Reactivity of Tantalum Hydride Aryloxide Complexes toward Organic Isocyanide Reagents

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The tantalum monohydride compound $[Ta(OC_6H_3Pr^i_2\text{-}2,6)_2Cl_2(H)(PMe_2Ph)_2]$ (**1**) reacts with organic isocyanides RNC to produce the phosphine adduct η^2-iminoformyl complexes $[Ta(OC_6H_3Pr^i_2\text{-}2,6)_2Cl_2\{HC(PMe_2Ph)NR\}]$ (R = 2,6-diisopropylphenyl (**2a**), 2,6-dimethylphenyl (**2b**), *tert*-butyl (**2c**)). Compounds **2b**,**c** were only detected spectroscopically as intermediates, while **2a** was isolated and reacted with PMe_3 to produce the complex $[Ta(OC_6H_3Pr^i_2\text{-}2,6)_2Cl_2\{HC(PMe_3)NC_6H_3Pr^i_2\text{-}2,6\}]$ (**3**), which was structurally characterized. The structure of **3** is best described as trigonal bipyramidal about tantalum with a chloride atom and the phosphine adduct of an η^2-iminoformyl group occupying axial sites. Important structural parameters for **3** are Ta−N = 1.956(4), Ta−C = 2.210(5), and N−C = 1.421(7) Å. Compounds **2a** and **3** do not react with a further 1 equiv of 2,6-diisopropylphenyl isocyanide. In contrast **2b** reacts with 2,6-dimethylphenyl isocyanide to produce the ylide derivative $[Ta(OC_6H_3Pr^i_2\text{-}2,6)_3Cl_2\{RN{=}CHC(=PMe_2Ph)NR\}]$ (**4**) (R = $C_6H_3Me_2$-2,6), while **2c** reacts with an additional 2 equiv of Bu^tNC to produce the compound $[Ta(OC_6H_3Pr^i_2\text{-}2,6)_3Cl_2\{Bu^tN{=}CHC(=C{=}NBu^t)NBu^t\}]$ (**5**). Spectroscopic data on **4** and **5** and a single-crystal X-ray diffraction study of **5** show both molecules contain 2,5-diazacyclopent-2-ene rings with either ylide (**4**) or keteneimine (**5**) groups attached to the C-4 position. Addition of Bu^tNC to **2a** produces the complex $[Ta(OC_6H_3Pr^i_2\text{-}2,6)_2Cl_2\{RN{=}CHC(=C{=}NBu^t)NBu^t\}]$ (**6**) (R = $C_6H_3Pr^i_2$-2,6). The tantalum dihydride compound $[Ta(OC_6H_3Bu^t_2\text{-}2,6)_2Cl_2(H)(PMePh_2)]$ (**7**) reacts with RNC to produce the monocyclometalated derivatives $[Ta(OC_6H_3Bu^t\text{-}CMe_2CH_2)(OC_6H_3Bu^t_2\text{-}2,6)Cl_2\{N(R)CH_3\}]$ (**8**) (**a**, R = $C_6H_3Me_2$-2,6; **b**, R = Bu^t), in which a total of three hydride groups have been transferred to the isocyanide substrate to produce the dialkylamido ligand.

Introduction

The migratory insertion of carbon monoxide and isoelectronic small molecules into transition metal−ligand bonds has become an important area of research in organometallic chemistry.[1−5] A particularly significant development has been the demonstrated ability of high-valent early d-block, lanthanide, and actinide metal hydride, alkyl, and more recently silyl bonds to not only insert 1 equiv of CO but also to carry out the oligomerization of multiple equivalents of CO.[6−12] Crucial to an understanding of this chemistry is the structure and reactivity of the η^2-formyl, η^2-acyl, and η^2-silaacyl functional groups formed by the initial migratory insertion of 1 equiv of CO.[13] Isolated derivatives of these ligands along with related η^2-iminoacyl groups have been shown to undergo a large number of carbon−carbon bond-forming reactions. In this paper we report on the reaction of organic isocyanides with recently isolated hydride−aryloxides of tantalum.[14,15] These studies show that the initially formed η^2-iminoformyl complexes can undergo oligomerization reactions with further equivalents of isocyanide in reaction sequences that appear to parallel those previously documented for carbon monoxide.

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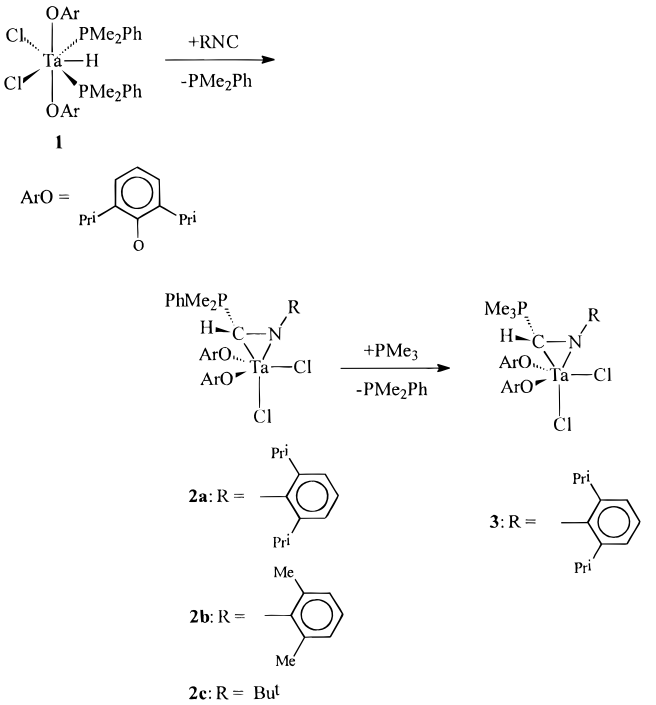
Scheme 1



Results and Discussion

Synthesis and Spectroscopy of Organometallic Products. The tantalum monohydride complex [Ta(OC$_6$H$_3$Pr$^i_2$-2,6)$_2$Cl$_2$(H)(PMe$_2$Ph)$_2$][14] (**1**) is only sparingly soluble in cold hydrocarbon solvents. Suspensions of colorless **1** in C$_6$D$_6$ solvent will react slowly over hours with a variety of organic isocyanides to produce much more soluble organometallic products. Due to its low solubility, **1** is exposed to large excesses of reagent throughout the course of these reactions. The progress of the reactions can be readily monitored by ^{1}H and ^{31}P NMR spectroscopy. Addition of the sterically very bulky reagent CNC$_6$H$_3$Pr$^i_2$-2,6 to **1** leads to formation of a single organometallic product [Ta(OC$_6$H$_3$Pr$^i_2$-2,6)$_2$Cl$_2${HC(PMe$_2$Ph)NC$_6$H$_3$Pr$^i_2$-2,6}] (**2a**) (Scheme 1). In the ^{1}H NMR of **2a** a sharp doublet at δ3.22 ppm can be assigned to the iminoformyl proton coupled to the phosphorus atom with a large, 36 Hz, coupling. The formulation of **2a** as a metal-bound phosphine adduct of an η^2-iminoformyl derivative is ruled out by ^{13}C and ^{31}P NMR data. Previous studies have shown that early d-block η^2-iminoacyl compounds containing aryloxide ancillary ligation are characterized by a very low field resonance for the η^2-iminoacyl carbon.[13] In **2a** a doublet at δ 51.1 ppm in the proton-decoupled ^{13}C NMR spectrum is too high for a simple η^2-iminoformyl group. The large, 71 Hz, coupling to ^{31}P along with the chemical shift of this phosphorus atom in the ^{31}P NMR spectrum is consistent with the formulation shown (Scheme 1). The literature contains examples of related adducts of acyl and formyl functional groups.[8] The addition of PMe$_3$ to solutions of **2a** was found to generate the corresponding adduct **3** which was structurally characterized (Figure 1, Table 1).

The reaction of **1** with the isocyanide CNC$_6$H$_3$Me$_2$-2,6 was found (^{1}H and ^{31}P NMR) to initially produce a mixture of products. One component of this mixture was identified on the basis of spectroscopic data as the adduct **2b** (Scheme 1). Over time the reaction mixture

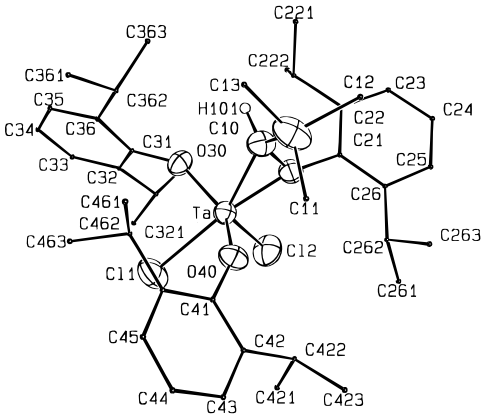
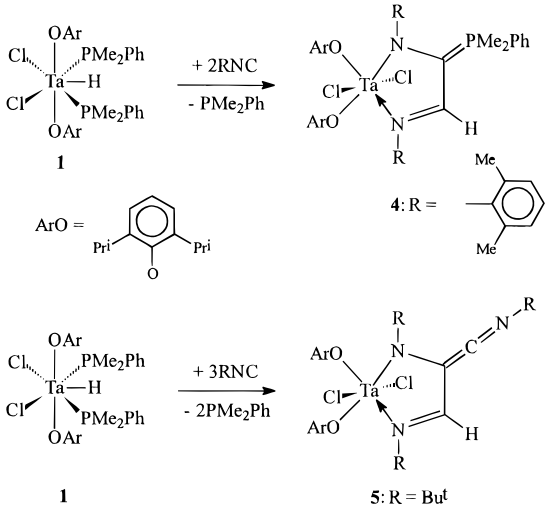


Figure 1. Molecular structure of [Ta(OC$_6$H$_3$Pr$^i_2$-2,6)$_2$-Cl$_2${HC(PMe$_3$)NC$_6$H$_3$Pr$^i_2$-2,6}] (**3**).

Table 1. Selected Bond Distances (Å) and Angles (deg) for [Ta(OC$_6$H$_3$Pr$^i_2$-2,6)$_2$Cl$_2${HC(PMe$_3$)NC$_6$H$_3$Pr$^i_2$-2,6}] (3)

Ta−O(30)	1.896(3)	Ta−N(20)	1.956(4)
Ta−O(40)	1.894(3)	Ta−C(10)	2.210(5)
Ta−Cl(1)	2.468(1)	N(20)−C(10)	1.421(7)
Ta−Cl(2)	2.354(1)	P(10)−C(10)	1.776(5)
Cl(1)−Ta−Cl(2)	86.33(6)	O(30)−Ta−O(40)	141.9(2)
Cl(1)−Ta−O(30)	84.1(1)	O(30)−Ta−N(20)	100.0(2)
Cl(1)−Ta−O(40)	82.2(1)	O(30)−Ta−C(10)	86.0(2)
Cl(1)−Ta−N(20)	169.0(1)	O(40)−Ta−N(20)	100.1(2)
Cl(1)−Ta−C(10)	151.7(1)	O(40)−Ta−C(10)	89.5(2)
Cl(2)−Ta−O(30)	105.5(1)	N(20)−Ta−C(10)	39.3(2)
Cl(2)−Ta−O(40)	108.8(1)	Ta−N(20)−C(10)	80.0(3)
Cl(2)−Ta−N(20)	82.8(1)	Ta−N(20)−C(21)	152.3(4)
Cl(2)−Ta−C(10)	121.9(1)	Ta−C(10)−P(10)	133.1(3)
Ta−O(30)−C(31)	148.7(3)	Ta−C(10)−N(20)	60.7(3)
Ta−O(40)−C(41)	149.9(3)	P(10)−C(10)−N(20)	119.4(4)

Scheme 2



was found to convert to a single organometallic product formulated as [Ta(OC$_6$H$_3$Pr$^i_2$-2,6)$_2$Cl$_2${RN=CH-C(PMe$_2$-Ph)NR}] (**4**) (R = C$_6$H$_3$Me$_2$-2,6) on the basis of its spectroscopic data (Scheme 2). The unique Ta−N=C*H* proton which originated from the hydride function is found as a doublet (5 Hz coupling to ^{31}P) at δ 6.42 ppm in the ^{1}H NMR spectrum. In the ^{13}C NMR spectrum two highly informative doublets are observed at δ 102.4 (111 Hz) and 148.9 (34.9 Hz). These can be assigned as the N*C*=P and N=*C*H carbons, respectively. Their coupling constants compare well with those reported for the compounds Cp*Cl$_3$Ta[O=C(SiMe$_3$)C(=PCy$_3$)O], Cp*$_2$-ThCl[O=C(CH$_2$Bu^t)C(=PPh$_3$)O], and Cp*$_2$ThCl[O=C-

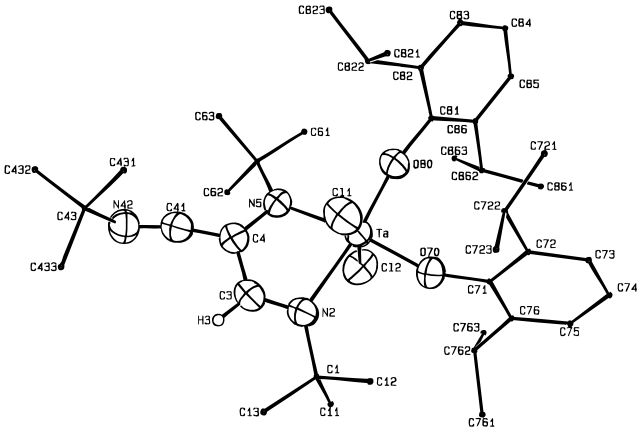


Figure 2. Molecular structure of $[Ta(OC_6H_3Pr^i_2\text{-}2,6)_2Cl_2\{Bu^tN{=}CHC(=C{=}NBu^t)NBu^t\}]$ (**5**).

Table 2. Selected Bond Distances (Å) and Angles (deg) for $[Ta(OC_6H_3Pr^i_2\text{-}2,6)_2Cl_2\{Bu^tN{=}CHC(=C{=}NBu^t)NBu^t\}]$ (5)

Ta−O(70)	1.919(2)	N(2)−C(3)	1.273(5)
Ta−O(80)	1.854(2)	C(3)−C(4)	1.423(6)
Ta−Cl(1)	2.387(1)	C(4)−N(5)	1.401(5)
Ta−Cl(2)	2.400(1)	C(4)−C(41)	1.338(6)
Ta−N(2)	2.271(3)	C(41)−N(42)	1.206(5)
Ta−N(5)	2.065(3)		
Cl(1)−Ta−Cl(2)	166.67(4)	O(70)−Ta−O(80)	92.6(1)
Cl(1)−Ta−O(70)	93.34(8)	O(70)−Ta−N(2)	94.3(1)
Cl(1)−Ta−O(80)	94.70(9)	O(70)−Ta−N(5)	171.3(1)
Cl(1)−Ta−N(2)	79.18(9)	O(80)−Ta−N(2)	171.0(1)
Cl(1)−Ta−N(5)	90.13(9)	O(80)−Ta−N(5)	95.1(1)
Cl(2)−Ta−O(70)	87.40(8)	N(2)−Ta−N(5)	78.5(1)
Cl(2)−Ta−O(80)	98.56(9)	Ta−N(2)−C(3)	107.9(3)
Cl(2)−Ta−N(2)	87.48(9)	Ta−N(5)−C(4)	111.2(2)
Cl(2)−Ta−N(5)	87.39(9)	N(2)−C(3)−C(4)	121.4(4)
Ta−O(70)−C(71)	158.8(2)	C(3)−C(4)−N(5)	117.9(3)
Ta−O(80)−C(81)	165.4(2)	C(4)−C(41)−N(42)	169.3(4)

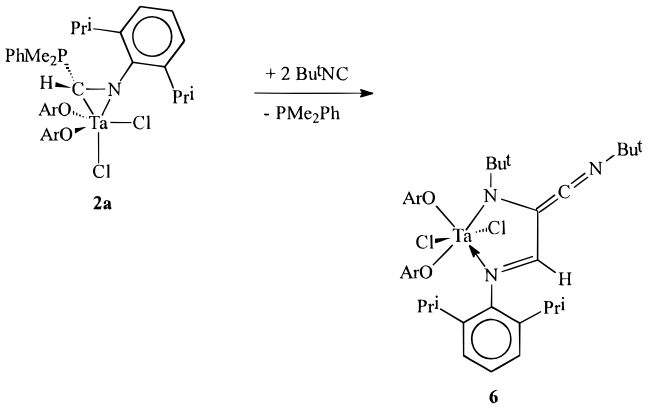
$(SiR_3)C(=PMe_2Ph)O]$.[7b,8b] The chemical shifts of these carbons also compare favorably with these other metal systems when one takes into account that **4** contains two NR groups instead of O.

Reaction of **1** with Bu^tNC in C_6D_6 solvent produces an intermediate adduct complex **2c** (identified spectroscopically), which is readily converted to a new non-phosphine-containing organometallic product **5** (Scheme 2). A single-crystal X-ray diffraction analysis of **5** (Figure 2, Table 2) shows it to contain 3 equiv of Bu^t-NC coupled by the single Ta−H functional group to produce a diazametallacycle with an exocyclic ketene-imine group. This compound is related to an oxa−aza metallacyclic analogue $[Cp^*_2ThCl\{OC(CH_2Bu^t)\text{-}C(=C{=}NR)NR\}]$ and the dioxa derivative $[Cp^*_2ThCl\text{-}\{OC(SiR_3)C(=C{=}NR)O\}]$.[7b,8a]

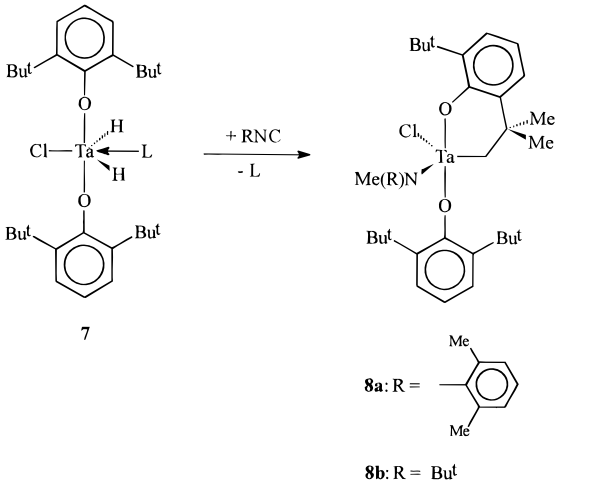
A direct analogue of **5** was obtained by addition of Bu^tNC to the iminoformyl complex **2a**. In this case incorporation of a further 2 equiv of isocyanide occurs with displacement of PMe_2Ph and formation of the organometallic compound $[Ta(OC_6H_3Pr^i_2\text{-}2,6)_2Cl\text{-}\{ArN{=}CHC(=C{=}NBu^t)NBu^t\}]$ (**6**) (Scheme 3; Ar = $C_6H_3Pr^i_2$-2,6). As expected, **6** has many spectroscopic similarities with **5**.

The six-coordinate dihydride complex $[Ta(OC_6H_3Bu^t_2\text{-}2,6)_2Cl(H)_2(PMePh_2)]$ (**7**) will also react with organic isocyanides. In this case, however, only 1 equiv of RNC is incorporated to produce the corresponding methyl, alkyl amido complexes **8** (Scheme 4). The spectroscopic

Scheme 3



Scheme 4



8b: R = Bu^t

data on **8** clearly show the presence of a cyclometalated 2,6-di-*tert*-butylphenoxide ligand.[16] We, therefore, conclude that intramolecular CH bond activation gives rise to the third equivalent of "hydride" needed to convert the original organic isocyanide into a dialkylamido function.

Structural Studies. The solid-state structure of **3** (Figure 1, Table 1) is best described as trigonal bipyramidal with a chloride atom and the phosphine adduct of an iminoformyl group occupying axial sites. The TaNC unit is oriented so that the NC vector lies coplanar with the equatorial Ta−Cl bond. The most interesting features of the structure of **3** relates to the structural parameters of the iminoformyl group. The literature presently contains no analogous phosphine adduct of an η^2-iminoformyl. There is, however, a related phosphine adduct of a silaacyl, $[Cp^*TaCl_3\{OC(SiMe_3)(PEt_3)\}]$, studied by Tilley et al.[8b,17] The Ta-N(20) distance of 1.956(4) Å in **3** is much shorter than the Ta−N distances of 2.15(5) and 2.165(5) Å in the η^2-iminoacyl compound $[Ta(OC_6H_3Me_2\text{-}2,6)_2(Me)(\eta^2\text{-}MeC\text{-}NAr)_2]$ (Ar = $C_6H_3Me_2$-2,6).[18] In contrast the Ta−C(10) distance of 2.210(5) Å in **3** is slightly longer than the Ta−C distances of 2.187(7) and 2.200(6) Å in the bis-(η^2-iminoacyl). The C−N distance in **3** of 1.421(7) Å is

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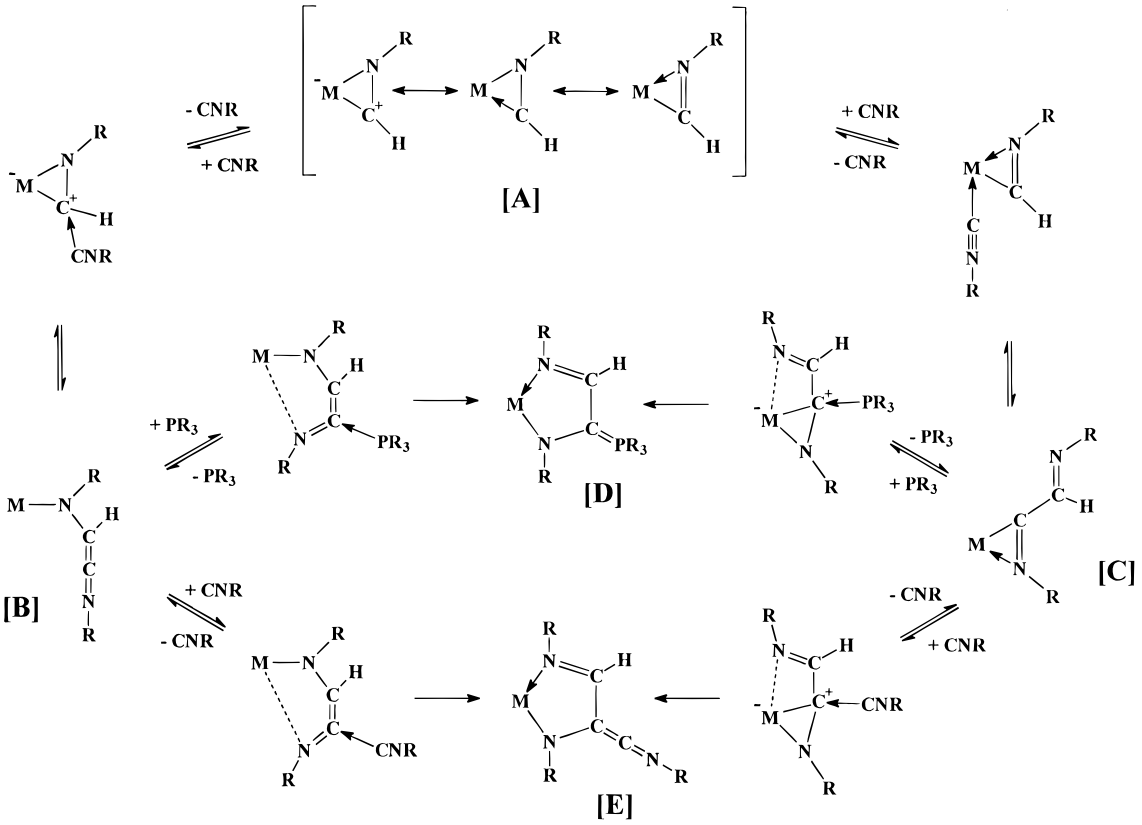
Scheme 5



much longer than the 1.28(8) and 1.286(8) Å distances found for the η^2-iminoacyl groups and is very close to that expected for a carbon−carbon single bond.

The solid−state structure of **5** (Figure 2, Table 2) shows a six-coordinate tantalum metal center with mutually *trans* chloride groups and *cis* aryloxide ligands. The geometry about tantalum is distorted, with both chloride ligands bent toward the atom N(2). This nitrogen atom is (*vide infra*) a datively bound imine function. Distortions of covalently bound ligands toward dative bonds is a characteristic feature of six-coordinate, d^0-metal complexes of this type, and a theoretical analysis has been carried out.[19] The most interesting structural features of **5** concern the parameters for the metallacyclic ring. Analysis of bond distances is entirely consistent with a 2,5-diazatantalacyclopent-2-ene ring as shown (Scheme 2). The Ta−N(2) distance of 2.271(3) Å is much longer than the Ta−N(5) distance of 2.065(3) Å. The former distance is comparable to the Ta−py distances of 2.315(6) Å in $[Ta(OC_6H_3Pr^i_2\text{-}2,6)_2Cl_3(py)]$,[19] while the latter is closer to distances of dialkylamido groups bound to tantalum; cf. distances of 1.963(5) and 1.954(5) Å in $[TaCl_3(NMe_2)_2(HNMe_2)]$.[20]

Mechanistic Considerations. The reaction of organic isocyanides with the tantalum hydride aryloxides **1** and **7** leads to a diverse series of organometallic compounds. The product molecules can, however, be accommodated into a unified reaction scheme in which the pivotal intermediate is the initial η^2-iminoformyl derivative. Previous synthetic and theoretical studies on the chemistry of η^2-acyl, η^2-iminoacyl, and related derivatives of high-valent d-block, lanthanide and actinide metals have characterized the carbon center as being electrophilic in nature.[6,13] Many possible resonance pictures for these functional groups have been proposed (e.g. [**A**] in Scheme 5). The structural studies of η^2-iminoacyl groups do show significant shortening of the metal−nitrogen bond below that expected for a simple dative interaction, but C−N distances clearly fall in the range expected for double bonds.[18] The phosphine adducts **2** obtained in this study are consistent with the carbon atom of the η^2-iminoformyl being highly electrophilic. In the case of the bulky nitrogen substituent 2,6-diisopropylphenyl (**2a**) the phosphine ligand has been shown to bind reversibly by exchange with PMe_3 to produce **3** (Figure 1).

The metallacyclic compounds obtained in this study can be envisaged as arising via two alternative pathways. Dissociation of phosphine from the adduct **2** leads to an η^2-iminoformyl complex [**A**], which can coordinate a second 1 equiv of isocyanide. This coordination can occur either at the electrophilic carbon or the electron-deficient metal center. The former would lead to an amido keteneimine [**B**] while the latter generates an η^2-iminoacyl [**C**] containing an imine group attached to the α-carbon. This latter reaction is the sequential migratory insertion of two isocyanide molecules into the tantalum−hydride bond. There is at present no precedence for the formation of compounds such as [**C**]. There is, however, excellent precedence for the formation of ketene and keteneimine functions by addition of CO or RNC to η^2-acyl groups.[7,8] The observed products can be generated from [**C**] by nucleophilic attack at the iminoacyl carbon either by phosphine, to produce [**D**], or by isocyanide, to produce [**E**] (Scheme 5). Although many ketene and keteneimine complexes had previously

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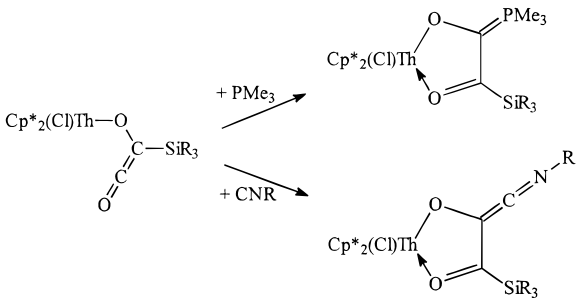
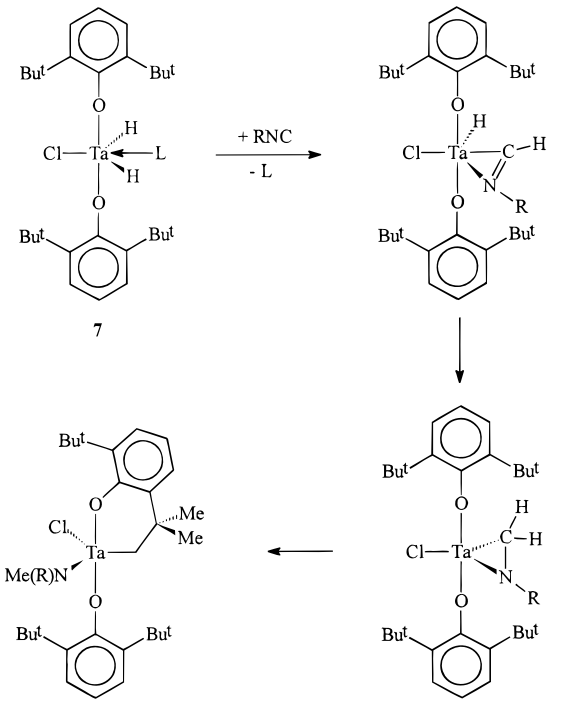
Scheme 6



Scheme 7



been isolated, direct evidence for their conversion to metallacycles such as [**D**] and [**E**] had been absent until very recently. In an important study Tilley et al. have shown that addition of PR_3 or RNC to a metallaoxyketene generates just such products (Scheme 6).[8a] On the basis of this work, we, therefore, now propose that the products obtained in this study originate from an undetected intermediate amido keteneimine [**B**] although we cannot conclusively rule out intermediates such as [**C**] on the basis of experiments in hand.

The cyclometalated compounds **8** (Scheme 4) arise from the addition of isocyanide to the dihydride **7**. Previous work has shown that η^2-iminoacyl ligands can be converted to η^2-imine groups by migration of a second alkyl substituent from the metal to the α-carbon. In the case of the formation of **8**, intramolecular CH bond activation in which the azametallacyclopropane is opened up leads to the final dialkylamide product (Scheme 7). The ligand 2,6-di-*tert*-butylphenoxide has been shown to undergo facile cyclometalation at early d-block metal centers with a variety of activating functional groups.[16]

Experimental Section

All operations were carried out under a dry nitrogen atmosphere or in vacuo either in a Vacuum Atmosphere Dri-Lab or by standard Schlenk techniques. Hydrocarbon solvents were dried by distillation from sodium/benzophenone and stored under dry nitrogen. 2,6-Diisopropylphenyl isocyanide was prepared by reported procedures. 2,6-Dimethylphenyl isocyanide was purchased from Fluka Chemical Co. Phosphines and *tert*-butyl isocyanide were all purchased from Strem Chemical Co. and were dried over 3 Å molecular sieves prior to use. $[Ta(OC_6H_3Pr^i_2\text{-}2,6)_2(Cl)_2H(PMe_2Ph)_2]$ (**1**) and $[Ta(OC_6H_3Bu^t_2\text{-}2,6)_2Cl(H)_2(PMePh_2)]$ (**7**) were prepared by reported procedures.[14] The ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on a Varian Associates Gemini 200 and a General Electric QE-300 spectrometer and were referenced to protio impurities of commercial benzene-d_6.

$[Ta(OC_6H_3Pr^i_2\text{-}2,6)_2Cl_2\{HC(PMe_2Ph)NC_6H_3Pr^i_2\text{-}2,6\}]$ (2a). To a suspension of $[Ta(OC_6H_3Pr^i_2\text{-}2,6)_2Cl_2(H)(PMe_2Ph)_2]$ (**1**) (0.5 g, 0.57 mmol) in benzene (5 mL) was added 2,6-diisopropylphenyl isocyanide (0.13 g, 0.68 mmol). The resulting red solution was stirred for 20 h. Slow cooling of a warmed toluene solution yielded product as colorless crystals, which were washed in hexane and dried *in vacuo* with high yield. ^1H NMR (C_6D_6, 30 °C, δ): 6.67−7.14 (m, 14H, aromatics); 4.07 (septet, 1H, C*H*Me); 3.87 (septet, 4H, C*H*Me); 3.22 (d, 1H, η^2-($C_6H_3Pr^i_2$-2,6)NC*H*), $^2J(^{31}P-^1H) = 35.7$ Hz; 3.11 (septet, 1H, C*H*Me); 1.64 (d, 3H, CH*Me*); 1.57 (d, 3H, CH*Me*); 1.40 (d, 12H, CH*Me*); 1.33 (d, 12H, CH*Me*); 1.23 (d, 3H, CH*Me*); 1.14 (d, 3H, CH*Me*); 0.89 (d, 6H, P−*Me*), $^2J(^{31}P-^1H) = 7.0$ Hz. ^{13}C NMR (C_6D_6, 30 °C, δ): 158.2 (TaO*C*); 120.5−150.0 (aromatics); 51.1 (η^2-ArN*C*H), $^1J(^{13}C-^{31}P) = 71.1$ Hz; 9.29−30.2 (aliphatics). ^{31}P NMR (C_6D_6, 30 °C): δ 25.6.

$[Ta(OC_6H_3Pr^i_2\text{-}2,6)_2Cl_2\{HC(PMe_2Ph)NC_6H_3Me_2\text{-}2,6\}]$ (2b). This compound was detected by ^1H and ^{31}P NMR in the reaction mixture of **3**. ^1H NMR (C_6D_6, 30 °C): δ 3.37 (d, 1H, η^2-($C_6H_3Me_2$-2,6)NC*H*), $^2J(^{31}P-^1H) = 34.0$ Hz. ^{31}P NMR (C_6D_6, 30 °C): δ 26.1.

$[Ta(OC_6H_3Pr^i_2\text{-}2,6)_2Cl_2\{HC(PMe_2Ph)NBu^t\}]$ (2c). This compound was detected by ^1H and ^{31}P NMR in the reaction mixture of **4**. ^1H NMR (C_6D_6, 30 °C): δ 2.60 (d, 1H, η^2-Bu^t-NC*H*), $^2J(^{31}P-^1H) = 42.0$ Hz. ^{31}P NMR (C_6D_6, 30 °C): δ 22.2.

$[Ta(OC_6H_3Pr^i_2\text{-}2,6)_2Cl_2\{HC(PMe_3)NC_6H_3Pr^i_2\text{-}2,6\}]$ (3). To a suspension of **1a** (0.5 g, 0.57 mmol) in benzene (5 mL) was added trimethylphosphine (0.85 mmol). The resulting solution was allowed to stand for 10 h to yield the crystalline product. The colorless crystals were washed with hexane and dried *in vacuo*; yield 0.4 g (81.2%). ^1H NMR (C_6D_6, 30 °C, δ): 6.92−7.43 (m, 9H, aromatics); 4.10 (septet, 1H, C*H*Me); 3.83 (septet, 4H, C*H*Me); 3.05 (septet, 1H, C*H*Me); 2.80 (d, 1H, η^2-($C_6H_3Pr^i_2$-2,6)NC*H*), $^2J(^{31}P-^1H) = 40.0$ Hz; 1.48 (d, 6H, CH*Me*); 1.36 (d, 12H, CH*Me*); 1.32 (d, 12H, CH*Me*); 1.18 (d, 6H, CH*Me*); 1.08 (d, 9H, P−*Me*), $^2J(^{31}P-^1H) = 3.3$ Hz. ^{31}P NMR (C_6D_6, 30 °C): δ 23.35.

$[Ta(OC_6H_3Pr^i_2\text{-}2,6)_2Cl_2\{(C_6H_3Me_2\text{-}2,6)N{=}CHC(PMe_2Ph)N(C_6H_3Me_2\text{-}2,6)\}]$ (4). To a suspension of $[Ta(OC_6H_3Pr^i_2\text{-}2,6)_2Cl_2(H)(PMe_2Ph)_2]$ (0.5 g, 0.57 mmol) in benzene (5 mL) was added 2,6-dimethylphenyl isocyanide (0.15 g, 1.13 mmol). The resulting dark red solution was stirred for 20 h. Removal of benzene solvent led to the crude product as a red-brown solid, which was washed with hexane and dried *in vacuo* to yield 0.56 g (98%). Anal. Calcd for $C_{50}H_{64}N_2PO_2Cl_2Ta$: C, 59.62; H, 6.41; N, 2.78; Cl, 6.95; P, 3.08. Found: C, 60.02; H, 6.70; N, 2.99; Cl, 6.66; P, 2.72. ^1H NMR (C_6D_6, 30 °C, δ): 6.55−7.25 (m, 17H, aromatics); 6.42 (d, 1H, *H*C=N), $^2J(^{31}P-^1H) = 4.8$ Hz; 4.05 (septet, 2H, C*H*Me); 3.80 (septet, 2H, C*H*Me); 3.01 (s, 3H, C*Me*); 2.45 (s, 3H, C*Me*); 1.19 (d, 12H, CH*Me*); 1.15 (d, 12H, CH*Me*); 0.59 (d, 6H, P−*Me*), $^2J(^{31}P-^1H) = 13.2$ Hz. ^{13}C NMR (C_6D_6, 30 °C, δ): 157.5 (TaO*C*); 153.5 (TaO*C*); 148.9 (N=*C*H), $^2J(^{13}C-^{31}P) = 34.9$ Hz; 122.5−138.2 (aromatics); 102.4 (N*C*=P), $^1J(^{13}C-^{31}P) = 111$ Hz; 14.37−26.36 (aliphatics); 11.28 (P−*Me*), $^1J(^{13}C-^{31}P) = 59.2$ Hz. ^{31}P NMR (C_6D_6, 30 °C); δ 3.43.

$[Ta(OC_6H_3Pr^i_2\text{-}2,6)_2Cl_2\{Bu^tN{=}CHC(=C{=}NBu^t)NBu^t\}]$ (5). To a suspension of $[Ta(OC_6H_3Pr^i_2\text{-}2,6)_2Cl_2(H)(PMe_2Ph)_2]$ (0.5 g, 0.57 mmol) in benzene (5 mL) was added *tert*-butyl isocyanide (0.09 g, 1.13 mmol). The dark red solution was stirred for 20 h. Slow cooling of a warmed hexane solution yielded

red crystals, which were washed in hexane and dried *in vacuo* with high yield. Anal. Calcd for $C_{39}H_{62}N_3O_2Cl_2Ta$: C, 54.67; H, 7.29; N, 4.90; Cl, 8.28. Found: C, 55.05; H, 7.59; N, 5.29; Cl, 8.37. ^{1}H NMR (C_6D_6, 30 °C, δ): 8.05 (s, 1H, N=CH); 7.17−6.90 (m, 6H, aromatics); 4.47 (septet, 2H, C*H*Me); 4.14 (septet, 2H, C*H*Me); 1.63 (s, 9H, C*Me*); 1.38 (d, 12H, CH*Me*); 1.30 (s, 9H, C*Me*); 1.15 (s, 9H, C*Me*); 1.14 (d, 12H, CH*Me*). ^{13}C NMR (C_6D_6, 30 °C, δ): 180.1 (C=C=N); 166.7 (N=*C*H); 156.7 (TaO*C*); 123.9−141.4 (aromatics); 95.6 (C=C=N); 64.4, 63.7, 63.3 (N*C*Me); 31.2, 30.4, 29.6 (NC*Me*); 24.4−26.6 (aliphatics).

[Ta(OC$_6$H$_3$Pr$^i_2$-2,6)$_2$Cl$_2${(C$_6$H$_3$Pr$^i_2$-2,6)N=CHC(=C=NBu^t)-NBu^t}] (6). To a concentrated solution of **2a** (0.1 g, 0.11 mmol) in benzene-d_6 (1 mL) was added *tert*-butyl isocyanide (0.03 g, 0.35 mmol). The product was only spectroscopically characterized. ^{1}H NMR (C_6D_6, 30 °C, δ): 7.95 (s, 1H, N=CH); 6.91−7.17 (m, 9H, aromatics); 4.45 (septet, br, 2H, C*H*Me); 4.17 (septet, br, 2H, C*H*Me); 3.03 (septet, 2H, C*H*Me); 1.70 (s, 9H, C*Me*); 1.44 (m, br, 12H, CH*Me*); 1.17 (d, 6H, CH*Me*); 1.07 (d, 6H, CH*Me*); 1.06 (s, 9H, C*Me*). ^{13}C NMR (C_6D_6, 30 °C, δ): 174.6 (N=*C*H); 156.9 (C=C=N); 148.2 (TaO*C*); 123.4−131.2 (aromatics); 96.1 (C=C=N); 65.1, 63.4, (N*C*Me); 30.9, 30.5 (NC*Me*); 23.1−29.8 (aliphatics).

[Ta(OC$_6$H$_3$Bu$^t_2$-2,6)(OC$_6$H$_3$Bu^{t}CMe$_2$CH$_2$)Cl{N(C$_6$H$_3$Me$_2$-2,6)CH$_3$}] (8a). To a suspension of [Ta(OC$_6$H$_3$Bu$^t_2$-2,6)$_2$Cl(H)$_2$ (PMePh$_2$)] (**7**) (0.5 g, 0.65 mmol) in benzene-d_6 (5 mL), was added 2,6-dimethylphenyl isocyanide (0.1 g, 0.78 mmol). The resulting red solution was stirred for 18 h. Removal of the benzene solvent led to the crude product as a red-brown solid. Layering a concentrated benzene solution with hexane yielded product as red crystals, which were washed with hexane and dried *in vacuo* with high yield. ^{1}H NMR (C_6D_6, 30 °C, δ): 6.58−7.25 (m, 9H, aromatics); 3.79 (s, 3H, NCH_3); 3.37 (d, 1H), 2.73 [d, 1H, Ta−CH_2, $^2J(^1H-^1H)$ = 15.8 Hz], 2.61 (s, 3H, C*Me*); 2.52 (s, 3H, C*Me*); 1.60 (m, 9H, C*Me$_3$*); 1.39 (s, 3H, C*Me$_2$*); 1.37 (s, 3H, C*Me$_2$*); 1.30 (m, 9H, C*Me$_3$*); 1.25 (s, 9H, C*Me$_3$*). ^{13}C NMR (C_6D_6, 30 °C, δ): 163.3 (TaO*C*); 156.4 (TaO*C*); 148.8 (N*C ipso*); 142.3 (*C*−CMe$_2$); 122.5−137.6 (aromatics); 94.8 (Ta*C*H$_2$); 45.9 (N*C*H$_3$); 32.0, 31.3 (TaCH$_2$C*Me$_3$*); 17.3−39.4 (aliphatics).

[Ta(OC$_6$H$_3$Bu$^t_2$-2,6)(OC$_6$H$_3$Bu^{t}CMe$_2$CH$_2$)Cl{N(Bu^t)CH$_3$}] (8b). To a suspension of [Ta(OC$_6$H$_3$Bu$^t_2$-2,6)$_2$Cl(H)$_2$(PMePh$_2$)] (0.1 g, 0.12 mmol) in benzene-d_6 (1 mL) was added *tert*-butyl isocyanide (0.03 g, 0.35 mmol). A yellow solution was observed. The product was only spectroscopically characterized. ^{1}H NMR (C_6D_6, 30 °C, δ): 6.78−7.29 (m, 6H, aromatics); 3.35 (s, 3H, NCH_3); 3.02 (d, 1H), 2.66 [d, 1H, Ta−CH_2, $^2J(^1H-^1H)$ = 16.6 Hz], 1.52 (m, 9H, N−^{t}*Bu*); 1.44 (s, 18H, C*Me$_3$*); 1.40 (s, 3H, C*Me$_2$*); 1.36 (s, 3H, C*Me$_2$*); 1.35 (m, 9H, C*Me$_3$*). ^{13}C NMR (C_6D_6, 30 °C, δ): 162.5 (TaO*C*); 158.2 (TaO*C*); 143.0 (*C*−CMe$_2$); 123.0−139.8 (aromatics); 101.4 (Ta*C*H$_2$); 61.5 (N*C*Me$_3$); 36.2 (N*C*H$_3$); 31.9, 30.1 (TaCH$_2$C*Me$_2$*); 18.5−40.7 (aliphatics).

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Supporting Information Available: Text describing the experimental procedures for X-ray diffraction studies and tables of positional and thermal parameters, bond distances and angles, and data collection parameters for **3** and **5** (42 pages). Ordering information is given on any current masthead page.

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