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Characterization of New Tungsten(VI) Amide Complexes

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Introduction

Several examples of W(VI) imide derivatives have been synthesized and studied for their role in the metathesis and polymerization of olefins and for their reactivity in competitive π bonding situations.[1–11] In contrast the syntheses of W(VI) amide complexes and their reactivities are less well developed.[12–17] Examples of tungsten imido and oxo complexes with amide coligands have been reported recently.[5,12] In earlier work, Bradley and Chisholm and co-workers have reported the syntheses and characterization of the homoleptic amide complex $W(NMe_2)_6$ and of some related derivatives.[13–15] In contrast to the reduced dinuclear amides $W_2(NR_2)_6$, for which an extensive reactivity at both the W≡W bond and at the terminal ligand sites has been developed,[18] viable ligand substitution reactions of the mononuclear W(VI) amide complexes were found to be quite limited.[14] We report here the syntheses and characterization of new tungsten(VI) amide–chloride complexes, and an examination of stability and reactivity relevant to the derivatization of the high-valent tungsten amide series.

Results and Discussion

Syntheses of Tris(amide) Complexes, $WCl_3(NR_2)_3$. The reaction of $WSCl_4$ with 3 or 4 equiv of *N,N*-dialkyl(trimethylsilyl)amine in THF at 0 °C led to the formation of a red solution, which, upon cooling, deposited a red or orange precipitate. This product was filtered and identified as $WCl_3(NR_2)_3$ (**1** when R = Me, **2** when R = Et, and **3** when NR_2 = pyrrolidine). Because of the low solubility of the products in the reaction solution, they could be isolated quite efficiently, but the percent yields of **1–3** that were formed in these reactions were quite low, 15–30%. The NMR spectrum of the filtrate from the reaction with Me_3SiNEt_2, for example, showed evidence for other complex(es) with coordinated diethylamide ligands. In the mass spectrum of this crude material, peaks with the tungsten isotope pattern corresponded to a complex with the formulation $W(S)Cl_3(NEt_2)$ and its fragmentation. However an attempt to isolate this complex by crystallization was unsuccessful. We have also attempted to prepare higher yields of mono- or bis(amide) complexes by using only 1 or 2 equiv of the amine, but discrete products could not be isolated.

The loss of the sulfido ligand from the starting reagent was not originally expected in these reactions since the W═S bond is usually considered to be quite strong.[19] At least part of the driving force for this metathesis reaction appears to lie in the formation of two strong W—N bonds at the expense of a single W═S bond. In the reported reaction of $WOCl_4$ with 4 equiv of $LiNMe_2$ at 0 °C, the terminal chalcogen ligand was also displaced and $W(NMe_2)_6$ was isolated in low yield.[20] It is interesting that attempts to prepare the tris amide complexes by the reactions of R_2NSiMe_3 with WCl_6 rather than $WSCl_4$ were not successful. Nor were we able to isolate clean products from the reactions of $WSCl_4$ with lithium amides or secondary amines. The fate of the sulfido ligand in the formation of **1–3** has not been established. The formation of bis(trimethylsilyl) sulfide was not observed when the formation of **2** was monitored by NMR spectroscopy in $CDCl_3$.

Characterization of Tris(amide) Complexes. The formulations of the tris(amide) complexes were confirmed by elemental analysis data. In particular, analysis of **2** for C, H, N, Cl, and S confirmed that the product did not contain a sulfido ligand. Mass spectral data for **1** showed the expected parent ion fragment, but in the mass spectra for **2** and **3** the highest molecular weight fragments corresponded to the P–Cl ion.

Each of the ^1H NMR spectra for **1–3** showed resonances for a single alkyl group at exceptionally low chemical shifts. For example, the spectrum of $WCl_3(NMe_2)_3$ shows one singlet at 5.46 ppm; in the spectrum of $WCl_3(NEt_2)_3$ the methylene quartet occurs at 5.46 ppm while the methyl triplet is observed at 1.25 ppm. For $WCl_3(N(CH_2)_4)_3$ two multiplets are observed at 6.38 and 1.78 ppm. The protons α to the amide nitrogens are more deshielded in these complexes than in other reported tungsten (VI) amides. For example, the *N*-methyl resonance in $W(OMe)_3(NMe_2)_3$ was reported at 3.9 ppm,[14] and the methylene protons in the amide ligands of $W(NEt_2)_2(NEt)_2$ occurred at 3.63 ppm.[13]

The spectrum of **2**, which was recorded in $CDCl_3$, remained unchanged at a temperature of −50 °C, suggesting that the complex is a single isomer of high symmetry. Similar single resonances for the NMe_2 ligands have been observed in low-temperature NMR spectra of $W(NMe_2)_6$,[13] *fac*-$W(NMe_2)_3(OMe)_3$,[14] and *fac*-$W(NMe_2)_3(O_2CNMe_2)_3$.[15] On the basis of the NMR data, the new products **1–3** were assigned as facial isomers of octahedral geometry. The large deshielding in the ^1H (and ^{13}C) NMR spectra was attributed to the effect of the chloride ion trans to each amide ligand.[21]

The new amide complexes reacted rapidly with water and other proton sources to lose dialkylammonium chloride. The complexes were stable at 25 °C in the solid state and in chloroform solution when protected from air and moisture, but decomposition of **1** and **2** in dried acetonitrile solution occurred over a period of 12–24 h. Alkylamido ligands in other high-valent metal complexes

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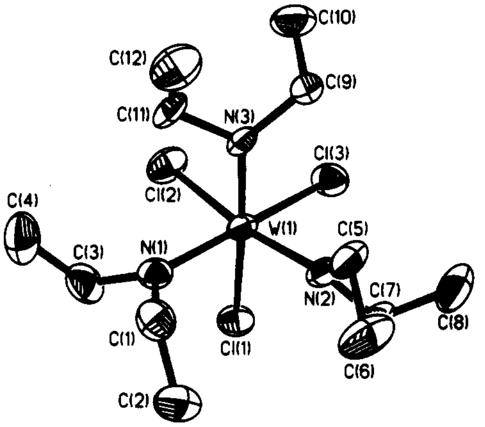

Figure 1. Perspective drawing and numbering scheme for $WCl_3(NEt_2)_3$, (**2**). Thermal ellipsoids are shown at the 50% probability level.

Table I. Atomic Coordinates[a] (×10⁴) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for $WCl_3(NEt_2)_3$ (**2**)

	x/a	*y/b*	*z/c*	*U*(eq)[b]
W(1)	56(1)	4894(1)	2520(1)	30(1)
Cl(1)	−848(2)	6816(2)	3573(1)	45(1)
Cl(2)	−928(2)	6548(2)	1456(1)	56(1)
Cl(3)	−3309(2)	3311(2)	2465(1)	50(1)
N(1)	2501(5)	6589(5)	2567(3)	36(1)
N(2)	306(6)	3329(6)	3348(3)	36(1)
N(3)	718(6)	3483(5)	1625(3)	33(1)
C(1)	4124(6)	6261(7)	3003(3)	47(2)
C(2)	4209(7)	6759(8)	3929(4)	64(2)
C(3)	2987(7)	8416(6)	2353(4)	52(2)
C(4)	4123(8)	8776(7)	1578(4)	71(2)
C(5)	1457(7)	2099(6)	3261(3)	45(2)
C(6)	2694(8)	2097(8)	4010(3)	65(3)
C(7)	−861(7)	3022(7)	4135(3)	48(2)
C(8)	−2126(9)	1186(7)	4172(4)	69(3)
C(9)	−440(7)	1729(6)	1389(3)	46(2)
C(10)	−1628(8)	1631(8)	605(3)	67(2)
C(11)	2209(7)	4193(6)	993(3)	51(2)
C(12)	3316(8)	3030(8)	682(4)	61(2)

[a] Atoms have occupancies of 1.0. [b] The equivalent isotropic *U* is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

have been observed to undergo β-hydrogen elimination from the amide ligand to form imine complexes.[22-24] However, when the thermal decomposition of **2** was carried out in the presence of Proton Sponge and monitored by ^1H NMR spectroscopy, a methyl doublet characteristic of an imine ligand, EtN=C(H)Me, was not detected. Another decomposition pathway identified for diethylamide complexes, usually at high temperatures, is the net loss of an ethyl group to form an ethanimide product.[13,23,25] Such products were not identified in the decomposition of **2**.

X-ray Diffraction Study of $WCl_3(NEt_2)_3$ (2). Single crystals of **2** were obtained from acetonitrile solution at −20 °C. The crystal structure identified a discrete six-coordinate complex of **2** with a distorted octahedral geometry. An ORTEP plot of **2** which provides the numbering scheme is shown in Figure 1. Atomic coordinates are given in Table I and selected bond distances and angles are listed in Table II. The structure confirms the presence of the facial isomer assigned above on the basis of NMR data. The distortion from an octahedral geometry involves Cl–W–Cl angles which are compressed to values less than 90° (86.0(1), 85.2(1), and 81.7(1)°), and N–W–N angles which are somewhat larger than 90° (102.5(2), 94.9(2), and 91.1(2)°).

The angles around the amide nitrogen atoms add up to 359–360°, indicating the planarity of each ligand and the involvement of the nitrogen lone pair in N–W p → dπ bonding. The W–N bond distances average 1.932(5) Å. This distance lies between those of two related facial $W(NR_2)_3X_3$ structures with oxygen donor ligands. In the monodentate carbamate complex $W(NMe_2)_3(O_2CNMe_2)_3$, the average W–N bond length was 1.922 (7) Å,[26] and in the silasesquioxane complex $(c\text{-}C_6H_{11})_7Si_7O_9(O_3W[NMe_2]_3)$, the distance was 1.958(5) Å.[17] The average W–N distance in $W(NMe_2)_6$, in which amide ligands must compete for π orbitals on the metal, is significantly longer, 2.032(25) Å.[27] A very short W–N distance of 1.881(5) Å was observed in the five-coordinate square pyramidal amide complex $W(O)(NEt_2)(CH_2\text{-}t\text{-}Bu)_3$.[12] We wondered whether the deshielding of the amide alkyl resonances in the NMR spectra could be directly related to the amount of π donation from the amide ligands. However, no correlation was observed between the chemical shifts of the amide alkyl resonances in the ^1H NMR spectra and the W–N bond distances in the known series of W(VI) complexes.

Table II. Selected Bond Distances and Angles for $WCl_3(NEt_2)_3$ (**2**)

Bond Lengths (Å)			
W(1)–Cl(1)	2.463(2)	W(1)–Cl(2)	2.440(2)
W(1)–Cl(3)	2.452(1)	W(1)–N(1)	1.931(3)
W(1)–N(2)	1.913(5)	W(1)–N(3)	1.938(5)
N(1)–C(1)	1.485(7)	N(1)–C(3)	1.479(6)
N(2)–C(5)	1.499(8)	N(2)–C(7)	1.503(6)
N(3)–C(9)	1.467(6)	N(3)–C(11)	1.495(6)
Bond Angles (deg)			
Cl(1)–W(1)–Cl(2)	85.9(1)	Cl(1)–W(1)–Cl(3)	85.1(1)
Cl(2)–W(1)–Cl(3)	81.8(1)	Cl(1)–W(1)–N(1)	85.3(1)
Cl(2)–W(1)–N(1)	89.0(1)	Cl(3)–W(1)–N(1)	167.1(1)
Cl(1)–W(1)–N(2)	93.4(1)	Cl(2)–W(1)–N(2)	168.5(1)
Cl(3)–W(1)–N(2)	86.7(1)	N(1)–W(1)–N(2)	102.5(2)
Cl(1)–W(1)–N(3)	175.6(1)	Cl(2)–W(1)–N(3)	89.7(1)
Cl(3)–W(1)–N(3)	94.5(1)	N(1)–W(1)–N(3)	94.5(2)
N(2)–W(1)–N(3)	90.9(2)	W(1)–N(1)–C(1)	121.2(3)

The average W–Cl distance in **2** of 2.450(2) Å is characteristic of a weak W–Cl bond which is trans to a π-donor ligand. Chloride ligands trans to a tungsten–nitrido and a tungsten–imido linkage were found to have W–Cl distances of 2.43 and 2.42 Å, respectively.[28,29] In contrast, the average W–Cl distance for chloride ligands cis to a π donor ligand in a series of tungsten(VI) derivatives was 2.33 Å.[30]

Reactivity of the Tris(amide) Complexes. The relatively long tungsten chloride bonds characterized in the structural study of **2** suggested that these tungsten amide complexes may undergo facile chloride substitution. We therefore attempted to prepare new tungsten amide complexes with other donor ligands. The reactions of **1** or **2** with a series of alkylating agents, including MeLi, PhLi, and Me_3SiCH_2MgCl, were studied. In some cases, tentative evidence for the formation of mixed alkyl-amide tungsten complexes was observed in the ^1H NMR spectra of the reaction solutions (see Experimental Section), but we were unsuccessful in isolating these products. The reaction of a less reducing reagent, PhZnCl, with **2** also failed to give a characterizable tungsten–aryl product.

Similar results were obtained when reactions of the tungsten derivatives with thiolate ligands were investigated. For example, unlike the reactions with NaSMe and NaS-*t*-Bu, the reaction of NaSPh with **2** proceeded to form new products, which, on the basis of NMR data, appeared to contain both amide and thiolate ligands. However these derivatives appeared to be quite unstable, and once again we were unsuccessful in our attempts to isolate them and obtain further characterization data. Our studies

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Table III. Crystallographic Data for $WCl_3(NEt)_3$[a]

chem formula	$C_{12}H_{30}N_3Cl_3W$	V, Å^3	913.4(4)
fw	506.6	Z	2
space group	$P\bar{1}$	d_{calc}, g cm^{-3}	1.842
a, Å	7.431(2)	temp, °C	22–24
b, Å	8.148(2)	abs coeff, mm^{-1}	6.897
c, Å	15.802(4)	λ, Å	0.710 73
α, deg	92.51(2)	R, %	3.44
β, deg	90.04(2)	R_w, %	4.80
γ, deg	107.12(2)		

[a] The quantity minimized in the least squares procedures is $\sum w(|F_o| - |F_c|)^2$. $R = R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. $R_w = R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$.

suggest that the strong donor properties of the amide ligands tend to destabilize complexation by other good donor ligands, thus limiting the derivatization chemistry for this system.

Experimental Section

All reactions were carried out under a nitrogen atmosphere by using standard Schlenk, glovebox, and vacuum line techniques. All solvents were distilled under nitrogen over appropriate drying agents. NMR solvents were dried over 5-Å sieves and degassed with a dry N_2 purge. ^1H and ^{13}C spectra were obtained on a Varian VXR-300 MHz spectrometer at 300 and 75.4 MHz, respectively. ^1H NMR spectra were referenced against the residual proton impurity in chloroform-d_1, while ^{13}C NMR spectra were referenced against the resonance representing the methine carbon of chloroform-d_1. Elemental analyses were performed by Desert Analytics, Tucson, AZ. *N,N*-diethyl(trimethylsilyl)amine, *N,N*-dimethyl(trimethylsilyl)amine, 1-(trimethylsilyl)pyrrolidine (Aldrich), and tungsten(VI) chloride were used as received. $WSCl_4$ was prepared by a slight alteration of the method described by Gibson.[31]

Synthesis of $WSCl_4$. WCl_6 (2.0 g, 5.0 mmol) in a Schlenk flask was dissolved in toluene (25 mL), giving a blue solution. $(Me_3Si)_2S$ (1.1 mL, 5.0 mmol) was added via syringe to the stirred solution at 0 °C resulting in a red solution and a red precipitate. The solution was stirred at 0 °C for 10 min and then allowed to warm to 20 °C. After $^1/_2$ h, the solvent was removed *in vacuo*, giving a red solid. Sublimation at 80 °C and 10^{-5} Torr resulted in isolation of $WSCl_4$ as a red powder (1.4 g, 78% yield).

Synthesis of $W(NMe_2)_3Cl_3$ (1). $WSCl_4$ (0.50 g, 1.4 mmol) in a Schlenk flask was dissolved in THF (15 mL), giving a red solution. Dimethyl(trimethylsilyl)amine (0.89 mL, 5.6 mmol) was added via syringe to the stirred solution at −78 °C. The solution was stirred at −78 °C for 30 min and then placed in the freezer for 2 days, giving a red solution with a red precipitate. The solution was removed from the red precipitate via cannula, and the solid was dried *in vacuo*. Yield: 0.18 g, 31%. ^1H NMR data ($CDCl_3$, 20 °C) $\delta = 5.53$ (12H, s, $N(CH_3)_2$). ^{13}C NMR data ($CDCl_3$, 20 °C) $\delta = 55.42$ ($N(CH_3)$). Anal. Calcd for $C_6H_{18}Cl_3N_3W$: C, 17.06; H, 4.30;N, 9.95. Found: C, 17.10; H, 4.16; N, 9.74. EI-MS (*m/e*): 423 ($W(NMe_2)_3Cl_3$), 379 ($W(NMe_2)_2Cl_3$), 343 ($W(NMe_2)_2Cl_2$), 316 ($W(NMe_2)_3$).

Synthesis of $W(NEt_2)_3Cl_3$ (2). $WSCl_4$ (0.98 g, 2.7 mmol) was reacted with diethyl(trimethylsilyl)amine (2.1 mL, 10.9 mmol) at 0 °C in a procedure similar to that described above. Yield: 0.29 g, 21%. Crystals suitable for X-ray analysis were obtained by concentrating a CH_3CN solution and cooling the solution to −20 °C for 3 days. ^1H NMR data ($CDCl_3$, 20 °C): $\delta = 5.46$ (12H, q, $J = 7.2$ Hz, $N(CH_2CH_3)_2$), 1.25 (18H, t, $J = 7.2$ Hz, $N(CH_2CH_3)_2$). ^{13}C NMR data ($CDCl_3$, 20 °C): $\delta = 57.06$ ($N(CH_2CH_3)_2$), 15.68 ($N(CH_2CH_3)_2$). Anal. Calcd for $C_{12}H_{30}Cl_3N_3W$: C, 28.45; H, 5.97; N, 8.29; Cl, 20.99. Found C, 28.38; H, 5.88; N, 8.20; Cl, 21.57. CI^+-MS (*m/e*): 472 ($W(NEt_2)_3Cl_2$), 435 ($W(NEt_2)_3Cl$), 400 ($W(NEt_2)_2Cl_2$).

Synthesis of $W(N(CH_2)_4)_3Cl_3$ (3). $WSCl_4$ (0.25 g, 0.70 mmol) was reacted with 1-(trimethylsilyl)pyrrolidine (0.49 mL, 2.8 mmol) at 0 °C in a procedure similar to that described above. Yield: 0.050 g, 14%. Analytically pure samples were obtained by recrystallization from CH_3CN. ^1H NMR data ($CDCl_3$, 20 °C): $\delta = 6.38$ (12H, m, NCH_2), 1.78 (12H, m, NCH_2CH_2). Anal. Calcd for $C_{12}H_{24}N_3Cl_3W$: C, 28.79; H, 4.83; N, 8.39. Found: C, 28.85; H, 4.74; N, 8.54. EI-MS (*m/e*): 465 ($W(N(CH_2)_4)_3Cl_2$), 429 ($W(N(CH_2)_4)_3Cl$), 394 ($W(N(CH_2)_4)_2Cl_2$), 360 ($W(N(CH_2)_4)_2Cl$).

X-ray Diffraction Study of $WCl_3(NEt_2)_3$ (2). Single crystals of **2** were isolated from an acetonitrile solution cooled to −20 °C, mounted on a glass fiber, and coated with epoxy. Details of the crystal structure study are given in Table III. The structure was solved by direct methods followed by Fourier techniques. For the final model all atoms except hydrogen were refined independently with anisotropic displacement parameters. Hydrogen atoms were included in idealized positions riding on the atom of attachment. Hydrogen atom isotropic thermal parameters were set equal to 0.08. Complete experimental details and structural data are given in the supplementary material.

Attempted Reactions with $WSCl_4$. (a) With *N,N*-diisopropyl(trimethylsilyl)amine. $WSCl_4$ (0.25 g, 0.70 mmol) in a Schlenk flask was dissolved in THF (15 mL) giving a red solution. *N,N*-diisopropyltrimethylsilylamine (1 equiv) was added via syringe to the stirred solution at 0 °C, and the solution was stirred at 0 °C for $^1/_2$ h. The solution was reduced until a precipitate began to form and then placed in the freezer overnight to give a brown precipitate and red solution. The precipitate was insoluble in $CDCl_3$, but was soluble in CD_3CN. ^1H NMR spectroscopy showed only one product, which was probably $HCl\cdot HN(i\text{-}Pr)_2$. ^1H NMR (CD_3CN): δ 3.11 (m, 1H, $CHMe_2$), 1.28 (d, 6H, Me). The soluble fraction appeared to be a mixture of products. These were not successfully separated or identified.

(b) With $LiNEt_2$. $WSCl_4$ (0.20 g, 0.56 mmol) in a Schlenk flask was dissolved in THF (15 mL). $LiNEt_2$ (0.18 g, 2.3 mmol) in a Schlenk flask was dissolved in THF and then added to the red $WSCl_4$ solution, resulting in a brown solution. After the mixture was stirred overnight the solvent was removed *in vacuo*. The brown solid was extracted with hexanes (20 mL) and filtered, giving a brown solution. The solution was cooled, but crystals were not obtained. The solvent was removed *in vacuo*, leaving a sticky brown solid. The ^1H NMR spectrum of the solid in C_6D_6 showed a complicated pattern of ethyl multiplets, suggesting a mixture, (multiplets at 5.3, 4.2, 3.6, 3.5, 2.8; six triplets between 0.8 and 1.6 ppm), and products were not successfully separated.

Attempted Reaction of WCl_6 with Me_3SiNEt_2. WCl_6 (0.25 g, 0.63 mmol) in an addition tube was added to a solution of *N,N*-diethyl(trimethylsilyl)amine (0.36 mL, 1.9 mmol) in THF (15 mL) at −78 °C. The solution was slowly warmed to 20 °C over 2 h resulting in an orange solution with an orange precipitate. The reaction flask was placed in the freezer overnight to produce a precipitate, which was filtered and dried. ^1H NMR data suggested this product was primarily $H_2NEt_2\cdot Cl$. ^1H NMR ($CDCl_3$): δ 9.5 (tr, NH), 3.0 (q), 1.4 (tr). The filtrate was evaporated and the residue was analyzed by NMR spectroscopy. The spectrum showed several ethyl resonances, but none corresponded to $W(NEt_2)_3Cl_3$. Attempts to synthesize $W(NEt_2)_3Cl_3$ from WCl_6 were also tried in CH_2Cl_2 and toluene solutions with similar results.

Attempted Reactions of $W(NR_2)_3Cl_3$. (a) With Alkylating Agents. $W(NEt_2)_3Cl_3$ (0.012 g, 0.024 mmol) in an NMR tube was partially dissolved in CD_3CN or THF-d_8 under nitrogen, and 1.4 M MeLi in ether (0.018 mL, 0.025 mmol) was added. The solution was frozen at −196 °C and the tube was sealed under vacuum. The reactions were monitored by ^1H NMR spectroscopy. In each case the spectrum showed a new multiplet at 4.9 ppm, which may correspond to a mixed amide–methyl complex. Broader ethyl resonances were also observed at 2.7 and 1.2 ppm. Other resonances were obscured by solvent.

A similar reaction was carried out on a larger scale. To a solution of **2** (0.10 g, 0.20 mmol) in THF was added 3 equiv of MeLi at 0 °C, and the solution was then warmed to room temperature over a period of 1 h. The resulting brown solution was filtered and evaporated to give a brown solid. The NMR spectrum showed resonances consistent with $WMe_3(NEt_2)_3$ as the major product. NMR ($CDCl_3$): δ 3.54 (q, 12H), 1.17 (t, 18H), 0.96 (s, 9H). However, attempts to recrystallize the product from dichloromethane/hexanes resulted in decomposition.

(b) With Thiolate Ligands. $W(NEt_2)_3Cl_3$ (0.002 g, 0.004 mmol) and NaSPh (0.002 g, 0.015 mmol) were placed in an NMR tube. CD_3CN was added to form a red solution. After 2 h, the solution was red with a white precipitate. The shift in the ethyl resonances to 4.6 ppm (q) and 1.1 ppm (t) and new aromatic resonances between 7.5 and 7.0 ppm suggested the formation of a mixed thiolate–amide complex. This reaction was repeated on a larger scale in CN_3CN at 0 °C. In addition to the quartet at 4.6 ppm, new quartets were observed in the spectrum at 4.1 and 3.6 ppm in equal intensities. Dynamic FAB on the latter product(s) showed tungsten fragments at *m/e* 684 and 552 ($W(SPh)_2Cl(NEt_2)(NEt)$.). The product(s) decomposed during attempted recrystallizations.

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Supplementary Material Available: Complete tables of crystallographic data, bond lengths, bond angles, anisotropic thermal factors and hydrogen atom coordinates (8 pages). Ordering information is given on any current masthead page.

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