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Synthesis of Molybdenum and Tungsten Silylimido Complexes. Structure of a Five-Coordinate Bis(silylimido) Complex

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Molybdenum(IV) and tungsten(IV) mono(silylimido) compounds, $M(NSiMe_3)Cl_2L_3$ (M = Mo, L = PMe_3 (**1**); M = W, L = PMe_3 (**2**), $PMePh_2$ (**3**)), have been prepared by the reaction of MCl_2L_4 with 1 equiv of trimethylsilyl azide. When M = W and L = $PMePh_2$, the addition of a second equivalent of trimethylsilyl azide produces a tungsten(VI) bis(silylimido) compound, $W(NSiMe_3)_2Cl_2(PMePh_2)$ (**4**). X-ray structural determination indicates that **4** possesses a five-coordinate trigonal-bipyramidal structure with cis equatorial imido ligands and short W-N bonds (1.70 (3) Å). The factors that influence the production of silylimido vs azido or nitrido compounds in this system are considered, and the synthesis of silylimido complexes is discussed in light of the reactivity of N-Si bonds.

Introduction

Interest in the study of transition-metal compounds containing terminal imido, nitrido, and oxo groups has stemmed from the wealth of reactivity associated with the metal-ligand multiple bonds found in these molecules.[1] Recently, we have been examining the chemistry of complexes with silyl-substituted imido ligands, $L_nM(NSiR_3)$, in order to probe the use of the nitrogen-silicon bond as an additional reactive site. We are particularly interested in silylimido complexes as precursors for nitride-bridged transition-metal compounds[2-4] and therefore have been exploring the influence of varied metal-ligand environments on both the synthesis of silylimido complexes and their conversion to nitrido derivatives.[2-5]

Silylimido compounds are rather rare,[6-9] in part because the reactive nature of the N-Si bond can preclude their synthesis by the methods usually used to prepare organoimido derivatives. We have developed routes to a variety of group V transition-metal mono(silylimido) complexes using hexamethyldisilazane as the source of the $NSiMe_3$ ligand.[4,5] In this paper, we describe the synthesis of molybdenum(IV) and tungsten(IV) mono(silylimido) and tungsten(VI) bis(silylimido) compounds by the reactions of trimethylsilyl azide with oxidizable molybdenum and tungsten derivatives.

Experimental Section

General Considerations. All manipulations were performed under a nitrogen atmosphere by using glovebox, Schlenk, or vacuum-line techniques. Hydrocarbon solvents were dried over activated 4-Å molecular sieves, stored over CaH_2, and vacuum-transferred prior to use; ethereal solvents were dried and stored over sodium benzophenone ketyl and vacuum-transferred prior to use. Trimethylsilyl azide (Petrach) was used as received. $MoCl_2(PMe_3)_4$,[10] $WCl_2(PMe_3)_4$,[11a,b] and $WCl_2(PMePh_2)_4$[11b] were prepared as previously reported. NMR spectra were recorded on Varian VXL300 (299.95 MHz, ^1H; 121.42 MHz, ^{31}P; 75.43 MHz, ^{13}C) and Bruker WM500 (500.14 MHz, ^1H) spectrometers at ambient temperatures in benzene-d_6; chemical shifts are reported relative to residual solvent signal in ppm downfield from $SiMe_4$ (^1H and ^{13}C NMR) and external PPh_3 in C_6D_6 (δ -5.8 relative to 85% H_3PO_4; ^{31}P NMR); coupling constants are reported in hertz. IR spectra were obtained as Nujol mulls with Perkin-Elmer 283 and 225 spectrometers. Elemental analyses were performed by Canadian Microanalytical Services, Ltd.

Table I. Crystallographic Data for $W(NSiMe_3)_2Cl_2(PMePh_2)$ (**4**)

formula	$C_{19}H_{31}Cl_2N_2PSi_2W$	T, °C	24
fw	629.37	λ(Mo Kα), Å	0.71073
space group	$Pna2_1$	ρ_{calcd}, g cm^{-3}	1.580
a, Å	18.678 (3)	μ, cm^{-1}	48.20
b, Å	9.461 (2)	transm coeff	0.996-0.533
c, Å	14.973 (3)	decay in intensity, %	3.0
V, Å^3	2646.0 (14)	$R(F_o)$	0.055
Z	4	$R_w(F_o)$	0.059

Synthesis. $Mo(NSiMe_3)Cl_2(PMe_3)_3$ (1). Trimethylsilyl azide (0.70 mL, 5.3 mmol) was added to a solution of $MoCl_2(PMe_3)_4$ (1.05 g, 2.2 mmol) in benzene (45 mL) at -78 °C. The mixture was allowed to warm to room temperature and was stirred for 2 days, producing a blue-green solution. The solvent and volatiles were removed under reduced pressure, and the product was crystallized from a mixture of diethyl ether and pentane. The resulting crystalline solid was collected by filtration, washed with cold pentane, and dried under vacuum, yielding 0.85 g of blue **1** (80%): ^1H NMR 1.44 (t, J_{PH} = 4), 1.28 (d, J_{PH} = 8), -0.05 (s); $^{13}C\{^1H\}$ NMR 23.6 (d, J_{PC} = 24), 18.1 (t, J_{PC} = 11), 1.2 (s); $^{31}P\{^1H\}$ NMR 10.2 (t, J_{PP} = 19), -0.8 (d, J_{PP} = 19); IR (cm^{-1}) 1421, 1296, 1274, 1243, 1107 s ($\nu_{Mo\equiv N}$), 944, 843, 760, 737, 723, 668, 633, 338, 263. Anal. Calcd for $C_{12}H_{36}Cl_2MoNP_3Si$: C, 29.88; H, 7.52; N, 2.90. Found: C, 29.81; H, 7.47; N, 3.59.

$W(NSiMe_3)Cl_2(PMe_3)_3$ (2). The above procedure was followed with 0.18 mL of trimethylsilyl azide (1.4 mmol) and 0.72 g of $WCl_2(PMe_3)_4$ (1.3 mmol) in toluene (30 mL) for 2 days, producing a brown residue on removal of solvent and volatiles. The product was crystallized from a mixture of toluene and pentane, collected by filtration, washed with cold diethyl ether until the washings no longer showed a black color, and dried under vacuum, yielding 0.16 g of violet **2** (38%): ^1H NMR 1.50 (t, J_{PH} = 4), 1.45 (d, J_{PH} = 8), -0.05 (s); $^{13}C\{^1H\}$ NMR 27.9 (d, J_{PC} = 32), 19.2 (t, J_{PC} = 13), 1.9 (s); $^{31}P\{^1H\}$ NMR -23.9 (d, J_{PP} = 2, J_{WP} = 218), -26.3 (t, J_{PP} = 2, J_{WP} = 413); IR (cm^{-1}) 1294, 1279, 1272, 1240, 1135 s ($\nu_{W\equiv N}$), 941, 842, 758, 735, 720, 710, 665, 630, 385, 335, 265, 260.

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Table II. Positional and Isotropic[a] Thermal Parameters for $W(NSiMe_3)_2Cl_2(PMePh_2)$ (**4**)

atom	*x*	*y*	*z*	*B*, Å^2
W	0.20254 (6)	0.07518 (10)	0.25000	3.75 (2)
Cl(1)	0.2192 (4)	0.3281 (6)	0.2595 (11)	5.5 (2)
Cl(2)	0.3283 (4)	0.0666 (9)	0.2800 (8)	7.7 (3)
P	0.0752 (4)	0.1678 (8)	0.2331 (5)	4.0 (2)
Si(1)	0.2005 (6)	−0.1580 (11)	0.0721 (7)	6.0 (2)
Si(2)	0.1404 (6)	−0.1445 (12)	0.4224 (8)	5.9 (3)
N(1)	0.195 (2)	−0.019 (3)	0.154 (2)	7.3 (8)
N(2)	0.173 (2)	−0.023 (3)	0.338 (2)	7.3 (8)
C(3)	0.048 (2)	0.274 (4)	0.332 (3)	7.2 (10)
C(11)	0.060 (2)	0.283 (3)	0.145 (2)	4.3 (7)
C(12)	0.102 (2)	0.272 (3)	0.067 (2)	5.4 (8)
C(13)	0.093 (2)	0.344 (4)	−0.013 (3)	6.8 (10)
C(14)	0.043 (2)	0.450 (4)	−0.010 (3)	6.8 (10)
C(15)	0.002 (2)	0.463 (4)	0.060 (3)	7.4 (10)
C(16)	0.006 (2)	0.384 (4)	0.139 (3)	8.7 (12)
C(21)	0.008 (1)	0.036 (2)	0.236 (2)	4.4 (7)
C(22)	0.023 (2)	−0.106 (3)	0.212 (2)	4.2 (7)
C(23)	−0.027 (2)	−0.212 (3)	0.217 (2)	5.8 (9)
C(24)	−0.100 (2)	−0.174 (3)	0.228 (2)	6.0 (9)
C(25)	−0.116 (2)	−0.037 (3)	0.232 (2)	4.8 (7)
C(26)	−0.063 (1)	0.067 (3)	0.241 (3)	5.9 (7)
C(101)	0.184 (2)	−0.332 (4)	0.125 (3)	7.1 (10)
C(102)	0.296 (2)	−0.156 (4)	0.027 (3)	7.8 (10)
C(103)	0.132 (2)	−0.110 (5)	−0.016 (3)	10.6 (15)
C(201)	0.131 (2)	−0.325 (4)	0.372 (3)	7.6 (11)
C(202)	0.210 (3)	−0.132 (5)	0.516 (4)	11.8 (15)
C(203)	0.056 (2)	−0.076 (4)	0.467 (3)	8.5 (11)

[a] Anisotropically refined atoms (W, Cl(1), Cl(2), and P) are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

Anal. Calcd for $C_{12}H_{36}Cl_2NP_3SiW$: C, 25.28; H, 6.36; N, 2.45. Found: C, 25.06; H, 6.15; N, 2.18.

$W(NSiMe_3)Cl_2(PMePh_2)_3$ (3). The above procedure was followed with 0.24 mL of trimethylsilyl azide (1.8 mmol) and 2.0 g of $WCl_2(PMePh_2)_4$ (1.9 mmol) in benzene (80 mL) for 1 day, producing a green residue on removal of solvent and volatiles. The product was crystallized from a toluene, diethyl ether, and pentane mixture, collected by filtration, washed with pentane, and dried under vacuum, yielding 1.3 g of green **3** (68%): ^{1}H NMR 7.87 (m), 7.59 (m), 7.50 (t, J = 8), 7.0 (m), 2.29 (t, J_{PH} = 4), 1.86 (d, J_{PH} = 8), −0.03 (s); $^{13}C\{^1H\}$ NMR 143.5 (d, J = 7), 138.9 (m), 134.2 (dt, J = 51, 4), 133.4 (d, J = 9), 132.5 (br), 24.6 (d, J_{PC} = 32), 17.7 (t, J_{PC} = 14), 1.5 (s); $^{31}P\{^1H\}$ NMR −2.9 (t, $J_{PP} < 2$, J_{WP} = 313), −3.1 (d, $J_{PP} < 2$, J_{WP} = 385); IR (cm^{-1}) 3045, 1585, 1569, 1311, 1287, 1250, 1185, 1153, 1105 s ($\nu_{W\equiv N}$), 1026, 997, 888, 846, 737, 691, 631, 501, 480, 450, 439, 405, 380, 342, 282, 270. Anal. Calcd for $C_{42}H_{48}Cl_2NP_3SiW$: C, 53.51; H, 5.13; N, 1.48. Found: C, 53.46; H, 5.26; N, 1.68.

$W(NSiMe_3)_2Cl_2(PMePh_2)$ (4). The above procedure was followed with 0.21 mL of trimethylsilyl azide (1.6 mmol) and 0.77 g of $WCl_2(PMePh_2)_4$ (0.77 mmol) in 45 mL of toluene for 1 day. Removal of solvent and volatiles under reduced pressure produced a dark brown oil that contained **4** (10% yield relative to $WCl_2(PMePh_2)_4$), free phosphine, and a reduced tungsten-containing species. Yellow crystals of **4** grew from the crude mixture over 1 week at room temperature: ^{1}H NMR 7.5 (m), 6.96 (m), 1.19 (d, J_{PH} = 10), 0.14 (s); $^{31}P\{^1H\}$ NMR 26.1 (s, J_{WP} = 355); IR (cm^{-1}) 1289, 1245, 1162, 1099, 1065, 998, 897, 838, 751, 739, 732, 693, 679, 630, 507, 466, 450, 425, 308, 282.

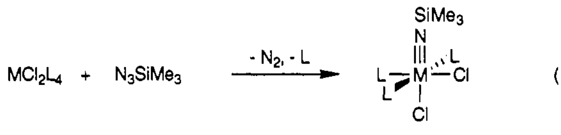
X-ray Structure Determination of $W(NSiMe_3)_2Cl_2(PMePh_2)$ (4). A thin yellow plate of dimensions 0.76 × 0.34 × 0.03 mm was mounted in a glass capillary under N_2. Data collection and refinement procedures have been described elsewhere.[2a] A summary of the crystallographic data is given in Table I. Precise unit cell parameters were calculated from a least-squares fit of the setting angles of 25 accurately centered reflections. A total of 2658 reflections with $2\theta \le 50°$ collected in the *hkl* octant yielded 1182 independent observed reflections ($I > 3\sigma_I$) after correction for Lorentz and polarization effects, decay, and absorption. Because the crystal quality is less than ideal and because the tungsten atom lies on what would be a mirror plane in the related centric space group, the choice of enantiomorph was clear only when a data set combining two nonaverageable octants (*hkl* and $hk\bar{l}$) was used to maximize the effect of the anomalous scattering. Final refinement was performed by using the *hkl* octant data, with the tungsten, chlorine, and phosphorus atoms anisotropic and with the hydrogen atoms fixed in calculated positions. Several atoms were poorly behaved during refinement and prevented complete convergence (final shift/error = 0.18). Positional and thermal parameters for non-hydrogen atoms are given in Table II; selected bond distances and angles are listed in Table III.

Table III. Selected Bond Distances (Å) and Angles (deg) for $W(NSiMe_3)_2Cl_2(PMePh_2)$ (**4**)

W–N(1)	1.70 (3)	W–Cl(1)	2.417 (6)
W–N(2)	1.70 (3)	W–Cl(2)	2.393 (8)
Si(1)–N(1)	1.80 (3)	W–P	2.548 (8)
Si(2)–N(2)	1.82 (3)		
W–N(1)–Si(1)	162.5 (20)	Cl(1)–W–P	77.7 (3)
W–N(2)–Si(2)	173.4 (2)	Cl(1)–W–N(1)	125.3 (11)
N(1)–W–N(2)	110.1 (14)	Cl(1)–W–N(2)	122.4 (11)
P–W–N(1)	91.1 (10)	Cl(2)–W–P	161.2 (3)
P–W–N(2)	87.8 (10)	Cl(2)–W–N(1)	102.8 (10)
Cl(1)–W–Cl(2)	84.0 (3)	Cl(2)–W–N(2)	98.9 (11)

Results

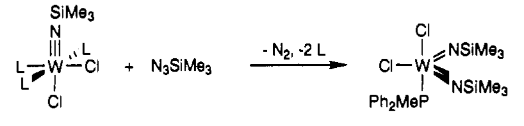
The reactions of MCl_2L_4 with 1 equiv of trimethylsilyl azide yield the six-coordinate molybdenum(IV) and tungsten(IV) mono(silylimido) complexes $M(NSiMe_3)Cl_2L_3$ (**1**–**3**) (eq 1). Blue **1**, violet **2**, and green **3** are isolated as air-sensitive crystalline solids. The cis,mer octahedral structure proposed for **1**–**3** (eq 1) is consistent with the spectral data for these compounds: the coupling and intensity patterns observed in the ^{1}H, ^{13}C, and ^{31}P NMR spectra indicate that the three phosphine ligands are meridional and two ν_{M-Cl} bands are observed in the IR spectra. This structure is analogous to that suggested for closely related (organoimido)molybdenum(IV)[12] and -tungsten(IV)[13a] derivatives, $M(NR)Cl_2L_3$. We have also observed (^{1}H and ^{31}P NMR) a related ethylene-substituted tungsten mono(silylimido) derivative, $W(NSiMe_3)Cl_2(C_2H_4)(PMePh_2)_2$, as the major product of the reaction of $WCl_2(C_2H_4)_2(PMePh_2)_2$[11a] with N_3SiMe_3.



(1)

M = Mo, L = PMe$_3$ **1**
M = W, L = PMe$_3$ **2**
M = W, L = PMePh$_2$ **3**

Addition of a second equivalent of N_3SiMe_3 to **3**, or reaction of $WCl_2(PMePh_2)_4$ with 2 equiv of N_3SiMe_3 (eq 2), produces a bis(silylimido) complex $W(NSiMe_3)_2Cl_2(PMePh_2)$ (**4**). In contrast, reactions of **1** or **2** with additional trimethylsilyl azide occur only at elevated temperatures and produce $ClSiMe_3$. ^{1}H NMR experiments indicate that **4** is generated in 30% yield; however isolated yields are significantly lower. Compound **4** is very soluble in the mixture produced on removal of the volatiles, which includes several equivalents of free $PMePh_2$. Additionally, **4** decomposes on attempted crystallization from a variety of organic solvents in the presence of this excess $PMePh_2$, producing a reduced tungsten-containing species currently under investigation.[14] Nonetheless, **4** is stable in the reaction residue and yellow air-sensitive crystals grow from this mixture over a week at room temperature. Note that no trimethylsilyl chloride is observed either



(2)

L = PMePh$_2$ **4**

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(14) Lichtenhan, J. D.; Doherty, N. M. Work in progress.

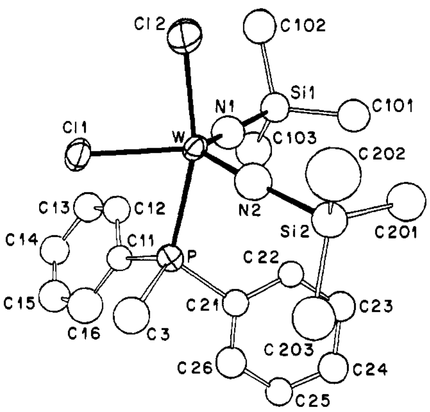


Figure 1. ORTEP drawing of $W(NSiMe_3)_2Cl_2(PMePh_2)$ (4) with 30% probability thermal ellipsoids for non-hydrogen atoms.

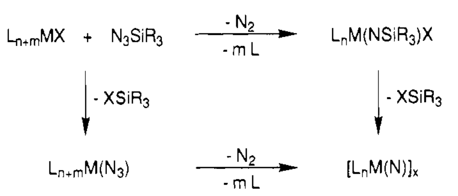
in reaction 2 or in the decomposition of **4** in the presence of excess $PMePh_2$.

The ^1H and ^{31}P NMR spectra of **4** are consistent with equivalent (trimethylsilyl)imido ligands and coordination of a single methyldiphenylphosphine to the tungsten(VI) center. An X-ray structural study further indicates that **4** possesses a roughly trigonal-bipyramidal structure in the solid state with the two (trimethylsilyl)imido ligands and one chloride in the equatorial plane (Figure 1). The axial chloride and phosphine ligands are bent away from the multiple-bonding imido ligands with a ClWP angle of 161°. The short W–N distances of 1.70 (3) Å and the WNSi angles of 163 and 173° are in the range normally reported for tungsten imido complexes[15] and are comparable to those of other structurally characterized bis(imido) derivatives.[16-18] The N–Si distances of 1.80 (3) and 1.82 (3) Å are long compared to the 1.65–1.75-Å range observed for silicon amides and amines, which are considered to possess nitrogen–silicon multiple-bond character, and approach the estimated N–Si single bond distance of 1.82–1.87 Å.[19] For comparison, the N–Si distances in structurally characterized silylimido compounds[7,8] range from 1.733 Å for $[Ta(NSiMe_3)(N(SiMe_3)_2)Br_2]_2$[8a] to 1.793 Å[7a] in the highly reactive[2] $V(NSiMe_3)Cl_3$.

Addition of 1 equiv of 2,2′-bipyridine or 4,4′-dimethyl-2,2′-bipyridine to samples of **4** in C_6D_6 produces $W(NSiMe_3)_2Cl_2(bpy)$ or $W(NSiMe_3)_2Cl_2(Me_2bpy)$, identified by ^1H and ^{31}P NMR. The d^0 electron counts and the NMR equivalence of both the (trimethylsilyl)imido ligands and the halves of the bipyridines suggest six-coordinate structures for these compounds with trans chloride and cis (trimethylsilyl)imido ligands as found for $W(NR)_2Cl_2(bpy)$.[16]

Preliminary experiments indicate that compounds **1**–**4** possess reactive N–Si bonds.[14] For example, **1** and **2** undergo room-temperature reactions with a variety of metal fluoride derivatives, producing fluorotrimethylsilane and metal-containing products currently under study. However, reactions of the N–Si bonds in these compounds do not yet extend to clean elimination of trimethylsilyl chloride and formation of nitrido products.

Scheme I



Discussion

Molybdenum and tungsten silylimido complexes have been prepared with trimethylsilyl azide as the source of $NSiMe_3$. These reactions proceed by the formal oxidative addition of this fragment to molybdenum(II), tungsten(II), or tungsten(IV) precursors. While addition of organoazides to metal centers is a common route to organoimido compounds,[20] the synthesis of silylimido complexes using N_3SiR_3 is rare.[6,7] This is because the N–Si bonds in these reagents can readily undergo reaction with metal–halogen bonds to produce the silyl halide and coordinated nitrido and/or azido ligands[21,22] (Scheme I). Note that both pathways in the scheme can potentially yield the metal nitride as the ultimate product. An initially formed azido species can undergo loss of N_2 to form the nitride.[23] Alternatively, loss of $XSiMe_3$ from an intermediate silylimido halide complex could also produce a nitride. Our report of the formation of polymeric and monomeric vanadium nitrido compounds from $V(NSiMe_3)Cl_3$ is the first well-characterized example of this reaction.[2]

Understanding the factors that control the competition between reaction of a metal center with the nitrogen–nitrogen vs the nitrogen–silicon bond of a silyl azide (Scheme I) is important for the synthesis and study of silylimido compounds. The molybdenum and tungsten complexes MCl_2L_4 undergo facile oxidative addition of N_3SiMe_3, yielding silylimido products. However, we have observed that the related complexes $MoCl_4(PMe_3)_3$,[10a] $WCl_4(PMe_3)_3$,[11a,c] and $WCl_4(PMePh_2)_2$[11b] produce $ClSiMe_3$ on reaction with trimethylsilyl azide. This could be because the molybdenum(IV) and tungsten(IV) complexes possess more reactive, or less stable, metal–chlorine bonds than those of the molybdenum(II) and tungsten(II) compounds. However, if this effect dominated, we might expect to observe a common reaction on addition of trimethylsilyl azide to the (silylimido)molybdenum(IV) and -tungsten(IV) derivatives **1**–**3**. Instead, reactions of **1**–**3** with N_3SiMe_3 occur at either the nitrogen–nitrogen or the nitrogen–silicon bond depending on the identity of the phosphine ligand. We can best explain the differences in the chemistry observed for this family of compounds by the requirement of labile phosphine ligand(s) in order for reaction with N_3SiMe_3 to produce a silylimido complex, suggesting that a vacant coordination site is

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necessary for this oxidative addition to occur.

The tetrakis(phosphine) complexes MCl_2L_4 are crowded molecules, as demonstrated by the X-ray structures of $MoCl_2(PMe_3)_4$[10b] and $WCl_2(PMePh_2)_4$,[13a] and, for WCl_2L_4, undergo ligand substitution[11a] and oxidative addition[9c,13a] reactions via initial loss of L. These derivatives react with N_3SiMe_3 to form silylimido compounds. In contrast, the MCl_4L_n derivatives have significantly less labile phosphine ligands and react with N_3SiMe_3, producing $ClSiMe_3$. Similarly, the lability of the phosphine ligands in **1**–**3** appears to be crucial in determining the course of further reaction with trimethylsilyl azide: **3**, with bulky, labile $PMePh_2$ ligands, reacts with a second equivalent of N_3SiMe_3 to produce **4**, whereas **1** and **2**, with smaller and therefore less labile PMe_3 ligands, yield trimethylsilyl chloride on further reaction with N_3SiMe_3. These observations parallel the substitution reactivity of the related oxo compounds $W(O)Cl_2L_3$ (L = PMe_3 or $PMePh_2$).[13]

Compound **4** is a rare example of a molecule with two terminal imido ligands in a five-coordinate structure. While a number of bis(imido) derivatives with coordination numbers of 4 and 6 are known,[16,17,22,24] significantly fewer $M(NR)_2L_3$ complexes have been reported.[18,25] The details of the structure of **4** are consistent with the trends observed for related compounds except for the long nitrogen–silicon bonds, which suggest that N–Si multiple bonding is less important in this compound than in silylamines and amides. While the size of the uncertainties in the bond distances calculated for **4** dictates caution in arguments based on these metrical data, the reactive nature of the N–Si bonds in **4** is consistent with weakened N–Si multiple bonding. Also consistent are the short W–N bond distances, since strong silylimido–tungsten π-donor interactions could weaken nitrogen–silicon π-bonding. The formal C_s symmetry in **4** permits formation of four π-bonds between the filled nitrogen p orbitals and the empty tungsten d orbitals and results in formal electronic saturation at the tungsten(VI) center in the five-coordinate structure. Nonetheless, there does not appear to be any barrier to addition of ligands to form six-coordinate tungsten(VI) bis(silylimido) derivatives, as demonstrated by the reaction of **4** with bpy and Me_2bpy. Therefore, the unusual trigonal-bipyramidal geometry observed for **4** is likely a further reflection of the controlling influence of the phosphine ligand on structure and reactivity in this system.

Conclusions

Trimethylsilyl azide can be used as a source of the (trimethylsilyl)imido ligand upon reaction with oxidizable metal chloride complexes. Coordinative unsaturation, which can be produced by loss of labile ligand(s), appears to be a prerequisite for this reaction, rather than the more usual formation of azido or nitrido derivatives, to occur.

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Supplementary Material Available: Tables of crystallographic data, anisotropic thermal parameters, hydrogen atom coordinates, bond distances and angles, torsional angles, and least-squares planes for **4** (7 pages); tables of observed and calculated structure factors for **4** (6 pages). Ordering information is given on any current masthead page.

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Synthesis, Structure, and Characterization of ((2-Aminophenyl)imido)dichlorobis(diethyldithiocarbamato)molybdenum(VI)

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The reaction of $MoOCl_2(S_2CN(C_2H_5)_2)_2$ with 1,2-phenylenediamine in the presence of 2 equiv of base produces the imido complex $Mo(NC_6H_4NH_2)Cl_2(S_2CN(C_2H_5)_2)_2$. The structure of $Mo(NC_6H_4NH_2)Cl_2(S_2CN(C_2H_5)_2)_2 \cdot CH_2Cl_2$ (I) has been determined by X-ray crystallography. The crystals are orthorhombic, of space group $Pc2_1n$, with a = 11.847 (5) Å, b = 13.836 (4) Å, and c = 17.522 (4) Å. The structure was refined to R = 7.13%, R_w = 6.47% by using 2658 independent reflections. The geometry of the complex is pentagonal bipyramidal. The Mo–N(3)–C(11) angle is 178° and the molybdenum–nitrogen distance 1.70 Å, indicating triple-bond character of the molybdenum–nitrogen bond. Compared to that in the previously reported structure of the corresponding *N*-phenyl complex, $Mo(NC_6H_5)Cl_2(S_2CN(C_2H_5)_2)_2 \cdot CHCl_3$ (II), the molybdenum–nitrogen distance is slightly shorter in I and the molybdenum–imido linkage is closer to 180°. The molybdenum–chloride bond distances, which are equal in II, differ in I: the axial molybdenum–chloride bond trans to the nitrene ligand is 0.06 Å longer than the equatorial molybdenum–chloride bond, showing a trans effect of the $-NC_6H_4NH_2$ group. The molybdenum center in I has a ^{95}Mo NMR signal at −164 ppm and is deshielded by 90 ppm compared to that of II. The imido nitrogen of I has a ^{14}N NMR signal at −19 ppm. Both I and II show irreversible two-electron reduction peaks in their cyclic voltammograms. Complex I has an absorption band at 465 nm that is absent in the UV–vis spectrum of II.

Introduction

Molybdenum(VI) compounds are of special interest due to the involvement of molybdenum(VI) in molybdenum hydroxylases, a group of enzymes that catalyze two-electron reduction or oxidation processes.[1] Molybdenum(VI) dioxo[2,3] and molybdenum(VI) monooxo complexes[2,4–6] have been studied extensively.

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