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Unexpected Formation of (Dimethylaminomethylene)methylamide Complexes from the Reactions between Metal Chlorides and Lithium Dimethylamide

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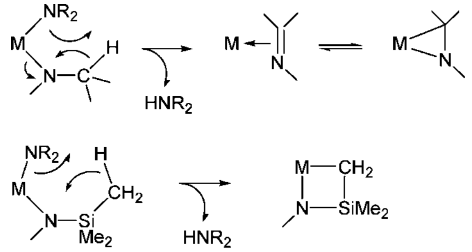
Summary: Reactions of MCl_5 (M = Nb, Ta) with $LiNMe_2$ have been found to yield $M(NMe_2)_4(\eta^2\text{-}MeNCH_2NMe_2)$ (M = Nb, ***2a****; Ta,* ***2b****) containing a chelating ligand (dimethylaminomethylene)methylamide, as confirmed by NMR spectroscopy, DFT calculations, and their reactivity studies.*

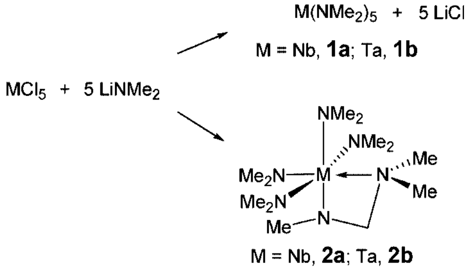
Introduction

Metathesis between transition metal halides and lithium amides is the most common route to amide complexes.[1,2] In particular, homoleptic amides complexes $M(NR_2)_n$ are almost exclusively prepared by the process shown in (1),[1a] and they have been used as precursors in the preparation of microelectronic thin films of metal[3] and oxides.[4] Although most metathesis reactions give amide complexes, there have been a few reports of β- and γ-H abstraction reactions yielding imine[5] and four-membered-ring metallaheterocyclic[6] complexes (Scheme 1).

Scheme 1



Scheme 2



$$MCl_n + nLiNR_2 \rightarrow M(NR_2)_n + nLiCl \qquad (1)$$

In our preparation of $M(NMe_2)_5$ (M = Nb, **1a**; Ta, **1b**) and $Ta(NMe_2)_4Cl$ from MCl_5 and $LiNMe_2$, we were surprised to isolate **2a** and **2b** as well in 5–10% yields (Scheme 2). **2b** was also observed in the reactions of $(Me_2N)_3TaCl_2$ with 2 equiv of $LiNMe_2$ and the reactions of $(Me_2N)_4TaCl$ with 1 equiv of $LiNMe_2$ in 0.9% and 2.9% yields, respectively. Our character-

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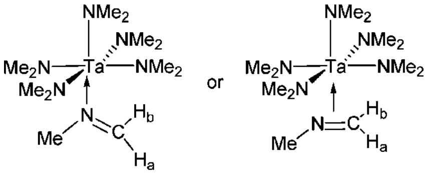
Scheme 3



3b **3b′**

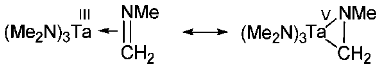
ization as well as experimental and theoretical studies of **2a**,**b** are reported.

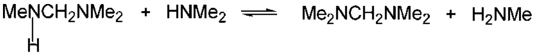
Results and Discussion

Sublimation at 70 °C (0.05 mmHg) of the product mixtures gave $M(NMe_2)_5$ (**1a**,**b**). Subsequent sublimation at 90 °C yielded crude **2a**,**b** as brown and pale yellow solids.[7] Recrystallization in Et_2O or pentane at −30 °C gave crystalline solids of **2a**,**b**. The ^1H resonances of $\mathit{Me}NCH_2-$, $-C\mathit{H}_2-$, and $-CH_2N\mathit{Me}_2$ of **2b** were observed as singlets at 3.13, 3.98, and 2.16 ppm (benzene-d_6), respectively. The four $-N\mathit{Me}_2$ ligands appeared at 3.30 ppm. The peak (2.16 ppm) of $-CH_2N\mathit{Me}_2$, which forms a N→Ta dative bond, is upfield-shifted from those of $-N\mathit{Me}_2$ and $\mathit{Me}NCH_2-$. The ^{13}C peaks of the $-N\mathit{Me}_2$, $-CH_2N\mathit{Me}_2$, and $\mathit{Me}NCH_2-$ were observed at 47.89, 47.29, and 39.13 ppm, respectively. DEPT-135 and HMQC experiments confirmed the assignment. In the ^1H-coupled ^{13}C NMR spectrum, the $-\mathit{C}H_2-$ resonance was a triplet at 82.67 ppm ($^1J_{C\text{-}H} = 141.1$ Hz). The crystal structures of **2a** and **2b** are isomorphous and disordered.[7] They are given in the Supporting Information. They are also isomorphous to that of $W(NMe_2)_6$.[8] Because of the disorder with the T_h symmetry, the presence of the η^2-$MeNCH_2NMe_2$ ligands in **2a**,**b** could not be confirmed by single-crystal X-ray diffraction. C, H, and N elemental analyses of **2a**,**b** are consistent with their compositions.[8] It should be noted that, in the reaction of MCl_5 (M = Nb, Ta) with 5 equiv of $LiNMe_2$, the total yields of $M(NMe_2)_5$ (**1a**,**b**) and **2a**,**b**, based on MCl_5, are 55% and 54%, respectively. Thus it is conceivable that the use of $LiNMe_2$ to give $M(NMe_2)_4(\eta^2\text{-}MeNCH_2NMe_2)$ (**2a**,**b**), which consumes at least 6 equiv of $LiNMe_2$, may have contributed to the lower yields of $M(NMe_2)_5$ (**1a**,**b**).

Studies were also conducted to rule out that **2a**,**b** are imine complexes (Scheme 3).[5,9] In either σ-bonded **3b** or π-bonded **3b′**, H_a and H_b in the imine complexes are expected to be chemically inequivalent. Only one peak (e.g., 3.98 ppm for **2b**) was observed for the $-C\mathit{H}_2-$ moiety, and the ^1H-coupled ^{13}C resonance split into a triplet, indicating that the two H atoms are chemically equivalent. This observation rules out that **2a**,**b** are imine complexes (**3b** or **3b′**). In addition, the ^{13}C NMR resonance of the $-\mathit{C}H_2-$ moiety at 82.7 ppm is much shifted from those of coordinated imine C atoms around 140 ppm.[9b,10] There is no characteristic imine (N=C) band around 1600 cm^{-1} in the IR spectrum of **2b**.[7] Hydrolysis of a solution of **2b** in benzene-d_6 was conducted to confirm its structure.[7] A GC-MS and NMR analysis of the volatile products showed the formation of $Me_2NCH_2NMe_2$, H_2NMe, and $HNMe_2$. The formation of $Me_2NCH_2NMe_2$ and H_2NMe is perhaps not surprising, given that alkyl amines are known to undergo catalytic alkyl exchanges.[11] The hydrolysis may initially yield $HMeNCH_2NMe_2$ and $HNMe_2$ which then undergo the exchange in eq 2 catalyzed by Ta oxide/hydroxide. Although we cannot rule out the possibility that $Me_2NCH_2NMe_2$ and H_2NMe are the products of the hydrolysis of $Ta(NMe_2)_5(CH_2{=}NMe)$ (**3b**), the observation of $Me_2NCH_2NMe_2$ as a hydrolysis product as well as spectroscopic and DFT studies discussed below strongly suggest that **2b** is $Ta(NMe_2)_4(\eta^2\text{-}MeNCH_2NMe_2)$ containing the chelating (aminomethyl)amide ligand.

Scheme 4





$$\underset{\displaystyle H}{MeNCH_2NMe_2} + HNMe_2 \rightleftharpoons Me_2NCH_2NMe_2 + H_2NMe \qquad (2)$$

Experiments have been conducted to verify if $Ta(NMe_2)_5$ (**1b**) reacts with freshly generated imine $CH_2{=}NMe$ to yield **2b**. $CH_2{=}NMe$ was prepared from the thermal cracking of its trimer,[12] and was added directly to $Ta(NMe_2)_5$ (**1b**) in toluene-d_8 at −45 °C. Variable-temperature NMR spectra were monitored. Several tests failed to show the formation of **2b**. In many cases, only the polymerization of $CH_2{=}NMe$ was observed.[12a] The results support the conclusions from computations that will be discussed below. *It is not clear at the present time how* ***2b*** *is formed in the reaction between* $TaCl_5$ *and* $LiNMe_2$. It is likely that a $-NMe_2$ ligand undergoes the β-H abstraction reaction with another amide or chloride ligand to yield a Ta(III) imine complex (or its resonance, Scheme 4).[6b] This reaction is perhaps parallel to the metathesis between MCl_5 and $LiNMe_2$ to give $M(NMe_2)_5$ (**1a**,**b**). Subsequent oxidation by adventitious molecular oxygen perhaps returns the Ta(III) imine complex back to d^0 Ta(V) that is eventually converted to **2b** through the coupling of the imine and an amide ligand. There have been precedents in the use of molecular oxygen in the preparation of high-oxidation metal complexes.[8b,13,14] Chisholm and coworkers have reported the preparation of d^0 $Mo(NMe_2)_6$ from the reaction of d^2 $Mo(NMe_2)_4$ with O_2.[13] Wilkinson and coworkers found that WMe_6 could be obtained from the reaction of WCl_6 with 3 equiv of LiMe in the presence of adventitious molecular oxygen.[14] Adventitious molecular oxygen was also

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(7) See Supporting Information for details.

(8) Additional studies were conducted to rule out the possibility that *a small amount* of $W(NMe_2)_6$ was present in the samples of **2b**, and preferentially crystallized, giving the observed crystal structure. Resonances of $W(NMe_2)_6$ were *not* observed in the ^1H and ^{13}C NMR spectra of **2b**. In addition, the color of the crystals of **2b** is pale yellow, in contrast to the reported red color for $W(NMe_2)_6$.[8a,b] Analyses by X-ray photoelectron spectroscopy (XPS) of solids of **2b**, $Ta(NMe_2)_5$, and $W(NMe_2)_6$ [containing a small amount of $W_2(NMe_2)_6$] were conducted, and the XPS spectra suggest that **2b** contains tantalum and no tungsten.[7] (a) Bradley, D. C.; Chisholm, M. H.; Heath, C. E.; Hursthouse, M. B. *Chem. Commun.* **1969**, 1261. (b) Bradley, D. C.; Chisholm, M. H.; Extine, M. W. *Inorg. Chem.* **1977**, *16*, 1791.

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(10) It is likely that the ^{13}C resonance for η^2-imine C atoms is around 80–90 ppm,[5c] and the stretching band of the η^2-imine C−N band may appear below 1600 cm^{-1}. In addition the IR $v_{C=N}$ bands for σ-imine complexes could be difficult to observe.[9b]

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believed to play a role in the formation of d^0 $W(NMe_2)_6$ from reactions of d^1 WBr_5 or d^2 $WCl_4(THF)_2$ with $LiNMe_2$.[8b] A process involving disproportionation of the Ta(III) imine species into Ta(V) and new Ta species at a lower oxidation seems unlikely, as XPS analyses of the solid residue from the sublimation of $Ta(NMe_2)_4(\eta^2\text{-}MeNCH_2NMe_2)$ (**2b**) suggest that there was unlikely Ta(0) species in the residue.[7]

Another possible pathway leading to the formation of the (aminomethylene)amide $-N(Me)CH_2NMe_2$ ligand in **2b** is perhaps similar to that in the reaction of d^0 $Ta(NMe_2)_5$ (**1b**) with O_2,[4e] giving $-N(Me)CH_2NMe_2$ ligands in $(Me_2N)_4Ta_2[\eta^2\text{-}N(Me)CH_2NMe_2]_2(\mu\text{-}O)_2$ and $(Me_2N)_6Ta_3[\eta^2\text{-}N(Me)CH_2NMe_2]_2(\eta^2\text{-}ONMe_2)(\mu\text{-}O)_3$. DFT studies indicate that the reaction of $Ta(NMe_2)_5$ (**1b**) with O_2 yields a peroxide complex $(Me_2N)_4Ta(\eta^2\text{-}O\text{-}O\text{-}NMe_2)$. The peroxide ligand plays an important role, including oxidizing an amide to an imine ligand through the abstraction of a hydride. Insertion of $Me{-}N{=}CH_2$ into a Ta−amide bond yields the unusual $-N(Me)CH_2NMe_2$ ligands.[4e] There might be a similar pathway involving adventitious molecular oxygen in the reactions of $TaCl_5$ with $LiNMe_2$, leading to the formation of the (aminomethyl)amide $-N(Me)CH_2NMe_2$ ligand in **2b**.

In the current work, **2b** was found to be inert to molecular oxygen, although it is easily hydrolyzed. Exposure of a solution of **2b** in benzene-d_6 to 1 atm of O_2 at 23 °C for 17 h showed no decay of **2b**.[7] Thus a trace amount of **2b** in $Ta(NMe_2)_5$ (**1b**) does *not* participate in the reaction with O_2.[4e] It should be noted that hexacoordinated $Mo(NMe_2)_6$ reacts with O_2 to give unknown species,[13] while $W(NMe_2)_6$ is inert to O_2.[15]

DFT calculations[16] have been conducted in the current work to help elucidate the structures of **2b** and **3b**. The optimized structures are shown in Figure 1. Among the six ligands in **3b**, the imine coordinates to the Ta center with a long dative bond (2.554 Å). The average length of the six Ta−N bonds is 2.142 Å, longer than the average [2.075(6) Å] in the crystal structure.[7] Each of the five amide planes is neither parallel nor perpendicular to the octahedral skeleton. The tilt angle of each amide plane with repsect to the octehdral skelton is in the range of 10–25°. **2b** adopts almost C_s symmetry. The tilt angles of the amide planes to the octahedral skeleton are smaller, ca. 3–12°. However, the octahedral skelton is much more distorted, with a small N−Ta−N angle of 58.5° in the $Ta(\eta^2\text{-}MeNCH_2NMe_2)$ moiety. The $N_{amine}{-}Ta$ distance is 2.629 Å, resulting in an average Ta−N bond length of 2.146 Å, also longer than the average [2.075(6) Å] in the crystal structure.[7]

NMR chemical shifts for **2b** and **3b** have been calculated with the DFT method and are given in Figure 1. They show that experimental values are close to calculated shifts of **2b**, and are different from those of **3b**. The calculated chemical shifts of H_a and H_b in **3b** are at ca. 7.3–7.4 ppm and the $=CH_aH_b$ are at 153.3 ppm. Both are much downfield shifted from the observed values.

For the energetic consideration, the computational studies reveal that the complexation between **1b** and imine (to give **3b**) is an unfavorable process and the conversion of **3b** to **2b** is a feasible process that has a low barrier and is exothermic (Scheme 5). Both **1b** + imine and **2b** are ca. 14 kcal/mol more stable than the imine complex **3b** in free energy, suggesting that **3b** is not a stable intermediate to be isolated. Even if **3b** is a possible intermediate, the calculation results show that its imine ligand likely departs from the metal center or undergoes a coupling reaction with an amide ligand, yielding the η^2-$MeNCH_2NMe_2$ ligand in **2b**. The calculation results given in Scheme 5 show that the formation of **2b** via **3b** from the reaction of **1b** with imine requires a very high barrier of ca. 37 kcal/mol in free energy, suggesting that **2b** may not directly come from the complexation of **1b** with imine. These results are consistent with the experimental observations described above that $Ta(NMe_2)_5$ (**1b**) does not react with imine $CH_2{=}NMe$.

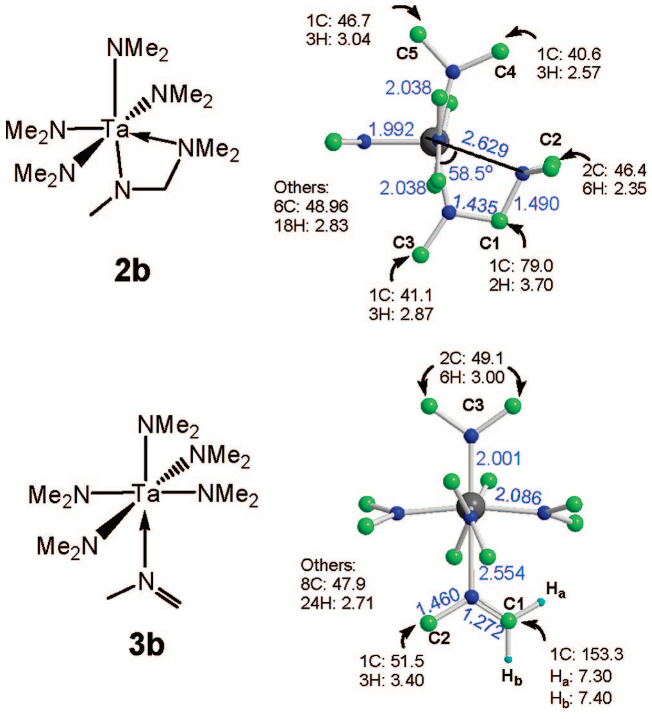

Figure 1. Calculated structures and NMR chemical shifts of **2b** and **3b** (bond distances in Å; NMR chemical shifts in ppm). Most H atoms are omitted for clarity.

It is not clear at the present time how the η^2-$MeNCH_2NMe_2$ ligands in **2a**,**b** are formed in the metathesis reactions between metal halides and lithium amides. The current work shows that the metathesis may be complex. The formation of **2a**,**b** helps shed light on the nature of the metathesis reactions, the most common route to homoleptic metal amides.

Experimental Section

All manipulations, unless noted, were performed under a dry N_2 atmosphere with the use of Schlenk techniques. All solvents were purified by distillation from K/benzophenone ketyl. Benzene-d_6 was dried over molecular sieves and stored under N_2. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker AC-250 or AMX-400 spectrometer. They were referenced with residual protons and solvent, respectively. FT-IR spectra of KBr pellets were recorded on a Bio-Rad FTS-60A spectrometer. A Hewlett-Packard 6890 gas chromatograph (GC) with a 5793 mass selective (MS) detector (MSD) was used to obtain GC/MS data. Elemental analyses were performed by E+R Microanalytical Laboratory, Corona, New York.

Preparation of $(Me_2N)_4Nb(\eta^2\text{-}MeNCH_2NMe_2)$ (2a). $NbCl_5$ (8.07 g, 29.9 mmol) in THF (30 mL) was added dropwise to 5

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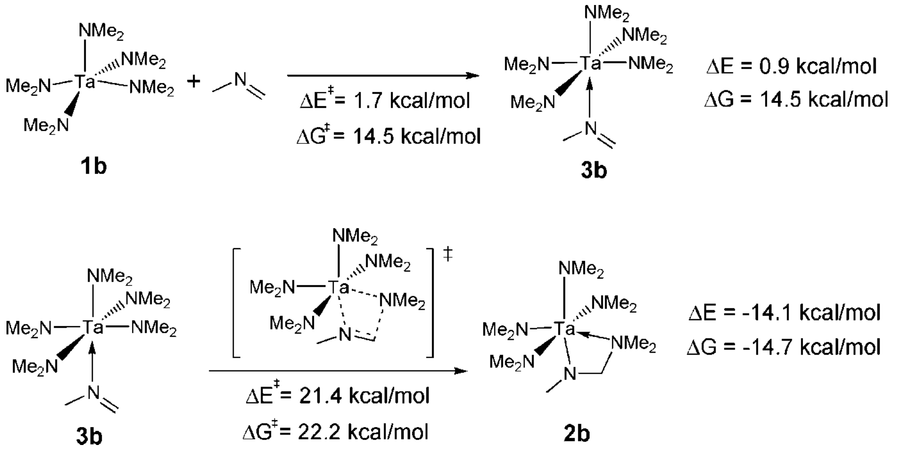
Scheme 5. Calculated Activation Energies (free energies) and Reaction Energies (free energies) of the Complexation of Imine to 1b and the Transformation of 3b to 2b



equiv of $LiNMe_2$ (7.62 g, 149 mmol) in THF (50 mL) at −78 °C with vigorous stirring. The dark brown solution was warmed to room temperature in 40 min. The mixture was stirred at room temperature for another 23 h. All volatiles were removed in vacuo, and the solid was extracted with hexanes. The solvent was then removed from the filtrate in vacuo. Sublimation at 60 °C gave 5.77 g of a mixture of 92 mol % $Nb(NMe_2)_5$ (**1a**) and 8 mol % $(Me_2N)_4Nb(\eta^2\text{-}MeNCH_2NMe_2)$ (**2a**), as revealed by the ^1H NMR spectrum of the mixture. Initial recrystallization of the mixture in *n*-pentane at −30 °C yielded crystals of **1a** (4.82 g. 15.3 mmol, 51.0% yield). Afterward, the supernatant solution was concentrated and cooled to −30 °C to give brown crystals of **2a** (0.385 g, 1.08 mmol, yield 3.6%). ^1H NMR (benzene-d_6, 399.9 MHz, 23 °C) δ 3.76 (s, 2H, Me_2NCH_2NMe), 3.20 (s, 24 H, NMe_2), 3.09 (s, 3H, Me_2NCH_2NMe), 2.13 (s, 6H, Me_2NCH_2NMe). ^{13}C NMR (benzene-d_6, 100.6 MHz, 23 °C) δ 84.0 (Me_2NCH_2NMe), 48.5 (NMe_2), 47.6 (Me_2NCH_2NMe), 40.4 (Me_2NCH_2NMe). Anal. Calcd for $C_{12}H_{35}N_6Nb$: C, 40.45; H 9.90. Found: C, 40.21; H 9.83. In addition, EA shows no lithium within experimental error, suggesting that **2a** is *not* π-bonded $Li_2[Nb(NMe_2)_5(\eta^2\text{-}CH_2{=}NMe)]$.

Preparation of $Ta(NMe_2)_4(\eta^2\text{-}MeNCH_2NMe_2)$ (2b). To a slurry of $LiNMe_2$ (5.36 g, 105 mmol) in hexanes (100 mL) was added $TaCl_5$ (7.16 g, 20 mmol) slowly at −30 °C with stirring. The mixture was stirred overnight at room temperature, and volatiles were removed in vacuo to give dark brown solid. The solid was sublimed in vacuo at 70 °C to give $Ta(NMe_2)_5$ (3.51 g, 8.74 mmol, 43.8%) on a coldfinger at −5 °C. The residue was then further sublimed in vacuo at 90 °C to give crude **2b** as a pale yellow solid (0.89 g, 2.0 mmol, 10%). The solid was crystallized in Et_2O at −30 °C to give pale yellow crystals of **2b**. ^1H NMR (benzene-d_6, 250.1 MHz, 23 °C) δ 3.98 (s, 2H, CH_2), 3.30 (s, 24H, NMe_2), 3.13 (s, 3H, $MeNCH_2$), 2.16 (s, 6H, CH_2NMe_2). ^{13}C NMR (benzene-d_6, 62.9 MHz, 23 °C) δ 82.7 (CH_2, $^1J_{C\text{-}H} = 141.1$ Hz), 47.9 (NMe_2, $^1J_{C\text{-}H} = 131.5$ Hz), 47.3 (CH_2NMe_2, $^1J_{C\text{-}H} = 135.5$ Hz), 39.1 ($MeNCH_2$, $^1J_{C\text{-}H} = 131.8$ Hz). HMQC NMR of **1b** is consistent with the assignments. Anal. Calcd for $C_{12}H_{35}N_6Ta$: C, 32.43; H, 7.94; N, 18.91. Found: C, 32.27; H, 7.86; N, 18.73.

Hydrolysis of 2b. To **2b** (37.5 mg, 0.084 mmol) in benzene-d_6 in a Young's tube was added 6 equiv of H_2O (9 μL, 0.504 mmol). The products were immediately analyzed by ^1H NMR, ^{13}C NMR, ^1H-coupled ^{13}C NMR, HMQC, and GC/MS. In a separate test, 2 equiv of H_2O was added to a solution of **2b** in benzene-d_6. Unhydrolyzed **2b**, $Me_2NCH_2NMe_2$, $HNMe_2$, and H_2NMe were observed in ^1H NMR.

Determination of X-ray Crystal Structures of 2a,b. The data for the X-ray crystal structures of **2a**,**b** were collected on a Smart 1000 X-ray diffractometer equipped with a CCD area detector fitted with an upgraded Nicolet LT-2 low-temperature device. The data were obtained with use of a graphite-monochromated Mo source (Kα radiation, 0.71073 Å). Suitable crystals were coated with paratone oil (Exxon) and mounted on loops under a stream of nitrogen at the data collection temperature. The structures were solved by direct methods.

Non-hydrogen atoms were anisotropically refined. All hydrogen atoms were treated as idealized contributions. Empirical absorption correction was performed with SADABS.[17b] In addition the global refinements for the unit cells and data reductions of the two structures were performed with the Saint program (version 6.02). All calculations were performed with the SHELXTL (version 5.1) proprietary software package.[17b]

Computational Details

All calculations were performed by using the Gaussian 03 package[16] with density functional theory at the B3LYP level. Full geometry optimizations were carried out with the basis set LanL2DZ with f polarization functions[18] for Ta and 6-31G* for the rest of the elements. Vibration frequency calculations were performed for all the calculated structures. The calculated relative energies shown in the text have been corrected with zero-point energy (ZPE). NMR shielding tensors were calculated by using the Gauge-Independent Atomic Orbital (GIAO) method[19] with the same DFT method used in the geometry optimization. The NMR shielding tensor of tetramethylsilane (TMS) was calculated as the reference.

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Supporting Information Available: Experimental section for XPS studies; DFT calculations, including calculated total energies and structures with Cartesian coordinates; crystallographic data and ORTEP views of **2a**,**b**; XPS and IR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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