethylphosphine.⁷ By contrast, vanadocene forms complexes⁸ with a wide variety of π -acceptors such as carbon monoxide, olefins, acetylenes, and bipyridine. Similarly, chromocene reacts with CO to give the 18-electron complex $\text{Cr}(\text{C}_5\text{H}_5)_2(\text{CO})$, although this complex is not particularly stable.⁹ The lack of reactivity of $\text{V}(\text{C}_5\text{H}_5)_2$ and $\text{Cr}(\text{C}_5\text{H}_5)_2$ towards Lewis bases is not entirely unexpected considering the rather stable low-spin nature of these metallocenes. The chemical anomaly is not that $\text{V}(\text{C}_5\text{H}_5)_2(\text{dmpe})$ and $\text{Cr}(\text{C}_5\text{H}_5)_2(\text{dmpe})$ do not exist, but that $\text{Mn}(\text{C}_5\text{H}_5)_2(\text{dmpe})$ *does*. The unusual electronic and magnetic properties of manganocene are undoubtedly responsible for this behaviour.

Experimental

Microanalyses were by Pascher (Bonn). Melting points in sealed tubes under argon are uncorrected. Spectrometers: n.m.r., JEOL FX 90 Q, δ values in p.p.m. in C_6D_6 at 25°C , referenced to SiMe_4 ; i.r., Perkin-Elmer 683, spectra in Nujol mulls; e.s.r., Varian E12 (X-band).

All operations were carried out under vacuum or under purified argon. Solvents were distilled from sodium or sodium-benzophenone under nitrogen before use. The light petroleum used had b.p. $40\text{--}60^\circ\text{C}$.

[1,2-Bis(dimethylphosphino)ethane]bis(η^5 -cyclopentadienyl)-titanium(II).—(a) From $\text{TiCl}_2(\text{dmpe})_2$. To a solution of $\text{TiCl}_2(\text{dmpe})_2$ (0.33 g, 0.79 mmol) in diethyl ether (50 cm^3) was added sodium cyclopentadienide (0.75 cm^3 of a 2 mol dm^{-3} solution in tetrahydrofuran, 1.50 mmol). The solution turned yellow-orange, and was stirred for 2 h. The solvent was removed, and the residue extracted with light petroleum (50 cm^3). The filtered extract was concentrated to *ca.* 40 cm^3 , and cooled to -20°C to give orange-black prisms. Yield 0.20 g, 77%; m.p. 195°C (decomp.) (Found: C, 57.7; H, 8.1; P, 18.5. $\text{C}_{16}\text{H}_{26}\text{P}_2\text{Ti}$ requires C, 58.6; H, 8.0; P, 18.8%). N.m.r.: ^1H , 4.60 (s, C_5H_5), 0.81 (s, PMe_2), and 0.72 (t, PCH_2 , $^2J_{\text{PH}} + ^3J_{\text{PH}} = 12\text{ Hz}$); ^{31}P - $\{^1\text{H}\}$, 50 (br s).

(b) By reduction of $\text{Ti}(\text{C}_5\text{H}_5)_2\text{Cl}_2$. To a solution of $\text{Ti}(\text{C}_5\text{H}_5)_2\text{Cl}_2$ (0.52 g, 2.09 mmol) in toluene (25 cm^3) and diethyl ether

Table 2. Atomic fractional co-ordinates for $\text{Ti}(\text{C}_5\text{H}_4\text{Me})_2(\text{dmpe})$

| Atom | x | y | z | Atom | x | y | z |
|-------|-----------|------------|------------|-------|-----------|-----------|------------------------|
| Ti(1) | -439(1) | 2 094(0.5) | 1 458(0.5) | C(6a) | -3 677(5) | 867(3) | 409(3) |
| P(1) | 1 091(1) | 2 767(1) | 257(1) | C(1b) | 1 624(5) | 1 346(3) | 2 402(3) ^a |
| C(11) | 2 223(6) | 2 084(3) | -482(3) | C(2b) | 2 075(4) | 1 284(3) | 1 551(3) ^a |
| C(12) | 62(5) | 3 533(3) | -519(3) | C(3b) | 820(5) | 757(3) | 1 094(3) ^a |
| C(13) | 2 730(5) | 3 546(3) | 677(3) | C(4b) | -351(5) | 524(2) | 1 680(3) ^a |
| P(2) | 1 025(1) | 3 452(1) | 2 146(1) | C(5b) | 139(5) | 887(2) | 2 490(3) ^a |
| C(21) | 2 838(5) | 3 358(3) | 2 904(3) | C(6b) | -669(6) | 752(4) | 3 296(3) ^a |
| C(22) | -92(6) | 4 341(3) | 2 677(3) | C(1c) | -193(12) | 667(11) | 2 040(11) ^b |
| C(23) | 2 012(6) | 4 143(3) | 1 332(3) | C(2c) | 197(12) | 569(11) | 1 294(11) ^b |
| C(1a) | -2 740(4) | 2 520(2) | 516(2) | C(3c) | 1 555(12) | 985(10) | 1 325(10) ^b |
| C(2a) | -2 455(4) | 3 181(2) | 1 164(2) | C(4c) | 1 904(12) | 1 359(11) | 2 083(11) ^b |
| C(3a) | -2 785(4) | 2 765(2) | 1 954(2) | C(5c) | 718(12) | 1 141(11) | 2 497(11) ^b |
| C(4a) | -3 244(4) | 1 872(3) | 1 769(2) | C(6c) | 500(12) | 1 353(11) | 3 457(11) ^b |
| C(5a) | -3 219(4) | 1 723(2) | 891(2) | | | | |

Occupancy factor = 0.85. ^b Occupancy factor = 0.15.

(25 cm³) was added dmpe (0.4 cm³, 2.67 mmol). The solution was transferred to excess of sodium amalgam (1 g in 5 cm³), and stirred for 12 h. The solvent was removed and the residue treated as above. Yield 0.35 g, 52%.

[1,2-Bis(dimethylphosphino)ethane]bis(methylcyclopentadienyl)titanium(II).—To a solution of $\text{TiCl}_2(\text{dmpe})_2$ (0.81 g, 2.54 mmol) in diethyl ether (50 cm³) was added sodium methylcyclopentadienide (4 cm³ of a 1 mol dm⁻³ solution in tetrahydrofuran, 4.0 mmol). The yellow-orange solution was stirred for 2 h, and the solvent removed. The residue was extracted into light petroleum (80 cm³), the extract filtered, concentrated to 50 cm³, and cooled to -20 °C to give orange-black prisms. Yield 0.57 g, 68%; m.p. 140–144 °C (Found: C, 60.2; H, 8.3; P, 17.2. $\text{C}_{18}\text{H}_{30}\text{P}_2\text{Ti}$ requires C, 60.7; H, 8.4; P, 16.6%). N.m.r.: ¹H 4.6 (s, $\text{C}_5\text{H}_4\text{Me}$), 4.34 (s, $\text{C}_5\text{H}_4\text{Me}$), 1.75 (s, $\text{C}_5\text{H}_4\text{Me}$), 0.84 (t, PMe_2 , ² $J_{\text{PH}} + ^4J_{\text{PH}} = 4.5$ Hz), and 0.80 (t, PCH_2 , ² $J_{\text{PH}} + ^3J_{\text{PH}} = 12.2$ Hz); ³¹P-{¹H}, 50 (br s).

Reactions of $\text{VCl}_2(\text{dmpe})_2$ and $\text{CrCl}_2(\text{dmpe})_2$ with $\text{Na}(\text{C}_5\text{H}_5)$.—To a suspension of $\text{VCl}_2(\text{dmpe})_2$ (0.13 g, 0.31 mmol) in diethyl ether (50 cm³) was added sodium cyclopentadienide (0.3 cm³ of 2 mol dm⁻³ solution in tetrahydrofuran, 0.60 mmol). The initially purple solution turned pale pink, and was stirred for 12 h. The solvent was removed, the residue extracted into toluene (50 cm³), and the filtered extract concentrated to 5 cm³. Cooling to -20 °C afforded purple crystals of vanadocene, identified by i.r. spectroscopy. Yield: 53%. The analogous reaction of $\text{CrCl}_2(\text{dmpe})_2$ with $\text{Na}(\text{C}_5\text{H}_5)$ gave chromocene as red crystals. Yield: 61%.

Interaction of $\text{V}(\text{C}_5\text{H}_5)_2$ with dmpe.—To a solution of vanadocene (0.10 g, 0.55 mmol) in toluene (10 cm³) was added dmpe (0.2 cm³, 1.33 mmol). No change in the colour of the solution occurred. A portion of the solution was transferred to an e.s.r. tube, and its e.s.r. spectrum recorded as a glass at -196 °C. The spectrum was identical with that of pure vanadocene.¹⁰

X-Ray Studies.—Crystals used for X-ray work were sealed under argon in Lindemann capillaries. Unit-cell and intensity data were obtained at 295 K using a Nonius CAD 4 diffractometer operating in the ω -2 θ scan mode and using graphite-monochromated $\text{Mo-K}\alpha$ radiation ($\lambda = 0.71069$ Å) in a manner previously described in detail.¹¹ The structure was solved and refined via routine procedures. Although one of the $\text{C}_5\text{H}_4\text{Me}$ rings [C(1)—C(6)] was completely ordered, the other

showed a small degree of disorder, with two orientations having occupancy factors of 0.85 and 0.15. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms on all carbons except those of the $\text{C}_5\text{H}_4\text{Me}$ ring in the low-occupancy site (which were included in idealized positions) were located on difference maps and refined with isotropic thermal parameters.

Crystal data. $\text{C}_{18}\text{H}_{30}\text{P}_2\text{Ti}$, $M = 356.29$, monoclinic, $a = 8.073(1)$, $b = 14.782(2)$, $c = 15.777(2)$ Å, $\beta = 93.34(3)^\circ$, $U = 1 879.7$ Å³, space group $P2_1/n$, $Z = 4$, $D_c = 1.26$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 5.39$ cm⁻¹, $F(000) = 760$.

Data recorded over $1.5 < \theta < 25.0^\circ$, with ω scan widths of $0.85 + 0.35 \tan \theta$, gave 3 303 unique data of which 2 513 were observed [$I > 1.5\sigma(I)$]. Final R and R' values were 0.0429 and 0.0450 for 349 parameters with least-squares weights of $w = 1/[\sigma^2(F) + 0.0005F^2]$. Final atomic fractional co-ordinates for non-hydrogen atoms are given in Table 2.

Acknowledgements

We thank the S.E.R.C. for support of the crystallographic studies, the National Science Foundation for a N.A.T.O. Postdoctoral Fellowship (to G. S. G.), and Dr. C. G. Howard for assistance.

References

- C. G. Howard, G. S. Girolami, G. Wilkinson, M. Thornton-Pett, and M. B. Hursthouse, *J. Am. Chem. Soc.*, 1984, **106**, 2033.
- J. G. Murray, *J. Am. Chem. Soc.*, 1961, **83**, 1287; J. L. Atwood, K. E. Stone, H. G. Alt, D. C. Hrcncir, and M. D. Rausch, *J. Organomet. Chem.*, 1977, **132**, 367; B. H. Edwards, R. D. Rogers, D. J. Sikora, J. L. Atwood, and M. D. Rausch, *J. Am. Chem. Soc.*, 1983, **105**, 416; M. Chang, P. L. Timms, and R. B. King, *J. Organomet. Chem.*, 1980, **199**, C3; A. M. McPherson, B. F. Fieselmann, D. L. Lichtenberger, G. L. McPherson, and G. D. Stucky, *J. Am. Chem. Soc.*, 1979, **101**, 3425.
- G. S. Girolami, G. Wilkinson, M. Thornton-Pett, and M. B. Hursthouse, unpublished work.
- K. I. Gell and J. Schwartz, *J. Am. Chem. Soc.*, 1981, **103**, 2687.
- J. L. Petersen and L. F. Dahl, *J. Am. Chem. Soc.*, 1975, **97**, 6422; R. Jungst, D. Sekutowski, J. Davis, M. Luly, and G. D. Stucky, *Inorg. Chem.*, 1977, **16**, 1645; P. L. Johnson, S. A. Cohen, T. J. Marks, and J. Williams, *J. Am. Chem. Soc.*, 1978, **100**, 2709; S. B. Jones and J. L. Petersen, *Inorg. Chem.*, 1981, **20**, 2889.
- R. D. Sanner, J. M. Manriquez, R. E. Marsh, and J. E. Bercaw, *J. Am. Chem. Soc.*, 1976, **98**, 8351; R. D. Sanner, D. M. Duggan, T. C. McKenzie, R. E. Marsh, and J. E. Bercaw, *ibid.*, p. 8358; T. C. McKenzie, R. D. Sanner, and J. E. Bercaw, *J. Organomet.*

- Chem.*, 1975, **102**, 457; S. A. Cohen, P. R. Auburn, and J. E. Bercaw, *J. Am. Chem. Soc.*, 1983, **105**, 1136.
- 7 P. M. Druce, B. M. Kingston, M. F. Lappert, T. Spalding, and R. Srivastava, *J. Chem. Soc. A*, 1969, 2106.
- 8 G. Fachinetti, S. Del Nero, and C. Floriani, *J. Chem. Soc., Dalton Trans.*, 1976, 1046; F. Calderazzo, G. Fachinetti, and C. Floriani, *J. Am. Chem. Soc.*, 1974, **96**, 3695; G. Fachinetti, C. Floriani, A. Chiesi-Villa, and C. Guastini, *Inorg. Chem.*, 1979, **18**, 2282; J. L. Petersen and L. Griffith, *ibid.*, 1980, **19**, 1852.
- 9 K. L. Wong and H. H. Brintzinger, *J. Am. Chem. Soc.*, 1975, **97**, 5143.
- 10 R. Prins, P. Biloen, and J. D. van Voost, *J. Chem. Phys.*, 1967, **46**, 1216.
- 11 M. B. Hursthouse, R. A. Jones, K. M. A. Malik, and G. Wilkinson, *J. Am. Chem. Soc.*, 1979, **101**, 4128.

Received 23rd January 1984; Paper 4/119