Crystal and Molecular Structure of [Ta(H)₂(OC₆H₃Prⁱ₂-2,6)₃(PMe₂Ph)]: a Distorted Six-coordinate Tantalum Dihydride

Valerie M. Visciglio, Phillip E. Fanwick and Ian P. Rothwell*

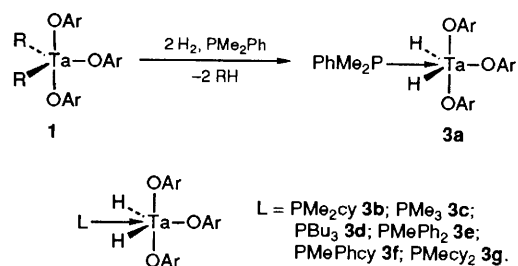*Department of Chemistry, 1393 Brown Building, Purdue University, West Lafayette, IN 47907, USA*

Reaction of [Ta(OC₆H₃Prⁱ₂-2,6)₃R₂] (R=CH₂C₆H₄-4-Me) with H₂ in the presence of phosphine ligands (L) leads to the dihydride compounds [Ta(H)₂(OC₆H₃Prⁱ₂-2,6)₃(L)], the solid-state structure of the PMe₂Ph derivative shows a geometry about the metal centre that is severely distorted from octahedral; hydrogenation of aryl-phosphines and other aromatic substrates is catalysed by these dihydride compounds.

The structure, spectroscopic properties and reactivity of transition metal hydride[1] and related dihydrogen[2] compounds continues to be a highly active area of chemical research. Here, describe the characterization of a series of reactive dihydride compounds of tantalum,[3-7] which contain an unusually distorted six-coordinate geometry about the metal centre.

The dialkyl compound [Ta(OC₆H₃Prⁱ₂-2,6)₃R₂] **1** (R = CH₂C₆H₄-4-Me) undergoes hydrogenolysis of the tantalum alkyl bonds over 24 h in cyclohexane solvent at 90 °C and 8 300 kPa of hydrogen. In the absence of added ligand, this reaction produces the monohydride compound [Ta(H)(OC₆H₃Prⁱ₂-2,6)₄] **2**, presumably by ligand-exchange reactions. Compound **2** shows a sharp singlet for the Ta–*H* resonance at δ 9.12 in the ¹H NMR spectrum and a band at 1586 cm⁻¹ in the IR spectrum assignable to ν (Ta–H). The hydrogenolysis of **1** in the presence of added PMe₂Ph (≥1 equiv.) leads to the formation of a highly soluble colourless dihydride compound [Ta(H)₂(OC₆H₃Prⁱ₂-2,6)₃(PMe₂Ph)] **3a** (Scheme 1). Com-

pound **3a** was obtained as colourless crystals from hexane once the *p*-xylene generated during the reaction was removed. The ¹H NMR spectrum of **3a** shows the hydride ligand as a downfield doublet at δ 14.89 due to coupling to the single

Scheme 1

R = CH₂C₆H₄-*p*-Me; OAr = OC₆H₃-2,6-Prʲ₂; cy = c-C₆H₁₁

L = PMe₂cy **3b**; PMe₃ **3c**; PBu₃ **3d**; PMePh₂ **3e**; PMePhcy **3f**; PMecy₂ **3g**.
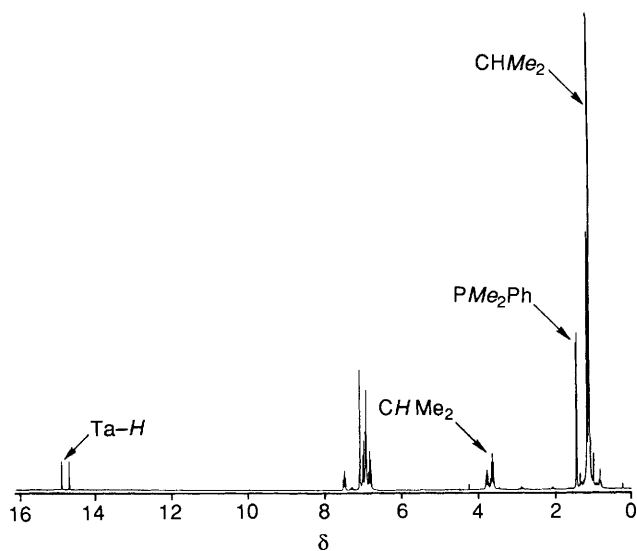
Fig. 1 ¹H NMR (300 MHz, C₆D₆) of **3a**

Fig. 2 ORTEP view of **3a** emphasizing the central coordination sphere. All hydrogen atoms except those bound to tantalum are removed for clarity. Selected bond distances (Å) and angles (°): Ta–P 2.650(1); Ta–O(20) 1.907(3); Ta–O(30) 1.912(4); Ta–O(40) 1.897(3); Ta–H(1) 1.74(4); Ta–H(2) 1.83(6); P–Ta–O(20) 89.3(1); –O(30) 174.5(1); –O(40) 85.4(1); –H(1) 69(1); –H(2) 64(3); O(20)–Ta–O(30) 92.0(2); –O(40) 173.3(1); –H(1) 89(1); –H(2) 91(2); O(30)–Ta–O(40) 93.6(2); –H(1) 116(1); –H(2) 109(2); O(40)–Ta–H(1) 86(1); –H(2) 91(2); H(1)–Ta–H(2) 135(3).

PMe₂Ph ligand (Fig. 1).† Two sharp sets of non-equivalent aryloxide ligands in the ratio of 2:1 are seen in the aliphatic region of the spectrum. Neither the P*Me₂*Ph nor aryloxide CH*Me₂* methyl groups are diastereotopic. These spectroscopic data are only consistent with the adoption of a geometry around the tantalum atom in **3a** with mutually *trans*-hydride ligands. This conclusion is supported by the solid-state structure of **3a** (Fig.2).‡ The aryloxide and phosphine ligands are arranged in a mutually square-planar arrangement about the metal centre. However, location and refinement of the two hydride ligands above and below this plane showed them to be significantly distorted from a linear arrangement. Instead the hydride ligands are both oriented towards the phosphorus atom with P–Ta–H angles of 66(2)° and 69(1)° and an H–Ta–H angle of only 135(3)°. An alternative description of the solid-state structure of **3a** begins with a trigonal-bipyramidal arrangement of the five covalently bound groups to which is attached the phosphine ligand with a long (stereochemically less active) dative bond between the two equatorial hydride groups. It has been recognized for some time,[8] and recently highlighted for aryloxide compounds,[9] that the structure of some main group compounds can be rationalized by recognizing the presence of primary (typically covalent) and secondary (dative) bonds.[10] Further support for the non-linear arrangement of the two hydride ligands in **3a** comes from its IR spectrum. The detection and assignment of metal–hydride vibrations is sometimes difficult

and ambiguous.[1] However, the spectrum of **3a** as a solution in Nujol shows two distinct bands at 1824 and 1758 cm⁻¹. If one tentatively assigns these bands to the symmetric and asymmetric tantalum–hydride stretches then their relative intensities[11] are not inconsistent with the observed H–Ta–H angles in **3a**.

Despite the distorted coordination geometry, dissociation of the PMe₂Ph ligand from **3a** is not rapid on the ¹H NMR timescale. Addition of PMe₂Ph to a solution of **3a** generates two sharp sets of phosphine signals and no loss of ³¹P coupling to the hydride ligands occurs. However, chemical exchange of coordinated phosphines can readily occur. Hence, addition of PMe₃ or PBu₃ to a solution of **3a** results in signals in the NMR spectra due to the formation of the corresponding phosphine adducts and free PMe₂Ph.

Solutions of **3a** in C₆D₆ undergo scrambling of the hydride ligands with D₂ (101.3 kPa) over a period of days at 25 °C. The hydride resonance of the isotopomer [Ta(H)(D)(OC₆H₃Prⁱ₂-2,6)₃(PMe₂Ph)] was observed by ¹H NMR at δ 14.84, an isotope shift of −0.05/D (upfield).[12] When the hydrogenolysis of **1** in the presence of PMe₂Ph was carried out for extended periods of time (>24 h) the formation of a new compound of formula [Ta(H)₂(OC₆H₃Prⁱ₂-2,6)₃(PMe₂cy)] **3b** was observed as a minor component of **3a** by ¹H and ³¹P NMR spectroscopy. Furthermore, use of the ligand PMePh₂ in the hydrogenolysis of **1** was found to yield only those products resulting from sequential hydrogenation of the aryl-phosphine ligands.[13] Analysis of the ³¹P NMR spectra from this reaction showed no phosphine compounds or complexes derived from partial hydrogenation of the aryl rings.

The dihydride compounds obtained in this study will also catalyse the regioselective hydrogenation of naphthalene and anthracene to 1,2,3,4-tetrahydronaphthalene and 1,2,3,4-tetrahydro- and 1,2,3,4,5,6,7,8-octahydro-anthracene, respectively. These hydrogenation reactions are inhibited by the presence of an excess of phosphine in the reaction mixture,

---

† *Selected spectroscopic data*: NMR data in C₆D₆ for each compound is listed as δ (Ta-*H*) [²*J*(³¹P-¹H)]; δ (Ta-*P*) **3a**: 14.89 (60.3), −6.5; **3b**: 14.65 (60.1), −3.6; **3c**: 14.46 (63.4), −17.4; **3d**: 14.67 (59.2), +10.7; **3e**: 15.34 (59.0), +8.2; **3f**: 15.23 (57.7), +11.9; **3g**: 14.82 (57.2), +18.2.

‡ *Crystallographic data* for **3a** at 20 °C: TaPO₃C₄₄H₆₄, *M* = 852.92, space group *P*2₁/*n*, (No. 14), *a* = 10.637(1), *b* = 12.820(2), *c* = 31.799(4) Å, β = 98.76(1)°, *U* = 4285(2) Å³, *D*c = 1.322 g cm⁻³, *Z* = 4. Of the 7944 unique reflections collected (4.0° ≤ 2θ ≤ 50.0°) with Mo-Kα (λ = 0.71073 Å) the 5127 with *I* > 3σ(*I*) were used in the final least-squares refinement to yield *R* = 0.029 and *R*w = 0.036. The two hydride ligands were located and refined. All other hydrogen atoms were placed in idealized positions. The highest peak in the final difference Fourier had a height of 0.49 e Å⁻³.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.
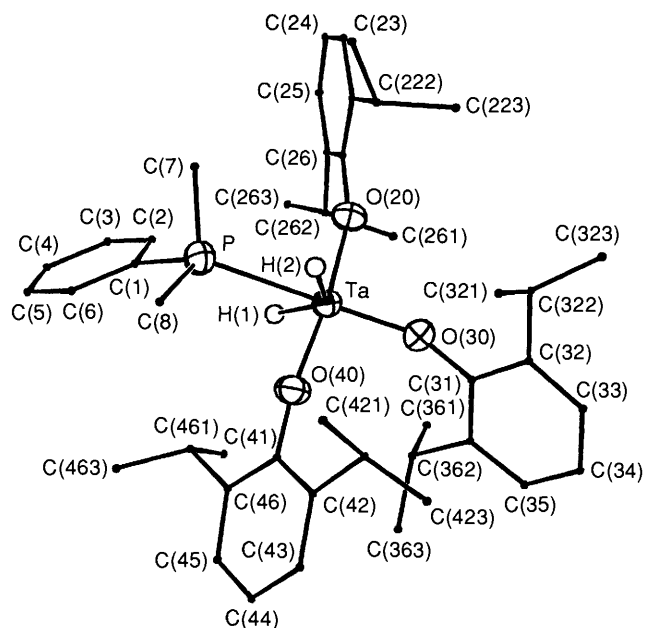
indicating that dissociation to form the dihydride [Ta-$(H)_2(OC_6H_3Pr^i_2-2,6)_3$] is a key step in these reactions.

References

1 R. H. Crabtree, in *Comprehensive Coordination Chemistry*, ed. G. Wilkinson, R. Gillard and J. A. McCleverty, Pergamon Press, New York, 1987; G. G. Hlatky and R. H. Crabtree, *Coord. Chem. Rev.*, 1985, **65**, 1; D. S. Moore and S. D. Robinson, *Chem. Soc. Rev.*, 1983, 415.

2 J. Eckert, G.J. Kubas and R. P. White, *Inorg. Chem.*, 1992, **31**, 1550; G. J. Kubas, *Acc. Chem. Res.*, 1988, **21**, 120; R.H. Crabtree and D. G. Hamilton, *Adv. Organomet. Chem.*, 1988, **28**, 299; R. H. Crabtree, *Acc. Chem. Res.*, 1990, **23**, 95.

3 F. N. Tebbe, *J. Am. Chem. Soc.*, 1973, **95**, 5823.

4 J. M. Mayer and J. E. Bercaw, *J. Am. Chem. Soc.*, 1982, **104**, 2157; J. M. Mayer, P. T. Wolczanski, B. D. Santarsiero, W. A. Olson and J. E. Bercaw, *Inorg. Chem.*, 1983, **22**, 1149.

5 R. E. LaPoint and P. T. Wolczanski, *J. Am. Chem. Soc.*, 1986, **108**, 3535.

6 A. J. Scioly, M. L. Luetkens, R. B. Wilson, J. C. Huffmanm and A. P. Sattelberger, *Polyhedron*, 1987, **6**, 741; M. L. Luetkens, W. L. Elcesser, J. C.Huffman and A. P. Sattelberger, *Inorg. Chem.*, 1984, **23**, 1718.

7 B. C. Ankianiec, P. E. Fanwick and I. P. Rothwell, *J. Am. Chem. Soc.*, 1991, **113**, 4710; R. D. Profilet, P. E. Fanwick and I. P. Rothwell, *Polyhedron*, 1992, **11**, 1559.

8 A. Haaland, *Angew. Chem. Int. Ed. Engl.*, 1989, **28**, 992; N. W. Alcock, *Adv. Inorg. Chem. Radiochem.*, 1972, **15**, 1.

9 S. C. Goel, M. Y. Chiang and W. E. Buhro, *J. Am. Chem. Soc.*, 1990, **112**, 6724.

10 M. D. Fryzuk, A. Carter and S.J. Rettig, *Organometallics*, 1992, **11**, 469.

11 F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 5th edn., John Wiley and Sons, New York, 1988, pp. 1035–1038.

12 X. L. Luo and R. H. Crabtree, *J. Am. Chem. Soc.*, 1990, **112**, 4813; D. G. Hamilton, X. L. Luo and R. H. Crabtree, *Inorg. Chem.*, 1989, **28**, 3198.

13 J. S. Yu and I. P. Rothwell, *J. Chem. Soc., Chem. Comm.*, 1992, 632.