Crystal and Molecular Structure of Di-μ-(tricarbonyl-π-cyclopentadienyltungsten-*OO'*)bisdimethylaluminium

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Summary The compound $[(C_5H_5)W(CO)_3AlMe_2]_2$ consists of molecules having twelve-membered rings with Al–O–C–W bridges between aluminium and tungsten.

IN many molecules, carbonyl groups form bridges by co-ordination of carbon to two or more metal atoms. We now describe a carbonyl bridge in which carbon is linked to one metal atom and oxygen to another.

Crystals of the compound $[(C_5H_5)W(CO)_3AlMe_2]_2$,[1] which is exceedingly reactive towards traces of air or moisture, were shaken from the reaction vessel, and sealed in evacuated thin-walled Pyrex capillaries. They were shown by *X*-ray methods to be monoclinic with $a = 18{\cdot}120(6)$, $b = 6{\cdot}188(3)$, $c = 22{\cdot}266(8)$ Å, $\beta = 93{\cdot}29(2)°$; $Z = 8$ {$[C_5H_5W(CO)_3AlMe_2]$ units}; space group $C2/c$. Intensity data for 1600 reflections with $F^2_{obs}/\sigma(F^2_{obs}) \geqslant 3{\cdot}0$ were observed

by four-circle automatic diffractometry using Mo-K_α radiation, and atomic parameters were found by Patterson, Fourier, and least-squares methods. All atoms were refined with anisotropic thermal parameters giving R 0·07 and further refinement with data corrected for absorption (μ 98·7 cm^{-1}) is proposed. The analysis shows well separated centrosymmetric dimeric molecules (Figure). Each tungsten is bound to a cyclopentadienyl group and to three carbonyl groups. The oxygen atoms of two of the carbonyls are linked to aluminium atoms making a slightly puckered twelve-membered ring. The tungsten achieves roughly octahedral co-ordination (with the cyclopentadienyl group occupying three co-ordination sites) and the aluminium is four-co-ordinate with the wide exocyclic C–Al–C angle found in other derivatives $(Me_2AlX)_n$ (n = 2,3; X = *e.g.*, Cl,Me,NR_2).[2] The nucleophile $[(C_5H_5)W(CO)_3]^-$ may thus serve as a bridging group between aluminium atoms in this class of compounds.

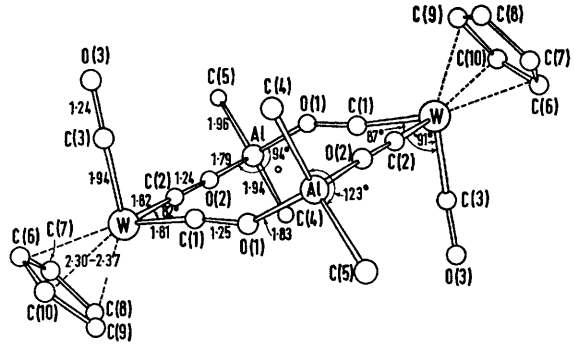

FIGURE. *Distances are in* Å.

Estimated standard deviations calculated from the inverse least-squares matrix are 0·03 (W–C, Al–C, Al–O) and 0·045 Å (C–C, C–O). Distances are uncorrected for thermal motion. The W–C bond lengths within the ring appear to be short compared with tungsten–terminal carbonyl bonds.[3] All C–O distances appear to be long compared with those in other carbonyl compounds, but discussion of molecular parameters is deferred until refinement is complete.

Similar carbonyl bridges between tungsten and aluminium in the ion $[(C_5H_5)W(CO)_3AlPh_3]^-$ were suggested[4] by i.r. spectroscopic data.

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