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Reactions of Tungsten(VI) Dialkyl Complexes with ^{t}BuNC: Synthesis and Characterization of New Square Pyramidal and Trigonal Bipyramidal Tungsten(VI) Complexes

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The complexes [(TMS)$_2$pda](NPh)WR$_2$ ((TMS)$_2$pda = *o*-(Me$_3$SiN)$_2$C$_6$H$_4$}$^{2-}$; R = CH$_3$ (**1**), CH$_2$CMe$_3$ (**4**)) react with ^{t}BuNC to form the octahedral monoadducts [(TMS)$_2$pda](NPh)WR$_2$(CN^{t}Bu) (**1a** and **4a**). **1a** is observed only at low temperature, while **4a** can be isolated. Both **1a** and **4a** react with ^{t}BuNC to form the corresponding trigonal bipyramidal bis(η^2-imino-acyl) species [(TMS)$_2$pda](NPh)W[η^2-(^{t}Bu)NCR]$_2$ (R = CH$_3$ (**2**), CH$_2$CMe$_3$ (**5**)), which have been isolated and characterized. Compound **2** isomerizes upon heating to the square pyramidal metallacycle [(TMS)$_2$pda](NPh)W[(^{t}Bu)NC(CH$_3$)=C(CH$_3$)N(^{t}Bu)] (**3**), which has been isolated as a red solid. X-ray crystal structures have been obtained for compounds **2** and **3**. Crystals of **2** are orthorhombic, space group $P2_12_12_1$, with a = 9.1175(3) Å, b = 17.9587(5) Å, c = 20.9435(6) Å, and Z = 4. Compound **2** has trigonal bipyramidal geometry with the imido N and one amido N in axial positions. Crystals of **3** are monoclinic, space group $C2/c$, with a = 35.1302(9) Å, b = 12.6459(2) Å, c = 16.2386(6) Å, β = 112.021(3)°, and Z = 8. **3** has distorted square pyramidal geometry with the imido moiety in the apical position.

Introduction

Recent work in our group has focused on the use of the chelating disubstituted phenylenediamide group {*o*-(Me$_3$SiN)$_2$C$_6$H$_4$}$^{2-}$ [(TMS)$_2$pda] as an ancillary ligand for high-oxidation-state metal centers such as W(VI) and Mo(VI).[1,2] The facile, high yield synthesis of several W(VI) dialkyl complexes of formula [(TMS)$_2$pda](NPh)WR$_2$[2] has provided us with the opportunity to investigate the chemistry of these d^0 dialkyl compounds. Until now, our efforts have been concentrated on the conversion of bulky, β-H-free dialkyls into alkylidene complexes and the subsequent use of the alkylidenes as olefin metathesis catalysts. We now report the reactivities of the dimethyl and dineopentyl complexes with isocyanides.

The reaction of alkyl isocyanides (RNC) with coordinatively unsaturated, electrophilic early transition metal alkyls typically results in the insertion of the isocyanide moiety into the metal−alkyl bond, frequently forming η^2-imino-acyl ligands.[3,4] These reactions are closely related to the reactions of CO with alkyl complexes that lead to the formation of metal acyls.[5,6] In the case of electrophilic metal centers like W, Mo, and Ta, the acyl functionality often adopts an η^2 structure involving coordination through both the carbon and oxygen atoms. The structure, spectroscopic properties, and reactivities of these η^2-acyls have been widely reported.[5,6] They are proposed to possess a significant amount of oxycarbene character,[3ef,7] supported by their ability to undergo both intra- and intermolecular coupling to make enediolates.[4a,7b,8] We report here the syntheses, characterizations, and X-ray crystal structures of several W(VI) η^2-imino-acyl complexes and the subsequent formation of diamide ligands through C−C coupling reactions of the η^2-imino-acyl groups.

Results and Discussion

Reaction of [(TMS)$_2$pda](NPh)W(CH$_3$)$_2$ (1) with ^{t}BuNC. When 2 equiv of ^{t}BuNC is added to a solution of **1**, the golden-brown mixture immediately turns

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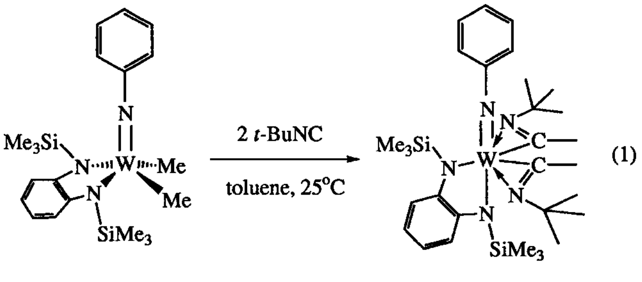
Table 1. ^{1}H NMR Data

compound	δ, ppm	mult	J, Hz	int	assnmt
W(NPh)[(TMS)$_2$pda](CH$_3$)$_2$ (CN^{t}Bu) (**1a**) at −60 °C in C$_7$D$_8$	0.56	s		9	−SiMe$_3$
	0.62	s		9	−CNC*Me*$_3$
	0.64	s		9	−SiMe$_3$
	0.81	br s			^{t}BuNC
	1.38	s		6	−CH$_3$
	6.60−7.50				aromatic
W(NPh)[(TMS)$_2$pda][η^2-(^{t}Bu) NCCH$_3$]$_2$ (**2**) in C$_6$D$_6$	0.15	s		9	−SiMe$_3$
	0.69	s		9	−SiMe$_3$
	1.21	s		18	−CMe$_3$
	2.69	s		6	−CH$_3$
	6.60−7.40			9	aromatic
W[N(^{t}Bu)C(CH$_3$)=C(CH$_3$)N(^{t}Bu)] [(TMS)$_2$pda](NPh) (**3**) in C$_6$D$_6$	0.45	s		18	−SiMe$_3$
	1.26	s		18	−CMe$_3$
	1.53	s		6	−CH$_3$
	6.74	m		2	aromatic
	6.79	t		1	*p*-H
	6.87	m		2	aromatic
	7.14	t		2	*m*-H
	7.40	t		2	*o*-H
W(NPh)[(TMS)$_2$pda](CH$_2$CMe$_3$)$_2$ (CN^{t}Bu) (**4a**) in C$_6$D$_6$	0.68	s		18	−SiMe$_3$
	0.76	s		9	−CNCMe$_3$
	1.15	s		18	−CMe$_3$
	1.84	d	12.6	2	−C*H*$_2$CMe$_3$
	2.73	d	12.6	2	−C*H*$_2$CMe$_3$
	6.75−7.70			9	aromatic
spectrum taken at −40 °C in C$_7$D$_8$	0.68	s		9	−CNCMe$_3$
	0.70	s		9	−SiMe$_3$
	0.73	s		9	−SiMe$_3$
	1.17	s		18	−CMe$_3$
	1.78	d	12.6	2	−C*H*$_2$CMe$_3$
	2.78	d	12.6	2	−C*H*$_2$CMe$_3$
	6.7−7.7			9	aromatic
W(NPh)[(TMS)$_2$pda][η^2-(^{t}Bu) NCCH$_2$CMe$_3$]$_2$ (**5**) in C$_6$D$_6$	0.27	s		9	−SiMe$_3$
	0.65	s		9	−SiMe$_3$
	1.06	s		18	−CMe$_3$
	1.43	s		18	−NCMe$_3$
	3.31	d	12.9	2	−C*H*$_2$CMe$_3$
	3.82	d	12.9	2	−C*H*$_2$CMe$_3$
	6.60−7.40			9	aromatic



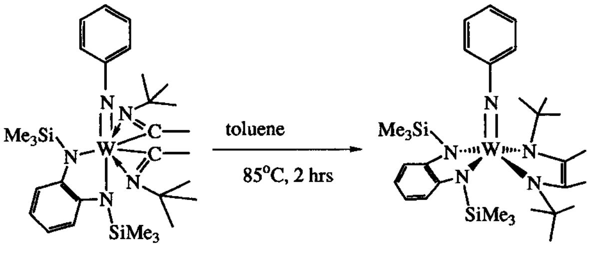
(1)

1 **2**

black. Concentration and cooling of this solution afford a black solid, **2**, which is extremely soluble in hydrocarbon solvents and ethers (eq 1). Compound **2** is air- and moisture-sensitive but is indefinitely stable in the solid state under an inert atmosphere. The ^{1}H NMR spectrum of **2** in C$_6$D$_6$ (Table 1) reveals peaks at 0.15 ppm (9H) and 0.69 ppm (9H), identified as inequivalent trimethylsilyl groups. A singlet at 1.21 ppm (18H) is assigned to equivalent *tert*-butyl groups, shifted downfield from free ^{t}BuNC (0.94 ppm). A singlet at 2.69 ppm (6 H) is identified as two equivalent methyl groups, while overlapping multiplets in the aromatic region integrate to a total of 9 protons.

The ^{13}C NMR spectrum in C$_6$D$_6$ (see Table 2) displays inequivalent TMS groups and equivalent *tert*-butyl and methyl groups. Additionally, a single peak at 210.48 ppm is consistent with the presence of an η^2-imino-acyl moiety.[6] The NMR data for compound **2** indicate that it is the trigonal bipyramidal bis(η^2-imino-acyl) complex [(TMS)$_2$pda](NPh)W[η^2-(^{t}Bu)NC(CH$_3$)]$_2$, in which one (TMS)$_2$pda nitrogen and the imido N occupy axial positions. This formulation has been confirmed by the solid state structure of **2**, as will be discussed below.

If left at room temperature for a period of weeks, a solution of **2** begins to take on a red color. Heating **2** to 80 °C for 24 h hastens the conversion of **2** to a new complex, **3**, which can be isolated as a deep red, air- and moisture-sensitive, crystalline solid (eq 2). Compound



(2)

2 **3**

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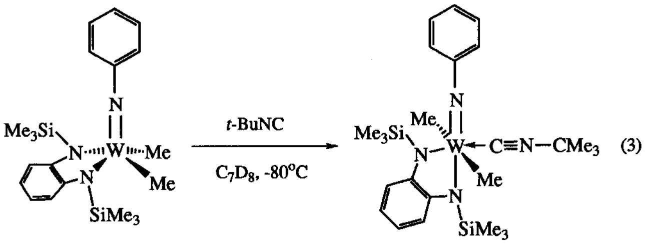
Table 2. ^{13}C NMR Data

compound	δ, ppm	mult	J, Hz	int	assnmt
W(NPh)[(TMS)$_2$pda][η^2-(^{t}Bu)NCCH$_3$]$_2$ (**2**) in C$_6$D$_6$	4.12	s			$-SiMe_3$
	5.25	s			$-SiMe_3$
	21.84	s			$-CMe_3$
	29.54	s			$-C\mathit{Me}_3$
	60.22	s			$-CH_3$
	116.09	s			aromatic
	116.27	s			
	117.71	s			
	117.79	s			
	124.35	s			
	125.24	s			
	150.26	s			
	152.88	s			
	156.21	s			
	210.48	s			(^{t}Bu)N*C*Me
W[N(^{t}Bu)C(CH$_3$)C(CH$_3$)N(^{t}Bu)][(TMS)$_2$pda](NPh) (**3**) in C$_6$D$_6$	3.39	s			$-SiMe_3$
	16.28	s			$C{=}C{-}\mathit{C}H_3$
	31.69	s			$-CMe_3$
	59.91	s			$-\mathit{C}Me_3$
	118.77	s			aromatic
	118.93	s			
	119.78	s			
	125.96	s			$C{=}C$
	128.47	s			aromatic
	128.60	s			
	148.97	s			
	157.14	s			
W(NPh)[(TMS)$_2$pda][η^2-(^{t}Bu)NCCH$_2$CMe$_3$]$_2$ (**5**) in C$_6$D$_6$	4.64	s			$-SiMe_3$
	6.41	s			$-SiMe_3$
	30.97	s			CH$_2$C*Me*$_3$
	31.84	s			NC*Me*$_3$
	32.96	s			CH$_2$*C*Me$_3$
	47.02	s			*C*H$_2$CMe$_3$
	62.95	s			N*C*Me$_3$
	115.95	s			aromatic
	116.54	s			
	118.32	s			
	118.82	s			
	125.53	s			
	150.36	s			
	152.84	s			
	155.50	s			
	213.28	s			$-$N*C*CH$_2-$

3 is extremely soluble in both hydrocarbon solvents and a variety of ethers and is indefinitely stable both in solid form and in solution at room temperature. The ^1H NMR spectrum of **3** in C_6D_6 displays a singlet at 0.45 ppm (18H), attributed to equivalent TMS groups, and a singlet at 1.26 ppm (18H) which is assigned to equivalent *tert*-butyl groups. An additional singlet at 1.53 ppm (6H) is assigned to equivalent methyl groups. The ^{13}C-$\{^1H\}$ NMR spectrum displays peaks assigned to the equivalent TMS, *tert*-butyl, and methyl groups and a singlet at 125.96 ppm that corresponds to the carbons of a C$-$C double bond. The NMR spectra of **3** are consistent with square pyramidal geometry about the W atom. The presence of the C$-$C double bond suggests that **3** is a metallacycle of formula [(TMS)$_2$pda](NPh)W-[(^{t}Bu)NC(CH$_3$)=C(CH$_3$)N(^{t}Bu)], with the imido moiety in the apical position (eq 2). This structural assignment has been confirmed by the crystal structure of **3**.

The fact that **1** is both electronically and coordinatively unsaturated suggests that the mono(isocyanide) adduct of **1** might be observable prior to insertion. This adduct is not observed at ambient temperature; the addition of 1 equiv of ^{t}BuNC to a solution of **1** in C_6D_6 at room temperature produces a clean 1:1 mixture of starting material (**1**) and the bis(η^2-imino-acyl) (**2**). When a sample of **1** and ^{t}BuNC was prepared and analyzed at -70 °C, the red monoadduct (**1a**) was indeed observed to form before insertion occurred. As for [(TMS)$_2$pda](NPh)WCl$_2$(L) (L = PMe$_3$, THF, 3-picoline, ^{t}BuNC, CH$_3$CN) and the PMe$_3$ adduct of **1**,[2] we expected the isocyanide to coordinate in the vacant site *trans* to the imido moiety and *cis* to the methyl groups. However, coordination *trans* to the imido group is not observed. Instead, the ^1H NMR of **1a** at -60°C in C_7D_8 reveals two TMS peaks at 0.56 ppm (9H) and 0.64 ppm (9H). The coordinated isocyanide appears at 0.62 ppm (9H), while free isocyanide appears at 0.81 ppm. Equivalent methyl groups appear as a singlet at 1.38 ppm (6H). These data reveal that complex **1a** has a pseudooctahedral structure with *trans* CH_3 groups, as shown in eq 3.



1

1a

There are three possible explanations for this somewhat surprising result. One possibility arises from the fact that even though the vacant coordination site on **1** is *trans* to the imido group, the LUMO of the complex is most likely the d_{xy} orbital (the W=N bond axis being defined as the *z* axis of the molecule).[12] This being the case, a Lewis base might be expected to attack the molecule at the LUMO and could generate the observed adduct directly. A second possibility is that the initial adduct that is formed has the isocyanide ligand coordinated *trans* to the imido group, but this rapidly rearranges to the observed product. A third possibility might be that **1** exists in solution as a rapidly equilibrating mixture of square pyramidal and trigonal bipyramidal isomers at all temperatures that have been probed via ^1H NMR (-80 to $+25$ °C). Assuming a trigonal bipyramidal structure akin to the observed structure of [(TMS)$_2$pda](NPh)W(CH$_2$CMe$_3$)$_2$ which has the alkyl groups in the equatorial positions, preferential coordination between the alkyl groups would then generate the observed product.

Reaction of [(TMS)$_2$pda](NPh)W(CH$_2$CMe$_3$)$_2$ (4) with ^{t}BuNC. When excess ^{t}BuNC is added to a golden-brown solution of **4**, the color of the solution changes to bright red. Concentration and cooling of this solution yield an air- and moisture-sensitive orange-red solid (**4a**) which is soluble in hydrocarbon solvents and diethyl ether and is only slightly soluble in diisopropyl ether

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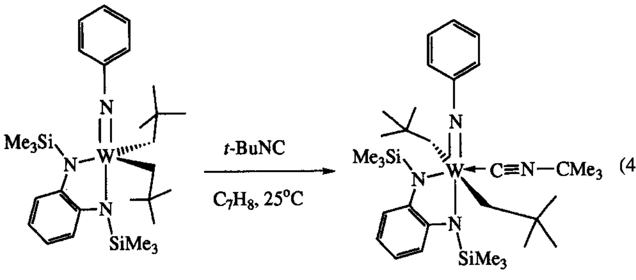
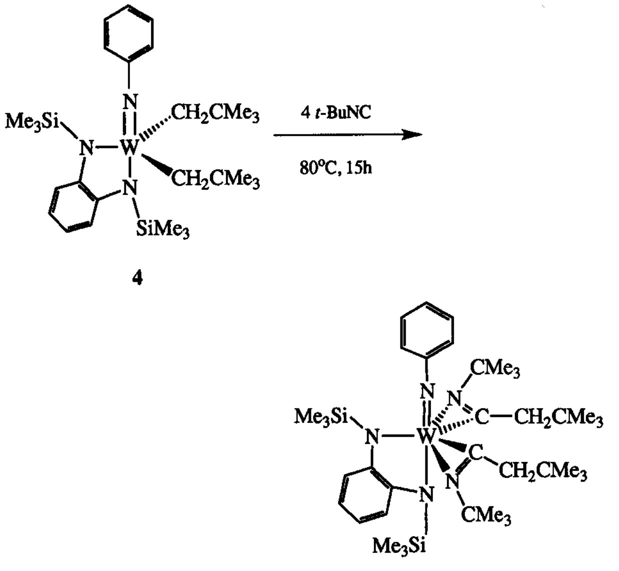
(eq 4). Complex **4a** begins to decompose to insoluble, unidentified products after only a few hours in solution at room temperature, which prevented the acquisition of ^{13}C NMR data for this compound. When stored in solid form under an inert atmosphere at room temperature, complex **4a** displays considerable decomposition after approximately 2 weeks.



4 **4a** (4)

The ^{1}H NMR spectrum of **4a** at room temperature shows a singlet at 0.68 ppm (18H), assigned to equivalent TMS groups. Another singlet at 0.76 ppm (9H) is attributed to 1 equiv of coordinated isocyanide. A peak at 1.15 ppm (18H) is assigned to equivalent *tert*-butyl groups on the neopentyl ligands. Two doublets at 1.84 ppm (2H) and 2.73 ppm (2H) ($J_{\mathrm{C-H}}$ = 12.6 Hz) are identified as the methylene protons on the α-carbons of the neopentyl groups. These data indicate that **4a** is the isocyanide adduct of the dineopentyl complex but do not uniquely identify the structure of the adduct. Low-temperature (−40 °C) ^{1}H NMR studies of **4a** display inequivalent TMS peaks, each integrating to 9 protons, which coalesce to a single peak at 13 °C. The two-site exchange approximation[11] allows us to estimate that $\Delta G^{\ddagger}$ for this process is 15.2 kcal/mol. These low-temperature NMR studies show that, like the mono(isocyanide) adduct of the dimethyl species, complex **4a** has a pseudooctahedral structure with the alkyl groups *trans* to one another. At this time, we do not know whether the fluxional process is an intramolecular rearrangement or involves dissociation of the ^{t}BuNC ligand.

Unlike **1**, the dineopentyl species, **4**, has trigonal bipyramidal geometry about the W atom in the solid state.[2] In solution at room temperature, however, only one TMS peak is observed in its ^{1}H NMR spectrum. At low temperature, the ^{1}H NMR spectrum of **4** displays two Me$_3$Si resonances, consistent with the solid state structure. It is likely that coordination of ^{t}BuNC to **4** occurs between the neopentyl groups (at the site of the LUMO) of the trigonal bipyramidal complex, giving the observed six-coordinate adduct, **4a**.



4 **5** (5)

When heated to 70 °C for 18 h with 4 equiv of ^{t}BuNC, the brownish-orange solution becomes emerald green. Upon concentration and cooling, a green solid, **5** (eq 5), can be isolated, which is soluble in hydrocarbon solvents and ethers and can be stored indefinitely under an inert atmosphere. The ^{1}H NMR spectrum of **5** in C$_6$D$_6$ shows two inequivalent TMS peaks at 0.27 ppm (9H) and 0.65 ppm (9H), a *tert*-butyl methyl peak from the neopentyl groups at 1.06 ppm (18H), and a *tert*-butyl peak from the isocyanide at 1.43 ppm (18H). The two doublets from the methylene protons on the neopentyl groups split farther apart and move downfield (Table 1). The ^{13}C NMR spectrum reveals one imino-acyl carbon resonance at 213.28 ppm. From these data, we have identified compound **5** as the trigonal bipyramidal bis(imino-acyl) insertion product of the dineopentyl complex, [(TMS)$_2$pda](NPh)W[η^2-(^{t}Bu)NCCH$_2$CMe$_3$]$_2$, analogous to complex **2**. Like complex **2**, compound **5** is expected to have η^2 coordination for each imino-acyl group, both groups being in the N-out position.

The formation of **5** from **4** requires the presence of excess ^{t}BuNC to give a clean product. When the reaction between **4** and 2 equiv of ^{t}BuNC was monitored by ^{1}H NMR spectroscopy at 25 °C, the initial formation of **4a** was observed, followed by incomplete conversion to a new species that we tentatively assign as the mono(imino-acyl)−mononeopentyl complex **6**.[7a] After the mixture is heated to 80 °C for 24 h, a complex mixture that contains unreacted starting material as well as compounds **5** and **6**, and other unidentified materials is formed. These data suggest that it is likely that the formation of **5** occurs in a stepwise fashion and that the presence of excess ^{t}BuNC is necessary to prevent other unidentified modes of reaction from occurring. Continued thermolysis of **5** does not result in isomerization to a metallacyclic diamide structure that would be analogous to **3**. It is possible that the further coupling of the imino-acyl groups is prevented by the steric bulk of the neopentyl groups.

The generation of the enediamidate ligand in compound **3** is similar the reactions of other early transition metal alkyls with isocyanides or CO. Migratory insertion reactions involving formation of bis(acyl) or bis(imino-acyl) ligands are well-known.[3e,6] Additionally, several examples of acyl−acyl and acyl−imino-acyl coupling to form metallacycles have been reported,[5c,9b,10] for example, the reaction of CO and (η^5-C$_5$Me$_5$)$_2$Zr(CH$_3$)$_2$ to produce the bis(acyl), which isomerizes to the enediolate complex Cp*$_2$Zr[O(CH$_3$)C=C(CH$_3$)O].[4a] Similar reactions have been reported for Cp*$_2$AnR$_2$ and CO (An = actinide).[4b]

Structural Studies. Single-crystal X-ray diffraction studies were performed on compounds **2** and **3**. The crystal structure of complex **1** was reported previously,[2] and that structure will be referenced for comparison. Thermal ellipsoid plots of complexes **2** and **3** are found in Figures 1 and 2, respectively, while selected bond

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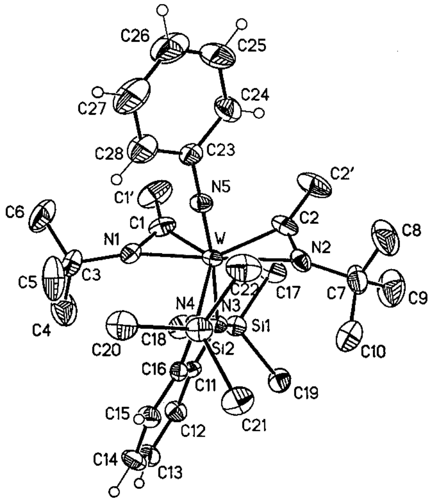

Figure 1. Thermal ellipsoid plot of **2**.

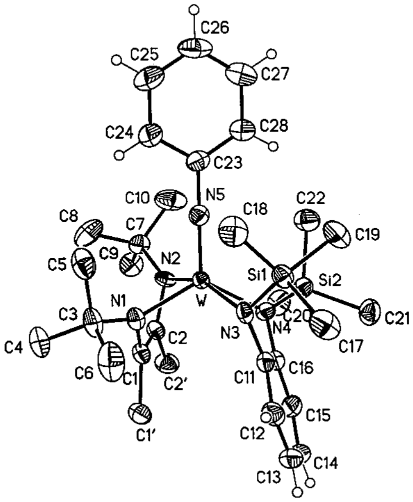

Figure 2. Thermal ellipsoid plot of **3**.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 2

1	2	3	1−2	1−2−3
N1	W	N2	2.157(3)	162.14(11)
N1	W	N3		82.88(11)
N1	W	N4		94.30(11)
N1	W	N5		92.45(12)
C1	W	N1	2.112(4)	34.47(13)
C1	W	C2		96.7(2)
C2	W	N1	2.110(4)	131.12(14)
N2	W	N3	2.149(3)	87.17(11)
N2	W	N4		98.03(11)
N2	W	N5		98.05(12)
N2	W	C1		129.81(13)
N2	W	C2		34.55(14)
N3	W	N4	2.179(3)	77.66(10)
N3	W	N5		174.57(12)
N3	W	C1		84.28(12)
N3	W	C2		93.01(12)
N4	W	N5	2.101(3)	100.01(11)
N4	W	C1		127.74(13)
N4	W	C2		132.50(13)
N5	W	C1	1.773(3)	93.46(13)
N5	W	C2		92.15(13)

lengths and angles are found in Tables 3 and 4. Abbreviated crystal data for both **2** and **3** are listed in Table 5.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for 3

1	2	3	1−2	1−2−3
N1	W	N2	1.957(3)	81.77(12)
N1	W	N3		91.09(12)
N1	W	N4		125.22(11)
N1	W	N5		112.97(13)
C1	W	N1	2.482(3)	34.01(11)
C1	W	C2		32.56(11)
C2	W	N1	2.531(3)	62.12(11)
N2	W	N3	2.025(3)	157.89(11)
N2	W	N4		89.55(12)
N2	W	N5		103.08(12)
N2	W	C1		62.26(11)
N2	W	C2		33.10(11)
N3	W	N4	2.117(3)	77.48(11)
N3	W	N5		98.97(12)
N3	W	C1		100.75(11)
N3	W	C2		125.87(11)
N4	W	N5	2.051(3)	121.67(12)
N4	W	C1		95.28(11)
N4	W	C2		81.90(11)
N5	W	C1	1.749(3)	141.09(13)
N5	W	C2		134.01(12)

Table 5. Crystallographic Data[a]

	2	3
A. Crystal Data (173 K)		
a, Å	9.1175(3)	35.1302(9)
b, Å	17.9587(5)	12.6459(2)
c, Å	20.9435(6)	16.2386(6)
β, deg	90.0	112.021(3)
V, Å^3	3451.8(2)	6687.8(3)
d_{calc}, g cm^{-3}	1.389	1.434
empirical formula	$C_{30}H_{51}N_5Si_2W$	$C_{30}H_{51}N_5Si_2W$
fw	721.79	721.79
cryst syst	orthorhombic	monoclinic
space group	$P2_12_12_1$	$C2/c$
Z	4	8
F(000), electrons	1472	2944
B. Structure Refinement		
refinement method	full-matrix least-squares on F^2	
S, goodness-of-fit	1.081	1.035
R_1/reflns	1.99/6592 > $2\sigma(I)$	2.66/5226 > $2\sigma(I)$
wR_2/reflns	4.81/6711	6.16/5744
R_{int}, %	3.61	3.76

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. w$R_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$. $S = [\sum[w(F_o^2 - F_c^2)^2]/(n - p)]^{1/2}$. $w = 1/[\sigma^2(F_o^2) + (0.0370p)^2 + 0.31p]$; $p = [\max(F_o^2,0) + 2F_c^2]/3$.

Some general comments about these structures are warranted. Both compounds have short W−N(imido) bond lengths (1.773(3) and 1.749(3) Å, respectively) and W−N−Ph angles (174.7(3) and 175.2(2)°, respectively) that are close to linear, as is consistent with the presence of W−N triple bonds.[12] Regardless of geometry, the phenylenediamide ligand retains a N−W−N angle of under 80°. Each of these angles (77.66° for **2** and 77.48° for **3**) reflects a decrease from that of the dimethyl complex (82.55°) possibly due to the increased steric congestion around the metal center.

Solid State Structure of 2. Complex **2** has trigonal bipyramidal geometry about the W center with both imino-acyls in the equatorial plane. The phenylenediamido ligand adopts an axial−equatorial coordination with one N *trans* to the imido moiety. A substantial *trans* influence is observed when the two amido W−N bond lengths are compared; the equatorial W−N bond is 2.101(3) Å, while the axial W−N bond (*trans* to the imido moiety) is longer, 2.179(3) Å. The solid state structure of **2** confirms η^2 coordination for both imino-acyl ligands. Both C−N distances are 1.265(5) Å, well within the range for the C−N double bond of a coordinated imino-acyl.[3] Additionally, the W−C1, W−C2, W−N1, and W−N2 bond lengths of the imino-acyls are consistent with reported bond lengths for η^2-imino-acyls

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on early transition metal centers.[7a,b,3] The W−C−N angles for each imino-acyl (74.7(2)° for N1−C1−W and 74.4(2)° for N2−C2−W) are also similar to published data.[3] Both imino-acyls bond in an N-out fashion with their bulky *tert*-butyl groups directed away from the metal center. This geometry is perfectly disposed to allow coupling of the imino-acyl carbon atoms to occur to generate the new diamido ligand in **3**.

Solid State Structure of 3. The structure of compound **3** reveals that the imino-acyl carbon atoms of **2** have coupled to generate a new enediamidate ligand. The compound has a distorted square pyramidal geometry about the metal center with the phenylimido moiety in the apical position. All four amido N's are in the equatorial plane. Although there is no crystallographic plane of symmetry that equates the ends of the amido groups, the librational motion of the bis(amido) chelate ligands about a plane of symmetry containing the phenylimido ligand and bisecting the N1−W−N2 and N3−W−N4 angles results in the equivalence of the ^{t}Bu and $SiMe_3$ groups in the ambient-temperature ^{1}H NMR spectrum of **3**. The distorted square pyramidal structure is similar to that of (NPh)W(NMe_2)$_4$,[13] which adopts an intermediate structure between a square pyramid and a trigonal bipyramid at low temperature which also equilibrates in solution at room temperature.

The bond lengths within the ^{t}Bu−NC(Me)C(Me)N−^{t}Bu ligand are consistent with this group being a bis(amido) ligand and not a diazabutadiene ligand. The N1−C1 and N2−C2 bond lengths are 1.392 and 1.386 Å, respectively, and are considerably longer than the related N−C bond lengths that are found in diazabutadiene ligands of *ca*. 1.27−1.30 Å.[14] Additionally, the C1−C2 bond distance (1.406(5) Å) in compound **3** is shorter than the corresponding bond lengths found in diazabutadiene complexes (*ca*. 1.44−1.46 Å), as is more consistent with a C−C double bond.[14] Thus, the structural details of **3** are consistent with a W(VI) bis(amide) complex and not a W(IV) diazabutadiene complex as might be expected given the relative stability of W(VI). It is likely that the bulk of the bis(amide) ligands in **3** causes the observed twisting of the both the newly formed metallacycle (W−N1−C1 = 94.2(2)°) and $(TMS)_2$pda (W−N3−C11 = 104.2(2)°) from the equatorial plane to accommodate the steric bulk of the *tert*-butyl and trimethylsilyl groups, respectively.

Summary and Conclusions

From our work with these dialkyl complexes and ^{t}BuNC, we have seen that complexes which contain bulky alkyl groups (compound **4**) undergo rapid interconversion between square pyramidal and trigonal bipyramidal isomers.[2] The dominant geometry is dictated by the steric bulk of the alkyl groups. In the case of bulky alkyl groups, isocyanide may react preferentially with the trigonal bipyramidal isomer, producing an octahedral adduct with one N atom of the $(TMS)_2$pda ligand occupying a position *trans* to the imido ligand. The NMR properties of the less sterically hindered dimethyl complex, **1**, do not allow us to assess whether it undergoes a fluxional process similar to that of **4**. However, there is no doubt that the same adduct isomer forms when either **4** or **1** interacts with ^{t}BuNC. The isocyanide adducts react with additional isocyanide to generate new trigonal bipyramidal bis(η^2-imino-acyl) complexes. Coupling of the imino-acyl ligands is possible, if the size of the carbon substituents permit, giving an enediamidate ligand. Further studies are underway to identify why the trigonal bipyramidal geometry appears to produce greater reactivity and to study how more hindered dialkyls such as metallacycles interact with isocyanide.

Experimental Section

Materials and Methods. All syntheses were carried out under dry argon atmospheres using standard Schlenk techniques. $[(TMS)_2pda](NPh)WMe_2$ (**1**) and $[(TMS)_2pda](NPh)W(CH_2CMe_3)_2$ (**4**) were synthesized according to published procedures.[2] ^{t}BuNC was purchased from Aldrich and used as received. Diethyl ether (Et_2O) and diisopropyl ether ($^iPr_2O$) were distilled from sodium benzophenone ketyl. Pentane, hexanes, and toluene were distilled from sodium. NMR solvents were stored over molecular sieves and degassed prior to use. NMR spectra were acquired on either a General Electric QE-300, a Gemini 300, or a Varian VXR-300 spectrometer. ^{1}H and ^{13}C chemical shifts are referenced to residual protons in deuterated solvents and are reported relative to TMS. Elemental analyses were performed by Atlantic Microlabs, Inc., Norcross, GA.

$[(TMS)_2pda](NPh)W[\eta^2\text{-}(^tBu)NCCH_3]_2$ (2). ^{t}BuNC (0.29 mL, 2.56 mmol) was added via syringe to a 15 mL pentane solution of $[(TMS)_2pda](NPh)W(CH_3)_2$ (705 mg, 1.27 mmol). The resulting black solution was stirred for 1 h at room temperature. Subsequent concentration and cooling to −78 °C for 1 h resulted in a black solid, which was isolated by filtration and dried under reduced pressure for 30 min. Crystals suitable for an X-ray diffraction study were grown from a concentrated diisopropyl ether solution at −20 °C over a period of 2 days. Yield: 662 mg (72%). Anal. Calcd for $C_{30}H_{51}N_5Si_2W$: C, 49.92; H, 7.14; N, 9.71. Found: C, 48.37; H, 7.01; N, 9.61.

$[(TMS)_2pda](NPh)W[(^tBu)NC(CH_3){=}C(CH_3)N(^tBu)]$ (3). A 10 mL toluene solution of **2** (620 mg, 0.859 mmol) in a round-bottom ampule was heated to 80 °C for 24 h. The resulting red solution was concentrated and cooled to −78 °C for 1 h. The resulting red solid was isolated by filtration and dried under reduced pressure for 1 h. Crystals of **3** suitable for an X-ray diffraction study were grown from a concentrated diisopropyl ether solution at −20 °C over a period of 2 days. Yield: 350 mg (56%). Anal. Calcd for $C_{30}H_{51}N_5Si_2W$: C, 49.92; H, 7.14; N, 9.71. Found: C, 48.49; H, 7.06; N, 9.69.

$[(TMS)_2pda](NPh)W(CH_2CMe_3)_2(CN^tBu)$ (4a). ^{t}BuNC (0.34 mL, 3.0 mmol) was added via syringe to a 10 mL diisopropyl ether solution of $[(TMS)_2pda](NPh)W(CH_2CMe_3)_2$ (495 mg, 0.74 mmol). The resulting orange-red solution was stirred for 10 min at room temperature. Concentration and cooling to −78 °C for 1 h produced an orange-red solid, which was isolated by filtration and dried under reduced pressure for 45 min. Yield: 430 mg (77%). Anal. Calcd for $C_{33}H_{58}N_4Si_2W$: C, 52.78; H, 7.80; N, 7.46. Found: C, 52.53; H, 7.85; N, 7.45.

$[(TMS)_2pda](NPh)W[\eta^2\text{-}(^tBu)NCCH_2CMe_3]_2$ (5). ^{t}BuNC (0.34 mL, 3.0 mmol) was added via syringe to a 15 mL diisopropyl ether solution of $[(TMS)_2pda](NPh)W(CH_2CMe_3)_2$ (500 mg, 0.75 mmol) in an ampule. The resulting solution was stirred for 24 h at 70°C, producing a green solution, which was allowed to cool to ambient temperature. Subsequent concentration and cooling to −78 °C for 1 h afforded a green solid, which was isolated by filtration and dried under reduced pressure for 1 h. Yield: 300 mg (48%). Anal. Calcd

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[13] Berg, D. M.; Sharp, P. R. *Inorg. Chem*. **1987**, *26*, 2959.
[14] van Koten, G.; Vrieze, K. *Adv. Organomet. Chem*. **1982**, *21*, 151.

for $C_{38}H_{67}N_5Si_2W$: C, 54.72; H, 8.11; N, 8.40. Found: C, 54.52; H, 8.06; N, 8.35.

X-ray Crystal Structures. Data for both compounds were collected at 173 K on a Siemens CCD SMART PLATFORM equipped with a CCD area detector and a graphite monochromator utilizing Mo Kα radiation ($\lambda = 0.710\,73$ Å). Cell parameters were refined using 8192 reflections from each data set. A hemisphere of data (1381 frames) was collected using the ω-scan method (0.3° frame width). 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 were applied using the psi scan data and the entire data set.

Both structures were solved by the direct methods in SHELXTL[15] and refined using full-matrix least-squares calculations on F^2. The non-H atoms were refined with anisotropic thermal parameters except for the disordered C atoms. All of the H atoms were included in the final cycle of refinement and were allowed to ride on the atoms to which they were bonded.

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Supporting Information Available: Tables of crystal data and structure refinement details, bond lengths and angles, and positional and thermal parameters (18 pages). Ordering information is given on any current masthead page.

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