Complexes of Organoaluminium Compounds. Part VIII.[1] Crystal and Molecular Structure, Infrared and Nuclear Magnetic Resonance Spectra, and Reactions of Di-μ-(tricarbonyl-η^5-cyclopentadienyltungsten-*OO'*)-bisdimethylaluminium and the Characterisation of Some Phosphine Derivatives †

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The compound $[\{(\eta\text{-}C_5H_5)W(CO)_3(AlMe_3)\}_2]$, made from trimethylaluminium or dimethylaluminium hydride and the hydride $[(\eta^5\text{-}C_5H_5)W(CO)_3H]$, crystallises in space group *C*2/*c* with a = 18.120(4), b = 6.188(2), c = 22.266(5) Å, β = 93.29(2)°, and Z = 4. The structure, determined by the heavy-atom method from *X*-ray diffractometer data (1 175 reflections), was refined by least-squares techniques to *R* 4.2%. The molecules have slightly puckered twelve-membered rings, in which carbonyl groups [C–O 1.22(2) Å] are linked through carbon to tungsten [W–C, 1.851(14) Å] and through oxygen to aluminium [Al–O, 1.81(1), Al–C, 1.94(2) Å; C–Al–C 123(1)°]. Co-ordination round tungsten is completed by cyclopentadienyl groups (W–C 2.31—2.36 Å) and by terminal carbonyl groups [W–C 1.97(2), C–O 1.19(3) Å]. Absorptions at *ca.* 1 550 cm^{-1} are associated with bridging carbonyl groups. The ring is easily broken by protonic species HX [X = Cl, OH, MeCOCHCOMe (acac)], yielding the hydride $[(C_5H_5)W(CO)_3H]$ and the compounds $(Me_2AlX)_n$, and by donors D (D = NMe_3 or OEt_2) giving complexes $[(C_5H_5)W(CO)_3(AlMe_2)]$,D. The compounds $[\{(C_5H_5)WL(CO)_2(AlMe_2)\}_m]$ (L = PPh_3, PMe_2Ph, or PEt_2Ph) were made from trimethylaluminium and the hydrides $[(C_5H_5)WL(CO)_2H]$: spectroscopic data suggest bridging carbonyl groups in the compounds where L = PMe_2Ph or PEt_2Ph, similar to those where L = CO. The reaction between dimethylaluminium hydride and pentacarbonylhydridorhenium gives the known hydride $[Re_3(CO)_{14}H]$.

PREVIOUS parts of this series have described reactions between organoaluminium compounds and main-group hydrides to give alkanes and oligomeric compounds $(R_2AlX)_n$.

$$nR^1_3Al + nHX \longrightarrow nR^1_3Al,HX \longrightarrow (R^1_2AlX)_n + nR^1H \;(X = NR^2_2 \text{ or } PR^2_2) \quad (1)$$

Analogous reactions with transition-metal hydrides also yielded alkanes and solids containing both aluminium and transition metal.[2,3] Two of these solids $[(C_5H_5)W(CO)_3(AlR_2)]$ (R = Me or Et) were dimeric in benzene.[3] The carbonyl stretching region in the i.r. spectrum of the dimethylaluminium derivative appeared to show only terminal carbonyl groups, suggesting a structure with

† No reprints available.

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[3] R. R. Schrieke and J. D. Smith, *J. Organometallic Chem.*, 1971, **31**, C46.

aluminium–tungsten bonds,[3] but an *X*-ray study[4] indicated that, in the crystal, the main group element and transition metal were linked by bridging carbonyl groups as in the compounds $[\{(C_5H_5)Mo(CO)_3\}_2Mg(C_5H_5N)_4]$ and $[\{(C_5H_5)W(CO)_3\}_3Al]$, 3 C_4H_8O.[5] In this paper we give more details of the crystal structure of the compound $[\{(\eta^5\text{-}C_5H_5)W(CO)_3(AlMe_2)\}_2]$ and resolve the discrepancy between the crystallographic and earlier spectroscopic data.

The first preparation of the compound $[\{(C_5H_5)W(CO)_3(AlMe_2)\}_2]$ was from dimethylaluminium hydride and tricarbonyl-η^5-cyclopentadienylhydridotungsten. It was later found that equally satisfactory yields could be obtained if the aluminium hydride was replaced by the more readily available trimethylaluminium, provided that a longer reaction time and a higher reaction temperature were allowed [equation (2), L = CO].

$$Me_6Al_2 + 2[HW(CO)_2L(C_5H_5)] \longrightarrow [\{Me_2Al(CO)_2LW(C_5H_5)\}_2] + 2\,MeH \quad (2)$$

The yellow crystalline product was extremely reactive towards air and moisture, but samples could be kept for long periods in sealed tubes at 20 °C.

EXPERIMENTAL

Because of the extreme sensitivity towards hydrolysis of the compounds described in this paper, special procedures were adopted for the transfer of small samples. Products were crystallised, filtered off, and washed in the reaction vessel (Figure 1A). Solid samples were then made into pellets within this vessel using a syringe carrying a glass or stainless-steel plunger. The syringe could be withdrawn into the head (Figure 1B) and samples (7 mm × 3 mm diameter for molecular-weight measurements or 3—5 mm × 1 mm diameter for microanalyses) could be discharged with a rapid argon stream into a purged receiver which could then be immediately evacuated.

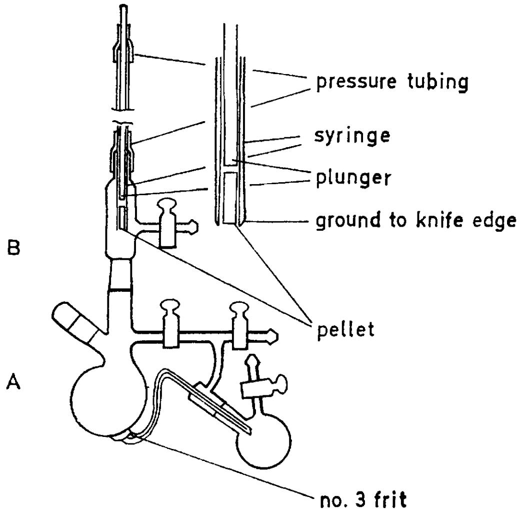

FIGURE 1 The reaction vessel and syringe

I.r. spectra were obtained from solutions in methylcyclohexane using matched 1-mm KBr cells which were flushed three times before use, either with the sample solution itself, or with a solution of trimethylaluminium in methylcyclohexane. Transfers were by syringe in an argon-filled drybag. For n.m.r. spectra, pellets of solid were transferred to sample tubes which, after condensation of solvent, were sealed. ^1H Spectra were recorded by Varian HA 100 or A60 instruments. ^{13}C Spectra were obtained, using a JEOL PFT100 spectrometer and a JEC 980A computer, from about 10^4 sweeps with a pulse width of 7 μs and a repetition time of 2.5 s. The addition of tris(acetylacetonato)chromium(III) as a relaxation agent[6] gave an improvement of only *ca.* 50% in the signal to noise ratio.

Preparation of the Compound $[\{(C_5H_5)W(CO)_3(AlMe_2)\}_2]$.—$Me_6Al_2$ (0.45 ml, 2.35 mmol), distilled through a trap at −4 °C to remove methoxides, was condensed onto $[(C_5H_5)W(CO)_3H]$ (1.08 g, 3.24 mmol) in methylcyclohexane (10 ml) at −196 °C. As the mixture warmed, no gas was evolved below 0 °C, but, after 20 h at 20 °C, methane (3.22 mmol) was collected by a Toepler pump and identified by its i.r. spectrum. The clear solution was concentrated and cooled to −78 °C when yellow crystals were obtained. The product appeared to be identical with that obtained previously[3] from the reaction between dimethylaluminium hydride and the hydride $[(C_5H_5)W(CO)_3H]$, except that the i.r. spectrum showed a group of strong absorptions at 1 981, 1 685, and 1 650 cm^{-1} as well as the group of absorptions at 2 020 and 1 936 cm^{-1} observed earlier.[3] Further investigation showed that the relative intensities of the peaks within each of these groups remained the same from preparation to preparation (using both trimethylaluminium and dimethylaluminium hydride as starting materials), but the intensities of one group, relative to the other, varied. The absorptions at 2 020 and 1 936 cm^{-1} could be reduced by various procedures (such as flushing the i.r. cell before use with a solution of trimethylaluminium in methylcyclohexane) designed to remove traces of water. We never, however, obtained a spectrum in which these bands were entirely absent. We now think that the spectrum originally given[3] for the compound $[\{(C_5H_5)W(CO)_3(AlMe_2)\}_2]$ was that of the hydride $[(C_5H_5)W(CO)_3H]$[7] formed by accidental hydrolysis during sampling, and that the true absorptions for the compound $[\{(C_5H_5)W(CO)_3(AlMe_2)\}_2]$ are at 1 981, 1 685, and 1 650 cm^{-1} (Table 1). These absorptions are similar to those found[3] for the diethylaluminium compound $[\{(C_5H_5)W(CO)_3(AlEt_2)\}_2]$ and it is unnecessary to postulate either that the molecular structure of $[\{(C_5H_5)W(CO)_3(AlMe_2)\}_2]$ is different in solution and in the solid, or that the structures of the dimethyl- and diethyl-aluminium compounds are different.

The difficulty of manipulating the sensitive compound $[\{(C_5H_5)W(CO)_3AlMe_2\}_2]$ as a solution rather than as a solid pellet was shown by comparison of i.r. and n.m.r. spectra from the same sample. Although the hydride absorptions showed strongly in the i.r. spectrum, the n.m.r spectrum (where absorptions due to hydride and $[\{(C_5H_5)W(CO)_3(AlMe_2)\}_2]$ are also easily distinguished) showed less than 2% of hydride.

The n.m.r. and carbonyl region of the i.r. spectra of a 2:1 mixture of the hydride $[(C_5H_5)W(CO)_3H]$ and Al_2Me_6 showed only peaks attributable to the hydride, Al_2Me_6, and the

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compound $[\{(C_5H_5)W(CO)_3AlMe_2\}_2]$. There were no new peaks which could be assigned to a complex $[(C_5H_5)W(CO)_3H],AlMe_3$, either similar to the complexes detected between the hydride $[(C_5H_5)_2WH_2]$ and several boron or aluminium acceptors,[8] or involving co-ordination of $AlMe_3$ at the carbonyl oxygen.[9]

Reactions.—(a) *With hydrogen chloride.* Samples (*ca.* 0.1 mmol) of $[\{(C_5H_5)W(CO)_3(AlMe_2)\}_2]$ were sealed in n.m.r. tubes with C_6D_6 (0.6 ml) and various measured amounts of HCl gas. Peaks at τ 5.02, assigned to $[\{(C_5H_5)W(CO)_3(AlMe_2)\}_2]$, and τ 5.31 and 16.75—16.95, assigned to hydride $[(C_5H_5)W(CO)_3H]$, appeared in samples with less than 2 mol HCl per $[\{(C_5H_5)W(CO)_3(AlMe_2)\}_2]$, but peaks at τ 9.73—9.78, assigned to CH_4, showed only in samples with more than 2 mol HCl per $[\{(C_5H_5)W(CO)_3(AlMe_2)\}_2]$. All peaks due to starting ring-compound $[\{(C_5H_5)W(CO)_3(AlMe_2)\}_2]$ had disappeared when 2 mol HCl had been added: only then, with further addition of HCl, were Al–C bonds broken. Samples with less than 2 mol HCl per $[\{(C_5H_5)W(CO)_3(AlMe_2)\}_2]$ gave only one *Al*–methyl signal, showing that exchange of methyl groups between $[\{(C_5H_5)W(CO)_3(AlMe_2)\}_2]$ and $(Me_2AlCl)_2$ was rapid on the n.m.r. time-scale at 38 °C. A parallel i.r. study confirmed that all the bridging carbonyl bands (Table 1) disappeared from the spectrum after addition of two equivalents of HCl.

TABLE 1

I.r. and n.m.r. data

Compound	I.r. (cm^{-1})				N.m.r. (τ) [a]
$[\{(C_5H_5)W(CO)_3(AlMe_2)\}_2]$ [b]	In C_7H_{14} [c]	1 981	1 865	1 650	In C_6H_5Me: 4.88 (C_5H_5); 10.17 (Me)
$[\{(C_5H_5)W(CO)_3(AlEt_2)\}_2]$ [b]	In C_7H_{14} [c]	1 986	1 692	1 659	In $C_6D_5CD_3$: 4.90 (C_5H_5); 8.81t, 9.86q (Et)
$[(C_5H_5)W(CO)_3(AlMe_2)],NMe_3$	In C_6H_6	1 960	1 857	1 569	In C_6H_6: 4.74 (C_5H_5); 8.06 (*N*-Me); 10.59 (*Al*-Me)
$[(C_5H_5)W(CO)_3(AlMe_2)],OEt_2$	In C_6H_6	1 948	1 854	1 562	In C_6H_6: 4.72 (C_5H_5); 6.41q, 9.06t (Et); 10.83 (*Al*-Me)
$[(C_5H_5)W(CO)_2(PPh_3)H]$	In CH_2Cl_2	1 939	1 840		In CD_2Cl_2: 2.60—2.63 (Ph); 4.88 (C_5H_5); 17.0d (*W*-H), ^2J(P–H) 56 Hz
$[(C_5H_5)W(CO)_2(PMe_2Ph)H]$	In C_6H_6 [d]	1 929	1 817		In CD_2Cl_2: 2.16—2.77 (Ph); 4.90 (C_5H_5); 8.08d (Me), ^2J(P–H), 9.0 Hz; 17.59d (*W*–H) ^2J(P–H): 46 Hz
$[(C_5H_5)W(CO)_2(PEt_2Ph)H]$	In CH_2Cl_2	1 920	1 825		In CD_2Cl_2: 2.29—2.90 (Ph); 4.82 (C_5H_5); 7.68—9.25c (Et); 17.70d (W–H), ^2J(P–H), 53 Hz, ^2J(W–H), 48 Hz
$[(C_5H_5)W(CO)_2(PPh_3)(AlMe_2)]$	Nujol mull	1 873	1 612		In CD_2Cl_2: 2.8—3.05 (Ph); 4.92 (C_5H_5); 10.15 (*Al*-Me)
$[(C_5H_5)W(CO)_2(PMe_2Ph)(AlMe_2)]$	Nujol mull	1 650	1 586		In C_6H_6: 4.83 (C_5H_5); 8.16d (*P*-Me), ^2J(P–C), 8.0 Hz; 10.04 (*Al*-Me)
$[(C_5H_5)W(CO)_2(PEt_2Ph)(AlMe_2)]$	Nujol mull	1 746	1 611		In C_6H_6: 4.84 (C_5H_5); 8.8—9.2c (Et); 10.03 (*Al*-Me)

[a] τ(Me_4Si) = 10; d, doublet; t, triplet; q, quartet; c, complex. [b] Ref. 3. [c] Methylcyclohexane. [d] 1 916 and 1 821 cm^{-1} in Nujol mull.

(b) *With acetylacetone* (Hacac). Acetylacetone (0.20 mmol) was added to $[\{(C_5H_5)W(CO)_3(AlMe_2)\}_2]$ (0.10 mmol) in benzene (1 ml). The n.m.r. spectrum of the clear solution, recorded after 20 min showed peaks at τ 5.19, 17.03 and at τ 4.95, 8.25, and 10.16 indicating complete conversion into the hydride $[(C_5H_5)W(CO)_3H]$ and acetylacetonatodimethylaluminium.[10] The carbonyl region of the i.r. spectrum confirmed that the bands due to the compound $[\{(C_5H_5)W(CO)_3(AlMe_2)\}_2]$ had disappeared.

(c) *With dimethylamine.* The n.m.r. spectrum of a sample of $[\{(C_5H_5)W(CO)_3AlMe_2\}_2]$, sealed with dimethylamine and benzene, showed no signals which could be assigned to the hydride $[(C_5H_5)W(CO)_3H]$ or methane. Thus the N–H bond of the amine was not broken. The signal ascribed to *N*-methyl protons appeared at higher field (τ 8.25) than that from the free amine (τ 7.67) or from $(Me_2NAlMe_2)_2$ (τ 7.89) and the signal due to *Al*-methyl protons (at τ 10.66) was also moved to higher field compared with that from $[\{(C_5H_5)W(CO)_3(AlMe_2)\}_2]$. This suggested formation of a complex $[(C_5H_5)W(CO)_3(AlMe_2)],NMe_2H$. When the sample was heated to 100 °C, some methane was detected; the solution darkened and unidentified solids were precipitated.

(d) *With trimethylamine.* A sample of $[\{(C_5H_5)W(CO)_3(AlMe_2)\}_2]$ (0.338 mmol) in benzene (7 ml) at 20 °C was exposed to an excess of NMe_3 gas. When no further pressure changes were observed, the solvent and unchanged amine were removed and it was found that 0.65 mmol of NMe_3 had been absorbed, suggesting formation of a complex $[(C_5H_5)W(CO)_3(AlMe_2)],NMe_3$. This conclusion was supported by the n.m.r. spectrum of the pale yellow residue (Table 1) which showed shifts to high field, compared with starting materials, for both *N*-methyl and *Al*-methyl resonances, and by the i.r. spectrum, which showed only one peak in the region characteristic of bridging carbonyl groups and two in the region characteristic of terminal groups.

(3) *With diethyl ether.* The reaction was similar to that with trimethylamine. Both i.r. and n.m.r. spectra (Table 1) suggested formation of a complex $[(C_5H_5)W(CO)_3(AlMe_2)],OEt_2$.

(f) *With pent-1-ene.* When a suspension of $[\{(C_5H_5)W(CO)_3(AlMe_2)\}_2]$ (0.071 g, 0.09 mmol) in pent-1-ene (1.45 g) was stirred for 16 h at 20 °C, no ethylene was detected on careful fractionation of the solvent. There was apparently no catalysis of olefin dismutation.

Compounds $[(C_5H_5)W(CO)_2L(AlMe_2)]$ (L = PPh_3, PMe_2Ph, or PEt_2Ph).—The hydride $[(C_5H_5)W(CO)_2(PPh_3)H]$ was made by heating triphenylphosphine with $[(C_5H_5)W(CO)_3H]$ in benzene.

$$[(C_5H_5)W(CO)_3H]) + L \longrightarrow [(C_5H_5)W(CO)_2LH] + CO \quad (3)$$

The yield (Table 2) was considerably improved compared

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[10] W. R. Kroll and W. Naegele, *J. Organometallic Chem.*, 1969, **19**, 439; S. Pasynkiewicz, and K. Dowbor, *ibid.*, 1972, **43**, 75.

with that given earlier.[11] The hydrides $[(C_5H_5)W(CO)_2(PMe_2Ph)H]$ and $[(C_5H_5)W(CO)_2(PEt_2Ph)H]$ were made similarly but with much shorter reaction times. Samples of each (*ca.* 1 g) were dissolved in toluene (20 ml) and a small excess of hexamethyldialuminium [20—30% more than shown by equation (2)] was condensed into the solution, which was then warmed until gas evolution was at a convenient rate. The yellow precipitates which formed were filtered off and recrystallised from methylcyclohexane. The triphenylphosphine derivative $[(C_5H_5)W(CO)_2(PPh_3)(AlMe_2)]$ was extremely insoluble in both aromatic solvents and dichloromethane and so the crystals precipitated during the reaction were simply filtered off and washed with cold toluene. Analytical data and details of i.r. and n.m.r. spectra are given in Tables 1 and 2.

Attempted Preparation of Tris(tricarbonyl-η⁵-cyclopentadienyltungsten)aluminium.— Bis(tricarbonyl-η⁵-cyclopentadienyltungsten)mercury reacted rapidly with aluminium powder in tetrahydrofuran to give the solvated derivative $[\{(\eta^5\text{-}C_5H_5)W(CO)_3\}_3Al],3C_4H_8O$.[5] An attempt to make the unsolvated compound by the same reaction in toluene was unsuccessful. After 20 h with vigorous stirring at 20 °C, the reaction mixture was filtered and the filtrate concentrated and cooled. The solid precipitated by addition of cold hexane was identified by i.r., n.m.r. spectroscopy, and m.p. as starting material $[\{(\eta^5\text{-}C_5H_5)W(CO)_3\}_2Hg]$, but it discoloured in air suggesting that perhaps reaction had occurred to a very small extent. Similar results were, however, obtained in another experiment in which the reaction mixture was heated for 16 days at 140 °C. An excess of the hydride $[(C_5H_5)W(CO)_3H]$ also failed to react with the compounds $[\{(C_5H_5)W(CO)_3(AlMe_2)\}_2]$ or $AlBu^i_3$ at temperatures low enough to prevent decomposition to unidentified brown solids.

TABLE 2

Yields and analytical data

Compound	M.p. (t/°C)	Conditions	Yield (%)	Found (%) C	Found (%) H	Found (%) W	Found (%) P	Calculated (%) C	Calculated (%) H	Calculated (%) W	Calculated (%) P
$[(C_5H_5)W(CO)_2(PPh_3)H]$ [a]	92	260 h/80 °C	91 [b]	52.7	3.70			52.8	3.70		
$[(C_5H_5)W(CO)_2(PMe_2Ph)H]$	75—76	3 h/80 °C	72 [b]	40.8	3.90			40.5	3.86		
$[(C_5H_5)W(CO)_2(PEt_2Ph)H]$	67—68	3 h/80 °C	76 [b]	43.2	4.60			43.2	4.49		
$[(C_5H_5)W(CO)_2(PPh_3)(AlMe_2)]$	228—230	2 h/60 °C	92 [c]	52.3	4.30	29.4	5.05 [d]	51.9	4.2	29.5	4.96
$[(C_5H_5)W(CO)_2(PMe_2Ph)(AlMe_2)]$	129—133d	48 h/20 °C	97 [c]	39.9	4.40	37.0	6.20	40.8	4.44	36.8	6.19
$[(C_5H_5)W(CO)_2(PEt_2Ph)(AlMe_2)]$	132—138d	46 h/20 °C	83 [c]	42.8	5.05	34.8	5.75	43.2	4.96	34.8	5.87

[a] See also ref. 11. [b] Based on amount of hydride $[(C_5H_5)W(CO)_3H]$ converted in reaction (3). [c] These figures indicate the quantity of methane evolved in reaction (2). Yields after recrystallisation were *ca.* 70%. [d] Al: found 4.55, calc. 4.32%.

Reaction between Dimethylaluminium Hydride and Pentacarbonylhydridorhenium.—The carbonyl hydride $[(OC)_5ReH]$ (0.378 g, 1.16 mmol) and hexane (5 ml) were sealed with Me_2AlH (0.255 g, 3.54 mmol), and the colourless solution was warmed to 20 °C. After 5 min, the mixture had darkened; after 13 h, large pale yellow crystals had precipitated; and after 47 h, a brown solid had also formed. The non-condensible products, separated by gas chromatography, were hydrogen (0.065 mmol) and, probably, carbon monoxide (0.435 mmol). The solid products were filtered off, washed with hexane, and then extracted with toluene. The toluene extract, on cooling, gave air-stable crystals which were shown to be the hydride $[HRe_3(CO)_{14}]$, m.p. 122 °C (yield: 25% based on $[(OC)_5ReH]$) (Found C, 17.4; H, <0.2%. Calc. for $C_{14}HO_{14}Re_3$: C, 17.7; H, 0.11%). The i.r., n.m.r., and mass spectra were identical with those previously reported.[12] No organic solvent was found for the material insoluble in benzene. It contained both aluminium and rhenium. It slowly dissolved in 1M-sulphuric acid, with formation of methane, and was pyrophoric in air, but no structural studies were made. Although the yield is not high, the hydride $[HRe_3(CO)_{14}]$ is the only soluble product, and so the separations needed in previously described preparations are not necessary.

Crystal Structure of $[\{(\eta\text{-}C_5H_5)W(CO)_3(AlMe_2)\}_2]$

Crystal Data.—$C_{20}H_{22}Al_2O_6W_2$, $M = 780.1$, Monoclinic, $a = 18.120(4)$, $b = 6.188(2)$, $c = 22.266(5)$ Å, $\beta = 93.29(2)°$, $U = 2\,492.5$ Å^3, $Z = 4$, $D_c = 2.08$, $F(000) = 1\,456$. $\mu(\text{Mo-}K_\alpha) = 98.6$ cm^{-1}. Space group $C2/c$ or Cc from systematic absences [hkl, $h + k = 2n + 1$; $h0l$, $l = 2n + 1$ $(h = 2n + 1)$], the former confirmed by successful refinement.

Crystallographic Measurements.—Irregularly shaped crystals, grown from toluene–methylcyclohexane at −20 °C, were shaken into thin-walled Pyrex capillaries joined directly to the reaction vessel, and sealed *in vacuo*. Weissenberg and precession photographs, taken by use of Cu-K_α radiation, established preliminary space-group data. Accurate lattice constants were obtained from settings of 12 reflections (mean 2θ, 25°) automatically centered on a Hilger and Watts Y 290 four-circle diffractometer, by use of Mo-K_α radiation ($\lambda = 0.709\,26$ Å); results from different crystals have led us to double values of estimated standard deviations obtained from the least-squares matrix. A crystal with dimensions 0.43 × 0.05 × 0.13 mm, mounted with the b axis coincident with that of the goniometer, gave multiple-film Weissenberg data for the six layers with indices $h0$—$5l$. Intensities of 1 333 reflections were estimated visually using a calibrated strip; multiple films were scaled using common reflections and data from different layers were correlated from exposure times. The structure was solved from this data set, but, because of the low resolution along b, the extreme absorption corrections, and uncertainty about possible slow decomposition (the crystal became progressively more opaque during photography), another crystal was examined in an attempt to improve data correlation.

This crystal, with dimensions 0.46 × 0.15 × 0.10 mm, gave good diffraction profiles but a small fragment (*ca.* 20% of the whole) adhered to the surface. To minimise multiple reflection effects[13] b^* was offset *ca.* 10° from the goniometer axis. Reflections from crystal and fragment proved to be sufficiently separated for the collection of an almost complete data set. Intensity measurements by use of Mo-K_α radi-

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[12] W. Fellmann and H. D. Kaesz, *Inorg. Nuclear Chem. Letters*, 1966, **2**, 63; J. M. Smith, K. Mehner, and H. D. Kaesz, *J. Amer. Chem. Soc.*, 1967, **89**, 1759.

[13] W. H. Zachariasen, *Acta Cryst.*, 1965, **18**, 705.

ation were made by the ω–2θ procedure, with background measurements at the extremities of each scan. Each background count was taken over 27 s and each peak count was accumulated over 54 steps of 0.01° with 1 s counts at each step. Integrated profiles of a range of reflections were printed to check for those affected by diffraction from the fragment. Most of the unique data set with $2 \leqslant \theta \leqslant 27°$ was obtained, and several shells of data were collected again to check for decomposition and crystal movement. As a further check, three standard reflections, well separated in reciprocal space, were measured after every 50 reflections. Fluctuations in standard intensities were a little more than usual (up to 3%) but decomposition was not significant. Data were processed as described elsewhere [14] with the instrumental factor p in the calculation [14] of the standard deviation $\sigma(I)$ set at 0.05. Values of I and $\sigma(I)$ were corrected for Lorentz and polarisation effects and a monochromatisation correction for an 'ideally imperfect' crystal [15] was included in the Lorentz factor. Intensities of 1 339 reflections with $I > 3\sigma(I)$ were used initially in the structure analysis. Absorption corrections were applied: [16] transmission coefficients (on I) were 0.21—0.44.

TABLE 3

Fractional atomic co-ordinates ($\times 10^4$) and thermal parameters ($Å^2 \times 10^3$),* with standard deviations in parentheses

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
W	867.7(4)	249.1(10)	1 493.3(3)	63.0(4)	71.1(4)	49.3(3)	9.6(3)	−1.7(2)	−8.3(4)
Al	−1 224(3)	3 330(9)	407(2)	76(3)	78(3)	49(3)	25(3)	0(2)	−7(2)
O(1)	−289(8)	2 730(26)	705(8)	82(9)	124(11)	128(13)	23(8)	−32(8)	−13(10)
O(2)	1 124(9)	−2 009(37)	301(7)	122(13)	236(21)	71(9)	49(13)	−5(8)	−79(12)
O(3)	−271(11)	−3 409(32)	1 784(9)	148(15)	124(14)	129(15)	−43(12)	41(12)	−22(12)
C(1)	139(10)	1 612(37)	1 038(8)	78(12)	126(16)	67(11)	32(11)	−26(9)	−43(11)
C(2)	1 025(10)	−1 226(33)	775(10)	70(11)	93(13)	100(15)	28(9)	1(10)	−35(11)
C(3)	124(13)	−1 944(38)	1 673(8)	110(16)	113(16)	46(14)	24(13)	6(9)	−1(10)
C(4)	−1 904(16)	1 696(49)	878(13)	124(20)	150(22)	111(19)	8(17)	40(15)	13(17)
C(5)	−1 298(18)	6 413(46)	279(14)	181(29)	104(19)	143(27)	34(18)	12(21)	34(18)
C(6)	1 482(15)	211(53)	2 445(9)	127(19)	169(26)	53(11)	−15(18)	−31(12)	19(14)
C(7)	1 987(12)	−76(39)	2 025(11)	91(13)	102(17)	90(15)	−2(12)	6(11)	−32(13)
C(8)	2 052(14)	1 652(51)	1 718(13)	99(17)	129(21)	122(21)	−29(16)	18(14)	−38(17)
C(9)	1 532(15)	3 238(43)	1 869(13)	120(20)	120(19)	119(21)	10(15)	−56(17)	−44(17)
C(10)	1 164(13)	2 279(60)	2 371(11)	95(16)	195(29)	67(14)	25(17)	−2(12)	−62(17)

* Thermal parameters U_{ij} are of the form $T = \exp - 2\pi^2[U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2(U_{12}hka^*b^* + U_{13}hla^*c^* + U_{23}klb^*c^*)]$.

Structure Analysis.—The tungsten atom was found from a three-dimensional Patterson synthesis by use of the film data, and all other non-hydrogen atoms were located from the resulting difference Fourier synthesis (R 0.18). Weights w were put equal to 1 in initial cycles. In all calculations, atomic scattering factors for tungsten, aluminium, oxygen, and carbon were taken from ref. 17, and values of $\Delta f'$ and $\Delta f''$ needed to correct for anomalous dispersion of tungsten from ref. 18. Refinement of scale factors and positional and isotropic thermal parameters for all atoms converged at R 0.15, R' 0.17 $[R' = (\Sigma w\Delta^2/\Sigma w|F_o|^2)^{\frac{1}{2}}]$. Further refinement was made by use of diffractometer data. With anisotropic temperature factors assigned to all atoms, convergence was reached after three cycles at R 0.066 and R' 0.084. A number of reflections which had been systematically affected by the fragment and which had eluded earlier checks were now rejected. Analysis of $\Sigma w\Delta^2$ showed a marked dependence on F_o and slight dependence on sin θ. With weights $w = XY$, where $X = \sin\theta/0.225$ for $\sin\theta < 0.225$, otherwise $X = 1.0$, $Y = 90/|F_o|$ for $|F_o| > 90$ otherwise $Y = 1.0$, refinement with 1 175 reflections converged in three cycles to R 0.042 and R' 0.051.* The maximum shift in the last cycle was 40% of its estimated standard deviation calculated from the least-squares matrix, and the mean shift-to-error ratio for all parameters was <5%. A final difference Fourier calculation showed no ripples >0.5 eÅ^{-3} except within 1 Å of the tungsten atom (up to 1.4 eÅ^{-3}). Only two of the five cyclopentadienyl hydrogen atoms were resolved at the noise level 0.5 eÅ^{-3}.

RESULTS AND DISCUSSION

Crystal Structure of $[\{(\eta\text{-}C_5H_5)W(CO)_3(AlMe_2)\}_2]$.—The solid consists of discrete dimeric centrosymmetric molecules (Figure 2). Tungsten and aluminium atoms are bridged by carbonyl groups with carbon bound to tungsten and oxygen to aluminium in slightly puckered

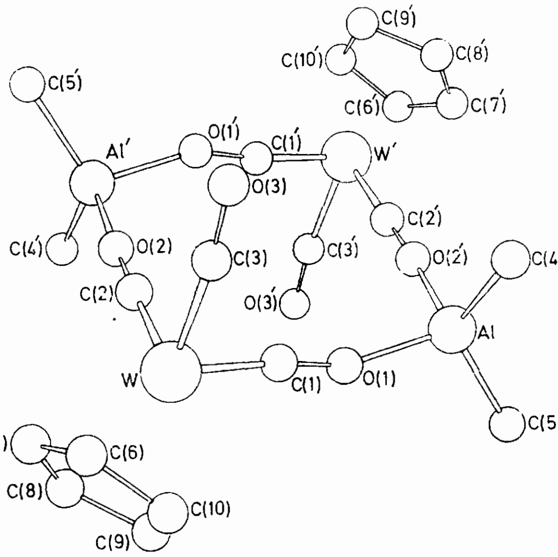

FIGURE 2 The molecule showing the atom numbering scheme

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* Final 1 175 values of $10|F_o|$ and $10F_c$ are listed in Supplementary Publication No. SUP 21444 (8 pp., 1 microfiche). See Notice to Authors No. 7, in *J.C.S. Dalton*, 1974, Index issue (items less than 10 pp. are supplied as full-size copies).

[14] P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, 1967, **6**, 197.

[15] U. W. Arndt and B. T. M. Willis, 'Single Crystal Diffractometry,' Cambridge University Press, Cambridge, 1966, p. 286.

[16] N. W. Alcock, *Acta Cryst.*, 1969, **A25**, 518.

[17] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104;

[18] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

twelve-membered rings. Final atomic and thermal parameters are given in Table 3 and bond lengths and angles in Table 4. Amplitudes of thermal vibration (Table 5) are large, but the directions of the principal axes of the vibrational ellipsoids shown in Figure 3 are chemically reasonable. Corrections to bond lengths involving tungsten using the usual model in which lighter atoms ride on heavier [19] lead to increases of $<1.5\sigma$. Corrections with aluminium as heavy atom give larger increases (up to 3σ); the mean Al–O distance is then 1.86 and Al–C 1.99 Å.

TABLE 4

Bond lengths (Å) and angles (°) for $[\{(C_5H_5)W(CO)_3(AlMe_2)\}_2]$*

(*a*) Distances

W–C(1)	1.825(19)	W–C(6)	2.34(2)
W–C(2)	1.878(21)	W–C(7)	2.30(2)
W–C(3)	1.970(23)	W–C(8)	2.34(3)
Al–O(1)	1.822(15)	W–C(9)	2.34(3)
Al–O(2′)	1.793(18)	W–C(10)	2.36(3)
Al–C(4)	1.95(3)	C(6)–C(7)	1.36(3)
Al–C(5)	1.93(3)	C(7)–C(8)	1.28(4)
C(1)–O(1)	1.25(3)	C(8)–C(9)	1.41(4)
C(2)–O(2)	1.18(3)	C(9)–C(10)	1.46(4)
C(3)–O(3)	1.19(3)	C(10)–C(6)	1.41(5)

(*b*) Angles

C(1)–W–C(2)	83.8(8)	W–C(2)–O(2)	175(2)
C(1)–W–C(3)	87.1(9)	W–C(3)–O(3)	174(2)
C(2)–W–C(3)	88.7(8)	Al–O(1)–C(1)	149(2)
O(1)–Al–O(2′)	95.1(8)	Al′–O(2)–C(2)	176(2)
O(1)–Al–C(4)	107.6(10)	C(6)–C(7)–C(8)	110(3)
O(1)–Al–C(5)	108.1(11)	C(7)–C(8)–C(9)	112(3)
O(2′)–Al–C(4)	109.6(11)	C(8)–C(9)–C(10)	104(3)
O(2′)–Al–C(5)	109.3(12)	C(9)–C(10)–C(6)	105(2)
C(4)–Al–C(5)	123.4(14)	C(10)–C(6)–C(7)	109(2)
W–C(1)–O(1)	172(2)		

* Estimated standard deviations in parentheses. These are minimum values since they take no account of interaction of positional and thermal parameters (see text).

TABLE 6

Molecular parameters for carbonyl and cyclopentadienyl derivatives of tungsten; distances (Å) angles (°)

	W–(C_5H_5) [a]	W–C	C–O	W–C–O
$[\{(C_5H_5)W(CO)_3\}_2]$ [b]		1.976	1.149	175.2
$[(C_5H_5)W(CO)_3Au(PPh_3)]$ [c]	2.01(2)	1.97(3)	1.16(4)	172(3)
$[(C_5H_5)W(CO)_3Ph]$ [d]		1.96(2)	1.18(3)	168
$[(C_4H_{10}S_2)W(CO)_3Cl(SnMeCl_2)]$ [e]		1.96	1.16(3)	175(2)
$[(C_{10}H_8N_2)W(CO)_3Br(GeBr_3)]$ [f]		1.91(4)	1.19(4)	171(3)
$[(C_5H_5)_2WS_4]$ [g]	2.01			
$[\{(C_6H_4)(SMe)_2\}W(CO)_4]$ [h]		2.00(4)	1.06—1.20	167
$[Et_4N][W(CO)_4Br_3]$ [i]		1.96	1.15(5)	
$[(Ph_2C_2)_3W(CO)]$ [j]		1.99	1.16	
$[\{(C_5H_5)W(CO)_3\}_3Al],3C_4H_8O$ [k]	2.04(1)	1.95(2) 1.85(2) [l]	1.16(2)	176(3)
$[\{(C_5H_5)W(CO)_3(AlMe_2)\}_2]$	2.016(11)	1.97(2) 1.85(2) [l]	1.19(3)	173(1)

[a] To centroid of cyclopentadienyl ring. [b] R. D. Adams, D. M. Collins, and F. A. Cotton, *Inorg. Chem.*, 1974, **13**, 1086. [c] J. B. Wilford and H. M. Powell, *J. Chem. Soc.* (*A*), 1969, 8. [d] V. A. Semion and Yu T. Struchkov, *J. Struct. Chem.*, 1968, **9**, 931. [e] M. Elder and D. Hall, *Inorg. Chem.*, 1969, **8**, 1273. [f] E. M. Cradwick and D. Hall, *J. Organometallic Chem.*, 1970, **25**, 91. [g] B. R. Davis and I. Bernal, *J. Cryst. Mol. Struct.*, 1972, **2**, 195. [h] R. Ros, M. Vidali, and R. Graziani, *Gazzetta*, 1970, **100**, 407. [i] M. G. B. Drew and A. P. Wolters, *J.C.S. Chem. Comm.*, 1972, 457. [j] R. M. Laine, R. E. Moriarty, and R. Bau, *J. Amer. Chem. Soc.*, 1972, **94**, 1402. [k] Ref. 5. [l] Carbonyl bound to Al.

There seems to be little significant variation (Table 6) in W–C or C–O (terminal) bond lengths over a range of oxidation states and geometries at tungsten. Our results for these lengths and for W–C–O angles are similar to those for other compounds, but the W–C (ring carbonyl) distances (mean 1.85 Å), the same as in the compound $[\{(\eta^5\text{-}C_5H_5)W(CO)_3\}_3Al]$, $3C_4H_8O$, are significantly short. The Al–C bond lengths are normal,[20,21] and Al–O distances are at the lower end of the range (Table 7) found in other compounds with carbonyl groups bound to aluminium.

TABLE 5

Root-mean-square amplitudes of vibrations (Å) for $[\{(C_5H_5)W(CO)_3(AlMe_2)\}_2]$

	Min.	Int.	Max.
W	0.216	0.238	0.285
Al	0.217	0.232	0.322
O(1)	0.24	0.34	0.41
O(2)	0.19	0.33	0.53
O(3)	0.30	0.33	0.45
C(1)	0.20	0.25	0.41
C(2)	0.21	0.28	0.37
C(3)	0.21	0.30	0.37
C(4)	0.29	0.37	0.40
C(5)	0.28	0.39	0.44
C(6)	0.20	0.36	0.43
C(7)	0.25	0.30	0.36
C(8)	0.28	0.31	0.42
C(9)	0.23	0.33	0.45
C(10)	0.20	0.30	0.48

The most interesting feature of the structure is the linking of tungsten and aluminium by two slightly different carbonyl bridges. One, W–C(2)–O(2)–Al′, is almost linear (angles 172—176°), and the other, W–C(1)–O(1)–Al is bent (angle 149°) at the oxygen atom. Unfortunately, the resolution obtained in this study is insufficient unambiguously to distinguish between bond lengths in these two bridges. Although the shorter W–C distance is associated with the longer C–O and Al–O distances, the two Al–O distances hardly differ significantly. Likewise,

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[19] W. R. Busing, K. O. Martin, and H. A. Levy, ORFFE, Report ORNL TM 306, Oak Ridge National Laboratory, Tennessee, U.S.A. 1964.

[20] G. M. McLaughlin, G. A. Sim, and J. D. Smith, *J.C.S. Dalton*, 1972, 2197 and refs. therein.

[21] Y. Kai, N. Yasuoka, N. Kasai, and M. Kakudo, *J. Organometallic Chem.*, 1971, **32**, 165; *Bull. Chem. Soc. Japan*, 1972, **45**, 3388, 3397, 3403.

the two C–O distances barely differ significantly from each other or from the C–O distance in the terminal carbonyl groups. Bond lengths in carbonyl compounds are not usually very sensitive to small changes in bond order,[22] so it is possible, in view of the high thermal motion of the ring atoms (Table 5 and Figure 3), that the two C–O bond lengths may not be differentiated, even if more complete *X*-ray data were obtained. In many compounds, the C–O–Al system is constrained within a five- or six-membered ring, but in acyclic systems the C–O–Al angle (Table 7) is in the range 138—163°. A linear C–O–Al system, as found here for the compound $[\{(C_5H_5)W(CO)_3(AlMe_2)\}_2]$ seems to be unusual, but it is associated with a very large amplitude of vibration perpendicular to the bonds.

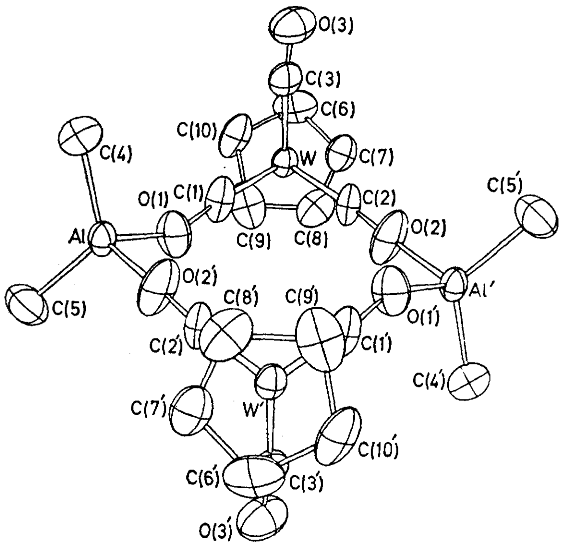

FIGURE 3 The molecule viewed approximately perpendicular to the cyclopentadienyl rings, with 40% thermal vibration ellipsoids for the anisotropic atoms

TABLE 7

Molecular parameters for carbonyl compounds bound to aluminium; distances (Å), angles (°)

	Al–O	Al–O–C	C–O
$[\{(C_5H_5)W(CO)_3\}_3Al],3C_4H_8O$ [a]	1.827(9)	140—163	1.25(2)
$[(C_5H_5)_2Fe_2(CO)_4],2AlEt_3$ [b]	2.00(2)	155(2)	
$[\{(C_5H_5)W(CO)_3(AlMe_2)\}_2]$	1.81(1)	149(2) 176(2)	1.22(2)
$ROCl,AlCl_3$ (R = Ar or Et) [c]	1.819—1.847	138—146	1.215—1.235
$(Me_2AlOCPhNPh)_2$ [d]	1.805(6)	134	1.28(1)
$[(C_{10}H_8NO)_2Al]_2O$ [e]	1.813(3)	118	1.333(5)
$(C_7H_5O_2)_3Al$ [f]	1.888(2)	155	1.291
$(Me_2AlOCPhNPh,MeCHO)_2$ [d]	2.045(7)	128	1.26(1)
$(Me_2AlOCPhNPh,MeCHO,AlMe_3)$ [d]	1.842(7)	125	1.26(1)
$(Me_2AlOCPhNPh,ONMe_3)$ [d]	1.770(6)	138	1.33(1)

[a] Ref. 5. [b] Ref. 23. [c] B. Chevrier and R. Weiss, *Angew. Chem.*, 1974, **86**, 12. [d] Ref. 21. [e] $C_{10}H_8NO$ = 2-methyl-8-quinolate; Y. Kushi and Q. Fernando, *J. Amer. Chem. Soc.*, 1970, **92**, 91. [f] $C_7H_5O_2$ = tropolonato; E. L. Muetterties and L. J. Guggenberger, *J. Amer. Chem. Soc.*, 1972, **94**, 8046.

Co-ordination of aluminium, by two oxygen atoms from bridging carbonyl groups and by two methyl groups, is similar to that in other dimethylaluminium compounds, and the large exocyclic C–Al–C angle reflects the transfer of charge from aluminium to tungsten, so that the form represented by the formula $[Me_2Al]^+[(C_5H_5)W(CO)_3]^-$ makes a contribution to the structure.[4] Co-ordination at tungsten is approximately octahedral, with the cyclopentadienyl group occupying three co-ordination sites. Thus, the carbon and oxygen atoms of carbonyl groups lie within 0.06 Å of three approximately perpendicular planes through tungsten (Table 8) and the approximate three-fold axis defined by the pyramidal $W(CO)_3$ group passes close to the centroid, G, of the cyclopentadienyl ring (Figure 3). The mean G–W–C(O) angle is 128°.

TABLE 8

Displacements (10^{-3} Å) of atoms from least-squares planes. Equations of planes in the form $Px + Qy + Rz = S$, where x,y,z are crystallographic fractional co-ordinates

(*a*) Displacements *

Plane (1): W, C(2), C(3), O(2), O(3)

W 8, Al′ −111, O(2) −21, O(3) 31, C(2) 33, C(3) −51

Plane (2): W, C(1), C(3), O(1), O(3)

W −12, Al 168, O(1) −4, O(3) −18, C(1) 5, C(3) 28

Plane (3): W, C(1) C(2), O(1), O(2)

W 37, Al −732, Al′ −59, O(1) 40, O(2) 14, C(1) −69, C(2) −22

Plane (4): C(6), C(7), C(8), C(9), C(10)

W −2 016

(*b*) Equations

Plane	*P*	*Q*	*R*	*S*	σ †
(1)	12.833	−3.322	9.287	2.410	0.036
(2)	−5.584	3.196	18.152	2.317	0.018
(3)	12.650	4.267	−5.167	0.395	0.046
(4)	11.952	2.302	13.676	5.153	0.023

(*c*) Angles (°) between planes: (1)–(2) 97, (1)–(3) 92, and (2)–(3) 89

* Primed and unprimed atoms are related by the centre of symmetry. † The root-mean-square deviation from the plane of the atoms defining the plane is denoted by σ.

A bridging atom linking two $[(C_5H_5)W(CO)_3]^-$ groups without distortion of the mutually perpendicular carbonyl groups requires a bond angle of 90° at the bridge. Compounds with Me_2Al groups bridging oxygen atoms, however, usually show angles of more than 90° between the bridge bonds.[21] Some puckering of the ring in $[\{(C_5H_5)W(CO)_3(AlMe_2)\}_2]$ is thus required to accommodate these conflicting requirements. The important features of the puckering observed are (*a*) that only one of the two carbonyl bridges is significantly bent and (*b*) that the aluminium atoms are close (Table 8) to the planes defined by the carbonyl groups at tungsten. The two different carbonyl bridges may be described as reflecting slightly different proportions of the two valence structures: $\mathrm{W{-}C{\equiv}O{:}Al}$ and $\mathrm{W{=}C{=}\dot{O}{\cdot}}\searrow$ Al

A χ-squared test on the mean plane through the atoms of the cyclopentadienyl ring shows that the ring is planar with a probability >80%. The observed C–C bond lengths (mean 1.38 Å) vary considerably, probably because of thermal motion. Individual C–C–C angles do not differ significantly from their mean, 108(2)°.

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[22] F. A. Cotton and R. M. Wing, *Inorg. Chem.*, 1965, **4**, 314.

The molecules pack in the crystal with the mean planes of the twelve-membered ring approximately normal to the short *b* axis (Figure 4). Only one intermolecular contact, between oxygen atoms of terminal carbonyl groups, is <3.55 Å.

Spectroscopic Studies.—Bridging carbonyl groups, with carbon bound to one metal atom and oxygen to the other, are associated with i.r. absorption in the range 1 530—1 680 cm^{-1}.[4,9,23,24] The three strong absorptions, one at higher frequency and the other two at much lower frequencies, observed in solutions of $[\{(C_5H_5)W(CO)_3(AlR_2)\}_2]$ (R = Me or Et) in hydrocarbons suggests that for both these compounds the twelve-membered rings persist in solution.

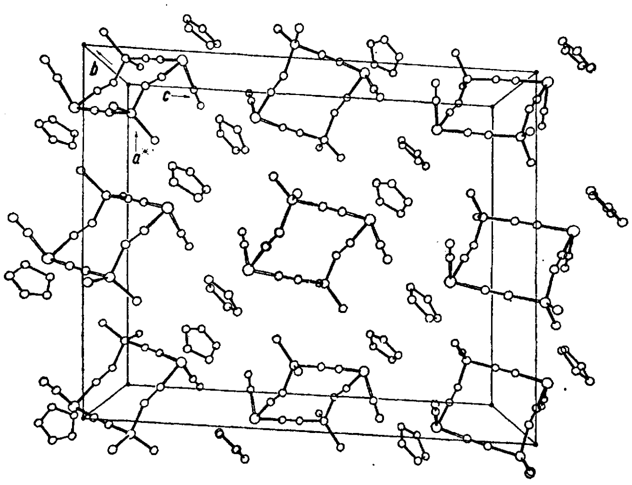


FIGURE 4 Packing diagram

The ^1H n.m.r. spectrum of the compound $[\{(C_5H_5)W(CO)_3(AlMe_2)\}_2]$ in toluene showed two sharp signals ascribed to protons of cyclopentadienyl and *Al*-methyl groups.[3] Two signals were also observed in the spectrum of a sample with an excess of hexamethyldialuminium at 20 °C, showing that exchange of methyl groups between the ring compound $[\{(C_5H_5)W(CO)_3(AlMe_2)\}_2]$ and hexamethyldialuminium was rapid on the n.m.r. time scale. When the sample was cooled to −65 °C, three peaks were obtained in the *Al*-methyl region; two of these, at τ 9.40 and 10.69, with relative intensities 1:2, were assigned to bridge and terminal groups of hexamethyldialuminium,[25] and the third at τ 9.89 to $[\{(C_5H_5)W(CO)_3(AlMe_2)\}_2]$. This resonance was considerably shifted from the position at room temperature.[3] There was no evidence for formation of a complex between trimethylaluminium and the oxygen atoms of the carbonyl groups in $[\{(C_5H_5)W(CO)_3(AlMe_2)\}_2]$, in accord with the generalisation[9] that terminal carbonyl groups are less basic than bridging carbonyl groups. There was also no peak attributable to ' mixed bridge ' species $Me_5Al_2X[X = (C_5H_5)W(CO)_3]$ such as those detected in spectra of several other $(Me_2AlX)_2$–Me_6Al_2 mixtures, *e.g.* for X = Ph, Cl, or NPh_2.[26] Mixed bridged species may, however, be intermediates in the exchange process. N.m.r. spectra from mixtures of the ring compounds $[\{(C_5H_5)W(CO)_3(AlMe_2)\}_2]$ and $(Me_2NAlMe_2)_2$ [27] at 38 °C showed two sharp signals at τ 10.19 and 10.45. Thus exchange of methyl groups between molecules of the two compounds was slow.

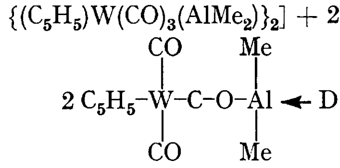
The proton decoupled ^{13}C n.m.r. spectrum of a saturated solution of $[\{(C_5H_5)W(CO)_3(AlMe_2)\}_2]$ at 32 °C showed peaks at −235.9(CO), −91.3(C_5H_5) and 10.5(Me) p.p.m. from Me_4Si, which are readily assigned by comparison with similar compounds.[6] The detection of only one signal due to ^{13}CO may imply a rapid ring-opening process, giving exchange between ring and terminal carbonyl groups. Alternatively, the observed signal may be that for the terminal carbonyl groups and the signal for the ring carbonyl groups may not be observed because the ^{13}C nuclei in the ring may have very long relaxation times. The multiple bonds in which they participate do not involve any other rapidly relaxing nuclei (*e.g.* ^1H) and may also be severely restricted with respect to rotation.

Reactions.—The compound $[\{(C_5H_5)W(CO)_3(AlMe_2)\}_2]$ was decomposed after heating at 70 °C for 18 h, with formation of an inflammable uncharacterised brown solid containing both aluminium and tungsten.

Several compounds HX reacted to give tricarbonyl-η^5-cyclopentadienylhydridotungsten and the aluminium compounds $(Me_2AlX)_n$. This reaction was very rapid for X = OH, Cl, or acac, but much slower for X = NMe_2. Aluminium–carbon bonds were attacked, with formation of methane, only when an excess of HX was available; and the ring was broken before substitution reactions were effected. A similar pattern of reactions was found for the ring-compounds $(R^1R^2NAlR^3{}_2)_m$.[28]

$$[\{(C_5H_5)W(CO)_3(AlMe_2)\}_2] + 2HX \longrightarrow 2[(C_5H_5)W(CO)_3H] + 2/n(Me_2AlX)_n \quad (4)$$

The twelve-membered ring was also broken by reaction with Lewis bases such as amines or ethers. Similar reactions have been described between Lewis bases and other weakly oligomerised derivatives Me_2AlX (X = halogen, SMe).[27]



$$\{(C_5H_5)W(CO)_3(AlMe_2)\}_2] + 2D \longrightarrow 2\,C_5H_5\text{–}\underset{CO}{\overset{CO}{W}}\text{–}C\text{–}O\text{–}\underset{Me}{\overset{Me}{Al}} \leftarrow D \quad (D = NR_3 \text{ or } OR_3) \quad (5)$$

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Related Compounds.—Several complexes $[(C_5H_5)W(CO)_2L(AlMe_2)]$ (L = PPh_3, PMe_2Ph, or PEt_2Ph) have been characterised. The presence of bands in the i.r. between 1 585 and 1 685 cm^{-1} (Table 1) suggests that the dimethyl- and diethyl-phosphine derivatives have carbonyl-bridged structures with the phosphine ligands replacing the terminal carbonyl groups of $[\{(C_5H_5)W(CO)_3(AlMe_2)\}_2]$. The structure of the extremely insoluble triphenylphosphine derivative, which gives a peak at 1 873 cm^{-1} in the i.r. spectrum, must at present remain in doubt.

An attempt to make a complex in which the $[(C_5H_5)W(CO)_3]^-$ fragment was replaced by $[Re(CO)_5]^-$ ion was not successful. The reaction between dimethylaluminium hydride and the hydride $[(OC)_5ReH]$ gave the known compound $[Re_3(CO)_{14}H]$ as the main product.

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