

Synthesis, characterization, and X-ray crystal structures of W(VI) alkyl complexes with chelating diamide and imido co-ligands ¹

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Abstract

The complex $\text{W(NPh)Cl}_2[o\text{-(NSiMe}_3)_2\text{C}_6\text{H}_4]$ **3** was synthesized from $\text{PhN=WCl}_4 \cdot \text{OEt}_2$ and $\text{N,N'-(Li}_2[o\text{-(NSiMe}_3)_2\text{C}_6\text{H}_4])$ and reacts with Lewis bases to form the adducts $\text{W(NPh)Cl}_2[o\text{-(NSiMe}_3)_2\text{C}_6\text{H}_4](\text{L})$ ($\text{L} = \text{PMe}_3$, THF, 3-picoline, ^tBuNC, MeCN) **4a–e**. Crystals of **4a** are triclinic, space group $P\bar{1}$, with $a = 9.562(1)$, $b = 10.277(1)$, $c = 14.920(2)$ Å, $\alpha = 82.15(1)$, $\beta = 80.18(1)$, $\gamma = 80.41(1)^\circ$, and $Z = 2$. The structure was solved by the heavy atom method and refined to $R = 0.0408$ for 4224 observed ($I > 2\sigma(I)$) reflections. The dialkyl complexes $\text{W(NPh)R}_2[o\text{-(NSiMe}_3)_2\text{C}_6\text{H}_4]$ ($\text{R} = \text{Me}$, Et, CH_2Ph , CH_2CMe_3 , $\text{CH}_2\text{CMe}_2\text{Ph}$) **5–9** are formed through subsequent reactions of **3** with the corresponding Grignard reagent. Crystals of complex **5** are monoclinic, space group $P2(1)/n$, with $a = 10.3545(2)$, $b = 17.9669(1)$, $c = 13.3168(1)$ Å, $\beta = 103.826(1)^\circ$, and $Z = 4$. The structure of complex **5** was solved by direct methods in SHELXTL5 and refined to $R = 0.0247$ for 4572 observed reflections. Compound **5** has a square pyramidal geometry in which the imido ligand occupies the apical position and reacts with PMe_3 to form the adduct $\text{W(NPh)Me}_2[o\text{-(NSiMe}_3)_2\text{C}_6\text{H}_4](\text{PMe}_3)$ **5a**. Crystals of complex **5a** are monoclinic, space group $C2/m$, with $a = 13.5336(1)$, $b = 14.4291(1)$, $c = 15.3785(1)$ Å, $\beta = 110.365(1)^\circ$, and $Z = 4$. The structure of compound **5a** was solved by direct methods in SHELXTL5 and refined to $R = 0.0272$ for 3057 observed reflections. Crystals of the bis-neopentyl complex **8** are monoclinic, space group $P2(1)/n$, with $a = 10.6992(4)$, $b = 18.3144(7)$, $c = 16.0726(6)$ Å, $\beta = 92.042(1)^\circ$, and $Z = 4$. The structure of **8** was solved by direct methods in SHELXTL5 and refined to $R = 0.0261$ for 5881 observed reflections. Complex **8** has a trigonal bipyramidal geometry with both neopentyl groups and one amido nitrogen in the equatorial plane.

1. Introduction

We have been interested in the chemistry of high oxidation state W, Mo, and Ta alkylidene complexes that contain chelating co-ligands as stabilizing groups [1]. Our interest in these compounds originated in a desire to create more thermally stable olefin metathesis catalysts that were specifically designed for use in acyclic diene metathesis (ADMET) polymerization reactions [2]. We have begun the study of the bidentate dianionic amide ligand $\{o\text{-(Me}_3\text{Si)N}_2\text{C}_6\text{H}_4\}^{2-}$ $[(\text{TMS})_2\text{pda}]$ as an ancillary ligand in this chemistry. These initial studies have resulted in the synthesis of a new alkylidene complex that is an effective olefin metathesis catalyst [3] and have revealed that a re-

versible metalation of the $(\text{TMS})_2\text{pda}$ ligand appears to enhance the catalytic properties of this complex [4].

As part of our investigation into the organometallic chemistry of complexes having the $(\text{TMS})_2\text{pda}$ ligand, we have synthesized a series of W(VI) alkyl complexes of formulae $[(\text{TMS})_2\text{pda}]\text{W(=NPh)R}_2$ and $[(\text{TMS})_2\text{pda}]\text{W(=NPh)R}_2(\text{PMe}_3)$. In this paper, we report the synthesis, characterization and structural studies of several of these complexes. Recently, related Group 4 complexes containing the $\{o\text{-(}^i\text{Pr}_3\text{Si)N}_2\text{C}_6\text{H}_4\}^{2-}$ ligand have been reported [5].

2. Results and discussion

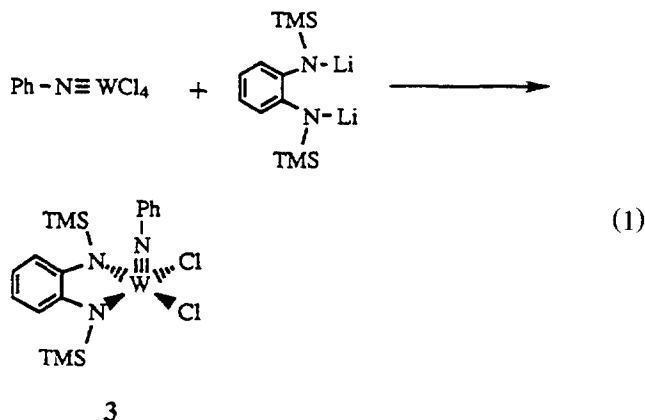
2.1. Synthesis

The synthesis of $\text{W(NPh)Cl}_2[(\text{NSiMe}_3)_2\text{C}_6\text{H}_4]$ **3** was achieved by reaction of the dilithium salt of

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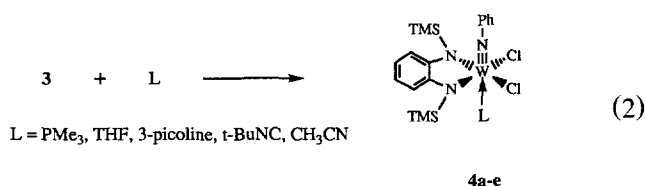
¹ Dedicated to Professor Malcolm L.H. Green on the occasion of his 60th birthday.

$[(\text{TMS})_2\text{pda}]^{2-}$ with $\text{PhN}=\text{WCl}_4 \cdot \text{OEt}_2$ in diethyl ether as shown in Eq. (1):



The yield of this reaction is high and it has been successfully carried out using up to 20 g of metal halide. Compound **3** is an air and water sensitive, orange microcrystalline solid which is stable in the solid state or in solution if stored under an inert atmosphere. The proton and ^{13}C NMR spectra of **3** are consistent with a square pyramidal geometry at W with an axial imido group. Proton and ^{13}C NMR data appear in Tables 1 and 2. The crystal structure of **3** has confirmed this geometry in the solid state [3].

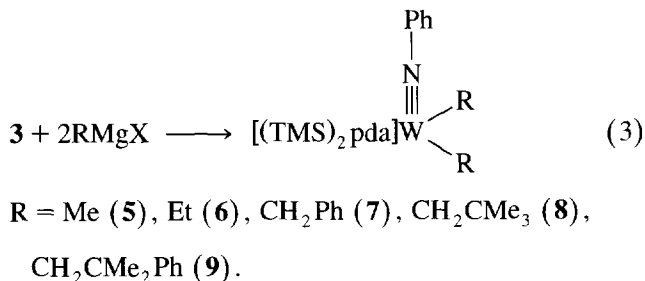
As expected for a 14 electron, five-coordinate complex, **3** reacts instantaneously with Lewis bases giving purple, six-coordinate Lewis base adducts **4a–e**, as shown in Eq. (2). Weak Lewis bases such as diethyl ether can be removed from the complex by exposure to reduced pressure at room temperature, while stronger Lewis bases form isolable adducts. The ^1H and ^{13}C NMR spectra (Tables 1 and 2) are consistent with a six-coordinate structure in which the imido group and Lewis base are *trans* to one another. This structure has been confirmed in the solid state and will be discussed in more detail below.



$\text{L} = \text{PMe}_3, \text{THF}, 3\text{-picoline}, \text{t-BuNC}, \text{CH}_3\text{CN}$

Compound **3** is a convenient starting material for the synthesis of a variety of alkyl complexes. As shown in Eq. (3), carbanions cleanly displace the Cl^- ligands of **3** giving the corresponding dialkyl complexes **5–9**. These reactions are most successful when Grignard reagents are employed as the alkylating agents. When

lithium reagents are employed, reduced yields are obtained and are accompanied by the formation of uncharacterizable decomposition products which have proven difficult to separate.



The dialkyl complexes **5–9** are extremely soluble in hydrocarbon solvents, which tends to complicate their isolation and purification. All of these compounds are air and moisture sensitive solids with the exception of complex **6**, which is an oil at room temperature. Despite their coordinative unsaturation, compounds **5–9** are indefinitely stable at room temperature if stored under an inert atmosphere. This is particularly surprising for complex **6**, which is a 14 electron, five-coordinate diethyl complex that is indefinitely stable with respect to $\beta\text{-H}$ elimination at room temperature.

The room temperature ^1H and ^{13}C NMR spectra of compounds **5–9** (Tables 1 and 2) display equivalent TMS methyl groups and alkyl groups as well as aa'/bb' patterns for the protons of the $(\text{TMS})_2\text{pda}$ phenyl group. The ^1H NMR spectra of complexes **5–7** are invariant as the temperature is decreased from room temperature to -80°C in toluene- d_8 . These observations are consistent with complexes **5–7** having square pyramidal geometry at all temperatures (and are consistent with the crystal structure of compound **5**).

When compounds **8** and **9** are cooled to -80°C , the TMS methyl resonances broaden and decoalesce into two peaks that integrate as 9 protons each, while the $(\text{TMS})_2\text{pda}$ phenyl protons split into four separate one proton resonances. Given that the crystal structure of compound **8** shows that it has trigonal bipyramidal geometry with the imido N and one amide group of the $(\text{TMS})_2\text{pda}$ ligand occupying axial positions, the observed NMR behavior of compounds **8** and **9** is consistent with a fluxional process that interconverts the inequivalent TMS groups. An intramolecular pseudo-rotation process or a process in which one arm of the $(\text{TMS})_2\text{pda}$ ligand dissociates will result in the exchange of the amide TMS groups. The coalescence temperatures for the TMS groups of complexes **8** and **9** are -45 and -42°C respectively. The two-site exchange approximation [6] allows us to estimate ΔG^\ddagger for the process at 46.4 and 56.5 kJ mol^{-1} for complexes **8** and **9**.

While complex **8** does not react with PMe_3 at room temperature [4], solutions of compound **5** change color

Table 1
¹H NMR Data

Compound	δ (ppm)	Mult.	J (Hz)	Int.	Assignment
1,2-[(CH ₃) ₃ SiNH] ₂ C ₆ H ₄ 1	0.18	s		18	–SiMe ₃
	3.00	br s		2	–NH
	6.83	m		2	aromatic
	6.89	m		2	aromatic
1,2-Li ₂ [(CH ₃) ₃ SiN] ₂ C ₆ H ₄ 2	0.22	s		18	–SiMe ₃
	6.59	m		2	aromatic
	6.87	m		2	aromatic
W(NPh)Cl ₂ [(Me ₃ SiN) ₂ C ₆ H ₄] 3	0.35	s		18	–SiMe ₃
	6.71	t	8	1	<i>p</i> -NPh- <i>H</i>
	6.94	m		2	aromatic
	7.01	t	8	2	<i>m</i> -NPh- <i>H</i>
	7.14	m		2	aromatic
	7.31	d	8	2	<i>o</i> -NPh- <i>H</i>
W(NPh)Cl ₂ (PMe ₃)[(Me ₃ SiN) ₂ C ₆ H ₄] 4a	0.42	s		18	–SiMe ₃
	0.79	d	² J _{P-H} = 9	9	–PMe ₃
	6.63	t	8		<i>p</i> -NPh- <i>H</i>
	6.83	m		2	aromatic
	7.01	m		2	aromatic
	7.17	t	8	2	<i>m</i> -NPh- <i>H</i>
	7.49	d	8	2	<i>o</i> -NPh- <i>H</i>
W(NPh)Cl ₂ (THF)[(Me ₃ SiN) ₂ C ₆ H ₄] 4b	0.41	s		18	–SiMe ₃
	0.92	qnt	3	4	–THF
	3.63	t	6	4	–THF
	6.62	t	8	1	<i>p</i> -NPh- <i>H</i>
	6.85	m		2	aromatic
	7.03	m		2	aromatic
	7.10	t	8	2	<i>m</i> -NPh- <i>H</i>
	7.47	d	8	2	<i>o</i> -NPh- <i>H</i>
W(NPh)Cl ₂ (3-Me-py)[(Me ₃ SiN) ₂ C ₆ H ₄] 4c	0.42	s		18	–SiMe ₃
	2.17	s		3	py-Me
	6.21	t	2	1	py-5- <i>H</i>
	6.33	d	8	1	py-4- <i>H</i>
	6.54	m		2	aromatic
	6.65	t	11	1	<i>p</i> -NPh- <i>H</i>
	6.76	m		2	aromatic
	7.18	t	9	2	<i>m</i> -NPh- <i>H</i>
	7.61	d	7	2	<i>o</i> -NPh- <i>H</i>
	8.72	s		1	py-1- <i>H</i>
	8.75	d	6	1	py-6- <i>H</i>
W(NPh)Cl ₂ (CNCMe ₃)[(Me ₃ SiN) ₂ C ₆ H ₄] 4d	0.47	s		18	–SiMe ₃
	0.54	s		9	–CNCMe ₃
	6.64	t		1	<i>p</i> -NPh- <i>H</i>
	6.92	m		2	aromatic
	7.11	t		2	<i>m</i> -NPh- <i>H</i>
	7.15	m		2	aromatic
	7.49	d		2	<i>o</i> -NPh- <i>H</i>
W(NPh)Cl ₂ (NCCCH ₃)[(Me ₃ SiN) ₂ C ₆ H ₄] 4e	0.38	s		18	–SiMe ₃
	0.49	s		3	–NCCMe
	6.67	t	7	1	<i>p</i> -NPh- <i>H</i>
	6.93	m		2	aromatic
	7.04	t	7		<i>m</i> -NPh- <i>H</i>
	7.14	m		2	aromatic
	7.34	d	7	2	<i>o</i> -NPh- <i>H</i>

Table 1 (continued)

Compound	δ (ppm)	Mult.	J (Hz)	Int.	Assignment
8 W(NPh)(CH ₂ CMe ₃) ₂ [(Me ₃ SiN) ₂ C ₆ H ₄] <i>Spectrum taken at -80°C in C₇D₈</i>	0.54	s		18	-Si Me ₃
	1.00	s		18	-C Me ₃
	2.13	d	10	2	-C H ₂ CMe ₃
			$^2J_{W-H} = 11$		
	2.29	d	10	2	-C H ₂ CMe ₃
			$^2J_{W-H} = 11$		
	6.83	t	7	1	<i>p</i> -NPh-H
	6.86	m		2	aromatic
	7.19	t	7	2	<i>m</i> -NPh-H
	7.25	m		2	aromatic
	7.59	d	7	2	<i>o</i> -NPh-H
	0.50	s		9	-Si Me ₃
	0.66	s		9	-Si Me ₃
	1.03	s		18	-C Me ₃
	2.24	d		2	-C H ₂ CMe ₃
2.36	d		2	-C H ₂ CMe ₃	
6.8 to 7.7			9	aromatic	
9 W(NPh)(CH ₂ CMe ₂ Ph) ₂ [(Me ₃ SiN) ₂ C ₆ H ₄] <i>Spectrum taken at -80°C in C₇D₈</i>	0.42	s		18	-Si Me ₃
	1.37	s		6	-C Me ₂ Ph
	1.38	s		6	-C Me ₂ Ph
	1.95	d	11	2	-C H ₂ C
			$^2J_{W-H} = 11$		
	2.94	d	11	2	-C H ₂ C
			$^2J_{W-H} = 11$		
	6.83	t	7	1	aromatic
	6.94	t	7	2	
	6.97	m		2	
	7.01	t	7	4	
	7.06	t	7	2	
	7.18	d	7	4	
	7.19	d	7	2	
	7.30	m		2	
	0.27	s		9	-Si Me ₃
	0.63	s		9	-Si Me ₃
	1.34	s		12	-C Me ₂ Ph
	1.61	d		2	-C H ₂ C
	3.36	d		2	-C H ₂ C
6.72-7.52		19		aromatic	
5 W(NPh)(CH ₃) ₂ [(Me ₃ SiN) ₂ C ₆ H ₄]	0.31	s		18	-Si Me ₃
	1.12	s	$^2J_{W-H} = 6$	6	W-Me
	6.86	t	8	1	<i>p</i> -NPh-H
	7.06	m		2	aromatic
	7.11	t	8	2	<i>m</i> -NPh-H
	7.32	d	8	2	<i>o</i> -NPh-H
	7.35	m		2	aromatic
	6 W(NPh)(CH ₂ CH ₃) ₂ [(Me ₃ SiN) ₂ C ₆ H ₄]	0.29	s		18
1.86		s		6	-CH ₂ CH ₃
1.91		m		2	-CH ₂ CH ₃
2.31		m		2	-CH ₂ CH ₃
6.86		t	8	1	<i>p</i> -NPh-H
7.04		m		2	aromatic
7.11		t	8	2	<i>m</i> -NPh-H
7.31		d	8	2	<i>o</i> -NPh-H
7.37		m		2	aromatic

Table 1 (continued)

Compound	δ (ppm)	Mult.	J (Hz)	Int.	Assignment
W(NPh)(CH ₂ Ph) ₂ [(Me ₃ SiN) ₂ C ₆ H ₄] 7	0.09	s		18	–SiMe ₃
	2.78	s		4	–CH ₂ Ph
	6.81	t	8	2	<i>p</i> -CH ₂ Ph–H
	6.88	t	8	1	<i>p</i> -NPh–H
	7.04				
	to				aromatic
	7.19				
	7.30	d	8	2	<i>o</i> -NPh–H
	7.37	m		2	aromatic
<i>Spectrum taken at +80°C in C₇D₈</i>					
	2.71	m	7	4	–CH ₂ Ph

from yellow–orange to red in the presence of PMe₃. Crystals of the complex [(TMS)₂pda]W(=NPh)Me₂-(PMe₃) **5a** can be isolated by cooling a pentane solution of compound **5** that contains excess PMe₃ to –40°C. These crystals readily lose PMe₃ if they are exposed to reduced pressure, and consequently must be isolated by filtration followed by drying under a gentle stream of Ar. The ¹H NMR spectrum of a C₆D₆ solution of complex **5a** displays shifted methyl and TMS groups relative to complex **5**. The chemical shift of the PMe₃ is identical to that of free PMe₃, suggesting that exchange between bound and free PMe₃ is rapid on the NMR timescale and is consistent with the weak binding of PMe₃ to compound **5**.

2.2. Structural studies

Single crystal X-ray diffraction studies were performed on compounds **4a**, **5**, **5a**, and **8**. The crystal structure of compound **3** was reported in a previous communication [3], and those results will be included in this discussion for comparison. Thermal ellipsoid plots of the compounds are found in Figs. 1–5, while selected bond lengths and angles are found in Tables 3–7. The set of compounds **3**, **5**, **4a** and **5a** gives a direct comparison of the five-coordinate dichloro and dimethyl complexes with their six-coordinate PMe₃ adducts.

Some general comments about these structures are warranted. All compounds have short W–N(imido) bond lengths and W–N–Ph angles that are close to linear, as is consistent with W–N triple bonds [7,8]. The W–alkyl bond lengths are also within the ranges expected for W(VI)–C distances [9]. Despite the 14e[–], coordinatively unsaturated nature of the complexes, there is no evidence for α or β agostic W–H–C interactions either structurally or spectroscopically.

The five-coordinate complexes **3** and **5** have square pyramidal coordination about the W atom with the imido group in the axial position. In both structures, the (TMS)₂pda ligand is obviously folded about the vector

that connects the two amido N atoms. This results in a dihedral angle between the phenyl ring of the (TMS)₂pda ligand and the plane defined by W and the amido N atoms of 130° in both complex **3** and complex **5**. This results in close contacts between the *ortho* carbon atoms of the phenyl ring of the (TMS)₂pda ligand and the metal center that range between 2.58 and 2.64 Å. The stronger σ donor properties of Me[–] relative to Cl[–] is reflected in the longer W–N(amido) bonds in compound **5** (2.006(3) Å) compared with compound **3** (1.951(11) Å).

The coordination of PMe₃ to give the six-coordinate complexes **4a** and **5a** results in a reduction in the fold of the (TMS)₂pda ligand as shown by the increased dihedral angle between the phenyl ring of the (TMS)₂pda ligand and the plane defined by W and the amido N atoms of 150°. The reduction in the fold of the ligand moves the *ortho* carbon atoms of the (TMS)₂pda ligand away from the metal center. Both complexes have rather long W–P bonds of 2.72 Å and show increased bond lengths between W and the other ligands, as expected with the increased coordination number relative to compounds **3** and **5**.

As can be seen in Fig. 5, the W atom in complex **8** adopts a trigonal bipyramidal coordination geometry with the imido N and one amido N occupying axial sites. The equatorial sites are occupied by the bulky neopentyl groups and the remaining amido N. In response to the greater steric demands of the ligands in compound **8**, the folding of the (TMS)₂pda ligand has decreased relative to the other compounds resulting in a dihedral angle between the phenyl ring of the (TMS)₂pda ligand and the plane defined by W and the amido N atoms of 164°. The W–N2 bond (2.133(3) Å) is significantly longer than the W–N3 bond (1.981(3) Å), and reflects the strong *trans* influence that is exerted by the imido group. The amido group *trans* to the imido group causes the W–N1 bond to be slightly longer than in complex **5**, though the W–N1 bond length is still within the range expected for a triply

Table 2
 ^{13}C NMR data

Compound	δ (ppm)	Mult.	J_{CH} (Hz)	Assignment
W(NPh)Cl ₂ [(Me ₃ SiN) ₂ C ₆ H ₄] 3	0.6	s		–SiMe ₃
	122.0	s		aromatic
	126.1	s		
	128.1	s		
	128.5	s		
	128.6	s		
	130.8	s		
W(NPh)Cl ₂ (PMe ₃)[(Me ₃ SiN) ₂ C ₆ H ₄] 4a	1.99	s		–SiMe ₃
	11.64	d	$^1J_{\text{C-P}} = 21$	–PMe ₃
	120.94	s		aromatic
	122.99	s		
	127.03	s		
	127.29	s		
	128.35	s		
	145.41	s		
W(NPh)Cl ₂ (THF)[(Me ₃ SiN) ₂ C ₆ H ₄] 4b	1.50	s		–SiMe ₃
	25.05	s		THF
	70.07	s		THF
	120.41	s		aromatic
	124.10	s		
	126.64	s		
	128.25	s		
	128.57	s		
	144.12	s		
W(NPh)Cl ₂ (3-Me-py)[(Me ₃ SiN) ₂ C ₆ H ₄] 4c	1.69	s		–SiMe ₃
	17.70	s		3-Me-py
	119.92	s		aromatic
	122.61	s		
	123.16	s		
	127.03	s		
	127.91	s		
	128.15	s		
	128.55	s		
	132.81	s		
	137.86	s		
	147.12	s		
	148.83	s		
	152.51	s		
W(NPh)(CH ₂ CMe ₃) ₂ [(Me ₃ SiN) ₂ C ₆ H ₄] 8	4.4	s		–SiMe ₃
	34.8	s		–CMe ₃
	38.3	s		–CMe ₃
	90.8	s	123	–CH ₂ CMe ₃
	118.9	s		aromatic
	119.3	s		
	126.0	s		
	128.5	s		
	129.2	s		
	144.2	s		
	155.8	s		

bonded imido group. The W–C1–C2 and W–C6–C7 angles are within the expected range for undistorted neopentyl groups.

Given the π bonding demands of the imido group as well as its strong *trans* influence, the square pyramidal structures found in compounds **3** and **5** are expected to

Table 2 (continued)

Compound	δ (ppm)	Mult.	J_{CH} (Hz)	Assignment
W(NPh)(CH ₂ CMe ₂ Ph) ₂ [(Me ₃ SiN) ₂ C ₆ H ₄] 9	4.1	s	126	–SiMe ₃
	32.5	s		–CMe ₂ Ph
	35.9	s		–CMe ₂ Ph
	44.2	s		–CMe ₂ Ph
	93.1	s		–CH ₂ CMe ₂ Ph
	119.4	s		aromatic
	119.8	s		
	125.5			
	125.6			
	126.1			
	128.2			
	128.4			
	129.2			
	143.8			
	153.4			
	155.2			
W(NPh)(CH ₃) ₂ [(Me ₃ SiN) ₂ C ₆ H ₄] 5	2.3	s	123	–SiMe ₃
	41.2	s		–CH ₃
	122.4	s		aromatic
	124.8	s		
	125.2	s		
	125.8	s		
	128.7	s		
	129.8	s		
	131.2	s		
W(NPh)(CH ₂ CH ₃) ₂ [(Me ₃ SiN) ₂ C ₆ H ₄] 6	1.5	s	120	–SiMe ₃
	17.4	s		–CH ₂ CH ₃
	58.4	s		–CH ₂ CH ₃
	122.3			
	123.9			
	125.0			
	125.6			
	128.8			
	135.1			
	156.2			
W(NPh)(CH ₂ Ph) ₂ [(Me ₃ SiN) ₂ C ₆ H ₄] 7	2.10	s		–SiMe ₃
	66.33	s		–CH ₂ Ph
	123.49	s		
	123.78	s		
	125.65	s		
	126.20	s		
	126.51	s		
	127.68	s		
	128.04	s		
	128.42	s		
	128.61	s		
	128.97	s		
	154.20	s		

be the most stable in this class of five-coordinate molecules because they maximize the imido–W π interaction [7,8]. Thus, the trigonal bipyramidal coordination geometry found in complex **8** most likely arises from the steric bulk of the neopentyl groups. As ex-

pected, the most sterically encumbered groups occupy the equatorial plane of the trigonal bipyramid with the smaller imido group occupying an axial position. The structure is clearly related to that of W(=NPh)(CH₂-^tBu)₃Cl, which has not been structurally characterized

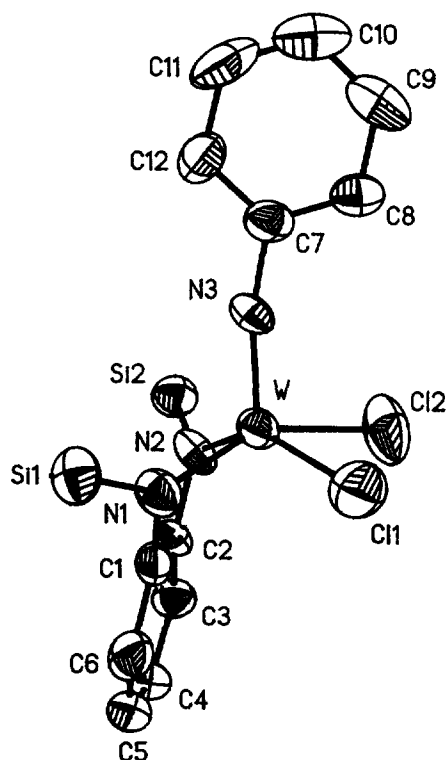


Fig. 1. Thermal ellipsoid plot of **3** (SiMe_3 methyls removed for clarity).

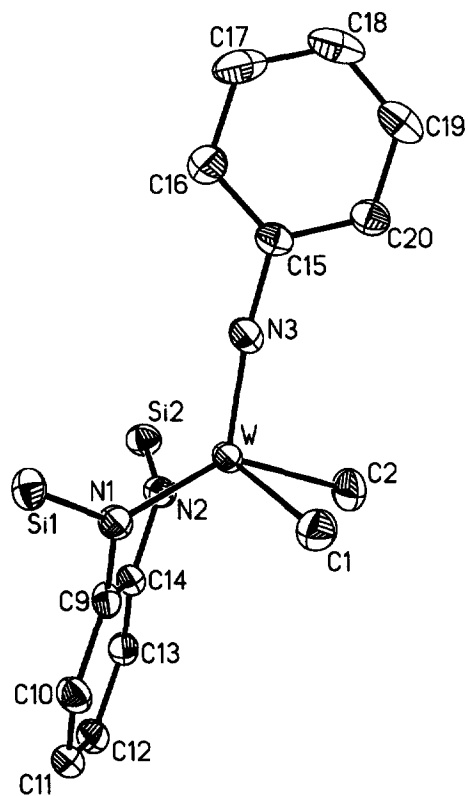


Fig. 3. Thermal ellipsoid plot of **5** (SiMe_3 methyls removed for clarity).

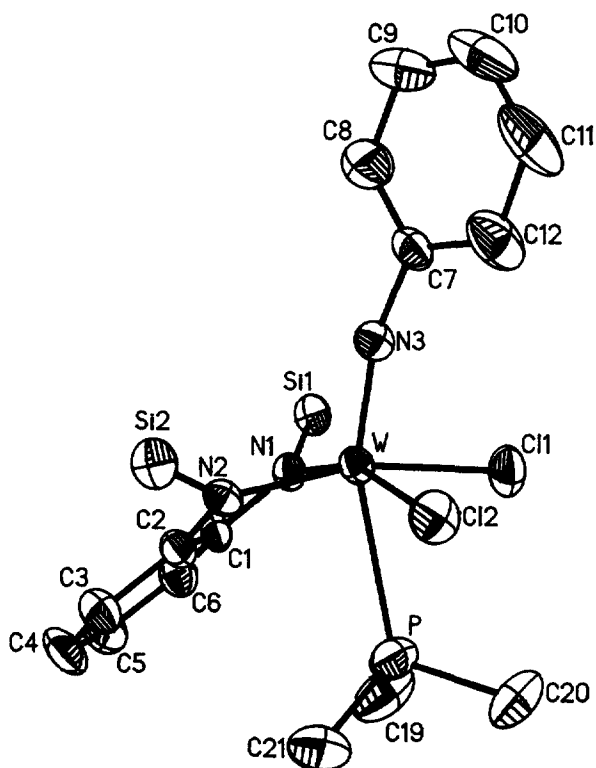


Fig. 2. Thermal ellipsoid plot of **4a** (SiMe_3 methyls removed for clarity).

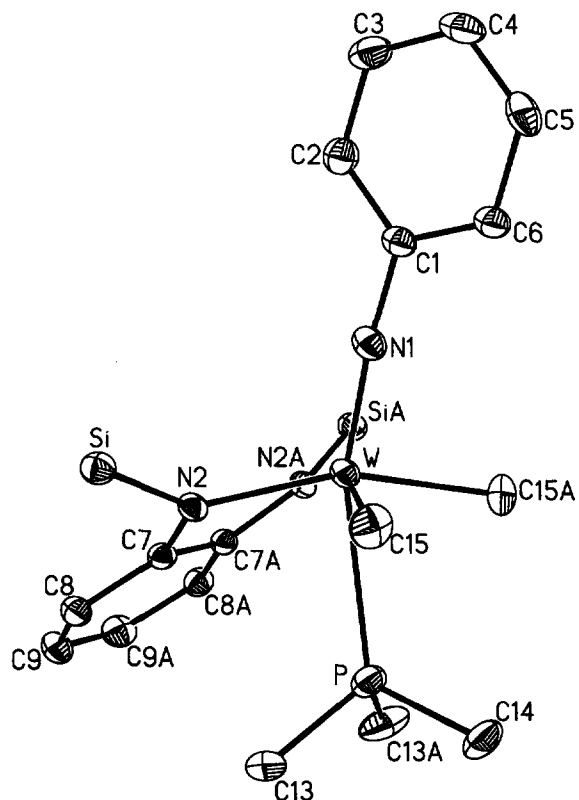
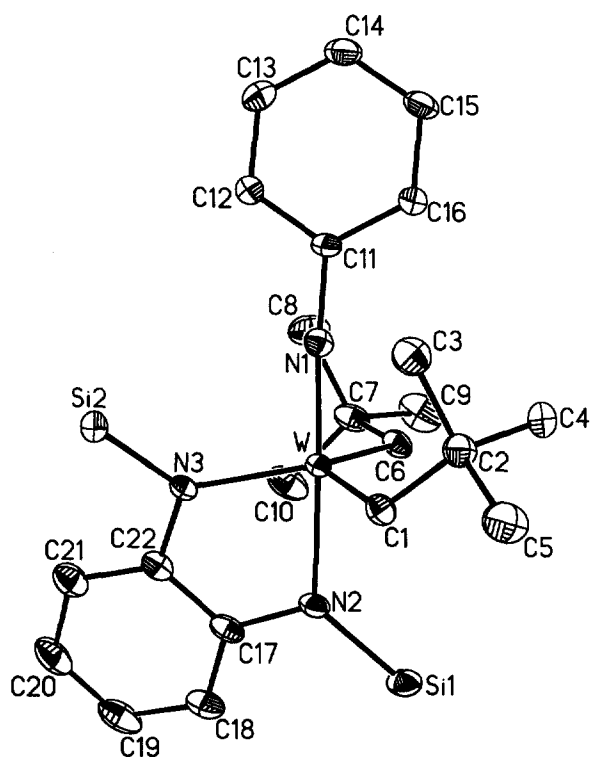


Fig. 4. Thermal ellipsoid plot of **5a** (SiMe_3 methyls removed for clarity).



but has been assigned a trigonal bipyramidal structure with equatorial neopentyl groups using NMR data [10].

It is clear that compound **3** is a convenient starting material for a variety of new W(VI) complexes. The steric flexibility of the (TMS)₃pda ligand may prove

1	2	3	1-2	1-2-3
C11	W	C12	2.383(4)	82.9(2)
C11	W	N1		87.7(3)
C11	W	N2		146.8(3)
C11	W	N3		102.9(4)
C11	W	C1		95.6(3)
C12	W	N1	2.387(4)	150.5(3)
C12	W	N2		88.9(3)
C12	W	N3		99.8(4)
C12	W	C1		120.5(3)
C12	W	C2		98.2(3)
N1	W	N2	1.951(11)	83.9(4)
N1	W	N3		109.5(5)
N1	W	C1		32.9(4)
N1	W	C2		61.9(4)
N2	W	N3	1.952(11)	110.2(5)
N2	W	C1		61.4(4)
N2	W	C2		32.4(4)
N3	W	C1	1.730(10)	137.4(4)
N3	W	C2		137.6(4)
C1	W	C2	2.582(13)	31.9(4)
C2	W	C11	2.582(13)	117.2(3)

1	2	3	1-2	1-2-3
C11	W	C12	2.449(2)	92.43(7)
C11	W	P		75.86(7)
C11	W	N1		91.2(2)
C11	W	N2		163.5(2)
C11	W	N3		90.4(2)
C11	W	C1		111.4(2)
C12	W	P	2.443(2)	75.70(7)
C12	W	N1		161.0(2)
C12	W	N2		90.7(2)
C12	W	N3		91.2(2)
C12	W	C1		135.07(14)
C12	W	C2		109.9(2)
P	W	N1	2.720(2)	87.2(2)
P	W	N2		89.2(2)
P	W	N3		160.3(2)
P	W	C1		74.25(14)
P	W	C2		75.3(2)
N1	W	N2	2.010(5)	80.8(2)
N1	W	N3		107.4(2)
N1	W	C1		28.3(2)
N1	W	C2		56.8(2)
N2	W	N3	1.990(5)	105.8(3)
N2	W	C1		56.5(2)
N2	W	C2		27.9(2)
N3	W	C1	1.747(6)	124.6(2)
N3	W	C2		123.6(2)
C1	W	C2	2.797(6)	29.7(2)
C2	W	C11	2.785(6)	137.4(2)

useful in the stabilization of coordinatively unsaturated complexes. This is demonstrated by the change in the degree of folding of the $(\text{TMS})_2\text{pda}$ ligand observed in the structures reported herein. The ability to fold along the N–N vector allows the $(\text{TMS})_2\text{pda}$ ligand to possess a variable steric “footprint” depending upon the needs of the metal center. Our studies on the thermolysis of **8** [4] have demonstrated that new alkylidene complexes containing the $(\text{TMS})_2\text{pda}$ ligand are accessible and are active olefin metathesis catalysts. Further studies directed towards understanding how the structural preferences identified in this paper affect and control the

1	2	3	1-2	1-2-3
N1	W	C1	2.007(3)	84.98(14)
N1	W	C2		141.7(2)
N2	W	N1	2.006(3)	82.55(11)
N2	W	C1		138.87(14)
N2	W	C2		85.5(2)
N3	W	N1	1.738(3)	117.64(13)
N3	W	N2		117.81(13)
N3	W	C1		102.7(2)
C1	W	C2	2.173(4)	80.5(2)
C2	W	N3		100.2(2)

Table 6
Selected bond lengths (Å) and angles (°) for **5a**

1	2	3	1–2	1–2–3
N1	W	N2	1.760(4)	110.99(12)
N1	W	N2a		110.99(12)
N1	W	C15		91.03(12)
N1	W	C15a		91.03(12)
N1	W	P		160.04(13)
N2	W	N2a	2.067(2)	77.30(14)
N2	W	C15		90.13(12)
N2	W	C15a		157.34(12)
N2	W	P		84.28(7)
N2a	W	C15	2.067(2)	157.34(12)
N2a	W	C15a		90.13(12)
N2a	W	P		84.28(7)
C15	W	C15a	2.218(3)	94.9(2)
C15a	W	P	2.218(3)	75.67(10)
P	W	C15	2.7148(12)	75.67(10)

Table 7
Selected bond lengths (Å) and angles (°) for **8**

1	2	3	1–2	1–2–3
N1	W	N2	1.775(3)	170.89(12)
N1	W	N3		99.58(12)
N1	W	C1		98.47(13)
N1	W	C6		88.62(13)
N2	W	C1	2.133(3)	90.40(12)
N2	W	C6		84.83(12)
N3	W	N2	1.981(3)	79.35(11)
N3	W	C1		108.93(12)
C1	W	C6	2.135(3)	122.40(13)
C6	W	N3	2.165(3)	126.15(12)
C2	C1	W		126.2(2)
C7	C6	W		120.6(2)

reactivity of these compounds with substrates such as H₂ and ethylene are in progress.

3. Experimental

3.1. Materials and experimental methods

All syntheses were carried out under dry argon atmosphere using standard Schlenk techniques. WCl₄-(=NPh)(OEt₂) was synthesized according to the literature procedure [10], while *o*-(Me₃SiNH)₂C₆H₄ **1** was synthesized as described below with a modification of the literature procedure [11]. Tetrahydrofuran (THF), diethyl ether (Et₂O), and diisopropyl ether (¹Pr₂O) were distilled from sodium benzophenone ketyl. Benzene and pentane were distilled from sodium. NMR solvents were stored over molecular sieves and degassed prior to use. NMR spectra were acquired on either General Electric QE-300 or Varian VXR 300 spectrometers. ¹H and ¹³C chemical shifts are referenced to residual pro-

tons in deuterated solvents and are reported relative to tetramethylsilane. Elemental analyses were performed by Atlantic Microlabs, Inc., or the analytical services of this department.

3.2. *o*-(Me₃SiNH)₂C₆H₄ **1**

1,2-phenylenediamine (3.146 g, 0.029 mol) was placed in a Schlenk tube and dried under reduced pressure for 30 min. The solid was dissolved in Et₂O (75 ml), and the resulting solution was cooled to 0°C. Si(CH₃)₃Cl (8.10 ml, 0.0638 mol) was added dropwise, giving a pink precipitate. The mixture was stirred for 30 min. NEt₃ (8.89 ml, 0.0638 mol) was added dropwise, and the thickened solution was stirred for 3 h at room temperature. After the mixture was allowed to settle, the solvent was filtered off, and the remaining solid was extracted with pentane (2 × 30 ml). The pentane and ether extracts were combined, and the solvent was removed under reduced pressure at 0°C to give a white solid. Yield: 6.105 g (83%).

3.3. N,N'-(Li₂[*o*-(NSiMe₃)₂C₆H₄], **2**

A solution of N,N'-bis(trimethylsilyl)-*o*-phenylenediamine (5.26 g, 20.9 mmol) in 75 ml of pentane was cooled to –78°C. To this solution, two equivalents of *n*-BuLi (16.8 ml, 41.9 mmol, 2.5 M solution in hexanes) was added slowly. A white precipitate formed as gas was evolved. Upon addition, a bubbler was attached and the reaction was stirred at room temperature for 2 h under a flow of argon. The mixture was filtered and the solid dried under reduced pressure. The volume of the filtrate was reduced to 25 ml under reduced pressure and cooled to –15°C to give colorless crystals. Yield: 4.93 g (combined) (89.5%).

3.4. W(NPh)Cl₂[*o*-(NSiMe₃)₂C₆H₄], **3**

N,N'-bis(trimethylsilyl)-*o*-phenylenediamine **1** (3.83 g, 15.16 mmol) was dissolved in 30 ml of Et₂O and cooled to –78°C. Two equivalents of *n*-BuLi (12.13 ml, 30.32 mmol, 2.5 M solution in hexanes) were then added. The reaction was warmed to room temperature and stirred for 1 h. The reaction was recooled, and 0.95 equivalents of W(NPh)Cl₄(OEt₂) (7.10 g, 14.4 mmol) in 20 ml of Et₂O was added. The reaction was stirred for 3 h, then filtered through a Celite pad, which, in turn, was rinsed with more Et₂O. Solvent was removed under reduced pressure. The dark red solid was washed with pentane until an orange powder remained. The powder was dried to yield 7.31 g of **3** (85.1%). Anal. Found: C, 35.91; H, 4.78; N, 6.78. C₁₈H₂₇N₃Cl₂Si₂W. Calc.: C, 36.25; H, 4.56; N, 7.05%.

3.5. $W(NPh)Cl_2(PMe_3)[o-(NSiMe_3)_2C_6H_4]$, **4a**

$W(NPh)Cl_2[(NSiMe_3)_2C_6H_4]$ **3** (0.68 g, 1.14 mmol) was slurried in 30 ml of pentane. Excess PMe_3 (4.55 ml, 2.00 mmol, 0.44 M in toluene) was added to the reaction. The reaction immediately turned from redish to deep purple. The reaction was cooled to $-78^\circ C$ to give **21** as 0.71 g of purple crystals, yield 90.5%. Satisfactory elemental analysis of this complex was not obtained, presumably due to the fact that PMe_3 is readily lost from the complex.

3.6. $W(NPh)Cl_2(L)[o-(NSiMe_3)_2C_6H_4]$, $L = THF$, 3-*picoline*, CH_3CN , $tBuNC$, **4b–e**

$W(NPh)Cl_2[(NSiMe_3)_2C_6H_4]$ **3** was dissolved in a minimum amount of the solvent L . The deep purple solution was then added slowly to a stirring pentane solution, which immediately turned purple. The solutions were then cooled to $-78^\circ C$ to give purple crystals of the mono-adduct in 70–90% yields. Satisfactory elemental analyses of these complexes were not obtained, presumably due to the fact that L is readily lost from the complexes.

3.7. $W(NPh)(CH_3)_2[o-(NSiMe_3)_2C_6H_4]$, **5**

CH_3MgI (1.17 ml, 3.52 mmol) was added via a syringe to a 25 ml 1Pr_2O solution of $[(TMS)_2pda](NPh)WCl_2$ (1.05 g, 1.76 mmol) at $-78^\circ C$. The reaction was allowed to warm to room temperature and was stirred for 2 h, during which time a brownish-gold color appeared and salts precipitated. The solvent was then removed under reduced pressure, and the remaining brown solid was dried for 2 h under reduced pressure. It was then extracted with pentane (2×15 ml), which was concentrated and cooled to $-78^\circ C$ for 2 h. The resulting golden solid was isolated by filtration and dried under reduced pressure for 1 h. Crystals suitable for X-ray diffraction study were isolated from the filtrate after further concentration. Yield: 675 mg (69%). Anal. Found: C, 42.89; H, 5.94; N, 7.29. $C_{20}H_{33}N_3Si_2W$ Calc.: C, 43.24; H, 5.99; N, 7.56%.

3.8. $W(NPh)(CH_2CH_3)_2[o-(NSiMe_3)_2C_6H_4]$, **6**

$W(NPh)Cl_2[(NSiMe_3)_2C_6H_4]$ **3** (1.12 g, 1.88 mmol) was dissolved in 25 ml of Et_2O and cooled to $-78^\circ C$. Two equivalents of $EtMgCl$ (1.88 ml, 3.76 mmol, 2.0 M solution in Et_2O) were then added. The reaction was allowed to warm to room temperature after 15 min. After 30 min, solvent was removed under reduced pressure. The solid was extracted with pentane until clear and filtered through a Celite pad. The solvent was removed under reduced pressure to yield 0.98 g of **6** as a thick red oil. Yield 89.3%.

3.9. $W(NPh)(CH_2Ph)_2[o-(NSiMe_3)_2C_6H_4]$, **7**

$W(NPh)Cl_2[(NSiMe_3)_2C_6H_4]$ **3** (2.02 g, 3.39 mmol) was dissolved in 25 ml of Et_2O and cooled to $-78^\circ C$. Two equivalents of $ClMgCH_2Ph$ (6.77 ml, 6.77 mmol, 1.0 M solution, in Et_2O) were then added. The reaction was allowed to warm to room temperature after 15 min. After 30 min, solvent was removed under reduced pressure. The solid was extracted with pentane until clear and filtered through a Celite pad. The solution was concentrated to 10 ml and cooled to $-78^\circ C$ to give 1.47 g of **7** as a dark solid. Yield 61.3%. Anal. Found: C, 53.98; H, 5.61; N, 5.69. $C_{32}H_{41}N_3Si_2W$ Calc.: C, 54.31; H, 5.84; N, 5.94%.

3.10. $W(NPh)(CH_2C(CH_3)_3)_2[o-(NSiMe_3)_2C_6H_4]$, **8**

$W(NPh)Cl_2[(NSiMe_3)_2C_6H_4]$ (2.78 g, 4.66 mmol) was dissolved in 30 ml of Et_2O and cooled to $-78^\circ C$. Two equivalents of $ClMgCH_2C(CH_3)_3$ (7.37 ml, 9.32 mmol, 1.27 M solution in Et_2O) were then added. The reaction was allowed to warm to room temperature after 30 min. After 1 h, solvent was removed under reduced pressure. The solid was extracted with pentane until clear and filtered through a Celite pad. The solution was concentrated to a total volume of about 10 ml and cooled in a $-78^\circ C$ cold bath to yield dark crystals of **8**. Yield: 2.19 g (70.1%). Anal. Found: C, 50.36; H, 7.04; N, 6.14. $C_{28}H_{47}N_3Si_2W$ Calc.: C, 50.52; H, 7.12; N, 6.31%.

3.11. $W(NPh)(CH_2C(CH_3)_2Ph)_2[o-(NSiMe_3)_2C_6H_4]$, **9**

$W(NPh)Cl_2[(NSiMe_3)_2C_6H_4]$ (2.04 g, 3.42 mmol) was dissolved in 30 ml of Et_2O and cooled to $-78^\circ C$. Two equivalents of $ClMgCH_2C(CH_3)_2Ph$ (6.55 ml, 6.84 mmol, 1.045 M solution in Et_2O) were then added. The reaction was allowed to warm to room temperature after 30 min. After 1 h, solvent was removed under reduced pressure. The solid was extracted with pentane until clear and filtered through a Celite pad. The solution was concentrated to a total volume of about 15 ml and cooled in a $-78^\circ C$ cold bath to yield 2.21 g (82.4%) of **9** as a light brown solid. Anal. Found: C, 57.95; H, 5.58; N, 5.29. $C_{38}H_{45}N_3Si_2W$ Calc.: C, 58.23; H, 5.79; N, 5.36%.

3.12. X-ray crystal structures

Compound 4a. $C_{21}H_{36}N_3PCl_2W$, $M_r = 672.43$, triclinic, $P\bar{1}$, $a = 9.562(1)$, $b = 10.277(1)$, $c = 14.920(2)$ Å, $\alpha = 82.15(1)$, $\beta = 80.18(1)$, $\gamma = 80.41(1)^\circ$, $V = 1415.6(3)$ Å³, $Z = 2$, $D_{calc} = 1.578$ g cm⁻³, Mo K α ($\lambda = 0.71073$ Å), $T = 298$ K. Data were collected on a Siemens R3m/V diffractometer equipped with a

graphite monochromator utilizing Mo K α radiation ($\lambda = 0.71073$ Å). 32 reflections with $20.0^\circ \leq 2\theta \leq 22.0^\circ$ were used to refine the cell parameters. 5312 reflections were collected using the ω -scan method. Four reflections were measured every 96 reflections to monitor instrument and crystal stability (maximum correction on I was less than 1%). Absorption corrections were applied based on measured crystal faces using SHELXTL PLUS [12,13]. The structure was solved by the heavy-atom method in SHELXTL PLUS from which the location of the W atom was obtained. The rest of the non-hydrogen atoms were obtained from a subsequent difference Fourier map. The structure was refined in SHELXTL PLUS using full-matrix least-squares. 271 parameters were refined in the final cycle of refinement using 4224 reflections with $I > 2\sigma(I)$ to yield $R = 4.08$ and $wR = 4.26$ respectively. Refinement of **4a** was done using F .

Compound 5. $C_{20}H_{33}N_3Si_2W$, $M_r = 555.52$, monoclinic, $P2(1)/n$, $a = 10.3545(2)$, $b = 17.9669(1)$, $c = 13.3168(1)$ Å, $\beta = 103.826(1)^\circ$, $V = 2405.65(5)$ Å³, $Z = 4$, $D_{\text{calc}} = 1.534$ g cm⁻³, Mo K α ($\lambda = 0.71073$ Å), $T = 173$ K. **5a.** $C_{23}H_{42}N_3PSi_2W$, $M_r = 631.60$, monoclinic, $C2/m$, $a = 13.5336(1)$, $b = 14.4291(1)$, $c = 15.3785(1)$ Å, $\beta = 110.365(1)^\circ$, $V = 1415.6(3)$ Å³, $Z = 4$, $D_{\text{calc}} = 1.5490$ g cm⁻³, Mo K α ($\lambda = 0.71073$ Å), $T = 173$ K. **8.** $C_{28}H_{49}N_3Si_2W$, $M_r = 667.73$, monoclinic, $P2(1)/n$, $a = 10.6992(4)$, $b = 18.3144(7)$, $c = 16.0726(6)$ Å, $\beta = 92.042(1)^\circ$, $V = 3147.4(2)$ Å³, $Z = 4$, $D_{\text{calc}} = 1.409$ g cm⁻³, Mo K α ($\lambda = 0.71073$ Å), $T = 173$ K. Data for **5**, **5a** and **8** were collected at 173 K on a Siemens SMART PLATFORM equipped with a CCD area detector and a graphite monochromator utilizing Mo K α radiation ($\lambda = 0.71073$ Å). Cell parameters were refined using the entire data set. A hemisphere of data (1321 frames) was collected for each crystal 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 less than 1%). ψ -Scan absorption corrections were applied based on the entire data set. The structures of **5**, **5a** and **8** were solved by direct methods in SHELXTL5 and refined using full-matrix least-squares. The non-H atoms were treated anisotropically, whereas the hydrogen atoms were calculated in ideal positions and were riding on their respective carbon atoms. 244, 151 and 307 parameters were refined in the final cycle of refinement for **5**, **5a** and **8** respectively, using 4572, 3057 and 5881 reflections for **5**, **5a** and **8** respectively with $I > 2\sigma(I)$ to yield R_1 and wR_2 values of 2.47 and 5.97, 2.72 and 7.12, 2.61 and 5.71 for **5**, **5a** and **8** respectively. Refinement of **5**, **5a** and **8** was done using F^2 .

4. Supplementary material available

Tables of bond lengths and angles, positional and thermal parameters.

Acknowledgements

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