(O5—C3—O8). Dans ces octaèdres, les distances Ti—O varie de 1,724 (6) à 2,164 (8) Å, les angles O—Ti—O (*trans*) sont compris entre 163,0 (3) et 176,4 (3)° et les angles O—Ti—O (*cis*) entre 77,6 (2) et 104,9 (3)°. Ces valeurs indiquent une certaine distorsion des octaèdres.

Les trois atomes de titane indépendants sont différenciés par la nature des groupements environnants: tous les atomes de titane sont liés à un oxygène μ_3-oxo et leur coordinance est complétée de la façon suivante: pour Ti1, trois atomes d'oxygène d'un groupement acétate pontant, un atome d'oxygène d'un groupe isopropoxyde terminal, un atome d'oxygène μ_2-oxo pontant; pour Ti2, trois atomes d'oxygène d'acétate pontant, un atome d'oxygène d'un groupe isopropoxyde pontant, un atome

d'oxygène μ_2-oxo pontant; pour Ti3 deux atomes d'oxygène d'un groupement acétate pontant, deux atomes d'oxygène de groupes isopropoxyde terminaux et un atome d'oxygène d'un groupe isopropoxyde pontant.

Cette structure est renforcée par l'existence de ponts acétate reliant entre eux les six atomes de titane. Les motifs d' hexamère sont indépendants les uns des autres.

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Structure of (Nonacarbonyl-1κ⁴C,2κ³C,3κ²C)-μ-(hydrido-2:3κ²H)-μ-(methoxymethylidyne-2:3κ²C)-(triphenylphosphine-3κP)-*triangulo*-triruthenium(3 Ru–Ru)

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Abstract. $[Ru_3H(CO)_9(C_2H_3O)\{(C_6H_5)_3P\}]$, $M_r = 861.5$, monoclinic, $C2/c$, $a = 21.793(3)$, $b = 15.945(2)$, $c = 18.648(4)$ Å, $\beta = 99.45(2)°$, $V = 6392.0$ Å^3, $Z = 8$, $D_x = 1.790$ g cm^{-3}, $D_m = 1.78(1)$ g cm^{-3}, $\lambda(Mo~K\alpha) = 0.71069$ Å, $\mu = 14.4$ cm^{-1}, $F(000) = 3360$, room temperature, $R = 0.035$ for 3780 unique observed reflections [$F > 3\sigma(F)$]. The three Ru—Ru distances are very similar (av. 2.833 Å) with the hydride and COMe groups bridging a common Ru—Ru distance. One of the Ru atoms involved in the bridge is coordinated by the Ph$_3$P ligand [P—Ru 2.320 (1) Å] which occupies an equatorial site with respect to the Ru$_3$ triangle. The solution ^{1}H, ^{13}C, and ^{31}P NMR data are discussed.

Introduction. In the course of the synthesis of a series of ruthenium–rhodium heteronuclear clusters, two minor by-products were identified in the synthesis of $[Ru_3H_2(CO)_9(\mu_3\text{-COMe})\{Rh(CO)_2PPh_3\}]$ from the reaction of $K[H_2Ru_3(CO)_9(\mu_3\text{-COMe})]$ and $[Rh(CO)_3(PPh_3)_2][PF_6]$ (Evans, Stroud & Webster, 1989). These were $[Ru_3H(CO)_9(PPh_3)(\mu\text{-COMe})]$ (I)

and $[Ru_3H(CO)_8(PPh_3)_2(\mu\text{-COMe})]$. The variable temperature ^{1}H NMR spectra of (I) showed the existence of two isomers. A crystal structure determination of (I) was undertaken both to identify the likely major isomer of (I) and also to investigate the structural distortions that the substitution of PPh$_3$ into $[Ru_3H(CO)_{10}(\mu\text{-COMe})]$ (II) (Johnson, Lewis, Orpen, Raithby & Süss, 1979) might induce into the cluster cage and the methoxymethylidyne bridging ligand.

Experimental. The title compound was isolated as a minor product (5%) of the reaction between equimolar amounts of $K[H_2Ru_3(CO)_9(\mu_3\text{-COMe})]$ and $[Rh(CO)_3(PPh_3)_2][PF_6]$ in methanol. The compound was purified by column chromatography [silica, 4:1 v/v petroleum ether (313–333 K)–CH$_2$Cl$_2$] (Stroud, 1989). Calc. for $C_{29}H_{19}O_{10}PRu_3$: C 40.4, H 2.2. Found: C 40.4, H 2.1%. FAB mass spectrum showed M^+ and loss of eight CO groups.

Air-stable yellow plate-like crystals were obtained from CH$_2$Cl$_2$–hexane solution and mounted in thin-wall glass capillaries. Preliminary photographic X-ray examination established the crystal system and

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cell dimensions, and the density was measured by flotation $(CCl_4/C_2H_4Br_2)$. Accurate cell dimensions were obtained from 25 centred reflections $(12\cdot4 < \theta < 13\cdot5°)$ using an Enraf–Nonius CAD-4 diffractometer fitted with a graphite monochromator and Mo radiation. The intensities of 6131 reflections were recorded (ω–2θ scan, $1\cdot5 < \theta < 25°$; h -25 to 25; k 0 to 19; l 0 to 22) using a crystal of dimensions $0\cdot5 \times 0\cdot25 \times 0\cdot1$ mm. The standard reflections (2) showed no change with time during the experiment and an empirical ψ-scan absorption correction was applied to the data (transmission factors min. 77·6, max. 99·9%). After the data reduction, there remained 5600 unique reflections ($R_{int} = 0\cdot008$) and 3780 with $F > 3\sigma(F)$ were used in the analysis. The normalized structure factors (E's) favoured the centrosymmetric space group $C2/c$ and the subsequent analysis confirmed this. The Ru atoms were located using the direct-methods strategy (*EEES*) available in *SHELX*76 (Sheldrick, 1976) and subsequent structure-factor and electron-density syntheses located the remaining non-H atoms of the cluster. The later electron-density maps gave evidence for the phenyl H atoms and these were introduced in geometrically calculated positions $[d(C—H) = 0\cdot95\ Å]$ with a common refined temperature factor. The difference electron-density map (at $R = 0\cdot037$) provided convincing evidence for a hydride atom. Thus it appeared as the highest peak in the map $(0\cdot68\ e\ Å^{-3})$, in a plausible position, and with other smaller peaks close to the heavy-atom framework. Blocked full-matrix least-squares refinement minimizing $\Sigma w(\Delta F)^2$ converged to $R = 0\cdot035$ {392 parameters (in 2 blocks), 3780 reflections, anisotropic (Ru,P,O,C) and isotropic (H) atoms, $w = 1/[\sigma^2(F) + 0\cdot0001F^2]$, max $\Delta/\sigma = 0\cdot03$, $wR = 0\cdot032$, $S = 1\cdot46$, with all unique data $R = 0\cdot079$, $wR = 0\cdot034$}. The residual electron density was in the range 0·6 to $-0\cdot4\ e\ Å^{-3}$. Scattering factors for neutral atoms and anomalous-dispersion corrections were taken from *SHELX*76 (Sheldrick, 1976) and *International Tables for X-ray Crystallography* (1974, Vol. IV, pp. 99–101) (Ru only). All calculations were carried out using *SHELX*76 (Sheldrick, 1976) and *ORTEP*II (Johnson, 1976) on an IBM 3090 computer. The final atomic coordinates are given in Table 1 and selected molecular geometry presented in Table 2.*

Discussion. The structure of the discrete molecule of (I) is shown in Fig. 1. The three metal atoms define

* Lists of structure factors, anisotropic thermal parameters, calculated H-atom positions and complete geometric details have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53160 (26 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic coordinates and equivalent isotropic temperature factors* ($Å^2 \times 10^3$)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Ru(1)	0·39670 (2)	0·01027 (3)	0·14614 (3)	45·0 (2)
Ru(2)	0·32878 (2)	−0·06971 (3)	0·02206 (2)	42·6 (2)
Ru(3)	0·26653 (2)	0·03462 (2)	0·10978 (2)	37·4 (2)
P(1)	0·16072 (6)	0·02759 (8)	0·06570 (7)	36·5 (6)
C(1)	0·4776 (3)	−0·0374 (4)	0·1470 (3)	57·8 (34)
O(1)	0·5249 (2)	−0·0665 (3)	0·1507 (3)	86·1 (31)
C(2)	0·4006 (3)	0·0727 (4)	0·2335 (4)	76·4 (44)
O(2)	0·4022 (3)	0·1070 (4)	0·2875 (3)	127·7 (46)
C(3)	0·3697 (3)	−0·0876 (4)	0·1928 (4)	61·7 (38)
O(3)	0·3569 (2)	−0·1441 (3)	0·2238 (3)	90·6 (34)
C(4)	0·4143 (3)	0·1100 (4)	0·0932 (4)	63·0 (37)
O(4)	0·4263 (2)	0·1706 (3)	0·0665 (3)	99·7 (38)
C(5)	0·4015 (3)	−0·0657 (4)	−0·0202 (3)	57·4 (35)
O(5)	0·4466 (2)	−0·0677 (3)	−0·0441 (3)	87·0 (32)
C(6)	0·3479 (3)	−0·1847 (4)	0·0576 (4)	68·3 (42)
O(6)	0·3583 (3)	−0·2508 (3)	0·0760 (4)	121·0 (45)
C(7)	0·2738 (3)	−0·1005 (4)	−0·0637 (4)	64·5 (38)
O(7)	0·2435 (2)	−0·1194 (4)	−0·1170 (3)	103·4 (38)
C(8)	0·2535 (3)	−0·0039 (4)	0·2049 (3)	59·4 (36)
O(8)	0·2479 (2)	−0·0260 (4)	0·2615 (3)	102·2 (38)
C(9)	0·2656 (2)	0·1493 (4)	0·1317 (3)	58·0 (36)
O(9)	0·2659 (2)	0·2193 (3)	0·1431 (3)	108·9 (39)
C(10)	0·3033 (2)	0·0506 (3)	0·0207 (3)	40·6 (27)
O(10)	0·3050 (2)	0·1162 (2)	−0·0214 (2)	52·5 (22)
C(11)	0·3361 (3)	0·1117 (4)	−0·0858 (3)	70·8 (41)
C(21)	0·1135 (2)	0·1099 (3)	0·0972 (3)	40·4 (27)
C(22)	0·0675 (2)	0·1524 (3)	0·0513 (3)	57·4 (34)
C(23)	0·0295 (3)	0·2096 (4)	0·0799 (4)	71·2 (43)
C(24)	0·0373 (3)	0·2248 (4)	0·1528 (4)	71·3 (45)
C(25)	0·0832 (3)	0·1839 (4)	0·1990 (4)	69·3 (42)
C(26)	0·1217 (3)	0·1274 (3)	0·1720 (3)	51·3 (32)
C(31)	0·1386 (2)	0·0305 (3)	−0·0324 (3)	40·2 (26)
C(32)	0·1580 (2)	0·0975 (3)	−0·0709 (3)	51·0 (32)
C(33)	0·1424 (3)	0·1006 (4)	−0·1456 (3)	64·8 (40)
C(34)	0·1075 (3)	0·0390 (5)	−0·1828 (3)	69·1 (41)
C(35)	0·0877 (3)	−0·0267 (4)	−0·1462 (3)	67·8 (39)
C(36)	0·1027 (2)	−0·0321 (4)	−0·0709 (3)	53·6 (33)
C(41)	0·1217 (2)	−0·0663 (3)	0·0929 (3)	39·0 (27)
C(42)	0·1531 (3)	−0·1418 (3)	0·1047 (4)	72·9 (42)
C(43)	0·1238 (3)	−0·2116 (4)	0·1264 (5)	88·6 (48)
C(44)	0·0636 (3)	−0·2088 (4)	0·1360 (4)	69·0 (41)
C(45)	0·0321 (3)	−0·1350 (4)	0·1254 (3)	58·2 (36)
C(46)	0·0606 (2)	−0·0644 (3)	0·1037 (3)	48·6 (30)
H(1)	0·2693 (23)	−0·0725 (32)	0·0854 (29)	80·0*

* Isotropic atom.

an approximately equilateral triangle, in which one edge is bridged by the H atom and the quaternary C atom of the COMe ligand, such that they subtend interplanar angles with the Ru_3 plane of 114 (3) and 94·1 (2)°, respectively. The Ru—C(carbyne) distances [Ru(2)—C(10) 1·996 (5), Ru(3)—C(10) 1·976 (5) Å] and the near planarity of the Ru(2), Ru(3), (COC) unit [Ru(x)—C(10)—O(10)—C(11) torsion angles: $x = 2$, $-4\cdot7°$; $x = 3$, 180·0°] are normal for an edge-bridging methoxymethylidyne ligand [the equivalent angles in (II) are 6·3 and 174·9°]. Compared to (II) the PPh_3 ligand can be seen to have been substituted on one of the bridged metal atoms [Ru(3)] in an equatorial site. The methyl group of the alkylidyne ligand is orientated away from the sterically demanding PPh_3 group, and the bond lengths and angles [C(10)—O(10) 1·312 (6),

O(10)—C(11) 1·475 (8) Å and C(10)—O(10)—C(11) 120·7 (4)°] are similar to those observed for (II) [1·299 (8), 1·427 (9) Å and 120·3 (6)°, respectively].

The carbonyl groups show a variation in Ru—C distance such that the ones *transoid* to the hydride are the shortest set (mean 1·88 Å), and those *transoid* to the carbyne the longest (mean 1·96 Å). This indicates a strong *trans* influence by the alkylidyne bridge.

Comparison with the structure of the parent complex (II) (Johnson, Lewis, Orpen, Raithby & Süss,

Table 2. *Selected distances* (Å) *and angles* (°)

Ru(1)—Ru(2)	2·836 (1)		Ru(2)—C(10)		1·996 (5)
Ru(2)—Ru(3)	2·831 (1)		Ru(3)—C(10)		1·976 (5)
Ru(3)—Ru(1)	2·833 (1)		C(10)—O(10)		1·312 (6)
P(1)—Ru(3)	2·320 (1)		O(10)—C(11)		1·475 (8)
P(1)—C(21)	1·824 (5)		Ru(2)—H(1)		1·89 (6)
P(1)—C(31)	1·814 (5)		Ru(3)—H(1)		1·77 (5)
P(1)—C(41)	1·834 (5)		C—H (fixed)		0·95

Ru—C	min.	1·875 (6)	max.	1·971 (6)	mean	1·92 (3)
C—O (carbonyl)	min.	1·120 (8)	max.	1·145 (8)	mean	1·134 (8)
Ru—C—O	min.	175·4 (6)	max.	178·2 (6)		
C—C (phenyl)	min.	1·353 (9)	max.	1·404 (8)	mean	1·38 (1)

Ru(1)—Ru(2)—Ru(3)	60·0 (1)		P(1)—Ru(3)—Ru(1)	167·4 (1)
Ru(2)—Ru(3)—Ru(1)	60·1 (1)		P(1)—Ru(3)—Ru(2)	108·0 (1)
Ru(3)—Ru(1)—Ru(2)	59·9 (1)		Ru(2)—H(1)—Ru(3)	101 (3)
Ru(3)—P(1)—C(21)	115·6 (2)		C(21)—P(1)—C(31)	103·7 (2)
Ru(3)—P(1)—C(31)	116·1 (2)		C(31)—P(1)—C(41)	103·9 (2)
Ru(3)—P(1)—C(41)	114·9 (1)		C(41)—P(1)—C(21)	100·8 (2)
C(10)—Ru(2)—Ru(3)	44·3 (2)		Ru(2)—C(10)—Ru(3)	90·9 (2)
C(10)—Ru(3)—Ru(2)	44·8 (1)		Ru(2)—C(10)—O(10)	137·6 (4)
C(10)—O(10)—C(11)	120·7 (4)		Ru(3)—C(10)—O(10)	131·4 (4)
C(10)—Ru(2)—Ru(1)	71·6 (1)		C(10)—Ru(3)—C(8)	161·7 (2)
C(10)—Ru(3)—Ru(1)	71·9 (1)		C(10)—Ru(3)—C(9)	94·5 (2)
C(10)—Ru(2)—C(5)	102·3 (2)		C(10)—Ru(3)—P(1)	103·0 (1)
C(10)—Ru(2)—C(6)	160·3 (3)			
C(10)—Ru(2)—C(7)	95·9 (2)			

Fig. 1. View of the discrete molecule showing the atom-numbering scheme. The atom surfaces are drawn at the 25% probability level and phenyl H atoms are omitted for clarity.
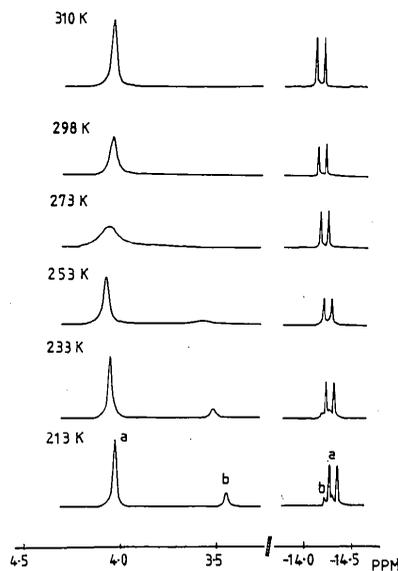
Fig. 2. Partial ¹H NMR spectra of (I) in CD₂Cl₂ solution (89·55 MHz), showing the CH₃ and Ru—H peaks of the major (a) and minor (b) isomers.

1979) indicates that the equatorial PPh₃ ligand has effected the following structural changes:

(a) the Ru—Ru bond distances have been slightly lengthened [mean Ru—Ru 2·833 Å in (I) and 2·811 Å in (II)].

(b) the O—C(Me) distance has been lengthened [1·475 (8) Å in (I), 1·427 (9) Å in (II)].

The ¹H NMR spectra of (I) in CD₂Cl₂ solution over the temperature range 213–310 K are shown in Fig. 2. At the lowest temperature, two isomers can be identified by their CH₃ and Ru—H resonances. The major isomer (a) exhibits its CH₃ proton resonance at δ 4·02, which is significantly closer to that reported for (II) (δ 4·46). This indeed suggests that the methyl group is oriented towards the unsubstituted end of the bridged bond in that isomer.

At 213 K the ³¹P{¹H} NMR spectrum of (I) contains two resonances at δ 41·1, [isomer (a)] and 39·4 [isomer (b)] relative to 85% H₃PO₄. Further indication of two such isomers is provided by their ¹³C{¹H} NMR spectra obtained at 233 K in CDCl₃ (Ph resonances omitted):

	Isomer (a)	Isomer (b)
C—OMe	372·1 (s)	369·2 (s)
C—O	207·0 [d, J(PC) 8, 1C]	206·6 [d, J(PC) 8, 1C]
	205·0 (s, 1C)	205·2 (s, 1C)
	204·6 (s, 1C)	204·3 (s, 1C)
	200·6 (s, 1C)	200·1 (s, 1C)
	200·0 [d, J(PC) 8, 1C]	201·3 [d, J(PC) 8, 1C]
	196·8 (s, 2C)	197·4 (s, 1C)
		196·4 (s, 1C)
	195·4 (s, 1C)	195·7 (s, 1C)
	188·3 (s, 1C)	188·8 (s, 1C)
CH₃	74·0 (s)	72·3 (s)

The close similarity of these data suggest that the isomers are based on a common coordination

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 ¹H 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 kJmol⁻¹ and −4 J K⁻¹mol⁻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(C₆H₇)(C₆H₁₆N₂)], 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, $\lambda(Mo\ K\alpha)$ = 0·71069 Å, μ = 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 (η⁵-C₅H₄CH₃) 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(CH₃)₃]₃-C₅H₂}Li.quinuclidine (Jutzi, Schlüter, Pohl & Saak, 1985) to 1·980 Å in {[Si(CH₃)₃]₃C₅H₂}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(CH₃)₃]₃C₅H₂}Li.quinuclidine (Jutzi, Schlüter, Pohl & Saak, 1985) and {[Si(CH₃)₃]₃C₅H₂}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(CH₃)₃]C₅H₄}Li.tmen (Lappert, Singh, Engelhardt & White, 1984), {[Si(CH₃)₃]₃C₅H₂}Li.tmen (Jutzi, Schlüter, Pohl & Saak, 1985) and {[Si(CH₃)₃]₃C₅H₂}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(CH₃)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

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