arrangement with the absence of any molecular symmetry. Clearly at 233 K the exchange rate is sufficiently rapid that line broadening is evident in the ^{1}H NMR spectrum (Fig. 2). The ratio of the major (a) to minor (b) isomers varies with temperature (in CD_2Cl_2 from 6·2:1 at 183 K through 5·4:1 at 213 K to 4·7:1 at 233 K). This allows estimates of ΔH and ΔS for the (a) to (b) equilibrium of 2 kJ mol^{-1} and -4 J K^{-1} mol^{-1} respectively, to be made in that solvent. The small entropy value would be expected for such a process, and the enthalpy difference favours the sterically more favoured form.

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(η⁵-Methylcyclopentadienyl)(N,N,N′,N′-tetramethylethylenediamine)lithium*

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Abstract. [Li(C_6H_7)($C_6H_{16}N_2$)], $M_r = 202·27$, orthorhombic, *Pbca*, $a = 11·238$ (2), $b = 16·014$ (3), $c = 14·522$ (3) Å, $V = 2613·5$ (8) Å³, $Z = 8$, $D_x = 1·028$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0·549$ cm^{-1}, $F(000) = 896$, $T \simeq 173$ K, $R = 0·042$ [1845 data, $I > 2\sigma(I)$]. The structure consists of discrete (η^5-$C_5H_4CH_3$) Li.tmen units (tmen = N,N,N',N'-tetramethylethylenediamine). The Li atom is coordinated by the methylcyclopentadienyl ring and the two N atoms of the chelating tmen ligand. The average Li—C distance is 2·258 Å; the Li—N distances are 2·130 (3) and 2·124 (3) Å.

Introduction. Molecular structures of several silylated cyclopentadienyl lithium derivatives have been reported in the literature. They all show the Li atom nearly symmetrically sited above the ring and coordinated by one additional mono- or bidentate Lewis base.

The distance between the Li atom and the ring plane ($= Z$) varies from 1·794 Å in {[Si(CH_3)$_3$]$_3$-C_5H_2}Li.quinuclidine (Jutzi, Schlüter, Pohl & Saak, 1985) to 1·980 Å in {[Si(CH_3)$_3$]$_3C_5H_2$}Li.tmen (Jutzi, Schlüter, Pohl & Saak, 1985). For coordination

number CN = 4 (the cyclopentadienyl ring is regarded as a tridentate ligand) as obtained for {[Si(CH_3)$_3$]$_3C_5H_2$}Li.quinuclidine (Jutzi, Schlüter, Pohl & Saak, 1985) and {[Si(CH_3)$_3$]$_3C_5H_2$}Li.THF (Jutzi, Leffers, Pohl & Saak, 1989), Li—Z is found to be 1·794 and 1·803 Å, respectively. In the five-coordinated species such as {[Si(CH_3)$_3$]C_5H_4}Li.tmen (Lappert, Singh, Engelhardt & White, 1984), {[Si(CH_3)$_3$]$_3C_5H_2$}Li.tmen (Jutzi, Schlüter, Pohl & Saak, 1985) and {[Si(CH_3)$_3$]$_3C_5H_2$}Li.pmdeta (pmdeta = pentamethyldiethylenetriamine) (Jutzi, Schlüter, Krüger & Pohl, 1983) values of 1·928 and 1·980 Å indicate that the increase in the Li—Z distance is not only due to the higher coordination number, five, but also to steric repulsions between the bulky Si(CH_3)$_3$ groups and the bidentate base. In order to reveal the parameters that determine the Li—Z distance we report here the structure of (methylcyclopentadienyl)(tetramethylethylendiamine)lithium, a compound without interligand repulsions.

Experimental. The title compound was prepared from freshly cracked methylcyclopentadiene and *n*-butyllithium in hexane/tetrahydrofuran (1/3) followed by crystallization from N,N,N',N'-tetramethylethylenediamine. Crystals were separated

* Coordination Geometry in Cyclopentadienyl Complexes. IV. Part III: Hammel & Weidlein (1990).

$[Li(C_6H_7)(C_6H_{16}N_2)]$

Table 1. Atomic coordinates and temperature factors

$$U_{eq} = -8\pi^2 U \sin^2\theta/\lambda^2.$$

	x	y	z	$U_{eq}(\text{Å}^2)$
Li	0·2118 (3)	0·3103 (2)	0·3976 (2)	0·027 (2)
N(1)	0·1221 (1)	0·3859 (1)	0·2989 (1)	0·022 (1)
N(2)	0·2282 (1)	0·4223 (1)	0·4750 (1)	0·023 (1)
C(11)	0·0058 (2)	0·3742 (1)	0·3131 (2)	0·036 (1)
C(12)	0·1486 (2)	0·3696 (1)	0·2017 (1)	0·034 (1)
C(21)	0·3542 (2)	0·4452 (1)	0·4713 (2)	0·035 (1)
C(22)	0·1907 (2)	0·4164 (1)	0·5715 (1)	0·041 (1)
C(111)	0·1582 (2)	0·4716 (1)	0·3236 (1)	0·027 (1)
C(222)	0·1553 (2)	0·4851 (1)	0·4265 (1)	0·026 (1)
C(1)	0·1729 (2)	0·1733 (1)	0·3681 (1)	0·024 (1)
C(2)	0·2861 (2)	0·1916 (1)	0·3334 (1)	0·028 (1)
C(3)	0·3599 (2)	0·2154 (1)	0·4071 (1)	0·031 (1)
C(4)	0·2919 (2)	0·2117 (1)	0·4877 (1)	0·029 (1)
C(5)	0·1776 (2)	0·1866 (1)	0·4638 (1)	0·026 (1)
C(6)	0·0686 (2)	0·1412 (1)	0·3142 (2)	0·039 (1)

Table 2. Selected distances (Å) and angles (°); Z = centre of the C5H4—CH3 ligand

Li—C(1)	2·278 (3)	Li—N(1)	2·130 (3)
Li—C(2)	2·276 (3)	Li—N(2)	2·124 (3)
Li—C(3)	2·258 (3)	N(1)—C(11)	1·464 (2)
Li—C(4)	2·240 (3)	N(1)—C(12)	1·466 (2)
Li—C(5)	2·236 (3)	N(1)—C(111)	1·475 (2)
C(1)—C(2)	1·400 (3)	C(111)—C(222)	1·511 (2)
C(2)—C(3)	1·407 (3)	N(2)—C(21)	1·464 (2)
C(3)—C(4)	1·399 (3)	N(2)—C(22)	1·466 (2)
C(4)—C(5)	1·391 (3)	N(2)—C(222)	1·476 (2)
C(5)—C(1)	1·406 (2)		
C(1)—C(6)	1·500 (3)	Li—Z	1·917
Li—N(1)—C(11)	107·3 (1)	Li—N(2)—C(21)	106·0 (1)
Li—N(1)—C(12)	116·7 (1)	Li—N(2)—C(22)	115·3 (1)
Li—N(1)—C(111)	103·6 (1)	Li—N(2)—C(222)	106·0 (1)
C(11)—N(1)—C(12)	108·2 (1)	C(21)—N(2)—C(22)	109·2 (1)
C(11)—N(1)—C(111)	110·8 (1)	C(21)—N(2)—C(222)	110·3 (1)
C(12)—N(1)—C(111)	110·1 (1)	C(22)—N(2)—C(222)	109·9 (1)
N(1)—C(111)—C(222)	111·6 (1)		
N(2)—C(222)—C(111)	111·2 (1)	N(1)—Li—N(2)	85·3 (1)

under Nujol and sealed in Lindemann capillaries. The specimen selected for X-ray analysis was 0·3 × 0·2 × 0·4 mm. Intensity data recorded on a Syntex $P2_1$ automatic diffractometer, graphite-monochromated Mo $K\alpha$ radiation (ω-scan mode). Cell parameters refined by least squares from angle data of 20 reflections ($20 < 2\theta < 30°$). Max. $(\sin\theta)/\lambda$ 0·650 Å^{-1}; hkl range 0–10, 0–20, 0–18. Two standard reflections (221, 132) measured after every 98 reflections showed no significant deviations from the mean. 2630 unique reflections measured in the range $2 < 2\theta < 55°$, 1845 considered observed $[I > 2\sigma(I)]$. Intensities corrected for Lorentz–polarization effects; systematic absences led to *Pbca*, No. 61 (*International Tables for X-ray Crystallography*, 1974, Vol. IV). Structure solved by direct (*SHELXS*86; Sheldrick, 1986) and Fourier methods (*XRAY*76; Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976), refinement on F. All H atoms taken from difference Fourier map and refined isotropically. 228 parameters, $R = 0·045$, $wR = 0·035$, $w = 1/[\sigma(F_o)]^2$, $S = 1·83$, $(\Delta/\sigma)_{max} = 0·0002$, $\Delta\rho$ in final difference Fourier map $< 0·2$ e Å^{-3}. Atomic scattering factors were those in *XRAY*76.

Discussion. Atomic parameters for the non-H atoms are listed in Table 1,* and selected distances and angles are listed in Table 2. Fig. 1 shows the molecule and the numbering scheme.

Unlike the silylated derivatives, $(\eta^5\text{-}C_5H_4\text{-}CH_3)Li$.tmen exhibits no disorder in the coordinated base or in the cyclopentadienyl ring. The cyclopentadienyl ring is planar within experimental error (0·004 Å). The methyl-group C atom is displaced from the ring plane away from the Li atom by

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, bond distances and angles involving H atoms and least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53152 (17 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Fig. 1. *ORTEP* (Johnson, 1976) drawing of Li(C5H4—CH3).tmen.

0·074 Å. The angle between the LiN_2 plane and the plane containing LiZ and the methyl group is 30·7°. For $[Si(CH_3)_3C_5H_4]Li$.tmen and $[CH_3C_5H_4]Li$.tmen, the geometrical parameters for the cyclopentadienyllithium fragment are identical within the combined e.s.d.'s. This is in agreement with the predictions based on our model of the 'cyclopentadienylkugel' (Hammel, Schwarz & Weidlein, 1989).

Comparison of the structural parameters of Lewis complexes with monodentate bases with those with bidentate bases shows that the Li—Z distance is mainly determined by the coordination number and to a smaller extent by steric repulsion between the coordinated base and the substituents on the ring. There is no observable change in the Li—Z distance on displacement of the N base by an O base or of the CH_3 group by an $Si(CH_3)_3$ group.

Based on these observations we describe the bonding between the Li atom and the cyclopentadienyl ring in these Lewis-base adducts as mainly ionic which is in agreement with the results obtained from SCF calculations on Lewis-base adducts of cyclopentadienyllithium with one, two or three molecules of ammonia (Blom & Faegri, 1990).

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Structure of 1,1,1,2,2,3,3-Heptacarbonyl-1,2,3-μ_3-ethylidyne-2,3-bis(triphenylphosphite)-*triangulo*-tricobalt(0)

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Abstract. $[Co_3(C_2H_3)(CO)_7(C_{18}H_{15}O_3P)_2]$, $M_r = 1020\cdot4$, triclinic, $P\bar{1}$, $a = 11\cdot311$ (5), $b = 11\cdot541$ (2), $c = 18\cdot805$ (3) Å, $\alpha = 99\cdot61$ (1), $\beta = 103\cdot21$ (2), $\gamma = 70\cdot93$ (3)°, $V = 2247\cdot3$ Å^3, $Z = 2$, $D_x = 1\cdot51$ g cm^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 12\cdot23$ cm^{-1}, $F(000) = 1036$, $T = 290$ K, $R = 0\cdot056$ for 3828 observed reflections with $F > 4\sigma(F)$. The Co atoms are arranged in a triangle, with Co—Co bond lengths in the range 2·478–2·493 (2) Å. The seven carbonyl ligands are all coordinated terminally, as are the two triphenylphosphite ligands which occupy equatorial positions *trans* to metal–metal bonds. The metal-atom triangle is capped by a μ_3-ethylidyne (μ_3-CCH$_3$) group, whose H atoms, successfully located in the electron-density map, take up staggered conformations with respect to the metal-atom positions.

Introduction. The structures of several μ_3-ethylidyne *triangulo*-tricobalt compounds have previously been reported; examples include $Co_3(\mu_3\text{-CCH}_3)(CO)_9$ (Sutton & Dahl, 1967), $Co_3(\mu_3\text{-CCH}_3)(CO)_7$dppm, where dppm is bisdiphenylphosphinomethane (Balavoine, Collin, Bonnet & Lavigne, 1985), $Co_3(\mu_3\text{-CCH}_3)(CO)_8(PPh_3)$ (Brice, Penfold, Robinson & Taylor, 1970) and $Co_3(\mu_3\text{-CCH}_3)(CO)_6$-$[P(OMe)_3]_3$ (Dawson, Robinson & Simpson, 1979). In the phosphine- and phosphite-substituted compounds, the ligand has always been found to be coordinated equatorially and *trans* to a metal—metal bond. In the case of the title compound, $Co_3(\mu_3\text{-CCH}_3)(CO)_7[P(OPh)_3]_2$, nuclear-magnetic-resonance data had provided conflicting evidence as to whether the ligands were equatorial or axial in solution (Heaton, Johnson & Kernaghan, 1988), and so the structure determination of the compound was undertaken to confirm the ligand positions in the crystal.

Experimental. Very dark red, almost opaque crystals were prepared from solution in heptane; crystals of rectangular cross section. The crystal used for data collection had dimensions $0\cdot50 \times 0\cdot25 \times 0\cdot15$ mm. Intensity data recorded from ω scans on a CAD-4 diffractometer at Queen Mary College, London (SERC service). 25 reflections, $20 < 2\theta < 40°$, used to determine accurate cell parameters. Data collected from $2\theta_{min} = 3$ to $2\theta_{max} = 44°$, $0 \leq h \leq 11$, $-12 \leq k \leq 12$, $-19 \leq l \leq 19$, using reflections $32\bar{8}$, $2\bar{5}\bar{3}$ and $0,1,\overline{10}$ as references. Maximum intensity variation of references <3%. No absorption correction. Of 5734 reflections measured, 5496 were unique.

Metal-atom positions found by the automatic Patterson search procedure of *SHELX*86 (Sheldrick, 1986); these were then used to phase subsequent Fourier syntheses in *SHELX*76 (Sheldrick, 1976), in which all other non-H atoms and ethyli-