

Reaction Pathways for the Oligomerization of Organic Isocyanides by Tantalum Hydride Reagents

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The tantalum monohydride compound $[\text{Ta}(\text{OAr})_2\text{Cl}_2(\text{H})(\text{PMe}_2\text{Ph})_2]$ (OAr = 2,6-diisopropylphenoxide) will react with one, two or three equivalents of organic isocyanides to produce a sequence of organometallic products resulting from initial insertion into the Ta–H bond and subsequent coupling reactions.

The migratory insertion of organic isocyanides into transition metal hydride bonds has been less extensively studied than the corresponding reaction with metal-alkyl compounds.¹ The initial products following insertion of RNC into $\text{L}_n\text{M}-\text{H}$ bonds have been used as models for the related hydrogenation of carbon monoxide.^{1,2} We report here our observation concerning the insertion of organic isocyanides into a single tantalum hydride bond. Steric control of the substituent on the RNC substrate has allowed isolation of a number of intermediates in the subsequent oligomerization process.

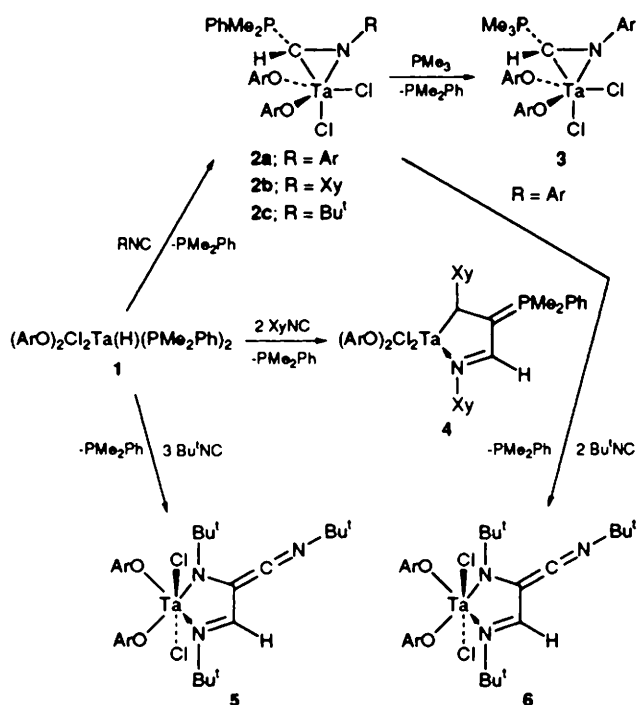
Treatment of benzene solutions of the trichloro compound $[\text{Ta}(\text{OAr})_2\text{Cl}_3]$ (OAr = 2,6-diisopropyl phenoxide)³ with one equivalent of Bu_3SnH in the presence of PMe_2Ph (≥ 2 equiv.) leads to the slow formation of the sparingly soluble, seven-coordinate mono-hydride compound **1** in 86% yield. Crystals of **1** will react slowly with hydrocarbon solutions or organic isocyanides to produce much more soluble organometallic products (Scheme 1). Reaction with an excess of 2,6-diisopropylphenyl isocyanide (ArNC) generates complex **2a** containing the phosphine adduct of an η^2 -iminoformyl ligand.^{4,5} Addition of PMe_3 to solutions of **2a** rapidly generated the new adduct **3** and free PMe_2Ph .

Compound **2a** does not react further with 2,6-diisopropylphenyl isocyanides. With the less bulky reagent 2,6-dimethylphenyl isocyanide (XyNC), the monohydride **1** produces a product **4** in which two equivalents of isocyanide have been coupled to produce a five-membered diazametallacycle with an exocyclic phosphorus ylide function. An intermediate η^2 -iminoformyl complex **2b** was detected by ^1H and ^{31}P NMR spectroscopy in the reaction mixture. Reaction of **1** with *tert*-butyl isocyanide (Bu^tNC) produces yet another organo-

metallic product **5** which contains three equivalents of Bu^tNC and no residual phosphine. Again an intermediate η^2 -iminoformyl **2c** was detected spectroscopically.

The assignment of the ^1H and ^{13}C NMR spectra of these new organometallic compounds was aided by the use of the mono-deuteride $[\text{Ta}(\text{OAr})_2\text{Cl}_2(\text{D})(\text{PMe}_2\text{Ph})_2]$ and are consistent with the formulations shown.[†] Furthermore, the solid state structures of compounds **3** and **5** have been determined by single crystal X-ray diffraction analysis and ORTEP representations of the molecular structures are shown in Figs. 1 and 2.[‡] The molecular structure of **3** (Fig. 1) is best described as distorted trigonal bipyramidal with the η^2 -C,N bound iminoacyl function occupying an axial site *trans* to a chloride ligand. The O–Ta–O angle of $141.9(2)^\circ$ within the equatorial plane is opened up presumably because of the steric bulk of the aryl oxide ligands. The central coordination sphere in compound **5** is a distorted octahedron with mutually *trans* chlorine atoms. The resonance form shown in Scheme 1 for the metallacycle in **5** is supported by the structural parameters. In particular Ta–N(2) and Ta–N(5) distances of 2.271(3) and 2.065(3) Å are consistent to the metal bonding to imine (simple dative bond) and amido ligands respectively. Furthermore, it can be seen that the two chlorine atoms are bent towards the weaker bound imine nitrogen N(2). A similar distortion has been noted in a previous six-coordinate complex of Ta^{V} .⁶

The reactivity of compounds **2** and **4** proved informative. Addition of Bu^tNC to **2a** was found to produce slowly a new



Scheme 1

[†] Selected spectroscopic data: NMR Data, C_6D_6 , 30°C : **1** ^1H : δ 18.93 (t, Ta–H) [$^2J(^{31}\text{P}-^1\text{H}) = 88.0$ Hz]; ^{31}P : δ 7.84. **2a** ^1H : δ 3.22 (d, η^2 -ArNCH) [$^2J(^{31}\text{P}-^1\text{H}) = 35.1$ Hz]; ^{13}C : δ 51.1 (η^2 -ArNCH) [$^1J(^{13}\text{C}-^{31}\text{P}) = 71.1$ Hz]; ^{31}P : δ 25.6. **2b** ^1H : δ 3.37 (d, η^2 -XyNCH) [$^2J(^{31}\text{P}-^1\text{H}) = 34.0$ Hz]; ^{31}P : δ 26.1. **2c** ^1H : δ 2.60 (d, η^2 -Bu^tNCH) [$^2J(^{31}\text{P}-^1\text{H}) = 42.0$ Hz]; ^{31}P : δ 22.2. **3** ^1H : δ 2.80 (d, η^2 -ArNCH) [$^2J(^{31}\text{P}-^1\text{H}) = 40.0$ Hz]; ^{31}P : δ 23.4. **4** ^1H : δ 6.42 (HC=NXY) [$^2J(^{31}\text{P}-^1\text{H}) = 4.8$ Hz]; ^{13}C : δ 140.7 (N=C=P) [$^1J(^{13}\text{C}-^{31}\text{P}) = 46.3$ Hz], δ 102.4 (N=CH) [$^2J(^{13}\text{C}-^{31}\text{P}) = 111$ Hz]; ^{31}P : δ 3.43. **5** ^1H : δ 8.05 (s, N=CH); ^{13}C : δ 180.1 (C=C=N), 166.7 (C=C=N), 95.6 (N=CH); **6** ^1H : δ 7.95 (s, N=CH); ^{13}C : δ 174.6 (C=C=N), 156.7 (C=C=N), 96.1 (N=CH). IR data, Nujol mull: **1** 1850 cm^{-1} ν (Ta–H).

[‡] Crystal data: For **3** at 20°C : $\text{TaCl}_2\text{PO}_2\text{NC}_6\text{H}_5$, $M = 870.77$, space group $P2_1/c$ (No. 14), $a = 10.7710(8)$, $b = 18.281(1)$, $c = 21.546(2)$ Å, $\beta = 102.771(7)^\circ$, $V = 4137(1)$ Å³, $D_c = 1.398$ g cm⁻³, $Z = 4$. Of the 5615 unique reflections collected ($4 \leq 2\theta \leq 45^\circ$) with Mo-K α ($\lambda = 0.71073$ Å), the 4080 with $I > 3\sigma(I)$ were used in the final least-squares refinement to yield $R = 0.024$ and $R_w = 0.029$. The unique hydrogen was located and refined. All other hydrogen atoms were placed in idealized positions. The highest peak in the final difference Fourier had a height of $0.34 \text{ e } \text{\AA}^{-3}$. For **5** at 20°C : $\text{TaCl}_2\text{O}_2\text{N}_3\text{C}_3\text{H}_6$, $M = 856.80$, space group $P\bar{1}$ (No. 2), $a = 10.0297(9)$, $b = 12.920(1)$, $c = 17.043(1)$ Å, $\alpha = 83.883(7)$, $\beta = 75.874(8)$, $\gamma = 84.246(8)^\circ$, $V = 2123.1(4)$ Å³, $D_c = 1.340$ g cm⁻³, $Z = 2$. Of the 5537 reflections collected ($4 \leq 2\theta \leq 45^\circ$) with Mo-K α ($\lambda = 0.71073$ Å), the 5017 with $I > 3\sigma(I)$ were used in the final least-squares refinement to yield $R = 0.022$ and $R_w = 0.029$. The unique hydrogen was located and refined. All other hydrogen atoms were placed in idealized positions. The highest peak in the final difference Fourier had a height of $0.98 \text{ e } \text{\AA}^{-3}$.

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.

product **6** along with free PMe_2Ph . The spectroscopic data for **6**[†] are consistent with it being related to **5** involving the selective coupling of one equivalent of 2,6-diisopropylphenyl isocyanide with two equivalents of Bu^tNC (Scheme 1). In

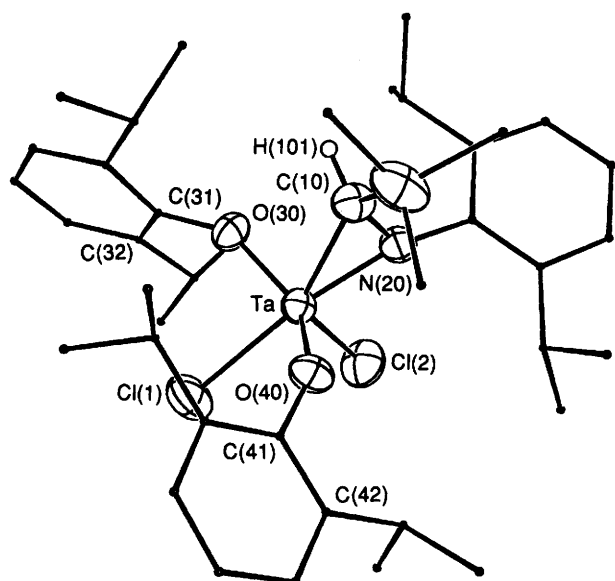
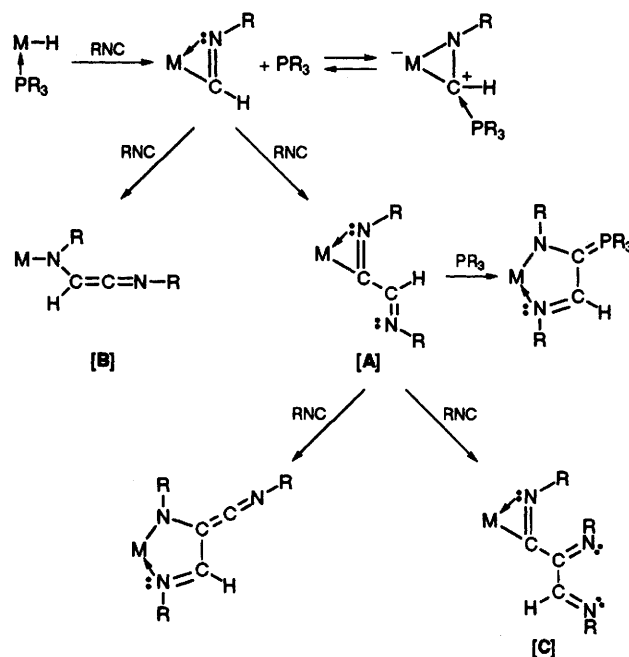


Fig. 1 ORTEP view of **3** emphasizing the central coordination sphere. All hydrogen atoms except one were removed for clarity. Selected bond distances (Å) and angles (°): Ta-Cl(1) 2.468(1); Ta-Cl(2) 2.354(1); Ta-O(30) 1.896(3); Ta-O(40) 1.894(3); Ta-N(20) 1.956(4); Ta-C(10) 2.210(5); N(20)-C(10) 1.421(7); Cl(1)-Ta-Cl(2) 86.33(6); -O(30) 84.1(1); -O(40) 82.2(1); -N(20) 169.0(1); -C(10) 151.7(1); Cl(2)-Ta-O(30) 105.5(1); -O(40) 108.8(1); -N(20) 82.8(1); -C(10) 121.9(1); O(30)-Ta-O(40) 141.9(2); -N(20) 100.0(2); -C(10) 86.0(2); O(40)-Ta-N(20) 100.1(2); -C(10) 89.5(2); N(20)-Ta-C(10) 39.3(2); Ta-O(30)-C(10) 148.7(3); Ta-O(40)-C(10) 149.9(3).

contrast, compound **4** does not react with either PMe_3 or an excess of Bu^tNC . These results imply a specific reaction pathway for the coupling or organic isocyanides by this tantalum monohydride system (Scheme 2). The migratory insertion of the first equivalent of isocyanide produces a highly electrophilic η^2 -iminoacyl which will readily (but reversibly) coordinate a phosphine ligand. Addition of a second equivalent of isocyanide can occur following phosphine dissociation and must lead to the double migratory insertion intermediate **[A]** shown (Scheme 2). Although it has precedent in



Scheme 2

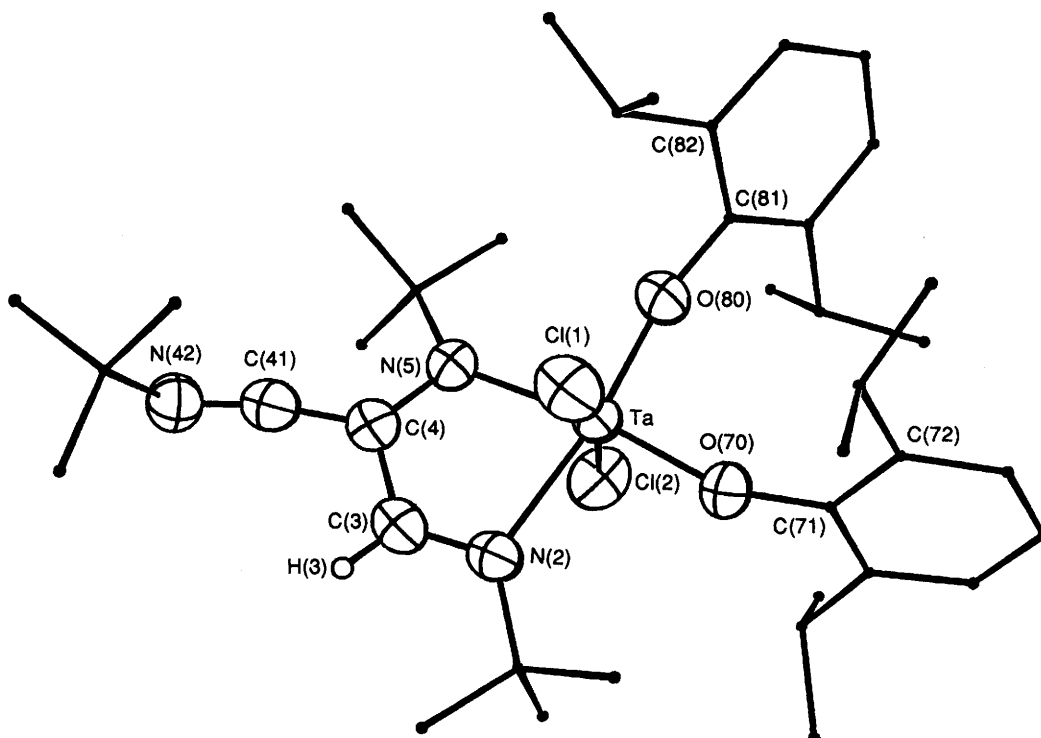


Fig. 2 ORTEP view of **5** emphasizing the central coordination sphere. All hydrogens except one have been removed for clarity. Selected bond distances (Å) and angles (°): Ta-Cl(1) 2.387(1); Ta-Cl(2) 2.400(1); Ta-O(70) 1.919(2); Ta-O(80) 1.854(2); Ta-N(2) 2.271(3); Ta-N(5) 2.065(3); C(4)-C(41) 1.338(6); N(42)-C(41) 1.206(5); N(2)-C(3) 1.273(5); N(5)-C(4) 1.401; C(3)-C(4) 1.423(6); Cl(1)-Ta-Cl(2) 166.67(4); -O(70) 93.34(8); -O(80) 94.70(9); -N(2) 79.18(9); -N(5) 90.13(9); Cl(2)-Ta-O(70) 87.40(8); -O(80) 98.56(9); -N(2) 87.48(9); -N(5) 87.39(9); O(70)-Ta-O(80) 92.6(1); -N(2) 94.3(1); -N(5) 171.3(1); O(80)-Ta-N(2) 171.0(1); -N(5) 95.1(1); N(2)-Ta-N(5) 78.5(1); Ta-O(70)-C(71) 158.8(2); Ta-O(80)-C(81) 165.4(2).

carbonylation chemistry,⁴ formation of the keteneimine [B] does not occur. Reaction of [A] with PMe_2Ph can occur irreversibly to produce a product of type 3. However, in the presence of an excess of a smaller, basic isocyanide such as Bu^tNC , formation of a keteneimine such as 5 and 6 occurs. The product of these reactions cannot be rationalised on the basis of an intermediate [C] formed by three sequential migratory insertion reactions.

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