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PREPARATION AND PROPERTIES OF MOLYBDENUM AND TUNGSTEN DINITROGEN COMPLEXES

XXI *. TRIMETHYLSILYLATION OF COORDINATED DINITROGEN

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Summary

The treatment of *cis*-[$W(N_2)_2(PMe_2Ph)_4$] with trimethylsilyl iodide in benzene gave two silylated compounds *trans*-[$WI(NNSiMe_3)(PMe_2Ph)_4$] and *mer*-[$WI_2(NNHSiMe_3)(PMe_2Ph)_3$], X-ray analyses of which disclosed the trimethylsilyldiazenido and trimethylsilylhydrazido(2 –) structures, respectively. Analogous products were also prepared from the reactions of *trans*-[$W(N_2)_2(dpe)_2$], *trans*-[$W(N_2)_2(dpe)(PPh_2Me)_2$] and *trans*-[$W(^nPrCN)(N_2)(dpe)_2$] (dpe = $Ph_2PCH_2CH_2PPh_2$) with trimethylsilyl iodide.

Introduction

Accumulated studies on the reactivities of dinitrogen coordinated to transition metals in an end-on fashion has shown that the terminal nitrogen atom in the dinitrogen ligand is generally susceptible to electrophilic attack by a variety of acids, which include both a series of protic acids and Lewis acids such as $AlMe_3$ and $MoCl_4(THF)_2$ [2]. We already reported briefly that trimethylsilyl iodide smoothly reacts with *cis*-[$W(N_2)_2(PMe_2Ph)_4$] to give *trans*-[$WI(NNSiMe_3)(PMe_2Ph)_4$] and *mer*-[$WI_2(NNHSiMe_3)(PMe_2Ph)_3$], where the trimethylsilyl group attacks the terminal nitrogen atom as electrophile [3]. This is the first demonstrated example of the nitrogen–silicon bond formation from a dinitrogen ligand, although the formation of tris(trimethylsilyl)amine was reported by Shiina in early 1970s by the reaction of trimethylsilyl chloride and lithium in the presence of transition metal salts (e.g.

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[*] For part XX: see ref 1. This article is dedicated to Prof. Sei Otsuka on the occasion of his 65th birthday.

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chromium chloride) under a nitrogen atmosphere [4]. We report here the detail of the syntheses and spectroscopic properties of trimethylsilylated dinitrogen complexes.

Results and discussion

Reaction of cis-[W(N$_2$)$_2$(PMe$_2$Ph)$_4$] with Me$_3$SiI

Preliminary experiments of the reaction of *cis*-[W(N$_2$)$_2$(PMe$_2$Ph)$_4$] with Me$_3$SiI in benzene at 50 °C resulted in the formation of separable yellow and red crystals after deposition of the products by the diffusion of hexane into a concentrated reaction solution. The yellow complex shows three characteristic strong bands at 1570, 1246 and 873 cm^{-1} in its IR spectrum, which are assignable to ν(N=N), δ(CH$_3$Si) and ν(SiN), respectively. In its ^{1}H NMR spectrum of C$_6$D$_6$ solution, two strong singlet peaks appear at 0.47 and 1.73 ppm, the former of which is assigned to Me$_3$Si protons and the latter to methyl protons of PMe$_2$Ph ligands, together with complicated peaks of phenyl protons in the region of 6.96–7.69 ppm. Though small peaks also exist in the PMe and SiMe proton region, they may be negligible as small amounts of decomposition or side products and it may be reasonable to conclude that the yellow complex has four PMe$_2$Ph ligands in the equivalent positions. Based on these spectroscopic results and the satisfactory elemental analysis data, we formulated the yellow complex as *trans*-[WI(NNSiMe$_3$)(PMe$_2$Ph)$_4$](I), which has been substantiated by the X-ray analysis (vide infra).

$$\textit{cis}\text{-}[\mathrm{W(N_2)_2(PMe_2Ph)_4}] + \mathrm{Me_3SiI} \rightarrow \textit{trans}\text{-}[\mathrm{WI(NNSiMe_3)(PMe_2Ph)_4}] + \mathrm{N_2}$$

On the other hand, the red complex shows ν(NN) at 1355 cm^{-1} and ν(NH) at 3450 cm^{-1} in addition to δ(CH$_3$Si) and ν(SiN) bands at 1250 and 840 cm^{-1}, respectively. In the ^{1}H NMR spectrum the singlet peak at −0.02 ppm is assigned to Me$_3$Si protons, whereas the NH proton appears at 2.13 ppm as a singlet peak with 1H intensity. Methyl protons of PMe$_2$Ph ligands were recorded as two triplets with very close chemical shifts at 2.29 ppm and a doublet at 1.46 ppm with 12H and 6H intensities, respectively. This pattern suggests the meridional configuration of three PMe$_2$Ph ligands. Thus the red complex was formulated as *mer*-[WI$_2$(NNHSiMe$_3$)(PMe$_2$Ph)$_3$] (II). The X-ray analysis of this complex was also successful as described later. The formation of the complex II with the complex I proceeds doubtlessly by the reaction of the latter with HI generated by the hydrolysis of excess Me$_3$SiI with adventitious water. Thus use of rigorously dry solvent and removal of HI before dissolving the dinitrogen complex into the Me$_3$SiI solution in benzene lead to the formation of the complex I as a major product. This condition was satisfied as follows: (1) extremely dry benzene was collected in the reaction vessel just before starting the reaction: (2) after the addition of only the stoichiometric amount of Me$_3$SiI into benzene the mixture was allowed to follow the freeze (at −45 to −50 °C)-pump-thaw-cycles to evaporate HI still contained (HI: m.p. −51 °C).

$$\textit{trans}\text{-}[\mathrm{WI(NNSiMe_3)(PMe_2Ph)_4}] + \mathrm{HI} \rightarrow \textit{mer}\text{-}[\mathrm{WI_2(NNHSiMe_3)(PMe_2Ph)_3}] + \mathrm{PMe_2Ph}$$

For the formation of the complex II as a major product, the dinitrogen complex was treated with excess Me$_3$SiI in a large volume of benzene and freeze-pump-thaw cycles were omitted. It is notable that even when treated with excess amount of Me_3SiI under extremely dry conditions the dinitrogen complex did not give bis(trimethylsilyl)hydrazido(2 –) complex. This is in sharp contrast to the formation of tris(trimethylsilyl)amine from Me_3SiCl, Li and N_2 by the catalysis of transition metal salts, although no information is available on the reaction mechanism of this amine formation.

Molecular structures of trans-[WI(NNSiMe$_3$)(PMe$_2$Ph)$_4$] (I) and mer-[WI$_2$(NNHSiMe$_3$)(PMe$_2$Ph)$_3$ (II)

X-Ray analyses of the single crystals of the complex I and II have determined the molecular structures of these complexes, which are shown in Figs. 1 and 2, respectively. Selected bond lengths and angles are summarized in Tables 1 and 2. The complex I has an octahedral structure. Four PMe_2Ph ligands lie on the basal plane whereas trimethylsilyldiazenido and iodide ligands occupy the remaining sites in the trans positions. The W–N–N linkage with the angle of about 168° is essentially linear and is close to the Mo–N–N linkage of diazenido complex *trans*-[MoCl(NNCOPh)(dpe)$_2$] (dpe = $Ph_2PCH_2CH_2PPh_2$) [5] (Table 3). Since the trimethylsilyldiazenido ligand having structure A functions as three-electron donor, the metal atom in complex I has an 18-electron configuration. However, the Si–N bond length of 1.680(30) Å observed for this complex is very short and approaches close to that of $(Me_3Si)_2N^-$ anion (Table 4). In general, the Si–N single bond is appreciably shorter than the sum of covalent radii (1.87 Å), because d_π–p_π interaction exists between the vacant 3*d* orbital of Si atom and the filled lone pair orbital of sp^2 hybridized N atom. In the $(Me_3Si)_2N^-$ anion, the formal negative charge on the N atom favours more effective delocalization of its lone pairs into the vacant orbital of the Si atom, which results in the unusually short Si–N bond length [6]. The fact that the complex I has a similar Si–N bond length to this anion indicates that the

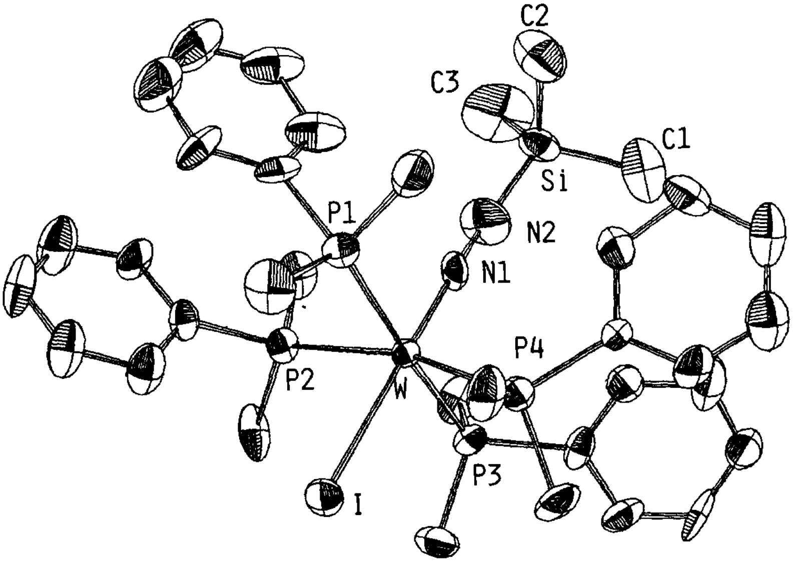


Fig. 1. An ORTEP drawing of the molecule *trans*-[WI(NNSiMe$_3$)(PMe$_2$Ph)$_4$] (I).

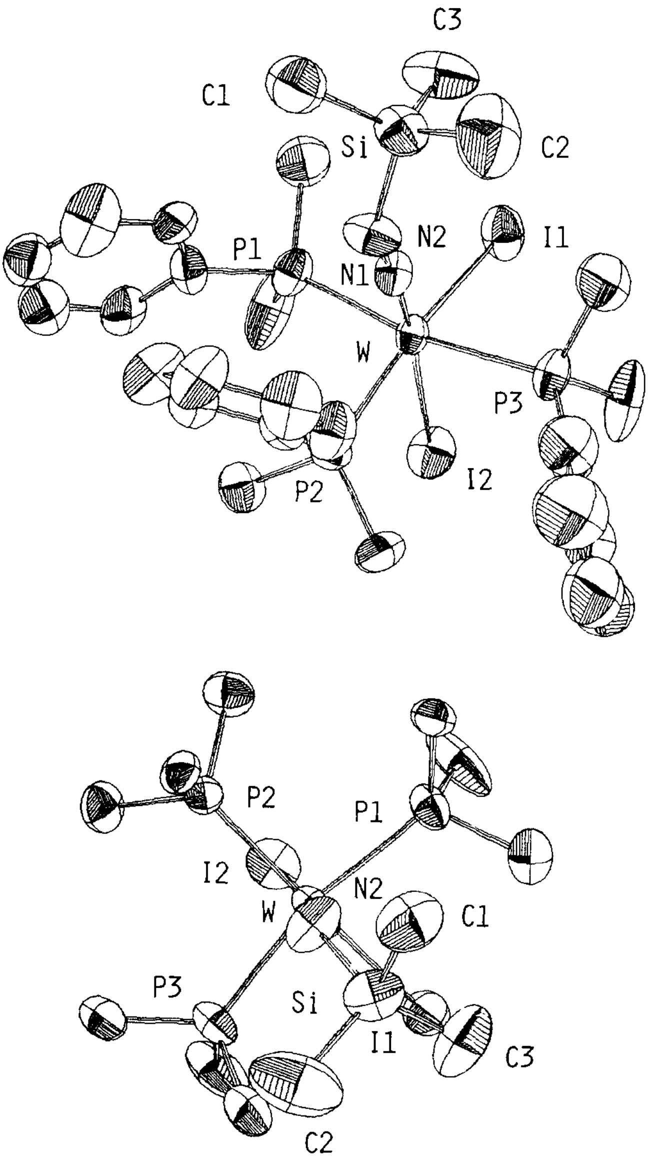
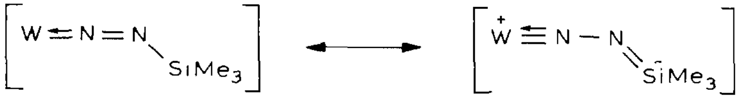


Fig. 2. An ORTEP drawing of the molecule *mer*-[$WI_2(NNHSiMe_3)(PMe_2Ph)_3$] (II) (upper); View showing the coordination around tungsten in the complex II (below).

W-N-N-$SiMe_3$ moiety can be represented by a combination of two resonance structures **A** and **B** and the latter structure contributes to a high degree in this complex. The difference of the Si-N-N angle of about 152° from the ideal 120°



(A) (B)

TABLE 1

SELECTED BOND LENGTHS AND ANGLES IN *trans*-$[WI(NNSiMe_3)(PMe_2Ph)_4]$

Bond Lengths (Å)		Bond Angles (°)			
W–I	2.917(2)	I–W–P(1)	94.9(1)	P(3)–W–N(1)	86.3(6)
W–P(1)	2.498(5)	I–W–P(2)	84.7(1)	P(4)–W–N(1)	102.4(6)
W–P(2)	2.507(5)	I–W–P(3)	90.0(1)	W–N(1)–N(2)	167.9(19)
W–P(3)	2.497(5)	I–W–P(4)	80.4(1)	N(1)–N(2)–Si	151.6(24)
W–P(4)	2.529(6)	I–W–N(1)	175.4(6)	N(2)–Si–C(1)	109.8(16)
W–N(1)	1.815(17)	P(1)–W–P(2)	88.9(2)	N(2)–Si–C(2)	114.4(15)
N(1)–N(2)	1.241(34)	P(1)–W–P(3)	174.8(2)	N(2)–Si–C(3)	105.0(18)
N(2)–Si	1.680(30)	P(1)–W–P(4)	92.5(2)	C(1)–Si–C(2)	106.7(16)
Si–C(1)	1.897(39)	P(1)–W–N(1)	88.7(6)	C(1)–Si–C(3)	107.6(19)
Si–C(2)	1.904(33)	P(2)–W–P(3)	89.8(2)	C(2)–Si–C(3)	113.1(18)
Si–C(3)	1.935(49)	P(2)–W–P(4)	165.1(2)		
		P(2)–W–N(1)	92.5(6)		
		P(3)–W–P(4)	90.1(2)		

TABLE 2

SELECTED BOND LENGTHS AND ANGLES IN *mer*-$[WI_2(NNHSiMe_3)(PMe_2Ph)_3]$

Bond Lengths (Å)		Bond Angles (°)			
W–I(1)	2.860(2)	I(1)–W–I(2)	85.7(1)	P(2)–W–N(1)	91.6(6)
W–I(2)	2.896(2)	I(1)–W–P(1)	84.2(2)	P(3)–W–N(1)	90.6(6)
W–P(1)	2.500(7)	I(1)–W–P(2)	164.2(1)	W–N(1)–N(2)	171.4(16)
W–P(2)	2.464(5)	I(1)–W–P(3)	82.7(2)	N(1)–N(2)–Si	126.6(17)
W–P(3)	2.511(7)	I(1)–W–N(1)	104.2(6)	N(2)–Si–C(1)	102.4(14)
W–N(1)	1.777(17)	I(2)–W–P(1)	93.0(2)	N(2)–Si–C(2)	108.8(17)
N(1)–N(2)	1.325(28)	I(2)–W–P(2)	78.5(1)	N(2)–Si–C(3)	109.3(15)
N(2)–Si	1.754(24)	I(2)–W–P(3)	88.0(2)	C(1)–Si–C(2)	109.5(19)
Si–C(1)	1.906(39)	I(2)–W–N(1)	169.7(6)	C(1)–Si–C(3)	114.6(17)
Si–C(2)	1.879(49)	P(1)–W–P(2)	94.8(2)	C(2)–Si–C(3)	111.8(20)
Si–C(3)	1.834(40)	P(1)–W–P(3)	166.8(2)		
		P(1)–W–N(1)	90.8(6)		
		P(2)–W–P(3)	98.3(2)		

TABLE 3

BOND LENGTHS AND ANGLES OF DIAZENIDO AND HYDRAZIDO(2–) COMPLEXES

Complex	M–N (Å)	N–N (Å)	M–N–N (°)	N–N–Si or N–N–C (°)	Ref.
trans-$[WI(NNSiMe_3)(PMe_2Ph)_4]$	1.815(17)	1.241(34)	167.9(19)	151.6(24)	[a]
trans-$[MoCl(NNCOPh)(dpe)_2]$	1.813(7)	1.255(10)	172.1(6)	116.7(7)	5
mer-$[WI_2(NNHSiMe_3)(PMe_2Ph)_3]$	1.777(17)	1.325(28)	171.4(16)	126.6(17)	[a]
trans-$[WBr(NNHMe)(dpe)_2]Br$	1.768(14)	1.32(2)	174(1)	121	7
trans-$[MoI(NNHC_8H_{17})(dpe)_2]I$	1.801(11)	1.259(14)	174(1)	120(1)	16

[a] This work.

TABLE 4

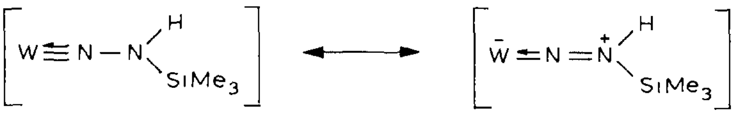
COMPARISON OF Si–N BOND LENGTHS

Compound	Si–N (Å)	Ref.
trans-[WI(NNSiMe$_3$)(PMe$_2$Ph)$_4$]	1.680(30)	^{a}
mer-[WI$_2$(NNHSiMe$_3$)(PMe$_2$Ph)$_3$]	1.754(24)	^{a}
K$^+$ (C$_4$H$_8$O$_2$)$_2$$^-$ N(SiMe$_3$)$_2$	1.64(1)	6
[(C$_5$H$_5$)MnNN(SiMe$_3$)$_2$]$_2$	1.743(8)	17
(Me$_3$Si)$_2$NN=NN(SiMe$_3$)$_2$ ^{b}	1.789(3), 1.770(4)	18
Me$_3$SiN=NSiMe$_3$	1.808(3)	19
[Me$_3$Si$^+$ (NC$_5$H$_5$)]I$^-$	1.858(9)	20

^{a} This work. ^{b} At −130 °C

expected for sp^2 hybridized N atom may come from the steric bulkiness of the Me$_3$Si group against the PMe$_2$Ph ligands.

The structure of the trimethylsilylhydrazido(2 −) ligand in complex II shows very good agreement with that of methylhydrazido(2 −) ligand in *trans*-[WBr(NNHMe)-(dpe)$_2$]Br [7]. The W–N–N linkage is essentially linear and the N–N distance of 1.325(28) Å corresponds to the bond order of 1.5. Dissociation of one PMe$_2$Ph ligand takes the steric repulsion away from the Me$_3$Si group and the Si–N–N angle approaches the nearly ideal value expected for sp^2 hybridized N atom. It is noteworthy that the Me$_3$Si group in the complex II is bent toward the site of iodide anion in the *cis* position, whereas the plane defined by the Si atom and two N atoms in complex I bisects the P–W–P angle. The Si–N distance of 1.754(24) Å in complex II is close to those of typical Si–N single bonds in silylamine derivatives. This indicates that d_π–p_π bonding between the Si and N atoms has smaller contribution in complex II than in complex I and the lone pair electrons on the N atom delocalize towards the metal instead of the Me$_3$Si group. This is reflected by the lower ν(SiN) of the complex II compared with that of the complex I. Thus the trimethylsilylhydrazido(2 −) ligand can be represented by the resonance of **C** and **D**.



(C) (D)

Reaction of the other dinitrogen complexes with Me$_3$SiI

The dinitrogen complexes *trans*-[W(N$_2$)$_2$(dpe)$_2$], *trans*-[W(N$_2$)$_2$(dpe)(PPh$_2$Me)$_2$] and *trans*-[W(^{n}PrCN)(N$_2$)(dpe)$_2$] also react with Me$_3$SiI to give trimethylsilyldiazenido and/or trimethylsilylhydrazido(2 −) complexes, which are summarized in Table 5. Characterization of these complexes is based on the elemental analyses and the appearance of a set of IR bands assigned to ν(NN), δ(CH$_3$Si) and ν(SiN) which shows a good agreement with those of the complexes I and II. Several attempts to record their ^{1}H NMR spectra were unsuccessful, since these complexes are unfortunately almost insoluble in usual organic solvents or decompose in common NMR solvents.

The complex *trans*-[W(N$_2$)$_2$(dpe)$_2$] reacts with Me$_3$SiI to give [WI(NN-

$SiMe_3$)(dpe)$_2$] or [WI(NNHSiMe$_3$)(dpe)$_2$]I, depending upon the procedures described above. Since the trimethylsilylation of this dinitrogen complex proceeds slower than that of *cis*-[W(N_2)$_2$(PMe_2Ph)$_4$], two molar equivalents of Me_3SiI were added to the former complex to obtain [WI($NNSiMe_3$)(dpe)$_2$]. On the other hand, preparation of a trimethylsilyldiazenido complex failed for *trans*-[W(N_2)$_2$(dpe)-(PPh_2Me)$_2$] and the trimethylsilylhydrazido(2 −) complex [WI_2($NNHSiMe_3$)-(dpe)(PPh_2Me)] was the sole isolable product even under the same condition as that for preparing [WI($NNSiMe_3$)(dpe)$_2$]. Surprisingly, only the complex [WI_2(N-$NHSiMe_3$)(dpe)(PPh_2Me)] was observed together with the unreacted dinitrogen complex at early stage of the reaction.

When *trans*-[W(^{n}PrCN)(N_2)(dpe)$_2$] was treated with two molar equivalents of Me_3SiI, trimethylsilylation occurred at the terminal nitrogen atom of the dinitrogen ligand without loss of the nitrile ligand, giving the trimethylsilylhydrazido(2 −) complex [W(^{n}PrCN)($NNHSiMe_3$)(dpe)$_2$]I_2. This reaction proceeds very fast even at room temperature, probably because the terminal nitrogen atom has more electron density than in *trans*-[W(N_2)$_2$(dpe)$_2$]. Replacement of one of the N_2 ligands by ^{n}PrCN results in increasing π-back donation from the W atom to the remaining N_2 ligand in the *trans* position. This is reflected in the lower ν(N≡N) in *trans*-[W(^{n}PrCN)(N_2)(dpe)$_2$] (1900 cm^{-1} [8]) than that in *trans*-[W(N_2)$_2$(dpe)$_2$] (1953 cm^{-1} [9]). It seems likely that this reaction proceeds analogously to the formation of [M(^{n}PrCN)(N_2H_2)(dpe)$_2$][HSO_4]$_2$ from *trans*-[M(^{n}PrCN)(N_2)(dpe)$_2$] and sulfuric acid (M = W, Mo) [8]. The ν(C≡N) in [W(^{n}PrCN)($NNHSiMe_3$)(dpe)$_2$]I_2 appears at 2255 cm^{-1}, which is higher than that in the starting complex (2175 cm^{-1}). A similar shift of the ν(C≡N) to a higher frequency is observed in the complex [W(^{n}PrCN)(N_2H_2)(dpe)$_2$][HSO_4]$_2$ (2260 cm^{-1} [8]).

When *trans*-[Mo(N_2)$_2$(dpe)$_2$] was treated with Me_3SiI in benzene at 50 °C, the color of the reaction mixture changed from orange to brown and a yellow solid precipitated as the product. However, this compound did not contain nitrogen and we have not yet succeeded in isolating the complexes with trimethylsilylated dinitrogen ligand. The characterization of the products from the reaction of a series of molybdenum dinitrogen complexes with Me_3SiI and the reactivities of trimethylsilyldiazenido and trimethylsilylhydrazido(2 −) ligands are under investigation.

Experimental

General

All experiments were carried out under nitrogen atmosphere. The complexes *cis*-[W(N_2)$_2$(PMe_2Ph)$_4$], *trans*-[W(N_2)$_2$(dpe)$_2$] [10], *trans*-[W(N_2)$_2$(dpe)(PPh_2Me)$_2$] [11], *trans*-[W(^{n}PrCN)(N_2)(dpe)$_2$] [8], and *trans*-[Mo(N_2)$_2$(dpe)$_2$] [10,12] were prepared by the reported methods. Trimethylsilyl iodide was prepared according to the literature [13] and stored in the refrigerator. IR spectra were recorded on Hitachi 215 spectrometer and ^{1}H NMR spectra on JEOL GX-400 spectrometer. All the trimethylsilylated dinitrogen complexes showed satisfactory elemental analysis data as given in Table 5.

Preparation of trans-[WI($NNSiMe_3$)(PMe_2Ph)$_4$]

After adding Me_3SiI (170 μl, 1.25 mmol) in the freshly distilled benzene (7 ml), the mixture was carefully degassed by freeze (at −45 to −50 °C)-pump-thaw cycles

TABLE 5

CHARACTERIZATION OF TRIMETHYLSILYLATED COMPLEXES

Complexes	Elemental analyses (Found (calcd.) (%))				Characteristic IR bands (cm^{-1}) [a]			
	C	H	N	I	ν(NN)	ν(SiN)	$\delta(CH_3Si)$	ν(NH)
Trimethylsilyldiazenido complexes								
trans-$[WI(NNSiMe_3)(PMe_2Ph)_4]$	43.66	5.95	2.82	13.14	1570	873	1246	–
	(43.58)	(5.55)	(2.90)	(13.16)				
$[WI(NNSiMe_3)(dpe)_2]$	53.58	4.45	1.82		1621	868	1246	–
	(54.63)	(4.75)	(2.32)					
Trimethylsilylhydrazido(2 –) complexes								
mer-$[WI_2(NNHSiMe_3)(PMe_2Ph)_3]$	33.93	4.79	2.85	26.20	1355	840	1250	3450
	(33.98)	(4.55)	(2.93)	(26.59)				
$[WI(NNHSiMe_3)(dpe)_2]I$	49.06	3.99	2.02		1358	848	1250	3195vw
	(49.41)	(4.38)	(2.10)					
$[WI_2(NNHSiMe_3)(dpe)(PPh_2Me)]$	44.70	4.25	2.37		1363	842	1251	3250
	(44.30)	(4.17)	(2.46)					
$[W(^nPrCN)(NNHSiMe_3)(dpe)_2]I_2$ [b]	48.50	4.71	2.81		1385	845	1253	3230vw
	(50.40)	(4.67)	(2.99)					

[a] KBr disks. [b] $\nu(C{\equiv}N)$: 2255 cm^{-1}

and then *cis*-[W(N_2)$_2$(PMe$_2$Ph)$_4$] (942 mg, 1.19 mmol) was added. After shielding from light, the mixture was stirred for 20 h at 50 °C. The brown solution obtained was concentrated in vacuo to about a half volume. Addition of freshly distilled hexane (4 ml) by trap to trap condensation gave yellow crystals, which were filtered off and dried in vacuo (776 mg, yield 67%).

Preparation of trans-[WI(NNSiMe$_3$)(dpe)$_2$]

After stirring a mixture of *trans*-[W(N_2)$_2$(dpe)$_2$] (994 mg, 0.958 mmol) and Me$_3$SiI (250 μl, 1.84 mmol) in benzene (15 ml) for 39 h in the dark, the yellow suspension obtained was reduced in volume to about 5 ml in vacuo. Trap to trap condensation of hexane (5 ml) to it gave a yellow solid, which was filtered off and dried in vacuo (1081 mg, yield 93%).

Preparation of [WI$_2$(NNHSiMe$_3$)(dpe)(PPh$_2$Me)]

A mixture of *trans*-[W(N_2)$_2$(dpe)(PPh$_2$Me)$_2$] (187 mg, 0.223 mmol) and Me$_3$SiI (60 μl, 0.441 mmol) in benzene (5 ml) was stirred for 24 h at 50 °C in the dark. The brown suspension obtained was concentrated to about half volume and trap to trap condensation of hexane (5 ml) to it gave a dark brown solid, which was filtered off and dried in vacuo (29 mg, yield 14%).

Preparation of [W(^{n}PrCN)(NNHSiMe$_3$)(dpe)$_2$]I$_2$

The suspension of *trans*-[W(^{n}PrCN)(N_2)(dpe)$_2$] (241 mg, 0.224 mmol) and Me$_3$SiI (65 μl, 0.478 mmol) in benzene (8 ml) was stirred at room temperature. Rapid color change from red to green was observed. After stirring for several hours, a pale green solid was filtered off, washed with hexane and dried in vacuo (83 mg, yield 25%).

Preparation of mer-[WI$_2$(NNHSiMe$_3$)(PMe$_2$Ph)$_3$]

Into a stirred solution of *cis*-[W(N_2)$_2$(PMe$_2$Ph)$_4$] (337 mg, 0.425 mmol) in benzene (10 ml) was added Me$_3$SiI (300 μl, 2.20 mmol) dropwise. After stirring overnight at 50 °C in the dark, the resultant red solution was evaporated in vacuo nearly to dryness. Crystallization of the residue from benzene/hexane gave red crystals of the title compound (220 mg, 54%).

Preparation of [WI(NNHSiMe$_3$)(dpe)$_2$]I

Into the suspension of *trans*-[W(N_2)$_2$(dpe)$_2$] (226 mg, 0.218 mmol) in benzene (15 ml) was added Me$_3$SiI (63 μl, 0.463 mmol) dropwise. After stirring for 14 h at 50 °C in the dark, a pink solid precipitated was filtered off, washed with benzene and dried in vacuo (165 mg, yield 57%).

Attempted reaction of trans-[Mo(N_2)$_2$(dpe)$_2$] with Me$_3$SiI

Into a mixture of Me$_3$SiI (60 μl, 0.441 mmol) and freshly distilled benzene (5 ml) was added *trans*-[Mo(N_2)$_2$(dpe)$_2$] (185 mg, 0.195 mmol). After stirring overnight at 50 °C in the dark, the brown suspension obtained was concentrated to about a half volume. Addition of hexane by trap to trap condensation gave a yellow solid, which was filtered off and dried in vacuo (155 mg). Elemental analysis of this compound showed the negligible content of nitrogen (Found: C, 53.97; H, 4.46; N, 0.32).

Crystallographic data

Yellow prism-like crystals of *trans*-[WI(NNSiMe$_3$)(PMe$_2$Ph)$_4$] (I) and red prism-

TABLE 6

CRYSTAL AND REFINEMENT DATA FOR *trans*-$[WI(NNSiMe_3)(PMe_2Ph)_4]$ (I) AND *mer*-$[WI_2(NNHSiMe_3)(PMe_2Ph)_3]$ (II)

	Complex I	Complex II
molecular weight	964.6 ($C_{35}H_{53}N_2SiP_4IW$)	954.3 ($C_{27}H_{43}N_2SiP_3I_2W$)
a (Å)	18.376(2)	17 418(4)
b (Å)	18.723(2)	18.031(5)
c (Å)	11.727(1)	11.370(2)
β (°)	96.082(10)	91.61(2)
V ($Å^3$)	4012.0	3569
Systematic absences	$0k0$, $k = 2n + 1$; $h0l$, $h + l = 2n + 1$	$0k0$, $k = 2n + 1$; $h0l$, $h + l = 2n + 1$
Space group	$P2_1/n$	$P2_1/n$
d_{calcd} (g/cm^3)	1.60	1.78
Z	4	4
Crystal dimensions (mm)	0.26×0.15×0.48	0.17×0.26×0.33
Linear abs coeff. (cm^{-1})	40.43	53.62
Data collection method	$2\theta-\theta$ scan	$2\theta-\theta$ scan
2θ-scan range (°)	2.5–60	2.5–60
Scan rate (2θ, °/min)	2	2
Scan range ($A + B\tan\theta$, °)	$A = 1.0$, $B = 0.35$	$A = 1.0$, $B = 0.45$
No. of standard reflections	3	3
No. of unique data collected	11640	10594
No. of data used ($F_o \geqq 3\sigma F_o$)	6482	6239
Data parameter ratio	13.6	16.2
Final *R*	0.10	0.12

like crystals of *mer*-$[WI_2(NNHSiMe_3)(PMe_2Ph)_3]$ (II) were prepared as described above and sealed in glass capillaries under nitrogen atmosphere. Data collection was carried out on an automatic Rigaku four-circle diffractometer, using LiF-monochromated Mo-K_α radiation. The lattice parameters of the crystals were determined with least-square fit to the setting angles for 37 and 40 hand-centered reflections with $24 < 2\theta < 32°$ for complex I and $24 < 2\theta < 34°$ for complex II, respectively. The intensity data were measured by the 2θ–θ scan mode, which prove the space group to be $P2_1/n$ for both crystals. In Table 6 are summarized the crystallographic data and details of data collection for both crystals. Lorentz and polarization corrections were applied to the data, followed by absorption correction.

Determination and refinement of the structures [14]

The crystal structures were solved by conventional Patterson synthesis to locate the tungsten atoms. Fourier syntheses were then carried out for the location of the remaining atoms except the hydrogen atoms. The positional parameters were refined by the block-diagonal least-squares technique [15]. Anomalous dispersion corrections were applied to the form factors for W, I, P, and Si atoms [15].

The quantity $w(|F_o| - |F_c|)^2$ was minimized and the weighting scheme was $w = 0.3$ for $F_o < F_{min}$, $w = 1.0$ for $F_{min} \leqq F_o < F_{max}$, and $w = (F_{max}/|F_o|)^2$ for $F_o > F_{max}$, where $F_{min} = 2.8$ and 2.6, $F_{max} = 14.4$ and 7.9 for the crystals of complexes I and II, respectively. In the final refinement, the *R* values were 0.10 for complex I and 0.12 for II. The standard deviations of an observation of unit weight defined as $[w(|F_o| - |F_c|)^2/(N - M)]$ were 0.99 and 0.58, where *N* and *M* are defined as the number of reflections and the number of refined parameters, respectively. The positional parameters obtained from the last cycle of refinement are listed in Tables 7 and 8 with the associated deviations estimated from the inverse matrix.

TABLE 7

FINAL POSITIONAL PARAMETER ($\times 10^4$) AND EQUIVALENT ISOTROPIC TEMPERATURE FACTORS ($\times 10$) FOR THE NON-HYDROGEN ATOMS OF *trans*-$[WI(NNSiMe_3)(PMe_2Ph)_4]$ (I)

Atom	x	y	z	B_{eq} [a]
W	2006.4(4)	1887.1(4)	736.0(6)	19
I	2938.9(9)	997.3(7)	−543.8(13)	35
P(1)	1056(3)	2087(3)	−920(4)	27
P(2)	2724(3)	2906(3)	36(4)	26
P(3)	2912(3)	1786(3)	2473(4)	27
P(4)	1499(3)	670(2)	1151(5)	27
Si	560(3)	3264(3)	2961(6)	35
N(1)	1493(9)	2473(9)	1590(12)	27
N(2)	1271(14)	2901(16)	2283(19)	61
C(1)	542(21)	2792(19)	4380(28)	66
C(2)	−347(15)	3207(17)	2134(27)	55
C(3)	913(23)	4235(13)	3297(41)	87
C(11)	84(13)	1874(14)	−720(24)	45
C(12)	1138(9)	1631(11)	−2269(17)	165
C(13)	875(10)	3020(10)	−1393(19)	30
C(14)	843(14)	3222(12)	−2470(22)	42
C(15)	701(17)	3948(20)	−2762(29)	67
C(16)	548(20)	4417(15)	−1935(30)	66
C(17)	578(15)	4229(16)	−818(31)	59
C(18)	748(16)	3472(17)	−542(27)	54
C(21)	2535(14)	3751(10)	733(20)	37
C(22)	3722(12)	2846(15)	261(19)	43
C(23)	2667(11)	3188(11)	−1452(16)	29
C(24)	2541(14)	3891(10)	−1877(20)	37
C(25)	2547(20)	4045(14)	−2986(22)	57
C(26)	2647(17)	3550(16)	−3805(21)	53
C(27)	2777(17)	2871(17)	−3454(21)	52
C(28)	2803(16)	2640(13)	−2332(20)	45
C(31)	3825(12)	1441(14)	2370(24)	43
C(32)	3121(14)	2658(12)	3164(19)	39
C(33)	2650(13)	1348(10)	3777(16)	31
C(34)	1918(13)	1396(12)	3978(19)	35
C(35)	1689(18)	1089(13)	4974(22)	49
C(36)	2164(15)	780(13)	5752(20)	41
C(37)	2902(17)	707(14)	5544(20)	52
C(38)	3110(13)	953(13)	4616(22)	41
C(41)	1098(16)	131(11)	−128(20)	44
C(42)	2180(15)	31(11)	1833(24)	44
C(43)	750(11)	555(10)	2061(16)	26
C(44)	615(13)	−37(10)	2677(20)	34
C(45)	51(18)	−99(16)	3296(23)	52
C(46)	−454(19)	450(19)	3366(23)	62
C(47)	−365(13)	1099(16)	2716(23)	46
C(48)	244(14)	1143(13)	3237(22)	41

[a] $B_{eq} = \frac{4}{3}(\beta_{11}a^2 + \beta_{22}b^2 + \beta_{33}c^2 + 2\beta_{13}ac\cos\beta)$.

TABLE 8

FINAL POSITIONAL PARAMETERS ($\times 10^4$) AND EQUIVALENT ISOTROPIC TERMPERATURE FACTORS ($\times 10$) FOR NON-HYDROGEN ATOMS OF *mer*-$[\mathrm{WI_2(NNHSiMe_3)(PMe_2Ph)_3}]$ (II)

Atom	x	y	z	B_{eq} [a]
W	3013.3(4)	1863.5(6)	1550 1(6)	28
I(1)	3725.1(10)	2965.6(11)	3024 6(16)	55
I(2)	3563.8(10)	806.5(11)	3295 9(14)	55
P(1)	4262(3)	1878(4)	519(5)	41
P(2)	2575(3)	682(3)	673(5)	34
P(3)	1888(3)	2103(4)	2830(5)	44
Si	2113(5)	3609(4)	−892(7)	54
N(1)	2568(9)	2379(10)	387(14)	35
N(2)	2210(13)	2665(10)	−552(16)	48
C(1)	2272(22)	3624(18)	−2543(26)	69
C(2)	1102(26)	3907(27)	−599(38)	107
C(3)	2819(23)	4142(17)	−13(34)	80
C(11)	4763(20)	2829(19)	286(33)	78
C(12)	5069(14)	1394(27)	1212(24)	86
C(13)	4312(12)	1567(13)	−1006(21)	43
C(14)	4713(11)	966(15)	−1372(22)	47
C(15)	4752(16)	758(18)	−2535(29)	66
C(16)	4371(19)	1156(19)	−3400(21)	65
C(17)	3942(16)	1731(24)	−3081(29)	76
C(18)	3908(15)	1969(13)	−1901(18)	46
C(21)	3323(14)	−8(14)	295(23)	50
C(22)	1921(16)	74(14)	1400(23)	53
C(23)	2069(11)	826(12)	−726(19)	40
C(24)	2437(14)	743(16)	−1821(23)	52
C(25)	2074(15)	920(19)	−2876(25)	63
C(26)	1329(15)	1126(19)	−2937(22)	62
C(27)	952(16)	1211(21)	−1866(28)	70
C(28)	1319(14)	1070(17)	−787(23)	56
C(31)	2098(18)	2096(26)	4438(23)	90
C(32)	1545(15)	3073(18)	2600(37)	74
C(33)	984(16)	1575(15)	2700(27)	58
C(34)	423(17)	1747(20)	1915(34)	73
C(35)	−249(21)	1335(28)	1530(51)	114
C(36)	−284(25)	730(27)	2514(49)	118
C(37)	130(28)	547(25)	3270(49)	113
C(38)	870(21)	946(20)	3448(32)	80

[a] $B_{eq} = \frac{4}{3}(\beta_{11}a^2 + \beta_{22}b^2 + \beta_{33}c^2 + 2\beta_{13}ac\cos\beta)$.

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