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Synthesis of Vanadium, Niobium, and Tantalum Silylimido Complexes and Reactivity of Their Nitrogen–Silicon Bonds

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A series of group V transition-metal (trimethylsilyl)imido compounds has been synthesized in which the $NSiMe_3$ groups derive from hexamethyldisilazane. Reaction of MCl_5 with 2 equiv of $NH(SiMe_3)_2$ produces $[M(NSiMe_3)Cl_3(NH_2SiMe_3)]_2$ (M = Nb, Ta). Pyridine and substituted pyridine adducts, $M(NSiMe_3)Cl_3L_2$ (M = Nb, L = py, 4-Mepy, or $^1/_2$ 4,4′-Me_2bpy; M = Ta, L = py), are prepared either by addition of ligand to the niobium dimer or by direct reaction of the metal halide with a mixture of hexamethyldisilazane and pyridine. Related vanadium (trimethylsilyl)imido compounds, $V(NSiMe_3)Cl_3L_2$ (L = 4-Etpy, 4-*t*-Bupy), are formed upon reaction of $V(NSiMe_3)Cl_3$ with added ligand in pentane. The vanadium compounds undergo fast, stoichiometric loss of chlorotrimethylsilane, yielding the nitrido derivatives $V(N)Cl_2L_2$, in contrast to slow, incomplete elimination of $ClSiMe_3$ from the niobium and tantalum complexes. The reactivity of nitrogen–silicon bonds in silylimido ligands is discussed in light of these observations.

Introduction

The utility of silicon compounds in synthetic organic chemistry has long been recognized.[1] Silicon's low electronegativity, its ability to expand its coordination sphere, and its strong bonds to electronegative elements allow it to serve in a variety of roles in the reactions of organic compounds. Silyl substituents can be employed to direct the course of reactions, to activate substrates, or to protect otherwise reactive sites in molecules. More recently, creative applications of silyl groups in the chemistry of organometallic and inorganic complexes have begun to appear, from the synthesis of reactive metal hydroxymethyl compounds via the (trimethylsiloxy)methyl ligand[2] to the substitution of sulfido for oxo ligands at metal centers using hexamethyldisilthiane.[3]

We recently reported a route to nitride-bridged transition-metal compounds that utilizes the reactivity of N–Si bonds in silylimido complexes: The condensation of silylimido complexes with metal halide derivatives accompanied by loss of silyl halide allows the preparation of both bimetallic and polymeric μ-nitride compounds (eqs 1 and 2).[4-6]

$$V(NSiMe_3)(OSiMe_3)_3 + M(F)L_n \rightarrow (Me_3SiO)_3V(\mu\text{-}N)ML_n + FSiMe_3 \quad (1)$$

$$V(NSiMe_3)Cl_3 + 2py \rightarrow [V(\mu\text{-}N)Cl_2(py)_2]_\infty + ClSiMe_3 \quad (2)$$

In order to explore the influence of varied metal–ligand environments on the nitride bridge and the generality of the condensation reaction, a range of silylimido compounds is needed. However, only a limited number of these derivatives have been reported to date,[7-10] in part because the reactive nature of the N–Si bond can preclude the synthesis of silylimido complexes by many of the general methods used to prepare organoimido derivatives.[11] We have recently described the preparation of a series of group VI transition-metal (trimethylsilyl)imido complexes using trimethylsilyl azide as the source of the $NSiMe_3$ ligand.[12] In this paper, we report the synthesis and characterization of a family of group V transition-metal (trimethylsilyl)imido compounds, $M(NSiMe_3)Cl_3L_n$, in which the $NSiMe_3$ group is derived from hexamethyldisilazane, $NH(SiMe_3)_2$. The variation in reactivity of the N–Si linkages in this series of compounds is also discussed.

Experimental Section

General Considerations. All manipulations were performed by using glovebox, Schlenk, or vacuum-line techniques. Solvents and pyridine were dried over activated 4-Å molecular sieves, stored over CaH_2, and vacuum-transferred prior to use. NMR solvents were dried over activated 4-Å molecular sieves. Hexamethyldisilazane (Petrach) and substituted pyridines (Aldrich) were purified by distillation under N_2; 4,4′-dimethyl-2,2′-bipyridine (Aldrich) was purified by vacuum sublimation. $NbCl_5$ (Alfa) and $TaCl_5$ (Strem) were sublimed under vacuum at least twice prior to use. $V(NSiMe_3)Cl_3$ (**5**) was prepared as previously reported.[6a] NMR spectra were recorded on Varian VXR300 (299.95 MHz, ^{1}H; 75.43 MHz, ^{13}C) and Bruker WM500 (500.14 MHz, ^{1}H) spectrometers at ambient temperatures in benzene-d_6 unless otherwise noted; chemical shifts are reported in ppm downfield from $SiMe_4$. IR spectra were obtained as Nujol mulls with Perkin-Elmer 283 and 1600 spectrometers. Elemental analyses were performed by Canadian Microanalytical Services, Ltd.

Syntheses. $[Nb(NSiMe_3)Cl_3(NH_2SiMe_3)]_2$ (1). $NH(SiMe_3)_2$ (3.2 mL, 15.2 mmol) was added to a suspension of $NbCl_5$ (2.0 g, 7.4 mmol) in benzene (20 mL), resulting in an orange solution that darkened to deep red over several hours at 22 °C. After being stirred approximately 18 h, the solution rapidly lightened to an olive color with deposition of a white microcrystalline solid. The solid was collected by filtration, washed with benzene (2 × 5 mL), and dried under vacuum, producing 2.4 g of **1** (86%): ^{1}H NMR 3.17 (br, 2 H), 0.25 (s, 9 H), 0.11 (s, 9 H); ^{13}C{^{1}H} NMR 0.4, 0.0; IR 3260, 3200, 1511, 1257, 1118, 1060, 1031, 848, 765, 694, 638, 569, 430, 373, 350, 327 cm^{-1}. Anal. Calcd for $C_6H_{20}Cl_3N_2NbSi_2$: C, 19.18; H, 5.37; N, 7.46. Found: C, 19.13; H, 5.39; N, 7.32.

$[Ta(NSiMe_3)Cl_3(NH_2SiMe_3)]_2$ (2). The above procedure was followed by using 2.0 g (5.6 mmol) of $TaCl_5$ and 2.3 mL (10.9 mmol) of $NH(SiMe_3)_2$, producing a yellow solution. After the solution was stirred for 20 h at 22 °C, a beige solid was isolated from the yellow-brown solution by filtration, washed with pentane (4 × 5 mL), and dried under vacuum, yielding 2.3 g of **2** (89%): ^{1}H NMR 4.32 (br, 2 H), 0.67 (s, 9 H), 0.62 (s, 9 H); IR 3190, 3168, 3155, 1520, 1435, 1271, 1158, 1100, 1032, 1019, 999, 872, 830, 784, 671, 653, 616, 574, 360, 314 cm^{-1}.

$Nb(NSiMe_3)Cl_3(py)_2$ (3a). Excess pyridine (5 mL) was added to a

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solution of **1** (0.60 g, 1.6 mmol) in toluene (25 mL) at −78 °C. The mixture was allowed to warm to 22 °C, producing a bright yellow solution, which was stirred for 1 h. The solvent and volatiles were removed under reduced pressure, resulting in a yellow oil. Trituration with pentane (5 mL) produced a yellow solid, which was collected by filtration, washed with pentane (3 × 5 mL), and dried under vacuum, yielding 0.57 g of **3a** (80%). Recrystallization from a toluene solution at −30 °C effects further purification: ^{1}H NMR (C_6D_6) 9.12 (d, J = 5 Hz, 2 H), 8.84 (d, J = 5 Hz, 2 H), 6.81 (t, J = 7 Hz, 1 H), 6.64 (t, J = 7 Hz, 1 H), 6.51 (m, 2 H), 6.27 (m, 2 H), 0.32 (s, 9 H); ^{1}H NMR (CD_2Cl_2) 8.90 (d, J = 3 Hz, 2 H), 8.82 (d, J = 5 Hz, 2 H), 7.94 (t, J = 7 Hz, 1 H), 7.82 (t, J = 7 Hz, 1 H), 7.41 (m, 4 H), 0.26 (s, 9 H); ^{13}C{^{1}H} NMR (C_6D_6) 152.7, 151.4, 138.6, 137.6, 124.2, 123.9, 0.3; IR 3145, 3050, 1610, 1604, 1591, 1450, 1410, 1252, 1224, 1158, 1112, 1075, 1052, 1045, 1020, 1011, 980, 852, 765, 706, 647, 632, 430, 390, 329, 302 cm^{-1}. Anal. Calcd for $C_{13}H_{19}Cl_3N_3NbSi$: C, 35.11; H, 4.31; N, 9.45; Cl, 23.92. Found: C, 35.45; H, 4.55; N, 9.34; Cl, 24.07.

Nb(NSiMe$_3$)Cl$_3$(4-Mepy)$_2$ (3b). The above procedure was followed by using 0.30 g (0.80 mmol) of **1** and 0.18 mL (1.9 mmol) of 4-methylpyridine, yielding 0.22 g of yellow **3b** (58%): ^{1}H NMR 9.08 (d, J = 4 Hz, 2 H), 8.77 (d, J = 6 Hz, 2 H), 6.42 (d, J = 4 Hz, 2 H), 6.16 (d, J = 6 Hz, 2 H), 1.60 (s, 3 H), 1.47 (s, 3 H), 0.37 (s, 9 H); ^{13}C{^{1}H} NMR 152.4, 151.9, 151.1, 149.5, 124.9, 124.8, 20.9, 20.8, 0.07; IR 3140, 1619, 1503, 1247, 1211, 1098, 1064, 1028, 1012, 843, 813, 754, 722, 631, 549, 533, 494, 383, 328 cm^{-1}. Anal. Calcd for $C_{15}H_{23}Cl_3N_3NbSi$: C, 38.11; H, 4.90; N, 8.89. Found: C, 38.51; H, 5.22; N, 8.71.

Nb(NSiMe$_3$)Cl$_3$(4,4′-Me$_2$bpy) (3c). Toluene (10 mL) was added to a mixture of **1** (210 mg, 0.56 mmol) and 4,4′-dimethyl-2,2′-bipyridine (73 mg, 0.40 mmol) at −78 °C. The mixture was allowed to warm to 22 °C and stirred for 1 h. The pale yellow solid was collected by filtration, washed with toluene (1 × 3 mL), and dried under vacuum, yielding 188 mg of **3c** (100%): ^{1}H NMR 9.32 (d, J = 6 Hz, 1 H), 9.15 (d, J = 6 Hz, 1 H), 6.87 (s, 2 H), 6.16 (d, J = 6 Hz, 1H), 6.08 (d, J = 6 Hz, 1 H), 1.63 (s, 3 H), 1.60 (s, 3 H), 0.49 (s, 9 H); IR 3140, 1624, 1620, 1552, 1409, 1309, 1253, 1249, 1121, 1103, 1081, 1026, 1019, 945, 923, 899, 846, 753, 727, 630, 561, 550, 521, 383, 324 cm^{-1}.

Ta(NSiMe$_3$)Cl$_3$(py)$_2$ (4). NH(SiMe$_3$)$_2$ (0.95 mL, 4.5 mmol) and excess pyridine (2.3 mL, 28 mmol) were added to a benzene suspension of $TaCl_5$ (1.50 g, 4.2 mmol), and the mixture was stirred at 22 °C for 20 h. The resulting yellow solution was decanted from an insoluble off-white material and filtered through Celite, and the solvent and volatiles were removed under reduced pressure, producing a yellow oil. Trituration with pentane (4 × 5 mL) produced a yellow solid, which was collected by filtration, washed with pentane (3 × 5 mL), and dried under vacuum, yielding 1.38 g. With hexamethylbenzene as an internal standard, the solid obtained in this reaction was determined to be 71% **4** by ^{1}H NMR spectroscopy. Attempts to purify **4** by recrystallization from a variety of solvents resulted in isolation of increasing amounts of insoluble off-white material. For **4**: ^{1}H NMR 8.97 (br, 2 H), 8.91 (d, J = 5 Hz, 2 H), 6.81 (m, 1 H), 6.59 (t, J = 8 Hz, 1 H), 6.49 (m, 2 H), 6.22 (m, 2 H), 0.37 (s, 9 H); ^{13}C{^{1}H} NMR 153.0, 151.5, 139.3, 137.5, 124.1, 123.9, 1.5; IR 1610, 1487, 1245, 1139, 1068, 1040, 1005, 842, 755, 697, 625 cm^{-1}.

V(NSiMe$_3$)Cl$_3$(4-Etpy)$_2$ (6a). A solution of 4-ethylpyridine (74 μL, 0.91 mmol) in pentane (3 mL) was added dropwise to a stirred solution of **5** (0.10 g, 0.41 mmol) in pentane (20 mL) at 22 °C, producing a mustard-colored precipitate. The solid was collected by filtration, washed with pentane (2 × 3 mL), and dried under vacuum, yielding 0.10 g of a mixture of **6a** and V(N)Cl$_2$(4-Etpy)$_2$ (**7a**): IR 1617, 1550, 1501, 1426, 1250, 1226, 1201, 1060, 1028, 1002, 962, 850, 825, 790, 716, 572, 513, 392 cm^{-1}.

V(NSiMe$_3$)Cl$_3$(4-*t*-Bupy)$_2$ (6b). The above procedure was followed by adding 4-*tert*-butylpyridine (0.12 g, 0.81 mmol) to **5** (0.10 g, 0.41 mmol) at −78 °C. A mustard yellow solid formed upon allowing the solution to warm to 22 °C with stirring. The solid was collected by filtration, washed with pentane (3 × 3 mL), and dried under vacuum, yielding 0.14 g of **6b** (64%): IR 1616, 1541, 1500, 1420, 1275, 1251, 1231, 1202, 1068, 1026, 1014, 844, 758, 728, 668, 572, 547, 459, 408 cm^{-1}.

Results

Niobium and Tantalum. The reaction of niobium or tantalum pentachloride with 2 equiv of hexamethyldisilazane in benzene at room temperature results in the formation of [M(NSiMe$_3$)Cl$_3$(NH$_2$SiMe$_3$)]$_2$ (M = Nb (**1**), Ta (**2**)) (eq 3). Monitoring

$$MCl_5 + 2NH(SiMe_3)_2 \rightarrow \tfrac{1}{2}[M(NSiMe_3)Cl_3(NH_2SiMe_3)]_2 + 2ClSiMe_3 \quad (3)$$
$$\mathbf{1},\ M = Nb$$
$$\mathbf{2},\ M = Ta$$

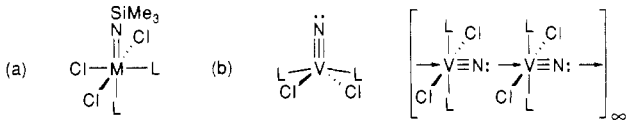

Figure 1. (a) Cis,mer geometry for M(NSiMe$_3$)Cl$_3$L$_2$. (b) Structures of [V(N)Cl$_2$L$_2$]$_n$.

reaction 3 by ^{1}H NMR spectroscopy indicates that 2 equiv of chlorotrimethylsilane is produced. White **1**, which is moderately soluble in benzene, or beige **2**, which is only sparingly soluble in benzene, deposits from the reaction mixture and is collected by filtration.

The ^{1}H NMR spectra of **1** and **2** (and the ^{13}C NMR spectra of more soluble **1**) show two singlets of equal intensity for two different trimethylsilyl groups. Broad singlets at δ 3.17 for **1** and at δ 4.32 for **2** for two equivalent nitrogen-bound protons are also observed by ^{1}H NMR spectroscopy. These data support formulation of **1** and **2** as (trimethylsilyl)imido/aminotrimethylsilane complexes rather than the alternative bis[(trimethylsilyl)amido] formulation, [M(NHSiMe$_3$)$_2$Cl$_3$]. This is further supported by the IR spectra of these compounds, which each show two sharp bands above 3100 cm^{-1} assignable to the symmetric and asymmetric combinations of the N–H stretches of a coordinated monosilylated amine.[13,14] Due to their limited solubility and by analogy to the closely related *tert*-butylimido/*tert*-butylamine derivatives,[15] we suggest that **1** and **2** are chloro-bridged dimers.

Addition of 2 equiv of pyridine or 4-methylpyridine or 1 equiv of 4,4′-dimethyl-2,2′-bipyridine to **1** in benzene at room temperature results in formation of yellow adducts Nb(NSiMe$_3$)Cl$_3$L$_2$ (**3a–c**) in good yield (eq 4). The monosilylated amine, NH$_2$SiMe$_3$,

$$\tfrac{1}{2}[Nb(NSiMe_3)Cl_3(NH_2SiMe_3)]_2 + 2L \rightarrow \underset{\mathbf{1}}{} Nb(NSiMe_3)Cl_3L_2 + \tfrac{1}{2}NH(SiMe_3)_2 + \tfrac{1}{2}NH_3 \quad (4)$$
$$\mathbf{3a},\ L = py$$
$$\mathbf{3b},\ L = 4\text{-}Mepy$$
$$\mathbf{3c},\ L_2 = 4,4'\text{-}Me_2bpy$$

which would be released from **1** on simple substitution, is reported to undergo rapid transamination, yielding the disilylated amine and ammonia,[16] and does so in reaction 4 as indicated by our observation of $^1/_2$ equiv of hexamethyldisilazane (^{1}H NMR).

The ^{1}H and ^{13}C NMR spectra of **3a–c** reveal that these molecules possess two inequivalent pyridine coordination sites, suggesting the cis,mer structure shown in Figure 1a. A preliminary X-ray crystallographic study of **3a** further supports this geometry.[17] The ^{1}H NMR spectrum of **3a** in C_6D_6 exhibits doublets at δ 9.12 and 8.84, multiplets at δ 6.51 and 6.27, and triplets at δ 6.81 and 6.64 for the ortho, meta, and para protons of two pyridine ligands, one of which (the ligand giving rise to the resonances at δ 9.12, 6.81, and 6.51) undergoes rapid exchange with added excess pyridine. Similarly, one of two sets of methyl and pyridine proton resonances observed in the ^{1}H NMR spectrum of **3b** undergoes broadening and shifting on addition of excess 4-methylpyridine. This suggests labilization of the pyridine trans to the silylimido group, consistent with the strong trans influence previously observed for organoimido ligands in octahedral electronically unsaturated complexes.[18] The dimethylbipyridine ligand in **3c** likewise coordinates to two inequivalent sites at the niobium center, resulting in two methyl singlets and four doublets for the aromatic 5,5′,6,6′-protons in the ^{1}H NMR spectrum. As expected,

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due to the chelating nature of dimethylbipyridine ligand, exchange between **3c** and free ligand is not observed on the NMR time scale.

An analogous tantalum complex, $Ta(NSiMe_3)Cl_3(py)_2$ (**4**), is prepared by the reaction of tantalum pentachloride with both hexamethyldisilazane and pyridine. The amount of **4** produced is optimized when the reaction is performed with roughly 1 equiv of $NH(SiMe_3)_2$ and 3 equiv of py, suggesting the stoichiometry shown in eq 5. ^1H and ^{13}C NMR spectra of **4** support a cis,mer

$$MCl_5 + NH(SiMe_3)_2 + 3py \rightarrow M(NSiMe_3)Cl_3(py)_2 + py\cdot HCl + ClSiMe_3 \quad (5)$$

3a, M = Nb
4, M = Ta

geometry for this compound with fast exchange occurring between excess free pyridine and the trans coordinated pyridine, analogous to the niobium system. Surprisingly, however, addition of pyridine to a benzene solution of **2** does not yield **4**; instead, nonstoichiometric amounts of $ClSiMe_3$ and $NH(SiMe_3)_2$ are observed (^1H NMR).

Compound **3a** can be prepared by reaction 5, although only in low yield. The difficulty in synthesizing the niobium complex by this direct reaction is presumably due to competing reduction of $NbCl_5$ by pyridine, which is reported to yield $NbCl_4(py)_2$; in contrast, addition of pyridine to $TaCl_5$ produces a tantalum(V) adduct, $TaCl_5(py)$.[19] Attempts to prepare the phosphine analogues of **3** and **4** by addition of PMe_3 to **1** or **2**, by direct reaction of MCl_5, $NH(SiMe_3)_2$, and PMe_3, or by addition of PMe_3 to **3a** or **4** did not yield tractable products, although very closely related *tert*-butylimido phosphine adducts, $M(NCMe_3)Cl_3(PMe_3)_2$, have been prepared by comparable methods.[15] Thus, group V transition-metal silylimido complexes appear to be very sensitive to the identity of ancillary ligands.

Samples of **4** contain a persistent insoluble byproduct, increasing amounts of which are formed on attempts to recrystallize this compound from benzene, toluene, or dichloromethane. The observation of accompanying formation of chlorotrimethylsilane (^1H NMR) indicates that **4** is undergoing decomposition via elimination of $ClSiMe_3$. Similarly, samples of **3a** decompose on heating in benzene or at room temperature in dichloromethane with loss of $ClSiMe_3$ and formation of an insoluble material. However, for decomposition of both **3a** and **4**, chlorotrimethylsilane is not produced in stoichiometric quantities: typically 60–90% of the possible $ClSiMe_3$ is observed even after exhaustive thermolysis, producing intractable off-white solids as the metal-containing products. Compounds **1** and **2** decompose similarly with nonstoichiometric loss of chlorotrimethylsilane and formation of orange solids of variable composition.

Vanadium. Substituted pyridine adducts of the vanadium(V) (trimethylsilyl)imido chloro compound, $V(NSiMe_3)Cl_3L_2$ (**6**), are prepared by the reaction of 2 equiv of 4-ethylpyridine or 4-*tert*-butylpyridine with $V(NSiMe_3)Cl_3$[6a,10] (**5**) in pentane at room temperature (eq 6). Mustard yellow **6a,b** immediately precipitate from these solutions and are collected by filtration.

$$\underset{\mathbf{5}}{V(NSiMe_3)Cl_3} + 2L \rightarrow \underset{\substack{\mathbf{6a},\ L = 4\text{-Etpy} \\ \mathbf{6b},\ L = 4\text{-}t\text{-Bupy}}}{V(NSiMe_3)Cl_3L_2} \quad (6)$$

In contrast to the niobium and tantalum silylimido compounds, **6a,b** are extremely reactive to loss of chlorotrimethylsilane. For example, solid samples of **6** in frozen C_6D_6 in sealed NMR tubes react immediately on melting to produce deep red solutions with ^1H NMR signals characteristic of the nitrido derivatives **7**[6] and chlorotrimethylsilane (eq 7). In the case of the *tert*-butylpyridine

$$\underset{\mathbf{6}}{V(NSiMe_3)Cl_3L_2} \rightarrow \underset{\mathbf{7}}{V(N)Cl_2L_2} + ClSiMe_3 \quad (7)$$

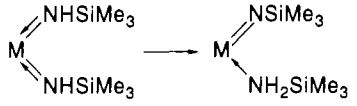
adduct, **6b**, addition of a known quantity of a standard indicates that loss of $ClSiMe_3$ and formation of the five-coordinate nitrido compound are quantitative (^1H NMR). Compounds **7a,b** were previously prepared by the rapid reaction of $V(NSiMe_3)Cl_3$ and 2 equiv of 4-ethylpyridine or 4-*tert*-butylpyridine in benzene[6] without observation of an intermediate adduct.

The stoichiometry observed in reactions 6 and 7 supports assignment of **6a,b** as bis(ligand) adducts, although as a consequence of their reactivity neither direct NMR observation nor elemental analysis of these compounds is possible. IR spectra provide additional support of their formulation. In particular, a series of bands characteristic of the trimethylsilyl group at roughly 1260, 850, and 750 cm^{-1} is observed.[13,20,21] The IR spectra also contain strong bands in the 900–1200-cm^{-1} region due to M=N and/or N—Si vibrations,[13,21,22] a series of bands for the coordinated pyridine ligands,[23] and strong bands in the 200–400-cm^{-1} region arising from metal–chloride stretches and/or metal–pyridine nitrogen stretches.[23,24] Additionally, weak IR bands consistent with contamination by the nitrido compounds $V(N)Cl_2L_2$ (**7**) are seen in all samples of **6a** and in some samples of **6b**.[25]

Discussion

Niobium and tantalum (trimethylsilyl)imido complexes have been prepared by using hexamethyldisilazane as the source of the $NSiMe_3$ ligand. These reactions produce the silylimido group from $NH(SiMe_3)_2$ by cleavage of one of its nitrogen–silicon bonds, yielding $ClSiMe_3$, and transfer of its proton to base. In the presence of pyridine, formation of py·HCl occurs (eq 5). In the absence of added base, net proton transfer to a second desilylated equivalent of amine results in formation of coordinated NH_2SiMe_3 (eq 3). Silylated derivatives of primary amines have frequently been used as the source of *organo*imido ligands upon reaction with metal halide or oxo complexes.[18] For example, the addition of *tert*-butyl(trimethylsilyl)amine to niobium or tantalum pentachloride produces dimeric *tert*-butylimido/*tert*-butylamine complexes, $[M(NCMe_3)(NH_2CMe_3)Cl_3]_2$,[15] direct analogues of **1** and **2**.

The monosilylated amine, NH_2SiMe_3, is unstable with respect to $NH(SiMe_3)_2$ and NH_3, which are observed on its dissociation from the metal centers in **1** and **2**. Therefore, it seems unlikely that free NH_2SiMe_3 is involved in the formation of these (trimethylsilyl)imido/aminotrimethylsilane products. This suggests the intermediacy of a bis[(trimethylsilyl)amido] species, such as $[M(NHSiMe_3)_2Cl_3]$, which subsequently undergoes interligand proton transfer (eq 8). An analogous bis(amido) $\rightleftarrows$ imido/amine



(8)

interconversion has been observed in the tungsten(VI) system $W(NH\text{-}t\text{-}Bu)_2(N\text{-}t\text{-}Bu)(O_2C_2X_4) \rightleftarrows W(NH_2\text{-}t\text{-}Bu)(N\text{-}t\text{-}Bu)_2(O_2C_2X_4)$, in which an equilibrium is established with its position depending on the glycolate ligand substituents, X.[26] There is precedent for bis(amido) compounds in this group V metal system: Bradley and co-workers have reported formation of a bis[bis(trimethylsilyl)amido]tantalum complex, $Ta[N(SiMe_3)_2]_2Cl_3$, on addition of $LiN(SiMe_3)_2$ to $TaCl_5$.[27] It is interesting to note that, in general, the reactions of metal chlorides with salts of hexa-

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(21) See the detailed assignment of IR data for $V(NSiMe_3)(OSiMe_3)_3$ in ref 9b.

(22) The controversial nature of the assignment of ν_{MN} for metal imido compounds has been discussed: Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; Wiley: New York, 1988; pp 123–125.

(23) Reference 14, pp 206–208.

(24) Reference 14, pp 324–331.

(25) Compounds **6a,b** are sufficiently reactive that care must be taken when Nujol mulls are prepared for IR spectra, since grinding can cause conversion to **7a,b**.

(26) Chan, D. M.-T.; Fultz, W. C.; Nugent, W. A.; Roe, D. C.; Tulip, T. H. *J. Am. Chem. Soc.* **1985**, *107*, 251–253.

(27) Bradley, D. C.; Hursthouse, M. B.; Abdul Malik, K. M.; Chota Vuru, G. B. *Inorg. Chim. Acta* **1980**, *44*, L5–L6. Note that $Ta[N(SiMe_3)_2]_2Cl_3$ does undergo subsequent reactions on addition of ligands, resulting in loss of $ClSiMe_3$ and formation of tantalum(V) silylimido derivatives.[8]

methyldisilazane, $M'N(SiMe_3)_2$ (M' = Li, Na, K), yield bis(trimethylsilyl)amido complexes,[28] in contrast to the synthesis of silylimido complexes from the amine.

Vanadium (trimethylsilyl)imido complexes **6a,b** are formed by addition of 2 equiv of ligand to $V(NSiMe_3)Cl_3$ (**5**) and can only be prepared in solvents from which they immediately precipitate. In solution, **6a,b** rapidly lose $ClSiMe_3$, yielding the previously reported nitrido complexes $V(N)Cl_2L_2$.[6] In contrast, we find that the analogous bipyridine complex, $V(NSiMe_3)Cl_3(bpy)$, reported by Dehnicke and co-workers,[10] requires hours at ambient temperature in benzene for elimination of $ClSiMe_3$ to occur, producing the nitrido derivative, $V(N)Cl_2(bpy)$.[29] Since loss of ligand is much less favorable for chelating bipyridines, as is observed for **3c**, this suggests that generation of a vacant coordination site at the metal center may be necessary for elimination of $ClSiMe_3$ and formation of the nitrido complex.[30] Alternatively, the lower reactivity of the bpy complex may reflect its poor solubility in benzene. Due to their high reactivity, **6a,b** are characterizable only by the products of their decomposition and by IR spectroscopy. Note that, as for the niobium and tantalum compounds described above, the (trimethylsilyl)imido ligands in **6a,b** originate from hexamethyldisilazane via $NH_4VO_3 + NH(SiMe_3)_2 \rightarrow V(NSiMe_3)(OSiMe_3)_3$[5,9a] $\rightarrow V(NSiMe_3)Cl_3$[6] $\rightarrow V(NSiMe_3)Cl_3L_2$.

The fast, clean elimination of $ClSiMe_3$ from the vanadium silylimido chloro compounds **5** and **6** contrasts with the slow, incomplete reactions of the niobium and tantalum derivatives **1-4**. The reasons that compounds **1-4** do not undergo stoichiometric loss of chlorotrimethylsilane are not clear but may possibly reflect an instability of M≡N: for niobium and tantalum. To date, all reported nitrido derivatives of these two metals have bridging structures with M—N distances in the range expected for double bonds;[31] there are no examples of niobium or tantalum terminal nitrido complexes. Likewise, triply bonded terminal oxo and imido complexes of niobium and tantalum are limited in number.[32] In contrast, vanadium forms short strong triple bonds to oxo and imido ligands in a wide range of compounds[32] and vanadium nitrido derivatives possess extremely short V-N triple bonds in both terminal and bridged linear-chain structures, $[V(N)Cl_2L_2]_n$[6a] (Figure 1b). If stoichiometric loss of $ClSiMe_3$ from the niobium and tantalum silylimido chloro compounds requires, at some point, a triply bonded terminal or highly asymmetric bridging nitride, this could prevent complete condensation. Instead of formation of $M(N)Cl_2L_2$, incomplete loss of $ClSiMe_3$ yielding small oligomeric or cluster nitride derivatives without niobium- or tantalum-nitrogen triple bonds, could be preferred.

Our work to date suggests that cleavage of the N-Si bonds of silylimido ligands is a general reaction, though not always stoichiometric. It is interesting to contrast this to the lack of reactivity of the N-C bond of organoimido ligands. The only reported example of cleavage of this bond is the formation of an osmium(VI) nitrido anion, $[Os(N)Cl_5]^-$, upon reaction of $Os(N\text{-}t\text{-}Bu)(O)_3$ and HCl.[33] Thus, despite the close similarity between *tert*-butylimido and (trimethylsilyl)imido ligands, complexes containing these ligands have significantly different chemistries. The features that have made silyl substituents so useful in organic chemistry clearly can be harnessed for both the synthesis and subsequent reactions of inorganic compounds. We are continuing to explore this rich area of chemistry.

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(30) Preliminary mechanistic evidence indicates that this is also the case for reactions 1 and 2: Jones, C. J.; Lerchen, M. E.; Doherty, N. M. Unpublished results.
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(32) Reference 22, Chapters 2 and 5.
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Models of Vitamin B_6 Enzymes. 3. Steric and Electronic Effects in Carbon-Hydrogen Bond Breaking Reactions of Bis(salicylideneglycinato)cobaltate(III) Anions

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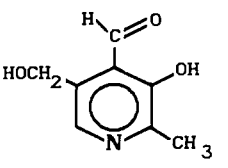
Salicylaldehydes readily form Schiff bases with glycine. These schiff bases form bis(salicylideneglycinato)cobaltate(III) complexes. Twelve cobalt(III) complexes have been synthesized with substituents variously on the 3-, 4-, 5-, and 6-positions of the aromatic ring of the salicylaldehyde moiety. The carbon-hydrogen bond breaking reactions of the two *gem*-methylenic protons of the glycine moiety have been studied by deuterium exchange. Rates are first order in complex and first order in hydroxide ion. Rates differ for the exchange of the two protons, and their ratio varies from 0.81 to 4.7. This demonstrates a reversal of stereoselectivity, depending on ring substituents. Rates vs substituents generally follow Hammett behavior. The structural and electronic features that lead to stereoselectivity are discussed.

Introduction

Stereo- and enantioselective reactions are of considerable current interest, as is the catalysis of reactions in which carbon-hydrogen bonds are broken. Vitamin B_6 model reactions offer approaches to the study of both these topics. Vitamin B_6 is, in one form, the heterocyclic aldehyde pyridoxal (I). It is an esssential cofactor



I

to many enzymes that catalyze a wide variety of reactions modifying the structure of amino acids.[1] The reactions proceed first

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