Preparation and Molecular Structure of $[Ta\{H_2Al(OC_2H_4OMe)_2\}(Me_2PC_2H_4PMe_2)_2]_2$, a Co-ordinatively Unsaturated Aluminohydride Adduct of Tantalum(I)

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Summary Reaction of $TaCl_2(Me_2PC_2H_4PMe_2)_2$ with $Na[H_2Al(OC_2H_4OMe)_2]$ affords $[Ta\{H_2Al(OC_2H_4OMe)_2\}(Me_2PC_2H_4PMe_2)_2]_2$, a co-ordinatively unsaturated complex based on an approximately square-pyramidal $P_4Ta\text{-}\mu\text{-}H_2\text{-}Al$ group.

TETRAHYDROALUMINATE salts and alkoxyaluminium hydrides are frequently used for the preparation of transition metal hydrides from the corresponding halogeno complexes.[1] Analogous reactions with tetrahydroborate ion often lead to $M(BH_4)$ complexes, most commonly containing a bidentate borohydride unit.[2] No definitive examples of tetrahydroaluminate or related alkoxyaluminium hydride complexes have been isolated.[3] We report the preparation and molecular structure of $[Ta\{H_2Al(OC_2H_4OMe)_2\}(dmpe)_2]_2$ (dmpe = $Me_2PC_2H_4PMe_2$), a remarkably stable 16-electron complex containing an approximately square-pyramidal $P_4Ta\text{-}\mu\text{-}H_2\text{-}Al(OR)_2$ unit. The $TaH_5(dmpe)_2$-catalysed $[^2H_2]$benzene exchange has been suggested to proceed *via* a low-valent Ta hydride.[4] The aluminohydride adduct may represent stabilization of the catalytic intermediate or a related species by the Ta–H–Al interaction.

Treatment of an ethereal solution of $TaCl_2(dmpe)_2$[5] with 2 equiv. of $Na[H_2Al(OC_2H_4OMe)_2]$ in the presence of CO rapidly affords $[TaCl(CO)_2(dmpe)_2]$.[5] Replacement of CO with ethylene does not lead to similar products; rather, crystals of $[Ta\{H_2Al(OC_2H_4OMe)_2\}(dmpe)_2]_2$ are slowly deposited. Ethylene was subsequently shown to be unnecessary.

Crystal data: triclinic, space group $P\bar{1}$, $a = 10{\cdot}899(3)$; $b = 11{\cdot}197(3)$; $c = 13{\cdot}579(4)$ Å; $\alpha = 99{\cdot}12(4)$; $\beta = 104{\cdot}69(4)$; $\gamma = 104{\cdot}21(4)°$; $Z = 1$. The 2558 reflections for which $F > 3{\cdot}92\,\sigma(F)$ were measured on a Syntex $P2_1$ automated diffractometer (crystal-monochromated Mo-K_α radiation). Full-matrix least-squares refinement of positional and anisotropic (Ta, P, Al) and isotropic (light atoms) thermal parameters for all atoms† has converged to a conventional R-factor of 0·071.

The essential features of the molecular structure of the complex, which is a centrosymmetric dimer with a bridging $H_2Al(OR)\text{-}\mu\text{-}(OR)_2\text{-}Al(OR)H_2$ species, are depicted in the Figure.‡

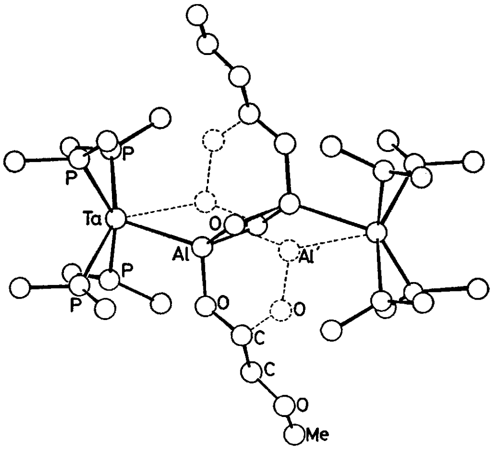

FIGURE. The molecular structure of $[Ta\{H_2Al(OC_2H_4OMe)_2\}(dmpe)_2]_2$. dmpe methylene carbon atoms are not included† and the $-CH_2CH_2OMe$ linkages on the bridging oxygen atoms have been omitted for clarity. In the actual structure, there are two orientations of the Al_2O_2 bridge unit in a 4 : 1 ratio. The 80% abundant form is shown in solid lines, while the 20% abundant form is indicated by the atoms (Al′ and O′) in dotted lines. Pertinent distances and angles are: Ta–Al, 2·733(9); Ta–Al′, 2·693(29); Ta–P, 2·500—2·536(9) Å; average P–Ta–P bite angle, 76·5(3)°.

Hydrogen atoms have not been located, but the presence of Ta–H–Al linkages is implied by chemical and spectroscopic evidence (*vide infra*). The salient features of the structure are as follows. (i) Each half of the dimer may be formally considered to be a distorted square-pyramid; 4P atoms form the basal plane (± 0·01 Å), while a $\mu\text{-}AlH_2$ unit approximately occupies the apex. The angle between the normal to the P_4 plane and the Ta–Al vector is 16·1°; that this angle is not near 0° suggests an $Al\text{-}\mu H_2\text{-}Ta$ interaction. The tantalum atom lies 0·64 Å out of the P_4 plane. There are no intermolecular contracts $\leqslant$ 4·0 Å to the tantalum atom. (ii) If one neglects the Ta–Al interaction, each aluminium atom is five-co-ordinate, *viz.*, AlO_3H_2. Five-co-ordinate aluminium has also been observed in the Lewis base adducts $AlH_3{\cdot}2NR_3$ and $(AlH_3{\cdot}NR_3)_2$.[6] (iii) The relatively short tantalum–aluminium distance, 2·733(9) Å, suggests interaction in view of distances reported for first- and second-row transition metal complexes, *e.g.*, Ti–Al, 2·79—3·13;[3c] Mo–Al, 2·65—2·99 Å.[3d]

Although the bridging hydrogen atoms have not been located crystallographically, two equally intense i.r. bands at 1605 and 1640 cm^{-1} are consistent with their presence.

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† Owing to severe disorder we were unable to locate the methylene carbon atoms in the two dmpe ligands, and thus these have not been included in the refinement. Further, there is a disorder involving the Al atom and the non-bridging oxygen atom directly attached to Al. However, this disorder is well resolved, and the affected atoms exhibit similar bond distances and angles in both forms. Refinement is continuing in both space groups $P1$ and $P\bar{1}$.

‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

A broad ^1H n.m.r. resonance at τ 16·30 of appropriate intensity is observed and is unchanged from 90 to −70 °C. Hydrolysis with DCl in benzene, neat CD_3OD, or D_2O gives D_2 and 2·0 ± 0·4 mol HD–Ta, consistent with the proposed structure and, together with the ^1H n.m.r. data, eliminating the possible existence of additional hydride ligands in the vacant co-ordination site.

The Ta–μ-H_2–Al unit is not easily degraded. The compound may be quantitatively recovered from triethylamine and is inert to CO. It does not catalyse the hydrogenation of oct-1-ene and is a poor catalyst for the isomerization of pent-1-ene. These observations suggest that the occasionally poor yields of metal hydrides obtained from alkoxyaluminohydrides and metal halides may be due to irreversible complex formation.[1,3a]

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