Preliminary communication

FACILE ACCESS TO METHYL TANTALUM DERIVATIVES BY UNPRECEDENTED PHOSPHORUS—METHYL BOND CLEAVAGE OF DIMETHYLPHENYLPHOSPHANE

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Summary

Reactions of the paramagnetic pentacoordinated $TaBr_3(PhPMe_2)_2$ adduct with strong bases, (RLi (R = Me, Bu) or 1,8-bis(dimethylamino)naphthalene) have been found to give methyltantalum(IV) derivatives as a result of P—Me bond cleavage.

Tertiary phosphanes are among the most extensively used ligands because of their versatility and inertness [1]. Our current studies of transition metal derivatives led us to the isolation of a paramagnetic Ta^{III} species, $TaBr_3(PhPMe_2)_2$ (1), the first monomeric halogeno Ta^{III} adduct structurally characterized [2]. Its coordinative and electronic unsaturation leads to unusual behavior in the solid as well as in solution. $TaBr_3(PhPMe_2)_2$ crystallises as stereodynamic (down to −150°C) square-pyramidal molecules with an apical bromine atom occupying either of the vacant sites of the basal plane and the two phosphorus ligands in *cis* positions. There is thus a pseudo-octahedral environment of the metal in the solid, and no interactions with hydrogen atoms are observed [3].

In solution, spontaneous C—H activation reactions provide an alternative way of relieving the unsaturation at the tantalum center and in CH_2Cl_2 agostic C—H interactions involving the phenyl groups are observed. In contrast, aliphatic carbon—hydrogen activation is favoured in CH_3CN, involving oxidative addition to Ta^V species having an η^2-CH_2PMePh moiety or the unusual $HC=TaPMePh$ metallocycle (2) (Scheme 1).
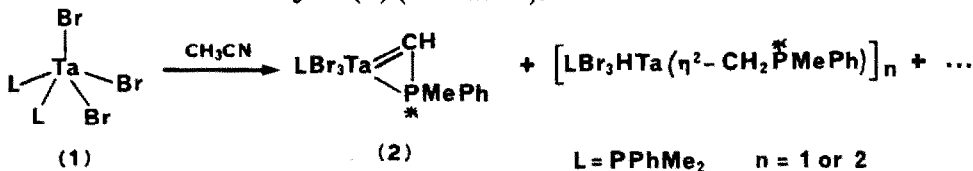
SCHEME 1

Attempts to enhance the selective formation of only one metallated phosphane species by reaction of $TaBr_3(PhPMe_2)_2$ in the presence of strong bases resulted in the unexpected formation of σ-methyl derivatives of tantalum. For example, the reaction between 1 and one equivalent of butyllithium in diethyl ether at room temperature gave a compound analysing* as $Ta_2Br_5(Me)L_3$ (L = $PhPMe_2$) but with spectral data, especially in the ^1H NMR**, more in agreement with a diamagnetic Ta^{IV} compound of formula $Ta_2Br_5(Me)_2(PhPMe)(PhPMe_2)_2$ (3). The formation of Ta—Me σ-bonds, for which chemical shifts would be in the observed range [4], is confirmed by the presence of a broad band at 450 cm^{-1} in the infrared. Dimeric structures (such as I), in which tantalum achieves its usual hexacoordination and the methyl groups and phosphanes occupy equivalent positions, can be assigned to 3.

L = PhPMe₂

(I)
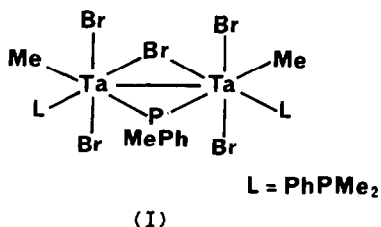
Dynamic equilibrium between geometrical isomers derived from structure I may account for the variation in the chemical shift for the tantalum-methyl protons as a function of the concentration and of the temperature, as well as for the appearance of several phosphorus resonances in the ^{31}P NMR spectrum.

Formation of σ-methyl derivatives of tantalum in high yield is general in reactions between 1 and a variety of strong bases, including methyllithium and the proton sponge 1,8-bis(dimethylamino)naphthalene, while lithium bis(trimethylsilyl)amide acts as a nucleophile. The formation of alkyl compounds (the only metal species isolated) and their stoichiometry (which depends on the base) implies the cleavage of a P—Me bond of a dimethylphenylphosphane ligand, even with methyllithium as the base. Various monitoring experiments have failed to detect any derivatives corresponding to some P—aryl cleavage.

Although phosphorus—carbon bond cleavage reactions are not unprecedented, they mainly involve P—aryl bonds in catalytic cycles: electron-rich metal derivatives, or high temperature or hydrogenolysis conditions [5]. For tertiary phosphanes, $P-C_{sp^3}$ cleavage appears to have been limited previously to symmetrical PR_3 (R = Me [6], ^tBu [7]. The cleavage of the P—aryl bond of $PhPMe_2$ is promoted by osmium derivatives [8a], but the cleavage of a P—Me bond rather than a P—aryl bond is to the best of our knowledge unprecedented. It is noteworthy that attempts to cleave a P—Me bond of $PhPMe_2$ using more classical routes, such as reactions with alkali metals, or use of electrochemical or γ-irradiation methods, were unsuccessful [8b].

The fact that the P—Me cleavages mediated by the tantalum center occurs under very mild conditions (even −20°C) may be a consequence of the high

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*Analytical data: Found: C, 24.96; H, 3.36; P, 7.35. $C_{25}H_{36}Br_5P_3Ta_2$ calcd.: C, 25.19; H, 3.04; P, 7.80%.

**NMR data for 3 in CD_3CN: ^1H: δ 4.02 (6H, CH_3), 2.12 (3H, d, ^2J(P—H) 15 Hz, PhPMe); 2.11 (12H, d, ^2J(P—H) 15 Hz, PhPMe₂). $^{31}P\{^1H\}$: +64 (PhPMe), 22.5, 5.7, −7.9 (PhPMe₂) ppm.

thermodynamic stability of the Ta—Me bond. The mean bond dissociation energy $\bar{D}$(Ta—Me) of 261 ± 6 kJ mol^{-1} estimated from the heat of dissocation of TaMe$_5$ [10], is quite high compared to the values found for most other methyl—metal bonds [11], and is comparable to the D(P—CH$_3$) bond energy (264 kJ mol^{-1}, for PMe$_3$) [12]. The formation of a μ-phosphidotantalum species and sometimes of LiPPhMe, which according to Issleib should be particularly stable [13], may act as an additional driving force in the P—Me bond cleavage.

The scope of P—C cleavage reactions for the preparation of other low-valent alkyl complexes of tantalum and niobium is under investigation [14].

References

1 R. Mason and D.W. Meek, Angew. Chem. Int. Ed., 17 (1978) 183. C.A. Tolman, Chem. Rev., 77 (1977) 314.
2 N. Hovnanian, L.G. Hubert-Pfalzgraf and G. Le Borgne, Inorg. Chem., Chem., in press.
3 M. Brookhart and M.L.H. Green, J. Organomet. Chem., 250 (1983) 295.
4 C.S. Santini-Scampucci and J.G. Riess, J. Chem. Soc. Dalton, (1973) 2436; J.A. Labinger, Comprehensive Organometallic Chemistry, Pergamon Press, vol. 3, 1982.
5 P.E. Garrou, Chem. Rev., 85 (1985) 17; T. Nishiguchi, K. Tanaka and K. Fukuzumi, J. Organomet. Chem., 193 (1980) 37; A.G. Abatjoglou, E. Billig and D.R. Bryant, Organometallics, 3 (1984) 923, 932.
6 K.W. Chiu, R.A. Jones, G. Wilkinson, A.M.R. Galas and M.B. Hursthouse, J. Chem. Soc. Dalton, (1981) 1892; N.F. Klein, J. Wenninger and U. Schubert, Z. Naturforsch. B, 34 (1979) 1391.
7 A.B. Goel and S. Goel, Inorg. Chim. Acta, 90 (1984) L33.
8 A.J. Deeming, R.E. Klimber and M. Underhill, J. Chem. Soc. Dalton, (1973) 2589.
9 E.I. Becker and M. Tsutsui (Ed.), Organometallic Reactions, vol. 5, 1970, Wiley-Interscience, NY; Organophosphorus Chemistry, Specialist Periodical Reports, The Chemical Society, London, 4 (1972); 8 (1977).
10 F.A. Adedeji, J.A. Connor, H.A. Skinner, L. Galyer and G. Wilkinson, J. Chem. Soc., Chem. Commun., (1976) 159.
11 J. Halpern, Acc. Chem. Res., 15 (1982) 238; M.L. Mandlich, F. Halle and J.L. Beauchamp, J. Am. Chem. Soc., 106 (1984) 4403.
12 J. Emsley and D. Hall, The Chemistry of Phosphorus, Harper, London, 1976.
13 K. Issleib, Z. Chem., 2 (1962) 163; K. Issleib and E. Tzchach, Chem. Ber., (1959) 1118.
14 C. Forano, N. Hovnanian and L.G. Hubert-Pfalzgraf, to be published.