

Direct observation of η^2 -imine formation through β -H abstraction between amide ligands. Neutron and X-ray diffraction structure of a dihydride imine ditantalum complex†

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Reactions of $\text{Ta}(\text{NMe}_2)_5$ with $\text{D}_2\text{SiR'Ph}$ ($\text{R}' = \text{Me, Ph}$) were found to give a dideuterio η^2 -imine complex $(\text{Me}_2\text{N})_3\text{Ta}(\mu\text{-D})_2(\mu\text{-N-}\eta^2\text{-N,C-CH}_2\text{NMe})\text{Ta}(\text{NMe}_2)_3$ (**1-d**) through C–H activation of an amide ligand *via* β -H abstraction, and the structure of **1** was confirmed by single crystal neutron and X-ray diffraction.

Imine complexes are of much current interest, especially in understanding the reactivity of amide ligands and mechanistic pathways in the reactions involving metal amide complexes.¹ There are relatively few known β -H abstraction reactions of amide ligands to yield imine complexes,¹ and several reported cases involve β -H abstraction of amide ligands by alkyl ligands.^{1i–k} The formation of imine complexes with M–C bonds from homoleptic $\text{M}(\text{NR}_2)_n$ is particularly significant to the understanding of mechanistic pathways and C incorporation into metal nitride thin films in chemical vapor deposition reactions.² Based on analysis of organic products^{2b} and spectroscopic,^{2c–e} theoretical,^{2f} and kinetic^{2g,h} studies, initial β -H abstraction between two amide ligands in $\text{M}(\text{NR}_2)_n$ to give an η^2 -imine moiety was postulated as the first step to establish M–C bonds in C incorporation into the nitride films. Reducing C incorporation has been actively studied in the formation of the metal nitrides as microelectronic materials. We have found that the reactions of $\text{Ta}(\text{NMe}_2)_5$ with silanes $\text{H}_2\text{SiR'Ph}$ ($\text{R}' = \text{Me, Ph}$) yielded an unusual bridging dihydride imine complex $(\text{Me}_2\text{N})_3\text{Ta}(\mu\text{-H})_2(\mu\text{-N-}\eta^2\text{-N,C-CH}_2\text{NMe})\text{Ta}(\text{NMe}_2)_3$ **1** (Fig. 1) with elimination of HNMe_2 . **1** is one of few structurally characterized η^2 -imine complex from β -H abstraction *between* amide ligands,^{1a,b,1} a step of mechanistic significance to the formation of M-bound carbon in CVD of metal nitrides and to the understanding of reactivities of amide ligands.² Analysis of both single crystal neutron diffraction data with the crystal at 20 K and single crystal X-ray diffraction data confirmed the structure of **1**. Molecules of **1** crystallize as racemates in the solid state. **1** is also a rare example of direct observation of H-transfer from silanes to transition metal amides^{3,4} and is one of the few Ta hydrides⁵ to be structurally characterized by neutron diffraction.⁶ Our preliminary results are reported here.

Compound **1** was prepared from $\text{Ta}(\text{NMe}_2)_5$ with $\text{H}_2\text{SiR'Ph}$ in almost quantitative yields (Scheme 1).† The by-product HNMe_2 was confirmed by its reactions, after its removal from the reaction mixture, with $\text{DCl/D}_2\text{O}$ to give $\text{H(D)NMe}_2\text{Cl}/(\text{D}_2\text{NMe}_2)\text{Cl}$ and with $(p\text{-MeC}_6\text{H}_4)\text{C(=O)Cl}$ to yield $(p\text{-MeC}_6\text{H}_4)\text{C(=O)NMe}_2$.† The separation of 2.18(2) Å between the two bridging hydrides in the neutron structure of **1** indicates that **1** is a dihydride (rather than dihydrogen) complex.†‡^{5a} In other words, in the structure derived from neutron diffraction data, the bond lengths of the four Ta–H bonds vary from 1.92(1)

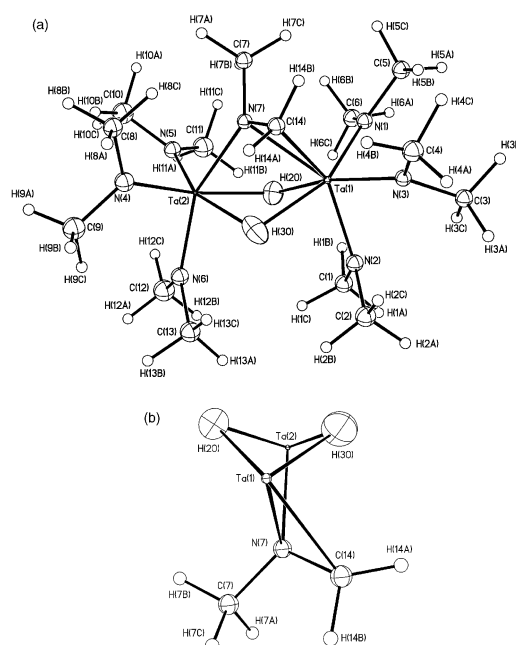
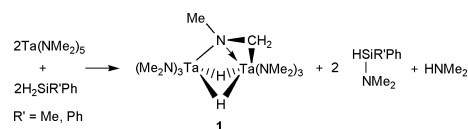


Fig. 1 Neutron structure of (a) **1** and (b) its core† showing 70% probability ellipsoids except for the methyl and methylene H atoms, which are shown with an arbitrary size for clarity. Selected bond distances (Å): Ta(1)–H(20) 1.994(10), Ta(1)–H(30) 1.957(10), Ta(2)–H(20) 1.977(9), Ta(2)–H(30) 1.923(11), Ta(1)–N(7) 2.224(5), Ta(2)–N(7) 2.149(5), Ta(1)–C(14) 2.223(6), Ta(1)–N(1,2,3)_{av} 2.035(9), Ta(2)–N(4,5,6)_{av} 2.003(9).

to 1.99(1) Å with an average value of 1.96(2) Å, and the average angles of Ta–H–Ta and H–Ta–H are 101.2(6) and 67.5(6)°, respectively. However, the shortest Ta–H bond is to Ta(2), which is not bonded to the methylene C(14), such that the inequivalent bond lengths appear to correlate with the inequivalent metal atom environments. The separation between the Ta atoms in **1**, 3.032(5) Å, is within the observed Ta–Ta bonding distances in Ta hydride complexes.⁷ If the imine ligand in **1** adopts metallacyclic bonding to the Ta atoms, there would be no direct metal–metal bonding between the d⁰ Ta atoms. The bridging imine N(7) is closer to Ta(2). This indicates that N(7) is likely bonded to Ta(1) through a dative bond by its lone pair electrons (Scheme 1).

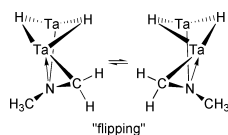
In ¹H NMR of racemic **1** in d₈-toluene at 23 °C, the two hydrides were observed as broad peaks at 8.47 and 6.57 ppm,



Scheme 1

† Electronic supplementary information (ESI) available: experimental section; X-ray ORTEP views of **1a** and **1b**; HMQC and NOESY NMR spectra. See <http://www.rsc.org/suppdata/cc/b1/b108913g/>

respectively. The diastereotopic methylene $-\text{CH}_2\text{H}_b-$ group was observed at $-28\text{ }^\circ\text{C}$ as two multiplets at 3.44 and 2.60 ppm in ^1H and 89.68 ppm in $^{13}\text{C}\{^1\text{H}\}$ NMR, respectively. HMQC studies of **1** confirmed the NMR assignments.[†] In the 2D-NOESY spectrum of **1** at $23\text{ }^\circ\text{C}$,[†] strong *positive* cross-peaks were observed between the two hydrides as well as between two methylene H atoms, respectively, indicating two exchange processes between these H atoms. One likely dynamic process between two enantiomers of **1** is shown in Scheme 2.



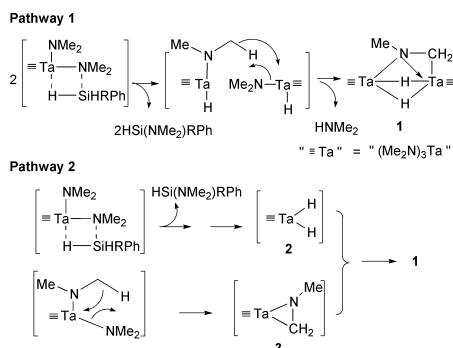
Scheme 2

The neutron structure of **1** confirmed the hydride ligands in **1**. The current studies (NMR of **1**, confirmation of the formation of HNMe_2 , and the neutron structure of **1**) showed that the reactions of an amide with silanes yielded hydride ligands. Such reactions are rare,^{4b,c} and the current work is the first direct confirmation of the hydrides in the product of such a reaction by single-crystal neutron diffraction.

Deuterium-labeling studies involving $\text{Ta}(\text{NMe}_2)_5$ and an excess of $\text{D}_2\text{SiR}'\text{Ph}$ showed the formation of 1-d_2 , $\text{HSi}(\text{NMe}_2)\text{R}'\text{Ph}/\text{DSi}(\text{NMe}_2)\text{R}'\text{Ph}$, $\text{HDSiR}'\text{Ph}$, and $\text{HNMe}_2/\text{DNMe}_2$ as a mixture with the remaining $\text{D}_2\text{SiR}'\text{Ph}$, indicating likely H/D exchanges among these compounds. However, *no* D incorporation into $-\text{CH}_2-$ in the imine ligand in 1-d_2 was observed in ^2H NMR, indicating that there is no exchange between $\text{Ta}^{\text{V}}-\text{D}-\text{Ta}^{\text{V}}$ and $-\text{CH}_2-$ in $\text{d}^0\text{1-d}_2$.⁸

The pathway in the formation of **1** is not clear. One *likely* pathway in the formation of **1** involves *direct* abstraction of a β -H atom in one amide by another amide in a bimolecular process to give the imine ligand (Scheme 3). In another possible pathway, two $\text{Ta}(\text{NMe}_2)_5$ molecules react with $\text{H}_2\text{SiR}'\text{Ph}$ and undergo β -H abstraction between two amide ligands, respectively, to give ' $\text{H}_2\text{Ta}(\text{NMe}_2)_3$ ' **2** and ' $\text{Ta}(\text{NMe}_2)_3(\eta^2\text{-N,C-CH}_2\text{NMe})$ ' **3**. **2** then reacts with **3** to yield **1**. Our earlier *ab initio* quantum chemical calculations showed that the bridging hydride ligands help stabilize hydride amide products.^{4c,d}

Particularly noteworthy is the β -H abstraction by an amide ligand to yield HNMe_2 and the η^2 -imine ligand with a direct Ta-C bond in **1**. The formation of η^2 -imine complexes through β -H abstraction was considered to be a relatively rare phenomenon.¹ NMR studies of reactions of MCl_5 ($\text{M} = \text{Ta}, \text{Nb}$) and WCl_6 with LiNEt_2 showed formation of imine-containing products,^{1g,h} and similar β -H abstraction was believed to occur in CVD of, *e.g.*, metal nitride films from homoleptic metal amides, leading to the formation of M-C bonds. The η^2 -imine ligand in **1** with a M-C bond constitutes one of few structurally characterized η^2 -imine ligands from β -H abstraction by another amide ligand. Previously reported examples include $[(\text{C}_2\text{N})_2\text{MCl}](\eta^2\text{-N,C-CyNC}_6\text{H}_{10})$ ($\text{M} = \text{Ta}, \text{Nb}$) from the reactions of TaCl_5 or $\text{NbCl}_4(\text{THF})_2$ with LiNCy_2 .^{1a,b,l} Such β -H abstraction between



Scheme 3

two amide ligands to give metal-bound carbon is of potential significance to the understanding of the formation of M-C bonds and C incorporation in metal nitride and M-Si-N ternary films from homoleptic metal amide precursors.

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† CCDC reference numbers 173742–173744. See <http://www.rsc.org/suppdata/cc/b1/b108913g/> for crystallographic data in CIF format.

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