Reaction of Trimethylgallium with Tricarbonyl-η^5-cyclopentadienylhydridotungsten and with Dicarbonyl-η^5-cyclopentadienylhydrido(triphenylphosphine)tungsten. Crystal and Molecular Structure of μ_3-Gallio-tris(tricarbonyl-η^5-cyclopentadienyltungsten)

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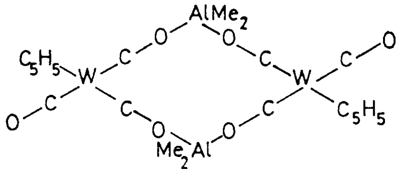
Trimethylgallium reacts with hydrides $[(C_5H_5)W(CO)_2LH]$ [(6) L = CO or (7) L = PPh_3] to give $[(C_5H_5)W(CO)_2L(GaMe_2)]$ [(2) L = CO or (5) L = PPh_3]. (2) Decomposes in hot hydrocarbon solution with formation of $[\{(C_5H_5)W(CO)_3\}_2GaMe]$, (3), and $[\{(C_5H_5)W(CO)_3\}_3Ga]$, (4). I.r. evidence suggests that (2) and (3), unlike $[\{(C_5H_5)W(CO)_3AlMe_2\}_2]$, do not have –C–O– bridges. An *X*-ray study of (4) shows that it crystallises in space group $P2_1/n$ with a = 13.464(4), b = 17.724(5), c = 11.296(3) Å, β = 101.72(2)°, Z = 4 (R 0.078 for 2 791 reflections). The co-ordination at gallium is planar, and the three tungsten neighbours are at 2.739(3) Å.

THE hydrides $[(C_5H_5)W(CO)_2LH]$ (L = CO, PPh_3, PMe_2Ph, or PEt_2Ph) react with hexamethyldialuminium to give methane and $[(C_5H_5)W(CO)_2LAlMe_2]$. For L = CO, the product is dimeric (1), with carbonyl groups linked through carbon to tungsten and through oxygen to aluminium.[1] Similar carbonyl bridges, which are associated with strong absorption in the i.r. between 1 550 and 1 650 cm^{-1}, were confirmed by *X*-ray methods in the compound $[\{(C_5H_5)W(CO)_3\}_3Al(C_4H_8O_2)_3]$.[2]



(1)

However, the compound $[(C_5H_5)Mo(CO)_3(TlMe_2)]$, obtained from the reaction between trimethylthallium and the hydride $[(C_5H_5)Mo(CO)_3H]$ below −50 °C, showed no i.r. absorption attributable to bridging carbonyl groups.[3] The reaction between trimethylindium and the hydrides $[(C_5H_5)M(CO)_3H]$ (M = Mo or W) gave as the only products the trisubstituted derivatives $[\{(C_5H_5)M(CO)_3\}_3In]$, which also showed no bands in the i.r. between 1 850 and 1 550 cm^{-1}.[4] A similar difference was observed between the analogous aluminium and indium derivatives $[Bu_4N][(C_5H_5)W(CO)_3(EPh_3)]$ (E = Al or In). The aluminium complex showed the strong absorption at 1 600 cm^{-1}, characteristic of a compound with a bridging carbonyl group between tungsten and aluminium, but the indium derivative showed no such absorption, suggesting that the anion $[(C_5H_5)W(CO)_3InPh_3]^-$ has a direct W–In bond.[5]

The reactions between trimethylgallium and the hydrides $[(C_5H_5)W(CO)_2LH]$ [(6) L = CO, (7) L = PPh_3] were examined to discover whether the structures of the gallium derivatives were, like those of the aluminium compounds, dominated by carbonyl bridges, or, like derivatives of the heavier Group III elements, based on main-group metal–transition-metal bonds. Trimethylgallium was assumed[6] to be co-ordinated to the oxygen atom of the carbonyl group in the 1 : 1 complex with $[Mo(phen)(PPh_3)_2(CO)_2]$, but no *X*-ray structural study was available to confirm this possibility.

The reaction of (6) with trimethylgallium was much slower than the corresponding reaction with hexamethyldialuminium. However, we isolated a yellow solid, which was analysed as $[(C_5H_5)W(CO)_3(GaMe_2)]$, (2), and which gave strong signals in the n.m.r. spectrum at τ 5.16 and 9.45. Crystals were obtained from methylcyclohexane solution by very slow cooling, and an *X*-ray structural investigation was begun. While this was in progress, several other samples were made and it became clear than the n.m.r. spectra of the products were not consistent from preparation to preparation. A check on the n.m.r. spectrum of the crystals used for the structure determination showed that they gave no resonance due to *Ga*Me protons, suggesting reorganisation reactions during recrystallisation.

$$\underset{(2)}{2[(C_5H_5)W(CO)_3(GaMe_2)]} \longrightarrow \underset{(3)}{[\{(C_5H_5)W(CO)_3\}_2GaMe]} + GaMe_3$$

$$\underset{(3)}{2[\{(C_5H_5)W(CO)_3\}_2GaMe]} \longrightarrow \underset{(4)}{[\{(C_5H_5)W(CO)_3\}_3Ga]} + \underset{(2)}{[(C_5H_5)W(CO)_3(GaMe_2)]}$$

The formation of (4) was confirmed by analysis and by the *X*-ray structure determination.

EXPERIMENTAL

Air and moisture were excluded as rigorously as possible from all manipulations. Trimethyl- and triethyl-gallium[7] and the hydrides (6) and (7) were made by established methods. Mass spectra (70 eV) were obtained by insertion of solid samples into the ionisation chamber of the spectrometer: peaks corresponding to the combinations WGa, W_2Ga, *etc.*, were easily identified by isotope patterns. Data

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are given (relative intensities in parentheses) only for ^{184}W and ^{69}Ga.

Tricarbonyl-η^5-cyclopentadienyl(dimethylgallio)tungsten, (2).—The hydride (6) (0.34 g, 1.02 mmol) and trimethylgallium (1.05 mmol) were heated in a sealed ampoule at 130 °C for 16 h. Methane (0.99 mmol) was removed through a break-seal, measured by a Töpler pump, and shown to be pure by its i.r. spectrum, and by g.l.c. The residue was dissolved in toluene. On addition of hexane, a yellow *solid*, m.p. 247—8 °C, was precipitated (Found: C, 27.7; H, 2.40; W, 42.9. $C_{10}H_{11}GaO_3W$ requires C, 27.7; H, 2.56; W, 42.5%); the mass spectrum showed peaks at 417(100) $[(C_5H_5)W(CO)_3GaMe]^+$, and at 389(36), 361(21), and 333(21), corresponding to successive loss of CO from the parent ion. The peak at 735(2) $[\{(C_5H_5)W(CO)_3\}_2Ga]^+$ probably showed the presence of reorganisation products as impurities.

cis-*Dicarbonyl-η^5-cyclopentadienyl(dimethylgallio)(triphenylphosphine)tungsten*, (5).—The hydride (7) (ref. 8) (1.25 g, 2.19 mmol) reacted with trimethylgallium (2.24 mmol) during 42 days at 140 °C to give methane (1.99 mmol) and a yellow solid, which was recrystallised from toluene and washed with hexane. The crystals apparently easily occluded solvent toluene, which was removed by heating for 4 h at 90 °C and 10^{-3} mmHg, m.p. 213—217 °C (decomp.) (Found: C, 48.5; H, 3.95; P, 4.6; W, 27.8. $C_{27}H_{26}GaO_2PW$ requires C, 48.6; H, 3.93; P, 4.6; W, 27.6%); the mass spectrum showed peaks at 666(1) $[(C_5H_5)W(CO)_2(PPh_3)(GaMe_2)]^+$, 651(31) corresponding to loss of Me, 623(1) and 595(3) from further successive loss of CO, 567(46), 538(3), 506(62), 427(31), 357(10), and 322(26) from fragmentation of $[(Ph_3P)W(C_5H_5)]^+$, 262(59) Ph_3P^+, 185(23) Ph_2P^+, 99 (>400) $GaMe_2^+$, 84(64) $GaMe^+$, and 69(100) Ga^+. The high intensities of the gallium-containing peaks with $m/e < 100$ may indicate reorganisation reactions in the spectrometer with formation of trimethylgallium.

TABLE 1

N.m.r. and i.r. spectra

No.	Compound	N.m.r.[a,b] (τ)	I.r.[b] (cm^{-1})
(2)	$[(C_5H_5)W(CO)_3(GaMe_2)]$	5.16(5), 9.45(6)	1 982s, 1 970,[c] 1 876s,[c] 1 858s
(3)	$[\{(C_5H_5)W(CO)_3\}_2GaMe]$	5.02(10), 8.94(3)	1 966s,[c] 1 916m, 1 896s, 1 878s,[c] 1 814m
(4)	$[\{(C_5H_5)W(CO)_3\}_3Ga]$	4.75	2 020s, 1 940s
(5)	$[(C_5H_5)W(CO)_2(PPh_3)(GaMe_2)]$	2.59—2.63(16), 4.98(5), 9.96(6) [d]	1 924m, 1 861m, 1 839m, 1 798s [e]

[a] Relative intensities in parentheses. [b] In benzene, except where indicated. [c] Not quite certain; peaks shown by compounds (2) and (3) are probably very close. [d] In CD_2Cl_2. [e] In dichloromethane; 1 926, 1 861, and 1 724 cm^{-1} in Nujol mull.

μ_3-Gallio-tris(tricarbonyl-η^5-cyclopentadienyltungsten), (4).—When a saturated solution of the compound (2) in methylcyclohexane was cooled from 100 to 20 °C during 72 h, yellow crystals of (4), m.p. 256—259 °C (decomp.), separated, and were washed with a little more solvent (Found: C, 26.8; H, 1.55; W, 51.8. $C_{24}H_{15}GaO_9W_3$ requires C, 27.0; H, 1.42; W, 51.6%). The mass spectrum showed only peaks from fragmentation of $[(C_5H_5)W(CO)_3]$; there was no evidence for ions containing gallium. In another experiment, bis(tricarbonyl-η^5-cyclopentadienyltungsten)mercury [9] (0.37 g, 0.43 mmol) was stirred with gallium metal (0.12 g, 1.74 mmol) in tetrahydrofuran (15 ml) at 35 °C. The melted gallium was dispersed as small droplets and separated in a finely divided state when the mixture was cooled to 20 °C. After further stirring for 6 weeks, the metal was filtered off and the volume reduced to 5 ml. The addition of hexane (5 ml) produced a yellow precipitate, shown by n.m.r. spectroscopy to be a mixture of (4) and $[\{(C_5H_5)W(CO)_3\}_2Hg]$; *ca.* 55% of the original mercury compound had been converted to the gallium derivative. No resonance attributable to co-ordinated solvent was observed. The reaction thus contrasts strongly with the analogous reaction with aluminium instead of gallium, which gives the solvated aluminium derivative $[\{(C_5H_5)W(CO)_3\}_3Al(C_4H_8O)_3]$ quantitatively in *ca.* 15 min.[2]

Tricarbonylcyclopentadienyl(diethylgallio)tungsten.— Triethylgallium (0.48 g, 3.1 mmol) was added to the hydride (6) (0.98 g, 2.9 mmol) in toluene (7 ml) at −78 °C. At 60—70 °C, ethane (1.8 mmol) was evolved in 2.5 h. The pale yellow solid, which separated on cooling, was washed with hexane and recrystallised from toluene–hexane, m.p. 30 °C (Found: C, 31.8; H, 3.50. $C_{12}H_{15}GaO_3W$ requires C, 31.3, H, 3.28%).

N.m.r. studies.—Mixtures of trimethylgallium, the hydride (6), and benzene were sealed in n.m.r. tubes. Spectra of samples initially showed resonancs at τ 5.19 and 17.14, ascribed to (6), and at τ 9.99, ascribed to trimethylgallium. After 1—2 h at 70 °C, the intensity of the high-field resonance had decreased, and new resonances had appeared in both the cyclopentadienyl and *Ga*Me regions, that at τ 9.67 being assigned to methane. During further periods at 70 °C, the relative intensities of the new resonances underwent further changes and the peaks due to (6) disappeared. By comparison with spectra from analytically pure samples of (2) and (4) (Table 1), it was possible to identify two additional resonances with intensities in the ratio 3.3 : 1, and these were assigned to compound (3). All the compounds (2)—(4) showed separate resonances in the cyclopentadienyl region of the spectrum. The compounds (2) and (3) showed separate signals in the *Ga*Me region, but mixtures of trimethylgallium and (2) at 30 °C gave only one resonance, indicating rapid exchange of methyl groups between gallium atoms in the two species. A consistent value for the chemical shift of the *Ga*Me protons in (2) was found from the observed mean chemical shift and the relative concentrations of $GaMe_3$ and (2) obtained by integration of the *Ga*Me and cyclopentadienyl resonances.

X-*Ray Crystal Structure of* $[\{(C_5H_5)W(CO)_3\}_3Ga]$, (4).—*Crystal data*. $C_{24}H_{15}GaO_9W_3$, M 1 068.5, Monoclinic, $a = 13.464(4)$, $b = 17.724(5)$, $c = 11.296(3)$ Å, $\beta = 101.72(2)°$, $U = 2\,639.4$ Å^3, $Z = 4$, $D_c = 2.69$ g cm^{-3}, $F(000) = 1\,936$. $\lambda(\text{Mo-}K_{\alpha1}) = 0.709\,26$ Å; $\mu(\text{Mo-}K_\alpha) = 149.2$ cm^{-1}. Space group $P2_1/n$ (No. 14) [10] from systematic absences: $h0l$ for $h + l$ odd, $0k0$ for k odd.

Intensity measurements and structure determination. Crystals were shaken from the reaction vessel into thin-walled Pyrex capillaries and sealed *in vacuo*. The crystal used throughout the data collection was a square plate

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[9] R. B. King and F. G. A. Stone, *Inorg. Synth.*, 1963, **7**, 104.

[10] 'International Tables for *X*-Ray Crystallography,' vol. I, Kynoch Press, Birmingham, 1962.

0.4 × 0.4 × 0.13 mm, mounted along a plate diagonal (*b*). The space group and preliminary cell dimensions were derived from Weissenberg and precession films; accurate cell dimensions were determined by use of a Hilger and Watts Y 290 four-circle diffractometer, from a least-squares treatment of setting angles for 12 reflections. Intensity data to θ 20° were collected by the ω—2θ scan technique by use of Mo-K_α radiation (graphite crystal monochromator).

TABLE 2

Final atom parameters

Atom positions and temperature factors, with estimated standard deviations in parentheses

	x	y	z	U/Å^2
Ga	0.178 64(22)	0.141 73(15)	0.369 93(25)	*
W(1)	0.252 81(9)	0.029 10(6)	0.530 35(10)	*
W(2)	0.125 55(9)	0.278 99(6)	0.454 00(10)	*
W(3)	0.158 22(10)	0.115 76(6)	0.129 20(10)	*
C(11)	0.340(2)	0.115(2)	0.536(3)	0.051(7)
O(11)	0.398(2)	0.168(2)	0.543(2)	0.092(8)
C(12)	0.120(3)	0.064(2)	0.542(3)	0.071(9)
O(12)	0.036(2)	0.082(2)	0.555(2)	0.090(7)
C(13)	0.278(3)	0.051(2)	0.700(3)	0.070(9)
O(13)	0.295(2)	0.060(2)	0.806(3)	0.100(8)
C(21)	0.070(3)	0.359(2)	0.343(3)	0.070(9)
O(21)	0.040(2)	0.411(2)	0.280(2)	0.091(7)
C(22)	0.236(2)	0.284(2)	0.370(2)	0.044(6)
O(22)	0.303(2)	0.294(1)	0.322(2)	0.068(6)
C(23)	0.014(2)	0.223(2)	0.362(3)	0.059(8)
O(23)	−0.062(2)	0.191(2)	0.308(2)	0.087(7)
C(31)	0.180(3)	0.017(2)	0.075(3)	0.068(9)
O(31)	0.190(2)	−0.043(2)	0.030(3)	0.117(10)
C(32)	0.300(2)	0.099(2)	0.216(3)	0.061(8)
O(32)	0.384(2)	0.097(2)	0.262(2)	0.088(7)
C(33)	0.065(3)	0.059(2)	0.200(3)	0.069(9)
O(33)	0.003(2)	0.020(2)	0.238(3)	0.103(9)
C(14)	0.272(2)	−0.057(2)	0.373(3)	0.058(8)
C(15)	0.198(2)	−0.083(2)	0.426(3)	0.064(8)
C(16)	0.238(3)	−0.102(2)	0.552(4)	0.091(12)
C(17)	0.340(3)	−0.083(2)	0.569(3)	0.078(10)
C(18)	0.368(3)	−0.056(2)	0.463(4)	0.083(11)
C(24)	0.084(3)	0.257(2)	0.636(4)	0.088(11)
C(25)	0.182(3)	0.250(3)	0.656(4)	0.093(12)
C(26)	0.222(3)	0.328(2)	0.635(3)	0.081(10)
C(27)	0.142(3)	0.369(2)	0.610(3)	0.084(11)
C(28)	0.058(3)	0.322(3)	0.612(4)	0.098(13)
C(34)	0.098(3)	0.236(2)	0.080(3)	0.076(10)
C(35)	0.188(3)	0.233(2)	0.051(3)	0.082(11)
C(36)	0.192(3)	0.184(3)	−0.034(4)	0.091(12)
C(37)	0.100(3)	0.153(2)	−0.068(3)	0.075(10)
C(38)	0.030(3)	0.186(3)	0.008(4)	0.103(13)

* Anisotropic temperature factors (Å^2 × 10^{-4}) in the form $T = \exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*]$, with parameters:

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ga	430(16)	335(15)	397(16)	−23(13)	−62(13)	15(12)
W(1)	508(7)	326(6)	412(7)	32(5)	0(5)	61(5)
W(2)	545(7)	356(7)	387(6)	−10(5)	−42(5)	−53(5)
W(3)	735(9)	300(6)	367(7)	116(6)	−61(6)	25(5)

Peak counts were taken over 60 steps with 1 s counts at each step and background was counted for 30 s at each end of the scan. The intensities of 3 standard reflections, monitored every 100 reflections, showed no significant changes. Data were corrected for Lorentz and polarisation effects. Of 3 415 reflections measured, 2 791 having $I > 3\sigma(I)$ were considered observed and used in the structure determination.

The structure was solved by the usual Patterson and Fourier techniques and full-matrix least-squares refinement[11] of atomic positions and thermal parameters (anisotropic for Ga and W) initially converged at R 0.15. After correction for absorption,[11] refinement continued smoothly to R 0.079. Hydrogen atoms were then included at calculated positions with B 7.0 Å^2 and data given empirical weights w defined as $w = 1/\{1 + [(|F_o| - 50)/112]^2\}$. The refinement was continued until the maximum shift-to-error ratio was <0.25 with R 0.078, and R' 0.097. A final difference-Fourier synthesis had large peaks $\leqslant 3$ eÅ^{-3} near the tungsten atoms but <1 eÅ^{-3} elsewhere. The rather high residual peaks probably result from difficulties in computing the absorption correction.

Initial data processing was with University of Sussex computer programs, and the '*X*-Ray' program system [12] was used for structure solution and refinement. Final structure-factor data and calculated hydrogen positions are given in Supplementary Publication No. SUP 21382 (20 pp., 1 microfiche).*

TABLE 3

Intramolecular distances and angles,* with estimated standard deviations in parentheses

(*a*) Interatomic distances (Å)

Ga–W(1)	2.744(3)	W(3)–C(33)	1.91(4)
Ga–W(2)	2.758(3)	W(3)–C(34)	2.31(4)
Ga–W(3)	2.716(3)	W(3)–C(35)	2.33(4)
W(1)–C(11)	1.91(3)	W(3)–C(36)	2.33(4)
W(1)–C(12)	1.92(4)	W(3)–C(37)	2.30(3)
W(1)–C(13)	1.92(4)	W(3)–C(38)	2.34(4)
W(1)–C(14)	2.39(3)	C(11)–O(11)	1.22(4)
W(1)–C(15)	2.36(3)	C(12)–O(12)	1.21(5)
W(1)–C(16)	2.36(4)	C(13)–O(13)	1.18(5)
W(1)–C(17)	2.30(4)	C(21)–O(21)	1.18(4)
W(1)–C(18)	2.39(4)	C(22)–O(22)	1.15(4)
W(2)–C(21)	1.94(3)	C(23)–O(23)	1.22(4)
W(2)–C(22)	1.93(3)	C(31)–O(31)	1.20(5)
W(2)–C(23)	1.92(3)	C(32)–O(32)	1.16(4)
W(2)–C(24)	2.28(4)	C(33)–O(33)	1.22(5)
W(2)–C(25)	2.31(4)	Ga ··· C(11)	2.60(3)
W(2)–C(26)	2.35(4)	Ga ··· C(12)	2.63(4)
W(2)–C(27)	2.36(4)	Ga ··· C(22)	2.64(3)
W(2)–C(28)	2.29(5)	Ga ··· C(23)	2.63(3)
W(3)–C(31)	1.90(4)	Ga ··· C(32)	2.72(4)
W(3)–C(32)	1.98(3)	Ga ··· C(33)	2.65(3)

(*b*) Angles (°)

W(1)–Ga–W(2)	120.0(1)	W(2)–Ga–W(3)	120.9(1)
W(1)–Ga–W(3)	119.1(1)		
Ga–W(1)–C(11)	65.2(8)	C(13)–W(1)–C(11)	79.9(14)
Ga–W(1)–C(12)	66.1(10)	C(13)–W(1)–C(12)	81.0(15)
Ga–W(1)–C(13)	118.7(11)	C(11)–W(1)–C(12)	108.4(14)
Ga–W(2)–C(22)	65.8(8)	C(21)–W(2)–C(22)	83.2(14)
Ga–W(2)–C(23)	65.5(10)	C(21)–W(2)–C(23)	82.6(13)
Ga–W(2)–C(21)	121.0(11)	C(22)–W(2)–C(23)	110.6(13)
Ga–W(3)–C(32)	68.7(10)	C(31)–W(3)–C(32)	79.9(13)
Ga–W(3)–C(33)	67.2(10)	C(31)–W(3)–C(33)	79.0(16)
Ga–W(3)–C(31)	119.2(10)	C(32)–W(3)–C(33)	111.5(14)
W(1)–C(11)–O(11)	177(2)	W(2)–C(23)–O(23)	174(3)
W(1)–C(12)–O(12)	176(3)	W(3)–C(31)–O(31)	174(3)
W(1)–C(13)–O(13)	176(3)	W(3)–C(32)–O(32)	173(3)
W(2)–C(21)–O(21)	176(3)	W(3)–C(33)–O(33)	176(3)
W(2)–C(22)–O(22)	174(3)		

* C_5H_5 ring: C–C 1.21(6)—1.53(7), mean 1.38 Å; C–C–C 103(4)—113(4), mean 108°.

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1974, Index issue.

[11] N. W. Alcock, *Acta Cryst.*, 1969, **A25**, 518, program ABSCOR, as implemented at Altas Computer Laboratory, Chilton, Didcot, Berkshire; scattering factors were taken from D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104; D. T. Cromer, *ibid.*, p. 17; R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

[12] J. M. Stewart, F. A. Kundell, and J. C. Baldwin, '*X*-Ray '67 ' System of programs (used on the 1906A computer at the Atlas Computer Laboratory), University of Maryland Technical Report TR 67-58, version of 1970.

DISCUSSION

μ_3-Gallio-tris(tricarbonyl-η^5-cyclopentadienyltungsten).—Final atomic positions and thermal parameters are listed in Table 2 and the atom numbering scheme is shown in Figure 1 (drawn by use of program ORTEP[13]). Distances and angles within the molecule are given in Table 3. The structure shows well-separated molecules with no crystallographically-imposed symmetry, and there are no intermolecular contacts significantly shorter than the sum of the relevant van der Waals radii.

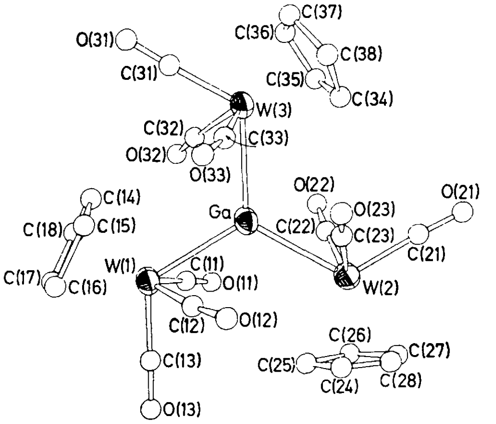

FIGURE 1 A drawing of the molecule $[\{(C_5H_5)W(CO)_3\}_3Ga]$, (4), showing 50% thermal vibration ellipsoids for anisotropic atoms

Each gallium atom is bound to three tungsten atoms, mean Ga–W 2.739(3) Å, although individual distances apparently differ significantly from this mean. The gallium–tungsten distance predicted[14-17] from the sum of the covalent radii is 2.83 Å, *ca.* 0.09 Å longer than that found. Tl–Mo[18] And Sn–Mo[19] distances found in *X*-ray studies of compounds with metal–metal bonds are also shorter than those derived from sums of radii.

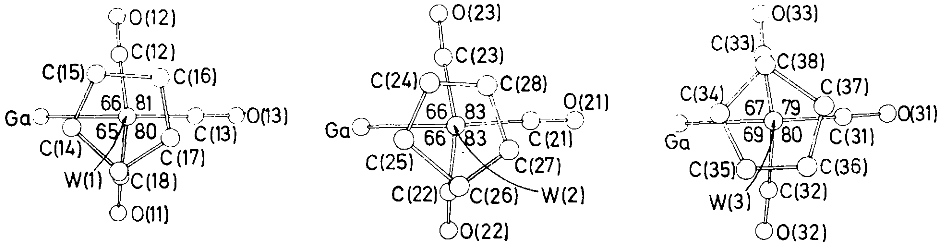

FIGURE 2 The co-ordination at tungsten viewed normal to the mean planes of the C_5H_5 groups

Mean bond distances in the remainder of the molecule [W–C(O) 1.916(17), C–O 1.20(2), W–C(C_5H_5) 2.342(13), C–C 1.40 (2) Å] are within ranges found for other cyclopentadienyltungsten derivatives (see ref. 1 for details), though the W–C(O) distance is shorter than in many other compounds. The gallium atom is within 0.002 Å of the plane determined by the three tungsten atoms (Table 4) in contrast to the compound $[\{(C_5H_5)Mo(CO)_3\}_3Tl]$,[18] in which the thallium atom is 0.59 Å from the plane defined by the three molybdenum atoms.

TABLE 4

Mean planes

Equations of planes in the form $pX + qY + rZ = s$, where X, Y, and Z are co-ordinates in Å with respect to the orthogonal axis set a,b,c^*. Deviations (Å) of relevant atoms from planes are given in square brackets

Plane (1): W(1)—(3)

$$-0.9414X - 0.3348Y - 0.0410Z = -2.4718$$

[Ga 0.00, C(31) 0.21, O(31) 0.36, C(21) 0.04, O(21) 0.00, C(13) −0.16, O(13) −0.26]

Plane (2): C(14)—(18)

$$0.2579X - 0.9311Y - 0.2581Z = 0.5977$$

[C(14) 0.00, C(15) −0.01, C(16) 0.01, C(17) −0.01, C(18) 0.01, W(1) −2.03]

Plane (3): C(24)—(28)

$$0.1293X - 0.2063Y - 0.9699Z = -7.8185$$

[C(24) 0.01, C(26) −0.01, C(26) 0.01, C(27), −0.01, C(28) 0.00, W(2) 2.01]

Plane (4): C(34)—(38)

$$-0.1322X + 0.7186Y - 0.6828Z = 2.2593$$

[C(34) 0.00, C(35) 0.01, C(36) −0.01, C(37) 0.00, C(38) 0.00, W(3) 2.00]

Angles (°) between planes: (1)–(2) 85, (1)–(3) 91, (1)–(4) 95, (2)–(3) 62, (2)–(4) 122, (3)–(4) 60°

Figures 1 and 2 show that, except for the C_5H_5 groups, the molecule as a whole has approximate C_{3h} symmetry with the GaW_3 plane defining an approximate non-crystallographic mirror plane which contains one carbonyl group on each tungsten atom and bisects the angle between the other two carbonyl groups. This high molecular symmetry probably arises from minimisation of intramolecular contacts, rather than packing forces. In the molecules of crystalline $[\{(C_5H_5)Mo(CO)_3\}_3Tl]$, however, where the Tl–Mo bonds are *ca.* 0.23 Å longer than the Ga–W bonds in (4), packing effects are presumably sufficiently large to remove the C_{3h} symmetry

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by rotations about Tl–Mo bonds.[18] In both molecules the co-ordination at molybdenum or tungsten is similar to that found in other compounds in which, assuming that the C_5H_5 ring occupies three co-ordination sites, the metal is seven-co-ordinate.[16,20] The mean angle (67°) made at tungsten between out-of-plane carbonyl groups and gallium atoms is significantly smaller (Figure 2) than that made between the out-of- and in-plane carbonyl groups (mean 81°). The steric requirements of the carbonyl ligands appear to be greater than those of the gallium-containing fragment. This results in a very short mean gallium–carbon distance [2.66(2) Å]. A similar pattern of angles at tungsten is observed in the crystal structure of the compound $[(C_5H_5)W(CO)_3Au(PPh_3)]$,[21] where corresponding mean angles are 67 and 79° though not in $[(C_5H_5)W(CO)_3Ph]$ [22] where the angles are 73 and 75°. The close proximity of the carbonyl groups to the atom, above and below the plane of the molecule, effectively precludes any intermolecular association involving gallium.

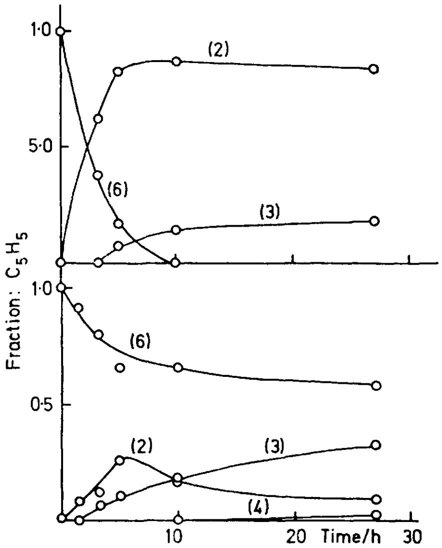
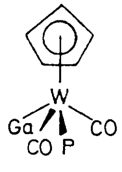


FIGURE 3 The fractions of $(C_5H_5)W(CO)_3$ groups in the compounds $[(C_5H_5)W(CO)_3H]$ (6), $[(C_5H_5)W(CO)_3(GaMe_2)]$ (2), $[\{(C_5H_5)W(CO)_3\}_2GaMe]$ (3), and $[\{(C_5H_5)W(CO)_3\}_3Ga]$ (4) after heating two mixtures of $GaMe_3$ and (6) in benzene for various times at 70°. Upper figure, Ga/W = 3; lower figure Ga/W = 0.7

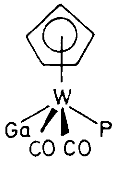
Reaction of Trimethylgallium with Tricarbonyl-η^5-cyclopentadienylhydridotungsten, (6).—Figure 3 shows the initial formation of the dimethylgallium derivative (2) and its subsequent reorganisation (or, perhaps, reaction with further hydride) to give the compounds (3) and (4). From reaction mixtures with a large excess of trimethylgallium, the initial hydride disappears rapidly and reorganisations are suppressed. It is probable that the symmetrical derivative (4) is the least soluble of the compounds (2)—(4) and that this is therefore isolated by slow recrystallisation. We have not isolated solid (3), but in one experiment in which a 1 : 0.9 mixture of hydride (6) and trimethylgallium was heated at 120 °C for 20 h the molar proportions of the products determined by n.m.r. were: (2) : (3) : (4) 17 : 70 : 12%. The equilibrium constant $K_1 = [(2)][(4)]/[(3)]^2$ at 70° may be estimated from the data of Figure 3 as *ca.* 2×10^{-2}; the value of $K_2 = [GaMe_3][(3)]/[(2)]^2$ is less certain, but it is probably *ca.* 10^{-1}.

There are no strong peaks (Table 1) in the carbonyl region of the i.r. spectra $<1\,810$ cm^{-1}, and the structures of the gallium compounds in solution do not therefore appear to involve carbonyl bridges of the kind found in the analogous aluminium derivatives. It is likely that all the molecules $[GaMe_nX_{3-n}]$ [$X = (C_5H_5)W(CO)_3$, $n = 0 — 2$] show gallium–tungsten bonds * and that the gallium is three-co-ordinate, as in trimethylgallium.[23]

The Compound $[(C_5H_5)W(CO)_2(PPh_3)(GaMe_2)]$, (5).—The phosphine derivative was made easily from the hydride (7) and trimethylgallium and no difficulty was found in its recrystallisation. No reorganisation products have been detected but a systematic search for them has not been made. Only one resonance was found in the cyclopentadienyl region of the n.m.r. spectrum. If the arguments applied to the hydride [8] can be transferred to the dimethylgallium derivative, this implies that the configuration at tungsten is *cis* (5a) rather than *trans* (5b).



(5a)



(5b)

The peak at 1 724 cm^{-1} shown in the i.r. spectrum from a mull, but not in those from solutions, may indicate a weak W–C–O–Ga bridge in the solid similar to those suggested for a zinc derivative.[24]

Mass Spectra.—The spectra of all the methylgallium compounds showed peaks corresponding to the loss of methyl groups from parent ions and to the subsequent successive elimination of carbonyl groups. Cyclopentadienyl and phosphine ligands were held strongly. Peaks from loss of methyl groups were stronger than in the mass spectra of analogous aluminium derivatives: this probably reflects the weaker Ga–Me, compared with Al–Me, bonds.

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* Professor J. P. Oliver has informed us that he has confirmed the presence of a Ga–W bond in solid $[(C_5H_5)W(CO)_3(GaMe_2)]$ by an *X*-ray study.

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