Aryloxide Ligand Dependent Reactivity of Tantalum Dihydride Compounds with Alkenes

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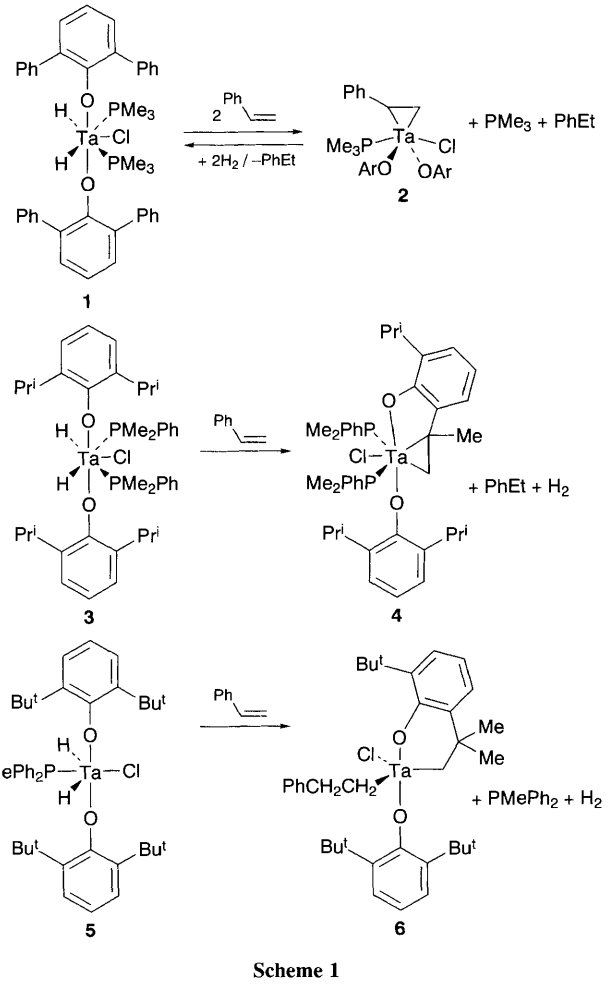
The tantalum dihydride compounds $[Ta(OAr)_2(L)_n(Cl)(H)_2]$ (n = 2, OAr = 2,6-diphenyl- and 2,6-diisopropylphenoxide; n = 1, OAr = 2,6-di-*tert*-butylphenoxide) react with styrene to produce different organometallic products depending upon the nature of the aryloxide ligand.

It has been shown recently that hydrido aryloxides of tantalum will catalyse the regio- and stereo-selective hydrogenation of arene rings.[1] As an extension of this work we have investigated the reactivity of some of these compounds towards alkenes and we report here our observation that the ancillary aryloxide ligand has a strong influence on the reaction path that is followed.

The seven-coordinate dihydride $[Ta(OC_6H_3Ph_2\text{-}2,6)_2(PMe_3)_2(Cl)(H)_2]$ **1**[2] reacts slowly with styrene in C_6D_6 solution to form 1 equiv. of ethylbenzene (^1H NMR) and the η^2-styrene complex **2** (Scheme 1).† The solid state structure of **2** (Fig. 1)‡ shows a coordination environment about tantalum best described as square pyramidal with the η^2-bound styrene occupying the axial site. The alkene C–C distance of 1.452(7) Å is significantly lengthened over the 1.339 Å distance found in ethylene,[3] implying the presence of a tantalacyclopropane ring.[4] Solutions of **2** and PMe_3 in C_6D_6 react slowly with H_2 (1 atm) to produce 1 equiv. of ethylbenzene and regenerate the dihydride **1**. In the presence of an excess of both styrene and hydrogen (20 psi; 1 psi = 6.8 × 10^{-2} atm), complex **1** will catalytically produce ethylbenzene at 25 °C in C_6D_6 solvent at a rate of only 1 equiv. per day. Monitoring this reaction by ^{31}P NMR showed the presence of **2** with small amounts of **1** in the reaction mixture during catalysis. Increasing the hydrogen pressure to 1200 psi increases the rate of formation of ethylbenzene to 1 equiv. per hour.



Scheme 1

The 2,6-diisopropylphenoxide dihydride $[Ta(OC_6H_3Pr^i{}_2\text{-}2,6)_2(PMe_2Ph)_2(Cl)(H)_2]$ **3**[2] also reacts in hydrocarbon solution with styrene to produce 1 equiv. of ethylbenzene. The reaction generates dihydrogen along with the tantalum compound **4** in which intramolecular dehydrogenation of an aryloxide isopropyl group has occurred (Scheme 1). The structure of **4** is based upon its spectroscopic data and comparison with related niobium complexes.[5] Studies utilizing the deuteride $[^2H_2]$**3** show that the generated hydrogen originates from the isopropyl group. A reaction pathway involving reductive elimination of ethylbenzene from an intermediate phenethyl hydride is implicated. Previous work has shown that tantalum(III) species have the ability to cyclometallate aryloxide ligands *via* oxidative addition of aliphatic CH bonds.[6] In the case of the 2,6-diphenylphenoxide **1** the coordination of styrene to the Ta^{III} intermediate is apparently favoured over CH bond activation leading to complex **2**.

The addition of styrene to the 2,6-di-*tert*-butylphenoxide dihydride $[Ta(OC_6H_3Bu^t{}_2\text{-}2,6)_2(PMePh_2)(Cl)(H_2)]$ **5**§ does not produce any ethylbenzene. Instead a phenethyl derivative **6** is

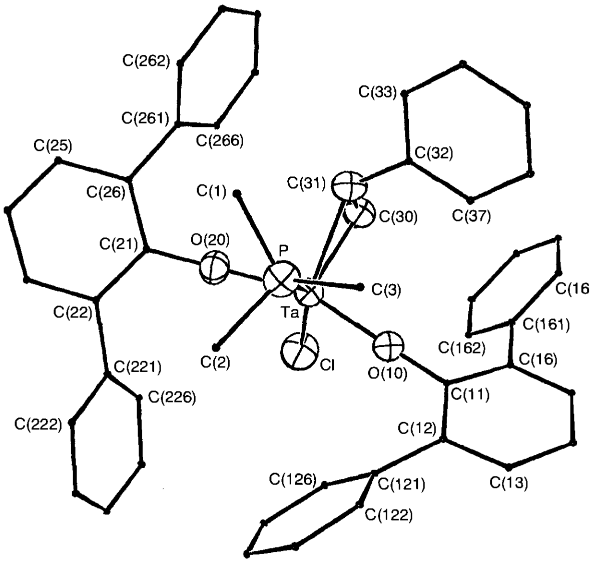


Fig. 1 Molecular structure of **2**. Selected interatomic distances (Å) and angles (°): Ta–Cl 2.44(1), Ta–P 2.609(1), Ta–O(10) 1.895(3), Ta–O(20) 1.915(3), Ta–C(30) 2.131(5), Ta–C(31) 2.242(5), C(30)–C(31) 1.452(7), O(10)–Ta–O(20) 158.9(1), Cl–Ta–P 150.88(5), Ta–O(10)–C(11) 174.7(3), Ta–O(20)–C(21) 165.8(3).

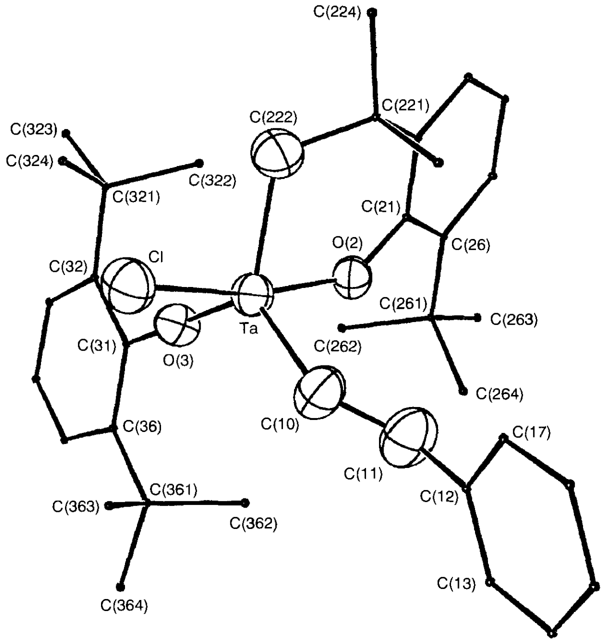


Fig. 2 Molecular structure of **6**. Selected interatomic distances (Å) and angles (°): Ta–Cl 2.383(2), Ta–O(2) 1.872(4), Ta–O(3) 1.863(4), Ta–C(10) 2.145(7), Ta–C(222) 2.171(7), Cl–Ta–O(2) 166.4(1), Ta–O(2)–C(21) 144.9(4), Ta–O(3)–C(31) 177.7(4), Ta–C(10)–C(11) 123.0(5).

produced along with dihydrogen (Scheme 1). Compound **6** contains a cyclometallated 2,6-di-*tert*-butylphenoxide ligand (Fig. 2) with a trigonal-bipyramidal geometry about tantalum. The addition of $[^2H_8]$styrene to the dideuteride $[^2H_2]$**5** was found to produce a phenethyl group containing some proton intensity (^{1}H NMR) in the β-methylene group. This result indicates that two pathways may be present for the formation of **6** from **5**. The initially formed phenethyl hydride can undergo cyclometallation and direct elimination of H_2 to form **6**. Alternatively, an intermediate styrene complex can be formed and CH bond activation occurs to open up the strained tantalacyclopropane ring. Further kinetic and mechanistic studies of these and related reactions are under way.

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Footnotes

† *Selected spectroscopic data* (solvent $[^2H_6]$benzene, 30 °C) for **2**: ^{13}C NMR δ 63.1 [d, $^2J(^{13}C–^{31}P)$ 8.0 Hz], δ 60.1 (s, Ta*C*H$_2$*C*HPh); ^{31}P NMR δ 1.46. For **4**: ^{1}H NMR δ 3.07 (m, 2H, Ta-C*H*$_2$), 2.40 (s, 3H, TaC*Me*); ^{13}C NMR δ 71.9 [d, Ta*C*Me, $^2J(^{13}C–^{31}P)$ 7.1 Hz], δ 68.2 [d, Ta*C*H$_2$, $^2J(^{13}C–^{31}P)$ 7.1 Hz]; ^{31}P NMR δ −0.67 (d), −4.73 [d, $^2J(^{31}P–^{31}P)$ 145 Hz]. For **6**: ^{1}H NMR δ 3.75 (m, 2H, PhC*H*$_2$CH$_2$), 2.82 (d, 1H), 2.64 [d, 1H, Ta-C*H*$_2$, $^2J(^1H–^1H)$ 15.2 Hz]; ^{13}C NMR δ 105.6 (Ta-*C*H$_2$CMe$_2$-), 97.8 (Ta-*C*H$_2$CH$_2$Ph).

‡ *Crystal data* For **2** at 20 °C: $TaClPO_2C_{47}H_{43}$, M = 887.24, space group $P2_1/n$ (No. 14), a = 9.810(1), b = 17.858(3), c = 22.981(4) Å, β = 100.57(1)°, V = 3957(2) Å^3, D_{calc} = 1.489 g cm^{-3}, Z = 4. Of the 8309 unique reflections collected (5.38 ⩽ 2θ ⩽ 52.64°) with Mo-Kα (λ = 0.71073 Å), the 5466 with $I > 3\,\sigma(I)$ were used in the final least-squares refinement to yield R = 0.029 and R_w = 0.036. The three hydrogen atoms on the styrene ligand were refined isotropically. All other hydrogen atoms were placed in idealized positions. The highest peak in the final difference Fourier had a height of 0.46 e Å^{-3}.

For **6** at 20 °C: $TaClO_2C_{36}H_{50}$, M = 731.20, space group $P2_1/c$ (No. 14), a = 10.0577(5), b = 18.590(2), c = 18.648(1) Å, β = 90.3(3)°, V = 3486.8(8) Å^3, D_{calc} = 1.393 g cm^{-3}, Z = 4. Of the 7311 unique reflections collected (4.9 ⩽ 2θ ⩽ 52.64) with Mo-Kα (λ = 0.71073 Å), the 4407 with $I > 3\,\sigma(I)$ were used in the final least-squares refinement to yield R = 0.033 and R_w = 0.039. The hydrogen atoms were located and added to the structure factor calculations but their positions were not refined. The highest peak in the final difference Fourier had a height of 1.12 e Å^{-3}.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

§ $[Ta(OC_6H_3Bu^t{}_2\text{-}2,6)_2(PMePh_2)(Cl)(H)_2]$ **5** was prepared as follows: to a mixture of $[Ta(OC_6H_3Bu^t{}_2\text{-}2,6)_2Cl_3]$ (1.0 g, 1.43 mmol) and $PMePh_2$ (0.43 g, 2.15 mmol) in benzene (5 ml), was added $Bu^n{}_3SnH$ (1.04 g, 3.58 mmol). The mixture was allowed to stand for 24 h and the resulting yellow crystals of **5** were washed with hexane and dried *in vacuo*; yield 0.64 g (54%). *Selected spectroscopic data* (solvent $[^2H_6]$benzene, 30 °C): ^{1}H NMR δ 17.69 [d, 2H, Ta-*H*, ^2J ($^{31}P–^1H$) 73.6 Hz], 7.68 (m, 4H, P-*Ph ortho*), 6.76–7.42 (m, aromatics), 2.02 [d, 3H, P-*Me*, ^2J ($^{31}P–^1H$) 7.43 Hz], 1.62 (s, 36H, C*Me*$_3$). ^{31}P NMR δ 24.1.

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