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Synthesis and Structural Investigation of Tungsten Imido Amidinate and Guanidinate Complexes

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The tungsten imido guanidinate and amidinate complexes $W(NR)Cl_3[R'NC(NMe_2)NR']$ and $W(NR)Cl_3[R'NC(Me)NR']$ ($R = Ph$, ${}^iPr$, Cy; $R' = {}^iPr$, ${}^tBu$, TMS) were synthesized by reacting the corresponding imido complex $W(NR)Cl_4(OEt_2)$ with the appropriate lithium amidinate or guanidinate. Crystallographic structure determination of $W(N^iPr)Cl_3[{}^iPrNC(NMe_2)N^iPr]$ and $W(N^iPr)Cl_3[{}^iPrNC(Me)N^iPr]$ allows comparison of structural features between the guanidinate and amidinate ligand in the presence of an identical ancillary ligand set.

Introduction

Guanidinate and amidinate anions have generated significant interest as ligands,[1,2] beginning with the first transition metal−guanidinate complexes that were reported in 1970 by Lappert.[3] These anions make attractive ligands because of their steric and electronic tunability through the programmed variation of the N and C substituents.[4−6] The ability of these anions to serve as alternatives to cyclopentadienyl has been confirmed, and they have been used extensively in the coordination chemistry of transition, f-block, and main-group metals.[7−21]

One motivation for exploring tungsten complexes that contain nitrogen-bound ligands is their application as single-source precursors for chemical vapor deposition (CVD) or atomic layer deposition (ALD) of tungsten nitride (WN_x) and tungsten carbonitride (WN_xC_y),[22,23] materials of interest to the semiconductor industry as potential diffusion barriers in copper metallization schemes.[24−31] Previously, we reported that the tungsten imido complexes $Cl_4(RCN)W(N^iPr)$, $Cl_4(RCN)W(NPh)$, and $Cl_4(RCN)W(NC_3H_5)$ ($R = Me$, Ph) could be used as single-source precursors for WN_x and WN_xC_y deposition.[32−35] Recently reported uses of guanidi-

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nate and amidinate complexes in the CVD of other materials[36−40] have suggested their use in the CVD/ALD of WN_x and WN_xC_y. In particular, it has been demonstrated that titanium guanidinate complexes can serve as precursors for the chemical vapor deposition of titanium carbonitride[40] and tantalum guanidinate complexes yield TaN by CVD.[41] We now describe the synthesis and structural characterization of a series of tungsten guanidinate and amidinate complexes derived from the series of $Cl_4(RCN)W(N^iPr)$, $Cl_4(RCN)W(NPh)$, and $Cl_4(RCN)W(NC_3H_5)$ compounds that we have previously used for CVD of WN_x and WN_xC_y.

Experimental Procedures

General Procedures. Unless otherwise stated, reactions and manipulations were performed in an inert atmosphere (N_2) glovebox or using standard Schlenk techniques. All reaction solvents were purified using an MBraun MB-SP solvent purification system prior to use. NMR solvents were degassed by three freeze−pump−thaw cycles and stored over 3 Å molecular sieves in an inert-atmosphere glovebox. ^1H and ^{13}C NMR spectra were recorded on Mercury 300, Gemini 300, or VXR 300 spectrometers using residual protons of deuterated solvents for reference. Infrared spectra were recorded as mineral oil mulls on NaCl plates on a Perkin-Elmer Spectrum One FT-IR spectrometer. UV−vis spectra were recorded on a Shimadzu UV-1650 UV−vis spectrophotometer. TGA analysis was carried out using a Perkin-Elmer TGA7 thermogravimetric analyzer under nitrogen with a heating rate of 10 °C/min (sample size $\approx$ 2 mg). Methyllithium, lithium dimethylamide, 1,3-diisopropylcarbodiimide, di-*tert*-butylcarbodiimide, and bis-trimethylsilylcarbodiimide were used as purchased from Aldrich. $W(NR)Cl_4(OEt_2)$ complexes were prepared by the method of Schrock.[42]

$W(NPh)Cl_3[^iPrNC(NMe_2)N^iPr]$ (1). A 250 mL Schlenk tube was charged with $LiNMe_2$ (0.156 g, 3.06 mmol) and 100 mL of Et_2O. The resulting colorless suspension was cooled to 0 °C, and 1,3-diisopropylcarbodiimide (0.48 mL, 3.1 mmol) was added dropwise via syringe. The reaction mixture was warmed to room temperature over 2 h. The resulting cloudy solution of lithium guanidinate reagent was cannula-transferred into a 250 mL Schlenk tube containing a solution of $W(NPh)Cl_4(OEt_2)$ (1.50 g, 3.06 mmol) in Et_2O (100 mL) at −78 °C. The reaction mixture was stirred for 20 min at −78 °C and was warmed to room-temperature overnight. Removal of solvent in vacuo, followed by extraction into Et_2O (200 mL) and filtration, yielded a purple solution. Et_2O was removed in vacuo to give crude **1** as an amber powder. Recrystallization from a toluene solution layered with hexane at −20 °C gave pure **1** as amber crystals (1.01 g, 60%). ^1H NMR (300 MHz, C_6D_6): δ 1.33 (d, 6H, $J = 6$ Hz, $CH(CH_3)_2$), 1.67 (d, 2H, $J = 6$ Hz, $CH(CH_3)_2$), 2.05 (s, 6H, $N(CH_3)_2$), 4.15 (septet, 1H, $CH(CH_3)_2$), 4.38 (septet, 1H, $CH(CH_3)_2$), 6.56 (t, 1H, $J = 8$ Hz, CH), 6.96 (t, 2H, $J = 8$ Hz, CH), 7.41 (d, 2H, $J = 8$ Hz, CH). ^{13}C NMR ($CDCl_3$): δ 22.8 ($CH(CH_3)_2$), 25.1 ($CH(CH_3)_2$), 40.8 ($N(CH_3)_2$), 50.1 ($CH(CH_3)_2$), 55.5 ($CH(CH_3)_2$), 128.0 (CH), 129.5 (CH), 130.9 (CH), 151.6 (C_{ipso}), 164.1 (N_2CCH_3). Anal. Calcd for $WC_{15}H_{25}N_4Cl$: C, 32.66; H, 4.57; N, 10.16. Found: 32.94; H, 4.72; N, 9.96.

$W(NCy)Cl_3[^iPrNC(NMe_2)N^iPr]$ (2). A 250 mL Schlenk tube was charged with $LiNMe_2$ (0.102 g, 2.01 mmol) and 100 mL of Et_2O. The resulting colorless suspension was cooled to 0 °C, at which temperature 1,3-diisopropylcarbodiimide (0.317 mL, 2.01 mmol) was added dropwise via syringe. The reaction mixture was warmed to room temperature over 2 h. The resulting cloudy solution of lithium guanidinate reagent was cannula-transferred into a 250 mL Schlenk tube containing a solution of $W(C_6H_{11})Cl_4(OEt_2)$ (1.00 g, 2.01 mmol) in Et_2O (100 mL) at −78 °C. The reaction mixture was stirred for 20 min at −78 °C and was warmed to room-temperature overnight in the absence of light. Removal of solvent in vacuo, followed by extraction into Et_2O (200 mL) and filtration, yielded a dark amber solution. Et_2O was removed in vacuo to give crude **2** as a dark amber powder. Recrystallization from a toluene solution layered with hexane at −20 °C yielded pure **2** as amber crystals (0.616 g, 55%). ^1H NMR (300 MHz, C_6D_6): δ 1.15 (m, 4H, CH_2), 1.48 (d, 6H, $J = 4$ Hz, $CH(CH_3)_2$), 1.72 (d, 6H, $J = 6$ Hz, $CH(CH_3)_2$), 1.78 (br, 2H, CH_2), 2.05 (br, 4H, CH_2), 2.15 (s, 6H, $N(CH_3)_2$), 4.08 (septet, 1H, $CH(CH_3)_2$), 4.41 (septet, 1H, $CH(CH_3)_2$), 5.47 (m, 1H, WNCH). ^{13}C NMR (C_6D_6): δ 23.4 (CH_2), 23.9 (CH_2), 25.5 (CH_2), 25.9 ($N(CH_3)_2$), 33.7 ($CH(CH_3)_2$), 39.9 ($CH(CH_3)_2$), 50.4 ($CH(CH_3)_2$), 53.9 ($CH(CH_3)_2$), 72.6 (WNC), 164.8 (N_3C). Anal. Calcd for $WC_{15}H_{31}N_4Cl_3$: C, 32.31; H, 5.60; N, 10.05. Found: C, 32.16; H, 5.65; N, 9.86.

$W(N^iPr)Cl_3[^iPrNC(NMe_2)N^iPr]$ (3). A 250 mL Schlenk tube was charged with $LiNMe_2$ (0.223 g, 4.38 mmol) and 100 mL of Et_2O. The resulting colorless suspension was cooled to 0 °C, at which temperature 1,3-diisopropylcarbodiimide (0.69 mL, 4.4 mmol) was added dropwise via syringe. The reaction mixture was warmed to room temperature over 2 h. The resulting cloudy solution of lithium guanidinate reagent was cannula-transferred into a 250 mL Schlenk tube containing a solution of $W(NCH(CH_3)_2)Cl_4(OEt_2)$ (2.00 g, 4.38 mmol) in Et_2O (100 mL) at −78 °C. The reaction mixture was stirred for 20 min at −78 °C and was warmed to room-temperature overnight in the absence of light. Removal of solvent in vacuo, followed by extraction into Et_2O (200 mL) and filtration, yielded a dark amber solution. Et_2O was removed in vacuo to give crude **3** as a dark amber powder. Recrystallization from a toluene solution layered with hexane at −20 °C yielded pure **3** as amber crystals (1.27 g, 56%). ^1H NMR (300 MHz, C_6D_6): δ 1.23 (d, 6H, $J = 6$ Hz, $CH(CH_3)_2$), 1.38 (d, 6H, $J = 7$ Hz, $CH(CH_3)_2$), 1.70 (d, 6H, $J = 6$ Hz, $CH(CH_3)_2$), 2.14 (s, 6H, $N(CH_3)_2$), 4.08 (septet, 1H, $CH(CH_3)_2$), 4.39 (septet, 1H, $CH(CH_3)_2$), 5.31 (septet, 1H, $WNCH(CH_3)_2$). ^{13}C NMR (C_6D_6): δ 23.3, 23.4, 25.4, 40.1 ($N(CH_3)_2$), 50.4 ($CH(CH_3)_2$), 53.8 ($CH(CH_3)_2$), 66.8 ($WNCH(CH_3)_2$), 164.7 (N_3C). IR (cm^{-1}): 2925 (s), 2854 (s), 1607 (w), 1461 (m), 1377 (m), 1278 (w). UV−vis [ether, λ_{max} (ϵ)]: 251 (1800), 309 (2800), 392 nm (1500 M^{-1} cm^{-1}). Anal. Calcd for $WC_{12}H_{27}N_4Cl$: C, 27.85; H, 5.26; N, 10.83. Found: C, 28.14; H, 5.52; N, 10.52.

$W(NPh)Cl_3[^tBuNC(Me)N^tBu]$ (4). Methyllithium (1.6 M in Et_2O, 2.29 mL, 3.7 mmol) was added dropwise to a solution of 1,3-di-*tert*-butylcarbodiimide (0.565 g, 3.66 mmol) in 100 mL of

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Et_2O at −30 °C. The mixture was warmed to room temperature and stirred for 4 h. The resulting colorless solution was then added to a solution of $W(NC_6H_5)Cl_4(OEt_2)$ (1.80 g, 3.66 mmol) in 50 mL of Et_2O at −30 °C. The reaction mixture was stirred overnight. All volatiles were then removed under reduced pressure, and the resulting solid was extracted with Et_2O (100 mL). The Et_2O extract was dried in vacuo to yield pure **4** as a purple powder (1.25 g, 62%). ^1H NMR (300 MHz, C_6D_6): δ 1.21 (s, 9H, $C(CH_3)_3$), 1.58 (s, 3H, N_2CCH_3), 1.62 (s, 9H, $C(CH_3)_3$), 6.51 (t, 1H, J = 8 Hz, CH), 6.83 (t, 2H, J = 8 Hz, CH), 7.31 (d, 2H, J = 8 Hz, CH). ^{13}C NMR (C_6D_6): δ 22.2 (N_2CCH_3), 31.4 ($C(CH_3)_3$), 32.1 ($C(CH_3)_3$), 59.9 ($C(CH_3)_3$), 63.4 ($C(CH_3)_3$), 130.0 (CH), 131.1 (CH), 173.1 (N_2CCH_3). There are two aromatic carbons that could not be located because of overlap with other peaks. Anal. Calcd for $WC_{16}H_{26}N_3Cl_3$: C, 34.90; H, 4.76; N, 7.63. Found: C, 35.39; H, 4.32; N, 7.36.

W(N^{i}Pr)Cl$_3$[^{t}BuNC(Me)N^{t}Bu] (5). Methyllithium (1.6 M in Et_2O, 1.64 mL, 2.6 mmol) was added dropwise to a solution of 1,3-di-*tert*-butylcarbodiimide (0.405 g, 2.62 mmol) in 100 mL of Et_2O at −30 °C. The mixture was warmed to room temperature and stirred for 4 h. The resulting colorless solution was then added to a solution of $W(NCH(CH_3)_2)Cl_4(OEt_2)$ (1.20 g, 2.62 mmol) in 50 mL of Et_2O at −30 °C. The reaction mixture was stirred overnight in the absence of light. All volatiles were then removed under reduced pressure, and the resulting solid was extracted with Et_2O (100 mL). The Et_2O extract was dried in vacuo to give pure **5** as a purple powder (0.880 g, 65%). ^1H NMR (300 MHz, C_6D_6): δ 1.22 (s, 9H, $C(CH_3)_3$), 1.28 (d, 6H, J = 6 Hz, $CH(CH_3)_2$), 1.56 (s, 3H, N_2CCH_3), 1.58 (s, 9H, $C(CH_3)_3$), 5.12 (septet, 1H, $WNCH(CH_3)_2$). ^{13}C NMR (C_6D_6): δ 22.1, 23.0, 31.4 ($C(CH_3)_3$), 32.0 ($C(CH_3)_3$), 67.1 ($C(CH_3)_3$), 68.4 ($C(CH_3)_3$), 88.9 ($NCH(CH_3)_2$), 167.1 (N_2CCH_3). IR (cm^{-1}): 2922 (s), 2849 (s), 1585 (w), 1463 (m), 1376 (m), 1259 (m), 1186 (m), 1097 (w), 827 (w). UV−vis [ether, λ_{max} (ϵ)]: 309 (4700), 478 nm (2100 M^{-1} cm^{-1}). Anal. Calcd for $WC_{13}H_{28}N_3Cl_3$: C, 30.23; H, 5.46; N, 8.13. Found: C, 29.99; H, 5.68; N, 7.91.

W(NCy)Cl$_3$[^{t}BuNC(Me)N^{t}Bu] (6). A solution of methyllithium (1.6 M in Et_2O, 1.26 mL, 2.01 mmol) in Et_2O was added dropwise to a solution of 1,3-di-*tert*-butylcarbodiimide (0.310 g, 2.01 mmol) in 100 mL of Et_2O at −30 °C. The mixture was warmed to room temperature and stirred for 4 h. The resulting colorless solution was then added to a solution of $W(NC_6H_{11})Cl_4(OEt_2)$ (1.00 g, 2.01 mmol) in 50 mL of Et_2O at −30 °C. The reaction mixture was stirred overnight in the absence of light. All volatiles were then removed under reduced pressure, and the resulting solid was extracted with hexane (100 mL). The hexane extract was dried in vacuo to yield pure **6** as a purple powder (0.65 g, 58%). ^1H NMR (300 MHz, C_6D_6): δ 0.28 (s, 3H, N_2CCH_3), 1.02 (br, 4H, CH_2), 1.25 (s, 9H, $C(CH_3)_3$), 1.60 (s, 9H, $C(CH_3)_3$), 1.87 (br, 6H, CH_2), 1.97 (s, 3H, N_2CCH_3), 5.22 (m, 1H, WNCH). ^{13}C NMR (C_6D_6): δ 22.2, 24.3, 25.7, 31.4, 32.0, 33.4, 59.6 ($C(CH_3)_3$), 61.9 ($C(CH_3)_3$), 73.5 (WNCH), 172.7 (N_2CCH_3). Anal. Calcd for $WC_{16}H_{32}N_3Cl_3$: C, 34.52; H, 5.79; N, 7.55. Found: 34.33; H, 5.53; N, 7.32.

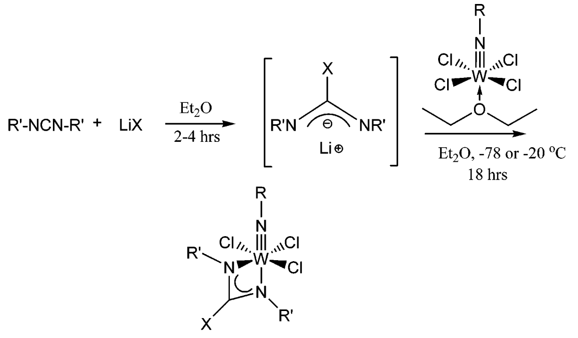
W(N^{i}Pr)Cl$_3$[Me$_3$SiNC(Me)NSiMe$_3$] (7). Methyllithium (1.6 M in Et_2O, 1.78 mL, 2.85 mmol) was added dropwise to a solution of 1,3-trimethylsilylcarbodiimide (0.531 g, 2.85 mmol) in 100 mL of Et_2O at −30 °C. The mixture was warmed to room temperature and stirred for 4 h. The resulting colorless solution was then added to a solution of $W(NCH(CH_3)_2)Cl_4(OEt_2)$ (1.30 g, 2.85 mmol) in 50 mL of Et_2O at −30 °C. The reaction mixture was stirred overnight in the absence of light. All volatiles were then removed under reduced pressure, and the resulting solid was extracted with hexane (100 mL). The hexane extract was dried in vacuo to give pure **7** as a pink powder (1.25 g, 62%). ^1H NMR (300 MHz,C_6D_6): δ 0.21 (s, 9H, $Si(CH_3)_3$), 0.56 (s, 9H, $Si(CH_3)_3$), 1.32 (d, 6H, J = 6 Hz, $CH(CH_3)_3$), 1.40 (s, 3H, N_2CCH_3), 5.23 (septet, 1H, $CH(CH_3)_2$). ^{13}C NMR (C_6D_6): δ 1.4 ($Si(CH_3)_3$), 2.1 ($Si(CH_3)_3$), 23.6 ($NCH(CH_3)_2$), 26.8 (N_2CCH_3), 66.6 ($NCH(CH_3)_2$), 170.5 (N_2CCH_3). HRMS (EI): calcd for $WC_{11}H_{28}N_3Si_2Cl_3$ $[M]^+$ m/z 547.0397; found 547.0385.

W(NPh)Cl$_3$[^{i}PrNC(Me)N^{i}Pr] (8). Methyllithium (1.6 M in Et_2O, 1.91 mL, 3.1 mmol) was added dropwise to a solution of 1,3-diisopropylcarbodiimide (0.48 mL, 2.9 mmol) in 100 mL of Et_2O at −30 °C. The mixture was warmed to room temperature and stirred for 4 h. The resulting colorless solution was then added to a solution of $W(NC_6H_5)Cl_4(OEt_2)$ (1.50 g, 3.06 mmol) in 50 mL of Et_2O at −30 °C. The reaction mixture was warmed to room temperature and stirred overnight. The liquid portion of the mixture was collected by filtration, and the solid residue was extracted with Et_2O (3 × 10 mL). The liquid portions were combined and dried under vacuum to yield pure **8** as a purple crystalline solid (1.06 g, 67%). ^1H NMR (300 MHz, $CDCl_3$): δ 1.49 (d, 6H, J = 6 Hz, $CH(CH_3)_2$), 1.51 (d, 6H, J = 6 Hz, $CH(CH_3)_2$), 2.07 (s, 3H, N_2CCH_3), 4.34 (septet, 1H, $CH(CH_3)_2$), 4.86 (septet, 1H, $CH(CH_3)_2$), 7.13 (t, 1H, J = 8 Hz, CH), 7.45 (d, 2H, J = 8 Hz, CH), 7.57 (t, 2H, J = 8 Hz, CH). ^{13}C NMR ($CDCl_3$): δ 12.9 (N_2CCH_3), 22.4 ($CH(CH_3)_2$), 24.9 ($CH(CH_3)_2$), 52.1 ($CH(CH_3)_2$), 56.3 ($CH(CH_3)_2$), 128.2 (CH), 129.4 (CH), 131.2 (CH), 151.7 (C_{ipso}), 172.1 (N_2CCH_3). Anal. Calcd for $WC_{14}H_{26}N_3Cl_3$: C, 32.18; H, 4.24; N, 8.04. Found: C, 32.46; H, 4.41; N, 7.86.

W(N^{i}Pr)Cl$_3$[^{i}PrNC(Me)N^{i}Pr] (9). Methyllithium (1.6 M in Et_2O, 1.78 mL, 2.9 mmol) was added dropwise to a solution of 1,3-diisopropylcarbodiimide (0.45 mL, 2.9 mmol) in 100 mL of Et_2O at −30 °C. The mixture was warmed to room temperature and stirred for 4 h. The resulting colorless solution was then added to a solution of $W(NCH(CH_3)_2)Cl_4(OEt_2)$ (1.30 g, 2.85 mmol) in 50 mL of Et_2O at −30 °C. The reaction mixture was warmed to room temperature and stirred overnight in the absence of light. The liquid portion of the mixture was collected by filtration, and the solid residue was extracted with Et_2O (3 × 10 mL). The liquid portions were combined and dried under vacuum to yield pure **9** as a purple crystalline solid (0.97 g, 70%). ^1H NMR (300 MHz, C_6D_6): δ 0.89 (s, 3H, N_2CCH_3) 1.23 (d, 6H, J = 6 Hz, $CH(CH_3)_2$), 1.26 (d, 6H, J = 7 Hz, $WNCH(CH_3)_2$), 1.60 (d, 6H, J = 6 Hz, $CH(CH_3)_2$), 3.71 (septet, 1H, $CH(CH_3)_2$), 4.00 (septet, 1H, $CH(CH_3)_2$), 5.24 (septet, 1H, $WNCH(CH_3)_2$). ^{13}C NMR (C_6D_6): δ 11.4 (N_2CCH_3), 22.5, 23.1, 24.7, 51.9 ($CH(CH_3)_2$), 54.2 ($CH(CH_3)_2$), 67.0 ($WNCH(CH_3)_2$), 171.5 (N_3C). IR (cm^{-1}): 2924 (s), 2853 (s), 2724 (w), 1462 (s), 1377 (m), 1303 (w), 1213 (w), 722 (w). UV−vis [ether, λ_{max} (ϵ)]: 307 (4100), 486 nm (1900 M^{-1} cm^{-1}). Anal. Calcd for $WC_{11}H_{28}N_3Cl_3$: C, 27.04; H, 4.95; N, 8.60. Found: C, 27.31; H, 4.77; N, 8.39.

W(NCy)Cl$_3$[^{i}PrNC(Me)N^{i}Pr] (10). Methyllithium (1.6 M in Et_2O, 1.59 mL, 2.5 mmol) was added dropwise to a solution of 1,3-diisopropylcarbodiimide (0.35 mL, 2.9 mmol) in 100 mL of Et_2O at −30 °C. The mixture was warmed to room temperature and stirred for 4 h. The resulting colorless solution was then added to a solution of $W(NC_6H_{11})Cl_4(OEt_2)$ (1.30 g, 2.54 mmol) in 50 mL of Et_2O at −30 °C. The reaction mixture was warmed to room temperature and stirred overnight in the absence of light. The liquid portion of the mixture was collected by filtration, and the solid residue was extracted with Et_2O (3 × 10 mL). The liquid portions were combined and dried under vacuum to give pure **10** as a purple crystalline solid (0.86 g, 64%). ^1H NMR (300 MHz, $CDCl_3$): δ 1.55 (m, 16H, $4CH_3 + 2CH_2$), 2.02 (s, 3H, N_2CCH_3), 2.05 (m, 6H, $3CH_2$), 4.23 (septet, 1H, $CH(CH_3)_2$), 4.77 (septet, 1H,

Scheme 1. Synthesis of Guanidinate and Amidinate Complexes



1 R = Ph, R' = ^{i}Pr, X = NMe_2
2 R = Cy, R' = ^{i}Pr, X = NMe_2
3 R = ^{i}Pr, R' = ^{i}Pr, X = NMe_2
4 R = Ph, R' = ^{t}Bu, X = Me
5 R = ^{i}Pr, R' = ^{t}Bu, X = Me
6 R = Cy, R' = ^{t}Bu, X = Me
7 R = ^{i}Pr, R' = TMS, X = Me
8 R = Ph, R' = ^{i}Pr, X = Me
9 R = ^{i}Pr, R' = ^{i}Pr, X = Me
10 R = Cy, R' = ^{i}Pr, X = Me

C*H*(CH_3)$_2$), 5.71 (m, 1H, WNCH). ^{13}C NMR ($CDCl_3$): δ 12.7 (N_2CCH_3), 22.4, 23.8, 25.1, 25.5, 33.5 (N_2CCH_3), 52.0 (*C*H(CH_3)$_2$), 55.0 (*C*H(CH_3)$_2$), 73.3 (WNCH), 171.5 (N_2CCH_3). IR (cm^{-1}): 2922 (s), 2849 (s), 2728 (w), 1608 (w), 1463 (s), 1377 (m), 1278 (w), 722 (w). UV−vis [ether, λ_{max} (ϵ)]: 307 (4600), 485 nm (2100 M^{-1}cm^{-1}). Anal. Calcd. for $WC_{14}H_{32}N_3Cl_3$: C, 31.81; H, 5.34; N, 7.95. Found: C, 31.89; H, 4.99; N, 7.66.

Crystallographic Structure Determination of 3 and 9. Data for both structures were collected at 173 K on a Siemens SMART PLATFORM equipped with a CCD area detector and a graphite monochromator utilizing Mo Kα radiation (λ = 0.71073 Å). Cell parameters were refined using up to 8192 reflections. A hemisphere of data (1381 frames) was collected using the ω-scan method (0.3° frame width) for each structure. The first 50 frames were remeasured at the end of data collection to monitor instrument and crystal stability (maximum correction on I was < 1%). Absorption corrections by integration were applied on the basis of the measured indexed crystal faces.

The structures were solved by the Direct Methods in *SHELXTL5*[43] and refined using full-matrix least squares. The non-H atoms were treated anisotropically, whereas the methyl hydrogen atoms were calculated in ideal positions and were riding on their respective carbon atoms. For compound **3**, the isopropyl moiety on N1 is disordered and is refined in two parts with their site occupation factors dependently refined. A total of 189 parameters were refined in the final cycle of refinement using 2299 reflections with $I > 2\sigma(I)$ to yield R_1 and wR_2 values of 2.64 and 4.87%, respectively. For compound **9**, the asymmetric unit consists of two chemically equivalent and crystallographically independent molecules. The N4 imido group was disordered and was refined in two parts with their site occupation factors dependently refined. A total of 362 parameters were refined in the final cycle of refinement using 20476 reflections with $I > 2\sigma(I)$ to yield R_1 and wR_2 values of 2.56 and 6.32%, respectively. Refinement was done using F^2.

Results and Discussion

The tungsten guanidinate and amidinate complexes **1**−**10** were synthesized by reacting the corresponding imido complex $W(NR)Cl_4(OEt_2)$ with the appropriate lithium amidinate or guanidinate (Scheme 1). The lithium salts were not isolated but were generated in situ as described by Bergman and Meyer.[10,44] The reactants were combined as diethyl ether solutions at either −78 or −20 °C. The reaction mixtures were then warmed to room temperature and stirred overnight to yield compounds **1**−**3** as amber solids after recrystallization. Complexes **4**−**10** are dark purple with the exception of **7**, which is pink. The ^{1}H and ^{13}C NMR spectra of complexes **1**−**10** all display inequivalence between the substituents of the chelating guanidinate or amidinate nitrogens, leading to their assignment as the mer isomers.

Table 1. Crystal Data and Structure Refinement for **3** and **9**

	3	**9**
empirical formula	$C_{12}H_{27}Cl_3N_4W$	$C_{11}H_{24}Cl_3N_3W$
fw	517.58	488.53
temp (K)	173(2)	173(2)
wavelength (Å)	0.71073	0.71073
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$
unit cell dimensions	a = 8.4844(7) Å b = 8.8717(8) Å c = 14.8556(13) Å α = 93.063(2)° β = 101.094(2)° γ = 116.862(2)°	a = 16.6234(11) Å b = 13.9173(9) Å c = 16.9854(11) Å α = 90° β = 114.095(2)° γ = 90°
vol (Å^3)	966.23(15)	3587.2(4)
Z	2	8
density (Mg/m^3)	1.779	1.809
abs coeff (mm^{-1})	6.389	6.876
$F_{(000)}$	504	1888
cryst size (mm^3)	0.06 × 0.05 × 0.01	0.22 × 0.16 × 0.06
θ range for data collection (deg)	1.42−24.60	1.97−27.28
index ranges	$-9 \le h \le 9$ $-9 \le k \le 9$ $-16 \le l \le 16$	$-20 \le h \le 17$ $-17 \le k \le 17$ $-21 \le l \le 20$
reflns collected	6201	20476
independent reflns (R_{int})	2732 (0.0465)	7210 (0.0622)
completeness to θ = 24.60 (%)	83.6	89.6
abs correction	integration	integration
max. and min. transmission	0.9390 and 0.6490	0.6719 and 0.2461
data/restraints/params	2732/1/189	7210/0/362
GOF on F^2	0.935	1.041
R_1[a]	0.0361	0.0325
wR_2[a]	0.0502	0.0660
largest diff. peak and hole (e·Å^3)	0.757 and −0.694	0.780 and −1.068

[a] $R_1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$; $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$; $S = [\Sigma[w(F_o^2 - F_c^2)^2]/(n - p)]^{1/2}$; $w = 1/[\sigma^2(F_o^2)+(mp)^2 + np]$; $p = [\max(F_o^2, 0)+ 2F_c^2]/3$.

Single crystals suitable for X-ray diffraction were obtained from **3** and **9**, and their structures were determined. Crystal data and structure refinement for these complexes can be found in Table 1. Compound **3** adopts a distorted octahedral geometry as shown in the ORTEP representation of **3** (Figure 1). The tungsten−chlorine bond distances are on the order of 2.38 Å, which is within the expected range for tungsten(VI)−chlorine bonds.[45] The W−N(3) bond length of 1.702(4) Å and the W−N(3)−C(10) bond angle of 168.4(8)° are consistent with the values previously reported for other W(VI) imido complexes that are expected to have a strong conjugation of the N lone pairs into empty metal d orbitals.[46,47] The W−N(2) bond length is 1.961(4) Å, while the W−N(1) bond length is 2.247(4) Å. The elongated bond

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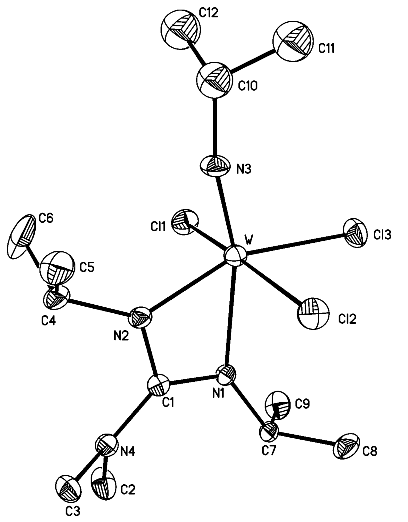

Figure 1. Thermal ellipsoid diagram of the molecular structure of **3**. Thermal ellipsoids are drawn at 40% probability, and the hydrogens have been omitted for clarity.

Table 2. Selected Bond Distances (Å) and Angles (deg) for Compound **3**

W−N1	2.247(4)	N1−W−N3	163.23(18)
W−N2	1.961(4)	N2−W−Cl3	155.81(13)
W−N3	1.702(4)	Cl1−W−Cl2	167.30(5)
W−Cl1	2.3752(15)	N2−W−N3	101.44(19)
W−Cl2	2.3819(16)	N1−W−N2	61.88(16)
W−Cl3	2.3833(14)	W−N1−C1	90.3(3)
C1−N2	1.399(6)	N1−C1−N2	107.8(4)
C1−N1	1.294(6)	W−N2−C1	100.0(3)
C1−N4	1.373(6)	W−N3−C10	168.4(8)

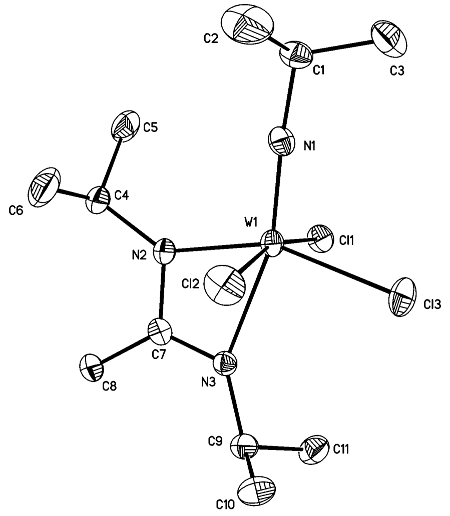

Figure 2. Thermal ellipsoid diagram of the molecular structure of **9**. Thermal ellipsoids are drawn at 40% probability, and the hydrogens have been omitted for clarity.

Table 3. Selected Bond Distances (Å) and Angles (deg) for Compound **9**

W−N1	1.720(3)	N1−W−N3	103.16(14)
W−N2	1.966(3)	N2−W−Cl3	154.12(9)
W−N3	2.290(3)	Cl1−W−Cl2	166.01(4)
W−Cl1	2.3750(9)	N2−W−N3	60.95(12)
W−Cl2	2.3754(11)	N1−W−N2	103.16(14)
W−Cl3	2.3679(10)	W−N2−C7	100.9(2)
C7−N2	1.407(5)	N2−C7−N3	108.0(3)
C7−N3	1.281(5)	W−N3−C7	90.1(2)
C7−C8	1.488(5)	W−N1−C1	174.0(3)

length of the latter is consistent with the strong trans influence of the imido ligand.[48] The C(1)−N(4), C(1)−N(1), and C(1)−N(2) bond distances in the guanidinate ligand are 1.373(6), 1.294(6), and 1.399(6) Å, respectively. All of these bond distances are roughly in the range for C(sp^2)−N(sp^2) bonds (ca. 1.36 Å).[49] This is an indication of lone pair donation from N(4) to C(1) and concomitant electron delocalization involving all three nitrogens of the chelating ligand. A sum of 357.6° for the three bond angles about N(4) is consistent with the sp^2 hybridization necessary for conjugation, although the torsional angle of 45.0° between the dimethylamido group and the chelating N−C−N core of the guanidinate ligand suggests that this interaction is somewhat limited. A list of selected bond lengths and angles for **3** is given in Table 2.

The structure of amidinate complex **9** (Figure 2) shows similarities to that of guanidinate complex **3**. The structure of **9** also exhibits a distorted octahedral geometry at tungsten. The W−N(1) bond length of 1.720(3) Å and the W−N(1)−C(1) bond angle of 174.0(3) suggest the presence of a W−N triple bond. The W−Cl bonds are on the order of 2.37 Å, as expected. A key difference between the structures of **3** and **9** can be noted in the bonding within the chelating ligand. The C(7)−N(3) bond length of **9** is 1.281(5) Å, somewhat shorter than the analogous C(1)−N(1) bond in **3**. The C(7)−N(2) bond length in **9**, however, is 1.407(5) Å, longer than the analogous C(1)−N(2) bond in **3**. This suggests that there is less electron delocalization between the chelating nitrogens in amidinate complex **9** than there is in guanidinate complex **3**. The W−N bond lengths for both ends of the chelating ligand in **3** are shorter than those in **9** (1.961(4) and 2.247(4) Å vs 1.966(3) and 2.290(3) Å, respectively) and the amidinate ligand of **9** is more unsymmetrically bound, revealing subtle but significant electronic differences between bonding in the guanidinate and amidinate ligands in a system where the steric differences at the metal center have been minimized. A list of selected bond lengths and angles for **9** appears in Table 3.

The thermal behavior of complex **3** was investigated as a representative case in conjunction with screening complexes **1**−**10** as precursors for MOCVD of WN$_x$. Sublimation of complex **3** was observed at 80 °C and 0.02 Torr, demonstrating its volatility. TGA experiments run with a heating rate of 10 °C/min from 25 to 900 °C resulted in a residual mass of 43% which was constant above 400 °C (Figure 3a). Examination of the derivative plot (not shown) reveals an inflection point corresponding to the onset of a decomposition process around 237 °C. A second inflection point appears at 315 °C and 49% residual weight, after which additional weight loss is slow. Isothermal studies of **3** at 120 °C for 180 min are depicted in Figure 3b. The thermal behavior of **3** strongly resembles that of the tantalum guanidinato complexes $[\mathrm{Ta(NR_1R_2)}\{{}^{i}\mathrm{PrNC(NR_1R_2)N}\text{-}{}^{i}\mathrm{Pr}\}_2(\mathrm{N}\text{-}{}^{t}\mathrm{Bu})]$ (R$_1$,

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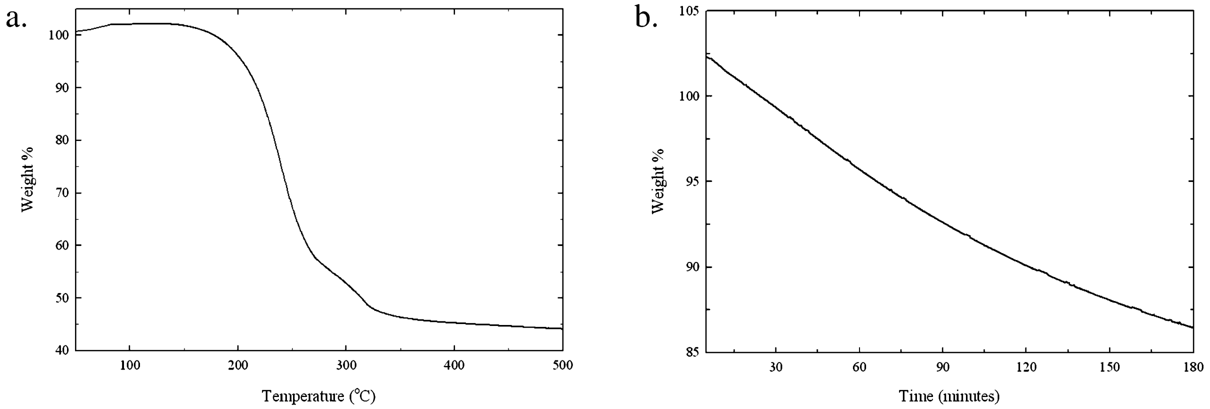

Figure 3. (a) TGA curve of compound **3** recorded at a heating rate of 10 °C/min under nitrogen. (b) Isothermal study of compound **3** at 120 °C under nitrogen.

R_2 = methyl, ethyl), which have been demonstrated to be CVD precursors to TaN.[41]

Conclusions

In conclusion, we have prepared the tungsten imido guanidinate and amidinate complexes W(NR)Cl$_3$[R′NC(NMe$_2$)NR′] and W(NR)Cl$_3$[R′NC(Me)NR′] (R = Ph, ^{i}Pr, Cy; R′ = ^{i}Pr, ^{t}Bu, TMS) (**1**−**10**) by reaction of the corresponding imido complexes W(NR)Cl$_4$(OEt$_2$) with the appropriate lithium amidinate or guanidinate. The crystallographic structure determination of W(N^{i}Pr)Cl$_3$[^{i}PrNC(NMe$_2$)N^{i}Pr] and W(N^{i}Pr)Cl$_3$[^{i}PrNC(Me)N^{i}Pr] allows comparison of structural features between the guanidinate and amidinate ligand in the presence of an identical ancillary ligand set. Complexes **1**−**10** are derivatives of the series of Cl$_4$(RCN)W(N^{i}Pr), Cl$_4$(RCN)W(NPh), and Cl$_4$(RCN)W(NC$_3$H$_5$) compounds we have previously used for CVD of WN$_x$ and WN$_x$C$_y$. The success of those experiments and the growing use of amidinate and guanidinate ligands in CVD and ALD precursors suggests deposition of WN$_x$ and WN$_x$C$_y$ from **1**−**10** should also be possible. CVD and ALD experiments with selected precursors from the series of complexes **1**−**10** are underway.

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Supporting Information Available: Tables of bond distances, bond angles, positional parameters, and anisotropic displacement parameters for **3** and **9** and crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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