space interactions. Our present data are ambiguous on the question of whether the $\Delta E_{1/2}$ value for the four-bond Cr_2 system is larger than the statistically predicted value, since the conditions for chemical reversibility of the (arene)-$Cr(CO)_3$ groups place limits on the voltammetric accuracy. Future work will hopefully be able to answer this question. The present results and those of ref 24 show that polynorbornyl spacers have promise for the investigation of relatively weak metal–metal interactions.

Acknowledgment. W.E.G. gratefully acknowledges the support of the National Science Foundation through Grant Nos. CHE-86-03728 and CHE-91-16332. M.N.P.-R. and A.M.O. thank the Australian Research Council for support and the award of an ARC postdoctoral fellowship, respectively. We thank a reviewer for helpful comments on the $\Delta E_{1/2}$ values.

Supplementary Material Available: Tables II–IV, listing atomic coordinates, isotropic and anisotropic thermal parameters, bond angles, bond lengths, and H atom positions for the three crystallographic determinations (17 pages). Ordering information is given on any current masthead page.

OM920311L

Novel Disilylation of a Dinitrogen Ligand in *cis*-$[W(N_2)_2(PMe_2Ph)_4]$. Synthesis and Reactivity of *mer*-$[WI_2(NNSiMe_2CH_2CH_2SiMe_2)(PMe_2Ph)_3]$[1]

Hiroyuki Oshita, Yasushi Mizobe, and Masanobu Hidai*

Department of Synthetic Chemistry, Faculty of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113, Japan

Received May 27, 1992

When treated with a mixture of $ClMe_2SiCH_2CH_2SiMe_2Cl$ and excess NaI in benzene, *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ afforded a novel disilylhydrazido(2−) complex *mer*-$[WI_2(NNSiMe_2CH_2CH_2SiMe_2)(PMe_2Ph)_3]$ (1). Reactions of 1 with CO, $CH_2{=}CH_2$, and nitriles gave a series of neutral disilylhydrazido(2−) complexes $[WI_2(NNSiMe_2CH_2CH_2SiMe_2)(PMe_2Ph)_2(L)]$ (**3**, L = CO; **4**, L = $CH_2{=}CH_2$; **5a**, L = MeCN; **5b**, L = EtCN; **5c**, L = *p*-MeC_6H_4CN; **5d**, L = *p*-$MeCOC_6H_4CN$), whereas treatment of 1 with *t*-BuNC afforded a cationic complex *mer*-$[WI(NNSiMe_2CH_2CH_2SiMe_2)(PMe_2Ph)_3(t\text{-}BuNC)]I$ (**6a**) as a major product together with a neutral complex $[WI_2(NNSiMe_2CH_2CH_2SiMe_2)(PMe_2Ph)_2(t\text{-}BuNC)]$ (**6b**). Furthermore, when 1 was allowed to react with CH_2X_2, paramagnetic disilylhydrazido(2−) complexes $[WX_3(NNSiMe_2CH_2CH_2SiMe_2)(PMe_2Ph)_2]$ (**7a**, X = Cl; **7b**, X = I) were formed. The molecular structures of 1, **5d**, and **7a** were determined by the X-ray analyses. Crystal data: 1, monoclinic $P2_1/n$, $a = 14.378$ (4) Å, $b = 25.657$ (4) Å, $c = 10.601$ (2) Å, $\beta = 95.58$ (2)°, $Z = 4$, and $R = 0.057$ for 7760 reflections; **5d**, monoclinic $P2_1/a$, $a = 20.423$ (6) Å, $b = 12.488$ (4) Å, $c = 16.150$ (4) Å, $\beta = 105.09$ (2)°, $Z = 4$, and $R = 0.067$ for 3649 reflections; **7a**, orthorhombic $P2_12_12_1$, $a = 24.778$ (4) Å, $b = 12.593$ (2) Å, $c = 10.024$ (2) Å, $Z = 4$, and $R = 0.055$ for 2882 reflections.

Introduction

We have previously reported that dinitrogen complexes $[M(N_2)_2(\mathbf{P})_4]$ (M = Mo, W; **P** = PMe_2Ph, $^1/_2$ dpe; dpe = $Ph_2PCH_2CH_2PPh_2$) react with Me_3SiX (X = I, CF_3SO_3) to give silyldiazenido complexes *trans*-$[MX(NNSiMe_3)(\mathbf{P})_4]$, which demonstrates the first clarified example of the Si–N bond formation at the coordinated dinitrogen (eq 1).[2]

$$[M(N_2)_2(\mathbf{P})_4] + Me_3SiX \rightarrow trans\text{-}[MX(NNSiMe_3)(\mathbf{P})_4] \qquad (1)$$

$$M = Mo, W;\ \mathbf{P} = PMe_2Ph,\ {}^1\!/_2\ dpe;\ X = I,\ CF_3SO_3$$

Importantly, this finding has led to the development of the novel catalytic N_2-fixing system promoted by these dinitrogen complexes, in which molecular nitrogen is converted into silylamines under mild conditions (eq 2).[3]

$$Me_3SiCl + Na + N_2 \xrightarrow[\text{THF, 30 °C, 4 h}]{cis\text{-}[Mo(N_2)_2(PMe_2Ph)_4]} N(SiMe_3)_3 + HN(SiMe_3)_2 \qquad (2)$$

This has prompted us to study more extensively the silylation reactions of coordinated dinitrogen, which has subsequently revealed that a variety of silyldiazenido complexes such as *trans*-$[WI(NNSiR_3)(PMe_2Ph)_4]$ (R_3 = Me_nPh_{3-n} (n = 0–3), Et_3, $Me_2(OMe)$, $Me(OMe)_2$)[4] and $[M(NNSiR_3)(\mathbf{P})_4](\mu\text{-}OC)[Co(CO)_3]$ (R_3 = $PhMe_2$, Ph_2Me)[5] can be readily prepared by the reactions of these dinitrogen complexes with R_3SiCl/NaI and $R_3SiCo(CO)_4$, respectively.

In relevance to the formation of $N(SiMe_3)_3$ and $HN(SiMe_3)_2$ in the catalytic reaction shown in eq 2, disilylation or trisilylation of the coordinated dinitrogen is of particular interest. However, in spite of the exploitation of various reactions forming silylated dinitrogen complexes, all the

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(1) Preparation and Properties of Molybdenum and Tungsten Dinitrogen Complexes. 40. Part 39: Ishii, Y.; Miyagi, H.; Jitsukuni, S.; Seino, H.; Harkness, B. S.; Hidai, M. *J. Am. Chem. Soc.*, in press.

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0276-7333/92/2311-4116$03.00/0

reaction systems shown above gave the monosilylated complexes as the only isolable products even when an excess of the silyl compound was used. Now we have found that a disilylhydrazido(2−) complex *mer*-$[WI_2(N\overline{NSiMe_2CH_2CH_2Si}Me_2)(PMe_2Ph)_3]$ (**1**) can be prepared when *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ (**2**) is reacted with a mixture of disilyl compound $ClMe_2SiCH_2CH_2SiMe_2Cl$ and NaI.[6] In this paper, we describe the details of preparation and characterization of **1**. Reactivities of **1** toward a series of ligands such as CO, $CH_2{=}CH_2$, *t*-BuNC, and nitriles, as well as CH_2X_2 (X = Cl, I), are also reported.

Experimental Section

General Methods. All experiments were carried out under dry nitrogen atmosphere by using thoroughly dried glassware. Complex **2** was prepared according to the literature methods.[7,8] Benzene, hexane, and ether were distilled from Na–benzophenone and carefully degassed just before use. Compounds CH_2Cl_2, CH_2I_2, MeCN, and EtCN were distilled from P_2O_5 and stored under N_2. Compounds $ClMe_2SiCH_2CH_2SiMe_2Cl$, *t*-BuNC, *p*-MeC_6H_4CN, and *p*-$MeCOC_6H_4CN$ were commercially obtained and used without further purification. IR spectra were recorded on a Shimadzu IR-400 or FT-8100M spectrometer, and ^1H NMR spectra were recorded on a JEOL JMN-GX-400 spectrometer. ESR spectra were obtained at X-band frequencies by using a JEOL JEX-FEIX spectrometer. Elemental analyses were performed at the Elemental Analysis Laboratory, Department of Chemistry, Faculty of Science, The University of Tokyo.

Preparation of *mer*-$[WI_2(N\overline{NSiMe_2CH_2CH_2Si}Me_2)(PMe_2Ph)_3]$ (1). A suspension of $ClMe_2SiCH_2CH_2SiMe_2Cl$ (719 mg, 3.40 mmol) and NaI (2.07 g, 13.4 mmol) in benzene (10.0 mL) was carefully degassed by freeze (at −40 to −50 °C)–pump–thaw cycles, and then **2** (1.36 g, 1.72 mmol) was added. After stirring of the mixture at 50 °C for 45 h in the dark, the dark brown product solution was separated from NaI and NaCl by filtration. Addition of hexane by trap to trap condensation to the filtrate concentrated in vacuo gave dark brown crystals, which were filtered off and dried in vacuo (1.33 g, 75.7%). Anal. Calcd for $C_{30}H_{49}N_2Si_2P_3I_2W$: C, 35.17; H, 4.82; N, 2.73; I, 24.77. Found: C, 32.45; H, 4.70; N, 2.63; I, 24.71 and C, 34.02; H, 4.63; N, 2.69. Two separate analyses were performed. We have experienced difficulty in obtaining good elemental carbon (but not hydrogen or nitrogen) analyses for several silyl–metal complexes described here. This is probably due to the formation of silicon carbide during combustion analysis as reported by another group.[9]

Preparation of $[WI_2(N\overline{NSiMe_2CH_2CH_2Si}Me_2)(CO)(PMe_2Ph)_2]$ (3). After stirring of a solution of **1** (256 mg, 0.250 mmol) in benzene (5.0 mL) under CO atmosphere (1 atm) for 15 h at room temperature, the resultant pale yellow solution was concentrated. Addition of hexane by trap to trap condensation gave a mixture of black crystals of **3** and a reddish brown solid. The black crystals were collected, washed with hexane, and dried (119 mg, 52.0%). Anal. Calcd for $C_{23}H_{38}N_2OSi_2P_2I_2W$: C, 30.21; H, 4.19; N, 3.06. Found: C, 28.45; H, 4.14; N, 2.91.

Preparation of $[WI_2(N\overline{NSiMe_2CH_2CH_2Si}Me_2)(CH_2{=}CH_2)(PMe_2Ph)_2]$ (4). After ethylene was bubbled through a solution of **1** (333 mg, 0.325 mmol) in benzene (5.0 mL) at room temperature for 10 min, the mixture was stirred under ethylene (1 atm) for 12 h at room temperature. The orange powder precipitated was collected by filtration, washed with a small amount of benzene and hexane, and then dried in vacuo. Addition of hexane by trap to trap condensation to the filtrate gave an additional amount of **4**. The total yield of **4** was 214 mg (72.1%). Anal. Calcd for $C_{24}H_{42}N_2Si_2P_2I_2W$: C, 31.53; H, 4.63; N, 3.06. Found: C, 28.97; H, 4.52; N, 2.85.

Preparation of $[WI_2(N\overline{NSiMe_2CH_2CH_2Si}Me_2)(MeCN)(PMe_2Ph)_2]$ (5a). To a solution of **1** (305 mg, 0.298 mmol) in benzene (5.0 mL) was added MeCN (16 μL, 0.30 mmol), and the mixture was stirred at room temperature for 15 h. During this period the initial dark brown solution changed to a brown suspension. Addition of hexane by trap to trap condensation gave a brown crystalline solid of **5a** and light brown powder. After removal of a slurry containing the latter powder through a cannula, the solid remained was dried in vacuo (112 mg, 40.4%). Anal. Calcd for $C_{24}H_{41}N_3Si_2P_2I_2W$: C, 31.08; H, 4.46; N, 4.53. Found: C, 30.42; H, 4.47; N, 3.72.

$[WI_2(N\overline{NSiMe_2CH_2CH_2Si}Me_2)(EtCN)(PMe_2Ph)_2]$ (5b). Complex **5b** was obtained as dark brown crystals by the same method as that for preparing **5a** (yield 42.6%). Anal. Calcd for $C_{25}H_{43}N_3Si_2P_2I_2W$: C, 31.90; H, 4.60; N, 4.46. Found: C, 31.51; H, 4.55; N, 3.81.

$[WI_2(N\overline{NSiMe_2CH_2CH_2Si}Me_2)(p\text{-}MeC_6H_4CN)(PMe_2Ph)_2]$ (5c). Into a solution of **1** (179 mg, 0.175 mmol) in benzene (7.0 mL) was added *p*-MeC_6H_4CN (21.3 mg, 0.182 mmol), and the mixture was stirred at room temperature for 12 h. A greenish brown solid deposited by addition of hexane was filtered off, washed with hexane, and then dried in vacuo (122 mg, 69.5%). Anal. Calcd for $C_{30}H_{45}N_3Si_2P_2I_2W$: C, 35.91; H, 4.52; N, 4.19. Found: C, 35.24; H, 4.63; N, 3.80.

$[WI_2(N\overline{NSiMe_2CH_2CH_2Si}Me_2)(p\text{-}MeCOC_6H_4CN)(PMe_2Ph)_2]$ (5d). Complex **5d** was obtained as a dark blue crystalline solid by the same procedure as that for preparing **5c** (yield 90.0%). Anal. Calcd for $C_{31}H_{45}N_3OSi_2P_2I_2W$: C, 36.10; H, 4.40; N, 4.07. Found: C, 36.18; H, 4.45; N, 4.06.

Preparation of *mer*-$[WI(N\overline{NSiMe_2CH_2CH_2Si}Me_2)(t\text{-}BuNC)(PMe_2Ph)_3]I$ (6a). Into a solution of **1** (417 mg, 0.407 mmol) in benzene (5.0 mL) was added *t*-BuNC (92 μL, 0.81 mmol). After the mixture was stirred overnight at room temperature in the dark, the brown suspension obtained was filtered off. Then the precipitate was washed with a small amount of benzene and dried in vacuo (97.2 mg, 21.6%). Anal. Calcd for $C_{35}H_{58}N_3Si_2P_3I_2W$: C, 37.95; H, 5.28; N, 3.79. Found: C, 36.98; H, 5.35; N, 4.00. Addition of hexane to the filtrate gave a solid. The ^1H NMR spectrum of the crude material showed the concurrent formation of **6b** with **6a** and uncharacterizable products. Crude yields of **6a** and **6b** in this solid were estimated as ca. 24% and 10%, respectively, on the basis of the relative intensities of the resonances due to the methyl protons of PMe_2Ph ligands. Isolation of each compound from this solid was unsuccessful.

Preparation of $[WI_2(N\overline{NSiMe_2CH_2CH_2Si}Me_2)(t\text{-}BuNC)(PMe_2Ph)_2]$ (6b). Into a reddish brown suspension of **5c** (106 mg, 0.105 mmol) in benzene (7.0 mL) was added *t*-BuNC (12 μL, 0.11 mmol). After the mixture was stirred for 3 h at 50 °C, the brown solution obtained was dried. Black cubic crystals deposited on crystallization from THF/hexane were washed with hexane and then dried in vacuo (76.0 mg, 74.7%). Anal. Calcd for $C_{27}H_{47}N_3Si_2P_2I_2W$: C, 33.45; H, 4.89; N, 4.33. Found: C, 33.75; H, 4.88; N, 4.20. Analogous treatment of **5d** with *t*-BuNC also gave **6b** (59.4% yield).

Preparation of $[WCl_3(N\overline{NSiMe_2CH_2CH_2Si}Me_2)(PMe_2Ph)_2]$ (7a). A solution of complex **1** (634 mg, 0.619 mmol) in CH_2Cl_2 (5.0 mL) was stirred for 2 h, and the resultant dark red solution was concentrated. Addition of hexane by trap to trap condensation gave dark red crystals of **7a** together with a pale yellow powdery byproduct. Only the dark red crystals were collected, washed with hexane, and then dried in vacuo. Crystals of **7a** were further obtained on cooling the filtrate at −20 °C. The combined yield of **7a** was 68.2 mg (14.9%). ESR ($CHCl_3$, room temperature): triplet, $g = 1.92$, $A(^{31}P) = 3.10$ mT. Anal. Calcd for $C_{22}H_{38}N_2Si_2P_2Cl_3W$: C, 35.76; H, 5.18; N, 3.79. Found: C, 32.59; H, 5.07; N, 3.30.

Preparation of $[WI_3(N\overline{NSiMe_2CH_2CH_2Si}Me_2)(PMe_2Ph)_2]$ (7b). A mixture of **1** (204 mg, 0.197 mmol) and CH_2I_2 (80 μL, 1.0 mmol) in benzene (10 mL) was stirred overnight in the dark, and the dark red suspension obtained was filtered. The filtrate was dried in vacuo, and the residue was crystallized from

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Table I. Crystallographic Data for *mer*-[$WI_2(NNSiMe_2CH_2CH_2SiMe_2)(PMe_2Ph)_3$] (1), [$WI_2(NNSiMe_2CH_2CH_2SiMe_2)(PMe_2Ph)_2(NCC_6H_4COMe$-*p*)] (5d), and [$WCl_3(NNSiMe_2CH_2CH_2SiMe_2)(PMe_2Ph)_2$] (7a)

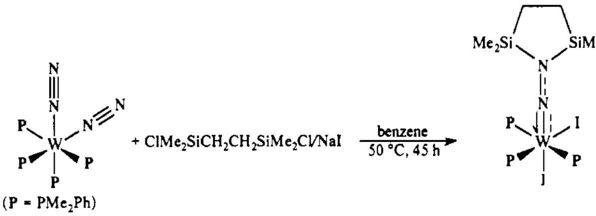
	1	5d	7a
		(a) Crystal Data	
formula	$C_{30}H_{49}N_2Si_2P_3I_2W$	$C_{31}H_{45}N_3OSi_2P_2I_2W$	$C_{22}H_{38}N_2Si_2P_2Cl_3W$
fw	1024.5	1031.5	738.9
cryst dimens, mm	0.5 × 0.7 × 0.8	0.20 × 0.30 × 0.25	0.19 × 0.19 × 0.19
cryst system	monoclinic	monoclinic	orthorhombic
space group	$P2_1/n$	$P2_1/a$	$P2_12_12_1$
cryst color	dark brown	dark purple	dark red
a, Å	14.378 (4)	20.423 (6)	24.778 (4)
b, Å	25.657 (4)	12.488 (4)	12.593 (2)
c, Å	10.601 (2)	16.150 (4)	10.024 (2)
β, deg	95.58 (2)	105.09 (2)	
V, $Å^3$	3891.9 (14)	3977.0 (20)	3127.7 (9)
Z	4	4	4
d_{calcd}, $g \cdot cm^{-3}$	1.748	1.722	1.569
$F(000)$, electrons	1984	1992	1468
μ_{calcd}, cm^{-1}	48.06	46.66	42.22
		(b) Data Collection	
diffractometer	Rigaku AFC-5R	MAC MXC-18	MAC MXC-18
monochromator		graphite	
radiatn (λ, Å)		Mo Kα (0.7107)	
temp		room temperature	
2θ range, deg	$5 < 2\theta < 60$	$3 < 2\theta < 55$	$3 < 2\theta < 50$
scan method	ω scan	ω–2θ scan	ω–2θ scan
scan speed, $deg \cdot min^{-1}$	8	10	16
abs corr	ψ scan method	Gaussian integration method	Gaussian integration method
transm factor	1.003–1.116	0.334–0.461	0.207–0.297
no. of reflcns measd	12316 ($\pm h,+k,+l$)	10186 ($\pm h,+k,+l$)	3139 ($+h,+k,+l$)
no. of data used	7760 ($\lvert F_o\rvert > 3\sigma(\lvert F_o\rvert)$)	3649 ($\lvert F_o\rvert > 5\sigma(\lvert F_o\rvert)$)	2882 ($\lvert F_o\rvert > 3\sigma(\lvert F_o\rvert)$)
		(C) Solution and Refinement	
no. of params refined	362	380	290
R	0.057	0.067	0.055
R_w	0.060	0.075	0.064
max resids, e $Å^{-3}$	1.8	1.6	2.9

CH_2Cl_2/hexane. The dark red crystals precipitated were filtered off, washed with ether, and dried in vacuo (123 mg, 60.8%). ESR (CH_2Cl_2, room temperature): $g = 2.04$. Anal. Calcd for $C_{22}H_{38}N_2Si_2P_2I_3W$: C, 26.08; H, 3.78; N, 2.76; I, 37.58. Found: C, 25.51; H, 3.73; N, 2.43; I, 38.93.

X-ray Crystallographic Analysis of 1, 5d, and 7a. An X-ray diffraction study was carried out by using single crystals sealed in glass capillaries under Ar or N_2. The orientation matrices and unit cell parameters were derived from a least-squares fit of about 20 machine-centered reflections with 2θ values between 25 and 35°. No significant decay in intensities of three standard reflections was observed for all three compounds during data collections. Intensity data were corrected for Lorentz and polarization effects, and absorption corrections were also performed. Details of the X-ray diffraction study of 1, 5d, and 7a are summarized in Table I. Positional parameters of the non-hydrogen atoms have been listed in Tables II–IV. Structure solution and refinements were performed at The Computer Center of The University of Tokyo, using the UNIX-III program package. The positions of W atoms were determined either by a direct methods program (MULTUN 78 for 1 and SHELXS 86 for 5d) or by the Patterson method for 7a. Subsequent cycles of difference Fourier syntheses and block-diagonal least-squares refinements revealed all non-hydrogen atoms, which were refined anisotropically. All hydrogen atoms were placed in calculated positions (d_{C-H}= 1.09 Å for methyl and methylene protons and d_{C-H} = 1.08 Å for phenyl protons). Anomalous dispersion effects were included, and the atomic scattering factors were taken from ref 10. Refinement of the structure of 7a with an opposite polarity did not result in the lower R values.

Results and Discussion

Preparation and Characterization of Disilylhydrazido(2–) Complexes. Treatment of *cis*-[$W(N_2)_2(PMe_2Ph)_4$] (2) with $ClMe_2SiCH_2CH_2SiMe_2Cl$ in the presence of excess NaI at 50 °C in benzene afforded a novel disilylhydrazido(2–) complex *mer*-[$WI_2(NNSiMe_2CH_2CH_2SiMe_2)(PMe_2Ph)_3$] (1) in moderate yield (eq 3).[11] Although a series of dinitrogen complexes



2 1 (3)

trans-[$M(N_2)_2(dpe)_2$] (M = Mo, W), *trans*–[$W(N_2)_2(dpe)(PPh_2Me)_2$], and *trans*-[$W(N_2)_2(PPh_2Me)_4$] were also treated with $ClMe_2SiCH_2CH_2SiMe_2Cl$/NaI, none of these gave the silylated dinitrogen complexes under conditions similar to those for preparing 1. Since 2 and $ClMe_2SiCH_2CH_2SiMe_2Cl$ do not afford 1 in the absence of NaI, the formation of 1 presumably takes place by the electrophilic attack of $IMe_2SiCH_2CH_2SiMe_2I$ or $IMe_2SiCH_2CH_2SiMe_2Cl$ generated in situ on the terminal nitrogen atom.[12–14] The second silylation is probably

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[10] *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

[11] The molybdenum disilylhydrazido(2–) complex *mer*-[$MoI_2(NNSiMe_2CH_2CH_2SiMe_2)(PMe_2Ph)_3$] was also prepared analogously by treatment of *cis*-[$Mo(N_2)_2(PMe_2Ph)_4$] with $ClMe_2SiCH_2CH_2SiMe_2Cl$/NaI at 40 °C. ^1H NMR (δ, C_6D_6): 6.7–7.7 (m, 15H, PPh), 2.14 (t, 6H, PMe), 2.08 (t, 6H, PMe), 1.36 (d, 6H, PMe), 0.53 (s, 4H, $SiCH_2$), 0.47 (s, 12H, SiMe). IR (KBr disk): ν(NN) 1302, δ(SiMe) 1252, ν(SiN) 857 cm^{-1}. Anal. Calcd for $C_{30}H_{49}N_2Si_2P_3MoI_2$: C, 38.47; H, 5.27; N, 2.99. Found: C, 38.10; H, 5.27; N, 2.77. Details of the preparation and properties of this complex will be reported elsewhere.

Table II. Positional Parameters (×10⁴) and Equivalent Temperature Factors for 1

atom	*x*	*y*	*z*	*B*(eq), Å²
W	2638.3 (3)	9109.3 (1)	6715.8 (3)	2.5
I(1)	3709.1 (6)	9432.4 (3)	4688.9 (7)	4.3
I(2)	1070.8 (5)	8989.8 (3)	4848.0 (7)	4.2
P(1)	3061 (2)	8177 (1)	6197 (3)	3.5
P(2)	4167 (2)	9241 (1)	7954 (3)	3.5
P(3)	2107 (2)	10045 (1)	6620 (3)	3.7
Si(1)	1612 (3)	9055 (2)	10546 (3)	5.0
Si(2)	307 (3)	8569 (2)	8510 (3)	4.9
N(1)	1991 (5)	8978 (3)	8004 (6)	2.6
N(2)	1400 (6)	8887 (4)	8911 (8)	3.8
C(1)	2369 (11)	8591 (6)	11504 (12)	5.9
C(2)	2029 (11)	9727 (6)	10788 (14)	6.6
C(3)	360 (11)	8967 (7)	10902 (13)	6.9
C(4)	−14 (10)	8477 (7)	10168 (14)	6.7
C(5)	414 (11)	7946 (6)	7652 (16)	7.1
C(6)	−574 (9)	9001 (6)	7626 (13)	5.5
C(11)	2224 (10)	7798 (5)	5192 (13)	5.5
C(12)	4077 (10)	8081 (5)	5276 (12)	4.8
C(13)	3258 (8)	7717 (4)	7506 (11)	3.8
C(14)	3697 (10)	7244 (5)	7382 (13)	5.8
C(15)	3834 (12)	6890 (5)	8356 (14)	6.7
C(16)	3559 (11)	6988 (5)	9500 (14)	6.5
C(17)	3082 (12)	7452 (6)	9660 (14)	7.0
C(18)	2925 (9)	7805 (5)	8643 (12)	5.1
C(21)	4743 (9)	9874 (5)	8003 (14)	5.5
C(22)	4104 (9)	9128 (6)	9652 (11)	5.3
C(23)	5149 (7)	8825 (5)	7682 (11)	3.8
C(24)	5241 (8)	8329 (5)	8232 (11)	4.4
C(25)	5963 (10)	8001 (6)	8016 (13)	5.8
C(26)	6614 (11)	8145 (6)	7248 (15)	7.0
C(27)	6583 (9)	8638 (6)	6710 (15)	6.6
C(28)	5832 (9)	8984 (6)	6897 (13)	5.4
C(31)	1763 (10)	10327 (5)	5062 (11)	4.9
C(32)	1007 (9)	10104 (5)	7345 (13)	5.1
C(33)	2799 (8)	10596 (4)	7329 (11)	4.1
C(34)	2677 (9)	10796 (5)	8517 (12)	5.0
C(35)	3173 (11)	11205 (6)	9026 (14)	6.5
C(36)	3808 (11)	11442 (5)	8353 (14)	6.3
C(37)	3961 (11)	11254 (6)	7165 (14)	6.1
C(38)	3454 (10)	10823 (5)	6669 (12)	5.0

Table III. Positional Parameters (×10⁴) and Equivalent Temperature Factors for 5d

atom	*x*	*y*	*z*	*B*(eq), Å²
W	2327.0 (4)	1951.6 (8)	7181.3 (6)	3.6
I(1)	3263 (1)	1384 (2)	6230 (1)	7.0
I(2)	3380 (1)	1628 (2)	8756 (1)	7.4
P(1)	2104 (3)	−9 (5)	7271 (4)	4.7
P(2)	2726 (3)	3856 (6)	7159 (5)	5.8
Si(1)	965 (4)	2286 (6)	4590 (4)	5.3
Si(2)	332 (3)	2915 (6)	5998 (4)	4.6
O	799 (10)	2405 (19)	12183 (11)	8.9
N(1)	1632 (8)	2247 (12)	6297 (10)	3.7
N(2)	1073 (8)	2451 (15)	5724 (11)	4.1
N(3)	1791 (8)	2243 (13)	8066 (12)	4.3
C(1)	1739 (14)	2642 (28)	4268 (18)	7.9
C(2)	748 (15)	873 (25)	4282 (18)	7.4
C(3)	221 (16)	3200 (28)	4230 (17)	8.6
C(4)	−198 (12)	3119 (29)	4889 (17)	7.8
C(5)	15 (11)	1896 (25)	6653 (19)	7.2
C(6)	523 (13)	4176 (20)	6650 (18)	6.2
C(11)	1685 (15)	−547 (22)	6243 (18)	7.2
C(12)	2825 (14)	−915 (22)	7599 (19)	7.2
C(13)	1601 (11)	−388 (17)	7983 (15)	4.6
C(14)	1873 (15)	−598 (28)	8840 (17)	8.0
C(15)	1454 (19)	−823 (37)	9376 (18)	11.5
C(16)	799 (18)	−850 (29)	9085 (26)	10.7
C(17)	511 (16)	−682 (33)	8252 (28)	12.1
C(18)	893 (13)	−462 (29)	7718 (24)	10.1
C(21)	3611 (13)	4172 (25)	7678 (21)	8.3
C(22)	2574 (21)	4396 (26)	6091 (20)	10.7
C(23)	2316 (11)	4879 (19)	7698 (15)	4.9
C(24)	2007 (14)	5800 (22)	7203 (25)	9.5
C(25)	1685 (16)	6504 (24)	7752 (26)	10.3
C(26)	1687 (14)	6271 (24)	8567 (24)	9.6
C(27)	1958 (13)	5364 (25)	8940 (21)	8.1
C(28)	2280 (12)	4639 (24)	8493 (19)	7.1
C(31)	1497 (10)	2332 (22)	8595 (15)	5.4
C(32)	1226 (10)	2473 (19)	9309 (14)	4.5
C(33)	655 (12)	3106 (26)	9252 (15)	6.7
C(34)	443 (12)	3251 (27)	9992 (16)	7.1
C(35)	776 (10)	2779 (18)	10765 (14)	4.6
C(36)	1359 (12)	2193 (19)	10779 (14)	5.5
C(37)	1573 (12)	2053 (23)	10081 (14)	5.9
C(38)	580 (13)	3014 (26)	11604 (16)	6.7
C(39)	143 (17)	3950 (35)	11614 (22)	10.5

enhanced by the concurrent cyclization affording a stable five-membered ring, which might be closely related to the facile formation of dialkyl- and diacylhydrazido(2−) complexes $[\mathrm{WBr}\{\mathrm{N}\overline{\mathrm{NCH_2(CH_2)_nCH_2}}\}(\mathrm{L\text{-}L})_2]\mathrm{Br}$ (n = 1–3)[15] and $[\mathrm{WF}(\mathrm{N}\overline{\mathrm{NCOCH_2CH_2CO}})(\mathrm{dpe})_2][\mathrm{BF_4}]$[16] by the reactions of $[\mathrm{W(N_2)_2(L\text{-}L)_2}]$ (L-L = diphosphines) with α,ω-dibromides and $[\mathrm{WF(NNH_2)(dpe)_2}][\mathrm{BF_4}]$ with succinyl chloride, respectively. As mentioned already, 1 is the first example of the disilylhydrazido(2−) complex derived from dinitrogen complexes, although some bis(trimethylsilyl)hydrazido(2−) complexes such as $[\mathrm{CpMNN(SiMe_3)_2}]_2$ (M = Cr, Mn)[17] and $\mathrm{Cp_2MNN(SiMe_3)_2}$ (M = Ti, V)[17,18] pre-

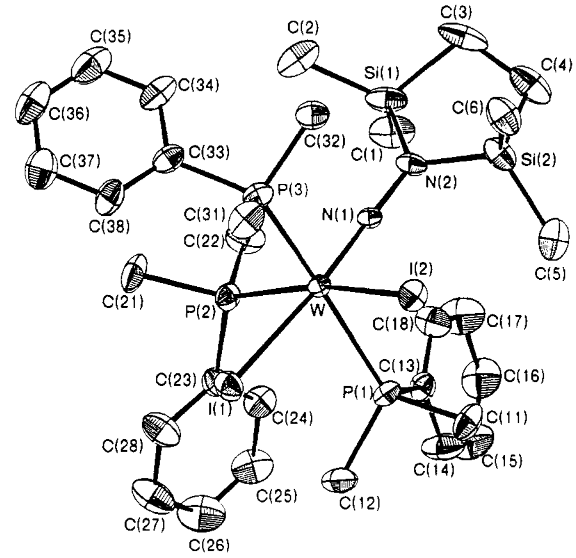

Figure 1. ORTEP diagram of *mer*-$[\mathrm{WI_2(N\overline{NSiMe_2CH_2CH_2SiMe_2})(PMe_2Ph)_3}]$ (1), showing the atom-labeling scheme.

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[12] The mixture of Me_3SiCl and NaI in MeCN can be used as a convenient and inexpensive alternative for Me_3SiI. See for example: Morita, T.; Okamoto, Y.; Sakurai, H. *Yuki Gosei Kagaku Kyokai Shi* **1981**, *39*, 973 and references cited therein.

[13] The radical mechanism proposed previously for the reaction of $[\mathrm{M(N_2)_2(L\text{-}L)_2}]$ (M = Mo, W; L-L = diphosphines) with alkyl halides to give alkyldiazenido (M=N=NR) complexes[14a,b] may be ruled out here because the silylation reaction carried out in toluene gave 1 in comparable yield (70%) to that in benzene (75%). Furthermore, the GLC analysis of the reaction mixture did not show the formation of any organic products derived from the benzyl radical. It is worth mentioning that alkylation of coordinated dinitrogen did not occur in the case of the monophosphine complex 2 and its Mo analogue,[14c] whereas silylation of coordinated dinitrogen proceeded smoothly.

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Table IV. Positional Parameters ($\times 10^4$) and Equivalent Temperature Factors for 7a

atom	*x*	*y*	*z*	*B*(eq), Å^2
W	1358.6 (3)	1969.9 (5)	684.3 (6)	3.1
Cl(1)	1397 (3)	881 (4)	2764 (5)	5.1
Cl(2)	1244 (3)	286 (4)	–462 (5)	5.8
Cl(3)	1494 (3)	3474 (4)	2169 (5)	4.9
P(1)	2366 (2)	1639 (4)	703 (6)	4.1
P(2)	359 (2)	1963 (5)	1244 (5)	4.3
Si(1)	1331 (3)	3015 (5)	–3459 (5)	4.5
Si(2)	1195 (3)	4823 (4)	–1552 (6)	4.8
N(1)	1330 (7)	2795 (9)	–737 (14)	4.0
N(2)	1279 (8)	3450 (10)	–1764 (13)	4.5
C(1)	969 (13)	1741 (20)	–3738 (22)	7.5
C(2)	2050 (11)	2947 (33)	–3959 (23)	9.0
C(3)	976 (12)	4198 (20)	–4194 (23)	7.0
C(4)	1124 (18)	5168 (22)	–3401 (26)	11.4
C(5)	606 (9)	5127 (17)	–438 (26)	5.8
C(6)	1826 (10)	5421 (19)	–856 (29)	6.5
C(11)	2544 (11)	209 (19)	593 (33)	7.4
C(12)	2716 (10)	2046 (26)	2231 (19)	6.4
C(13)	2776 (7)	2270 (14)	–552 (20)	3.9
C(14)	2813 (10)	3359 (16)	–579 (25)	6.0
C(15)	3135 (13)	3868 (26)	–1465 (33)	8.6
C(16)	3417 (10)	3282 (26)	–2383 (27)	8.4
C(17)	3370 (11)	2234 (25)	–2447 (26)	7.7
C(18)	3051 (9)	1712 (19)	–1515 (22)	5.7
C(21)	186 (9)	2535 (24)	2883 (24)	6.8
C(22)	53 (11)	638 (20)	1346 (31)	7.4
C(23)	–86 (9)	2599 (18)	72 (26)	5.5
C(24)	–475 (9)	3314 (20)	450 (30)	6.8
C(25)	–809 (11)	3793 (25)	–529 (41)	9.8
C(26)	–727 (11)	3614 (23)	–1812 (30)	7.8
C(27)	–346 (10)	2883 (24)	–2213 (28)	7.7
C(28)	–17 (11)	2393 (19)	–1265 (23)	6.0

Table V. Selected Bond Distances and Angles in 1

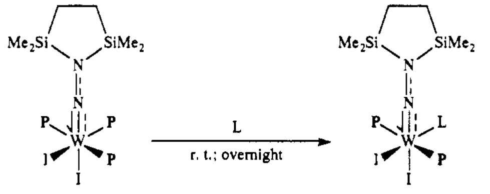
Bond Distances (Å)			
W–I(1)	2.884 (1)	W–I(2)	2.868 (1)
W–P(1)	2.541 (3)	W–P(2)	2.472 (3)
W–P(3)	2.519 (3)	W–N(1)	1.758 (7)
N(1)–N(2)	1.36 (1)	Si(1)–N(2)	1.78 (1)
Si(2)–N(2)	1.78 (1)		
Bond Angles (deg)			
I(1)–W–I(2)	87.53 (3)	I(1)–W–P(1)	87.3 (1)
I(1)–W–P(2)	81.1 (1)	I(1)–W–P(3)	83.0 (1)
I(1)–W–N(1)	174.2 (2)	I(2)–W–P(1)	86.5 (1)
I(2)–W–P(2)	168.5 (1)	I(2)–W–P(3)	81.9 (1)
I(2)–W–N(1)	94.4 (2)	P(1)–W–P(2)	91.4 (1)
P(1)–W–P(3)	165.1 (1)	P(1)–W–N(1)	98.2 (3)
P(2)–W–P(3)	98.2 (1)	P(2)–W–N(1)	97.1 (2)
P(3)–W–N(1)	91.9 (3)	N(2)–Si(1)–C(3)	95.1 (5)
N(2)–Si(2)–C(4)	97.3 (6)	W–N(1)–N(2)	173.4 (6)
N(1)–N(2)–Si(1)	125.7 (7)	N(1)–N(2)–Si(2)	120.4 (6)

pared by the reactions of $Me_3SiN{=}NSiMe_3$ with Cp_2M (M = Cr, Mn, V) or Cp_2TiCl_2 have been reported previously.

X-ray crystallography was performed for 1 to clarify the molecular structure of this disilylhydrazido(2–) complex. The ORTEP drawing of 1 is shown in Figure 1, while selected bond lengths and angles are summarized in Table V. Complex 1 has a slightly distorted octahedral configuration with three PMe_2Ph and two iodide ligands in mutually meridional and cis positions, respectively. In the disilylhydrazido(2–) ligand trans to one iodide ligand, the W–N–N linkage is essentially linear and the terminal N(2) atom binds two Si atoms, forming a five-membered ring. Two Si and two C atoms and one N atom consisting of this ring together with the inner N(1) and W atoms lie almost on the same plane. This planarity of the disilylhydrazido(2–) ligand as well as the N–N bond order larger than unity are ascribed to the sp^2 hybridization of the terminal N atom. The W–N bond distance is consistent with the W–N multiple bond. These structural features are also observed for the wide range of hydrazido(2–) complexes of this type as shown in Table VI. The Si–N bond distance of 1.78 (1) Å is slightly longer than a typical Si–N single bond (ca. 1.70–1.76 Å).[19]

Spectroscopic data for 1 are diagnostic of the structure clarified by the X-ray analysis. The IR spectrum shows characteristic ν(NN), δ(SiMe), and ν(SiN) bands (Table VII). The ^1H NMR spectrum of 1 exhibits two singlets assignable to methyl and methylene protons in the disilylhydrazido(2–) ligands in addition to the resonances due to the three meridional PMe_2Ph ligands, indicating that four methyl groups and four methylene protons are equivalent, respectively. This obviously results from the planar structure of the disilylhydrazido(2–) ligand manifested by the X-ray analysis.

Reactions of *mer*-[$WI_2(NNSiMe_2CH_2CH_2SiMe_2)(PMe_2Ph)_3$] (1) with CO, $CH_2{=}CH_2$, RCN, and *t*-BuNC. The study on the reactivities of 1 with several ligands such as CO, $CH_2{=}CH_2$, and RCN has shown that one PMe_2Ph ligand cis to the disilylhydrazido(2–) group is easily substituted by these molecules in benzene at room temperature to give new disilylhydrazido(2–) complexes *cis,trans*-[$WI_2(NNSiMe_2CH_2CH_2SiMe_2)(L)(PMe_2Ph)_2$] (3, L = CO; 4, L = $CH_2{=}CH_2$; 5a, L = MeCN; 5b, L = EtCN; 5c, L = *p*-MeC_6H_4CN; 5d, L = *p*-$MeCOC_6H_4CN$) (eq 4).



1 (P = PMe_2Ph; L = CO (3), $CH_2{=}CH_2$ (4), RCN (5)) (4)

The facile coordination of these molecules to the high-valent W(IV) center in 1 is of much interest. Closely relating substitution reactions of a phosphine ligand cis to the W(IV)–N multiple bond by π-acceptor ligands such as CO, isonitriles, and olefins have been recently observed for *mer*-[$WCl_2(NR)(P)_3$] (P = PPh_2Me, PMe_3),[20] *mer*-[$WCl_2(NN{=}CR_2)(PMe_2Ph)_3$],[21] and *mer*-[$WCl_2(NNH_2)(PMe_2Ph)_3$],[21] and the molecular orbital study has elucidated that these reactivities are ascribed to the substantial π-donating ability of the d^2 W centers in these particular complexes toward the cis direction with respect to the W–N multiple bonds.

Spectroscopic data for the disilylhydrazido(2–) complexes obtained here are summarized in Table VII. Three characteristic IR bands assignable to ν(NN), ν(SiN), and δ(SiMe) are observed for all complexes 3–5, indicating that the disilylhydrazido(2–) ligands remain intact after the reactions. The IR spectra of 3 and 5 further exhibit the strong ν(CO) or medium ν(C≡N) band, respectively. The ν(CO) value of 1931 cm^{-1} is comparable to those in [$WCl_2(NN{=}CMe_2)(CO)(PMe_2Ph)_2$] (1940 cm^{-1}) and [$WCl_2(NNH_2)(CO)(PMe_2Ph)_2$] (1940 cm^{-1}),[21] suggesting that the substantial π-donation from the d^2 W center to

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Table VI. Comparison of Bond Distances (Å) and Angles (deg) in Hydrazido(2−) Complexes of Tungsten

complex	W–N	N–N	N–Si	W–N–N	N–N–R	ref
mer-$[WI_2(NNHSiMe_3)(PMe_2Ph)_3]$	1.78 (2)	1.33 (3)	1.75 (2)	171 (2)	127 (2)	2b
trans-$[W(OH)(NNHSiPh_2Me)(dpe)_2][Co(CO)_4]$	1.78 (1)	1.36 (2)	1.76 (1)	169.3 (9)	131.8 (9)	5
mer-$[WI_2(N\overline{NSiMe_2CH_2CH_2Si}Me_2)(PMe_2Ph)_3]$	1.758 (7)	1.36 (1)	1.78 (1) 1.78 (1)	173.4 (6)	120.4 (6) 125.7 (7)	this work
$[WI_2(N\overline{NSiMe_2CH_2CH_2Si}Me_2)(PMe_2Ph)_2(p\text{-}MeCOC_6H_4C{\equiv}N)]$	1.77 (1)	1.29 (2)	1.80 (2) 1.78 (2)	172.1 (16)	124 (1) 122 (1)	this work
$[WCl_3(N\overline{NSiMe_2CH_2CH_2Si}Me_2)(PMe_2Ph)_2]$	1.76 (1)	1.33 (2)	1.79 (1) 1.75 (1)	175.9 (14)	123 (1) 122 (1)	this work
$[WCl_3(NNH_2)(PMe_2Ph)_2]$	1.75 (1)	1.30 (2)		178.7 (9)	110 107	33
$[WCl_3(NNHPh)(PMe_2Ph)_2]^a$	1.737 (5) 1.739 (5)	1.325 (8) 1.316 (8)		174.4 (5) 170.5 (6)	122.9 (7) 124.2 (7)	33
$[WBr(NNH_2)(NC_5H_4Me\text{-}4)(PMe_2Ph)_3]Br$	1.75	1.34		177		25
$[WF(N\overline{NCOCH_2CH_2C}O)(dpe)_2]BF_4$	1.75 (2)	1.39 (3)		174 (2)	120.5 125.9	16
$[WBr(N\overline{NCH_2CH_2C}H_2)(dtpe)_2]Br^b$	1.72 (6)	1.42 (6)		171 (5)	124 (5) 130 (7)	15b

[a] Two independent molecules in the crystal. [b] dtpe = $(4\text{-}MeC_6H_4)_2PCH_2CH_2P(C_6H_4Me\text{-}4)_2$.

the CO ligand is also present in **3**. The shifts of the $\nu(C{\equiv}N)$ values in **5** to the significantly lower frequencies than those of the free nitriles (23 cm^{-1} (**5a**), 34 cm^{-1} (**5b**), 54 cm^{-1} (**5c**), 87 cm^{-1} (**5d**)) are consistent with this feature of the W(IV) centers in **5**. Such a decrease of the $\nu(C{\equiv}N)$ values has been reported for several nitrile complexes with low-valent metal centers such as $[Mo(N_2)(RCN)(dpe)_2]$[22] and $[ReCl(RCN)(dpe)_2]$,[23] which has been ascribed to π donation from the metal center to the nitrile π^* orbital. On the other hand, coordination of nitriles to the high-valent metal center with less π-donating ability commonly results in the increase of $\nu(C{\equiv}N)$ values, which occurs predominantly by σ-bonding through the nitrile lone pair.

The mutually trans coordination of two PMe_2Ph ligands in **3**–**5** is evidenced by their ^1H NMR spectra. Thus, the methyl protons of two PMe_2Ph ligands appear as two triplets in these complexes. Selective displacement of the PMe_2Ph ligand trans to the iodide ligand in **1** observed here corresponds well to the results obtained by the reactions of the imido, diazoalkane, and hydrazido(2−) W(IV) complexes with CO, isonitriles, or olefins (vide supra).[20,21] The ^1H NMR spectrum of **4** unequivocally shows the coordination of $CH_2{=}CH_2$. Since the free rotation of the coordinated $CH_2{=}CH_2$ is inhibited by the substantial π-back-bonding between the W d orbital and C–C π^* orbital, the protons in the $CH_2{=}CH_2$ ligand are recorded as two multiplets both at room temperature and at 65 °C.

To confirm the structures of the complexes **3**–**5**, an X-ray analysis was performed for **5d**. Figure 2 depicts the molecular structure of **5d**, and selected bond distances and angles are given in Table VIII. These clearly indicate that the nitrile occupies the position cis to the disilylhydrazido(2−) ligand and trans to the iodide ligand in the octahedron as expected by the ^1H NMR spectrum. The bonding parameters in the disilylhydrazido(2−) ligand do not differ significantly from those in **1**. The W–N(3)–C(31) linkage in the nitrile ligand is essentially linear. The plane of this nitrile ligand defined by the N(3) and C(31) atoms as well as six aromatic carbons (C(32)–C(37)) is almost perpendicular (93.8°) to the basal plane including the W, I(2), two P, and N(1) atoms, while the dihedral angle between this nitrile ligand and the plane consisting of the W, two I, N(1), and N(3) atoms is 20.5°. Two phenyl rings in the PMe_2Ph ligands and the nitrile ligand are oriented toward a mutually parallel direction probably due to the stabilization by the π-stacking.

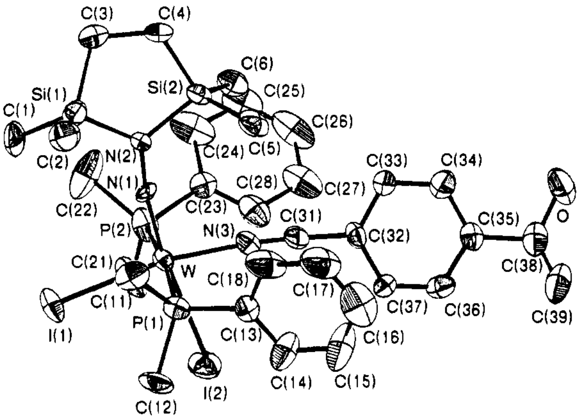
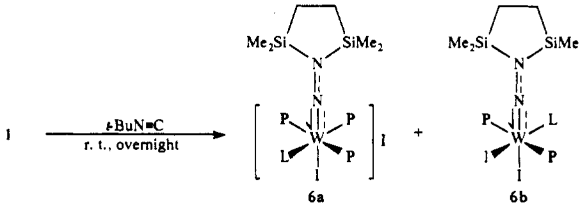


Figure 2. ORTEP diagram of $[WI_2(N\overline{NSiMe_2CH_2CH_2Si}Me_2)(p\text{-}MeCOC_6H_4CN)(PMe_2Ph)_2]$ (**5d**), showing the atom-labeling scheme.

In contrast to the reactions with CO, $CH_2{=}CH_2$, or nitriles, treatment of **1** with *t*-BuNC afforded predominantly the cationic disilylhydrazido(2−) complex *mer*-$[WI(N\overline{NSiMe_2CH_2CH_2Si}Me_2)(PMe_2Ph)_3(t\text{-}BuNC)]I$ (**6a**) resulting from the replacement of one iodide ligand by *t*-BuNC. Complex **6a** precipitated because of its low solubility in benzene and easily separated from the reaction mixture in analytically pure form by filtration. On the other hand, the spectroscopic data of the crude material obtained from the filtrate showed the concurrent formation of the neutral disilylhydrazido(2−) complex $[WI_2(N\overline{NSiMe_2CH_2CH_2Si}Me_2)(PMe_2Ph)_2(t\text{-}BuNC)]$ (**6b**) with **6a**,[24] but the isolation of pure **6b** was not successful (eq 5). Alternatively, **6b** could be readily prepared by



(P = PMe_2Ph; L = *t*-BuN≡C) (5)

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[24] The product ratio of **6a** and **6b** was about 5:1.

Table VII. IR and ^{1}H NMR Data for Disilylhydrazido(2–) Complexes [WX$_2$(NNSiMe$_2$CH$_2$CH$_2$SiMe$_2$)(L)(PMe$_2$Ph)$_2$] (1, 3–5, 6b, 7) and [WX(NNSiMe$_2$CH$_2$CH$_2$SiMe$_2$)(L)(PMe$_2$Ph)$_3$]X (6a)

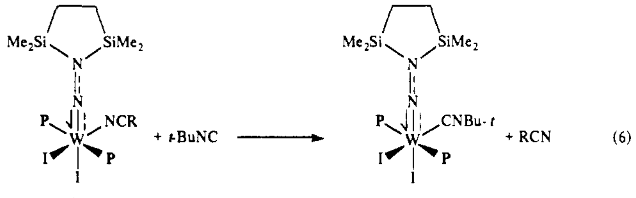
no.	X	L	IR[a]		^{1}H NMR[b]	
1	I	PMe$_2$Ph	1306	ν(NN)	0.47	s, 12H, SiMe
			1246	δ(SiMe)	0.59	s, 4H, SiCH$_2$
			858	ν(SiN)	1.52	d, 6H, PMe
					2.17	t, 6H, PMe
					2.20	t, 6H, PMe
3	I	CO	1364	ν(NN)	–0.03	s, 12H, SiMe
			1250	δ(SiMe)	0.33	s, 4H, SiCH$_2$
			864	ν(SiN)	2.10	t, 6H, PMe
			1931	ν(C≡O)	2.29	t, 6H, PMe
4	I	CH$_2$=CH$_2$	1356	ν(NN)	0.11	br s, 12H, SiMe
			1248	δ(SiMe)	0.39	s, 4H, SiCH$_2$
			864	ν(SiN)	1.98	m, 2H, CH$_2$=CH$_2$
					2.04	m, 2H, CH$_2$=CH$_2$
					2.16	t, 6H, PMe
					2.43	t, 6H, PMe
5a	I	MeCN	1352	ν(NN)	*c*	*c*
			1248	δ(SiMe)		
			860	ν(SiN)		
			2230	ν(C≡N)		
5b	I	EtCN	1348	ν(NN)	*c*	*c*
			1250	δ(SiMe)		
			860	ν(SiN)		
			2215	ν(C≡N)		
5c	I	*p*-MeC$_6$H$_4$CN	1354	ν(NN)	0.18	s, 12H, SiMe
			1246	δ(SiMe)	0.55	s, 4H, SiCH$_2$
			857	ν(SiN)	2.01	t, 6H, PMe
			2174	ν(C≡N)	2.07	s, 3H, CMe
					2.55	t, 6H, PMe
5d	I	*p*-MeCOC$_6$H$_4$CN	1352[d]	ν(NN)	0.18	s, 12H, SiMe
			1248[d]	δ(SiMe)	0.55	s, 4H, SiCH$_2$
			843	ν(SiN)	1.95	t, 6H, PMe
			2143	ν(C≡N)	2.08	s, 3H, COMe
			1676	ν(C=O)	2.49	t, 6H, PMe
6a	I	*t*-BuNC	1321	ν(NN)	0.18	s, 12H, SiMe
			1246	δ(SiMe)	0.77	s, 4H, SiCH$_2$
			860	ν(SiN)	1.22	s, 9H, CMe
			2122	ν(N≡C)	1.59	d, 6H, PMe
					1.94	t, 6H, PMe
					1.99	t, 6H, PMe
6b	I	*t*-BuNC	1356	ν(NN)	0.16	s, 12H, SiMe
			1250	δ(SiMe)	0.50	s, 4H, SiCH$_2$
			862	ν(SiN)	0.88	s, 9H, CMe
			2099	ν(N≡C)	2.08	t, 6H, PMe
			2051		2.45	t, 6H, PMe
7a	Cl	Cl	1383	ν(NN)		
			1248	δ(SiMe)		
			865	ν(SiN)		
7b	I	I	1373	ν(NN)		
			1248	δ(SiMe)		
			864	ν(SiN)		

[a] cm^{-1}; KBr disks. [b] ppm; C$_6$D$_6$ solution; referenced to a trace of C$_6$D$_5$H in C$_6$D$_6$ at 7.20 ppm; phenyl protons omitted. [c] Definite assignments could not be made due to instability in solution. [d] Obscured by the absorptions of the *p*-MeCOC$_6$H$_4$CN ligand.

Table VIII. Selected Bond Distances and Angles in 5d

Bond Distances (Å)			
W–I(1)	2.838 (3)	W–I(2)	2.900 (2)
W–P(1)	2.501 (7)	W–P(2)	2.518 (8)
W–N(1)	1.77 (1)	W–N(3)	2.05 (2)
N(1)–N(2)	1.29 (2)	Si(1)–N(2)	1.80 (2)
Si(2)–N(2)	1.78 (2)	O–C(38)	1.20 (3)
N(3)–C(31)	1.17 (3)		
Bond Angles (deg)			
I(1)–W–I(2)	89.4 (1)	I(1)–W–P(1)	86.9 (2)
I(1)–W–P(2)	87.8 (2)	I(1)–W–N(1)	97.3 (6)
I(1)–W–N(3)	168.9 (4)	I(2)–W–P(1)	85.3 (1)
I(2)–W–P(2)	88.6 (2)	I(2)–W–N(1)	172.9 (6)
I(2)–W–N(3)	79.7 (4)	P(1)–W–P(2)	172.0 (2)
P(1)–W–N(1)	97.5 (5)	P(1)–W–N(3)	89.7 (5)
P(2)–W–N(1)	89.2 (5)	P(2)–W–N(3)	94.4 (5)
N(1)–W–N(3)	93.7 (7)	N(2)–Si(1)–C(3)	97.0 (11)
N(2)–Si(2)–C(4)	97.1 (11)	W–N(1)–N(2)	172.1 (16)
N(1)–N(2)–Si(1)	123.8 (15)	N(1)–N(2)–Si(2)	122.3 (14)
W–N(3)–C(31)	174.9 (18)	N(3)–C(31)–C(32)	172.5 (20)

treatment of **5c** or **5d** with *t*-BuNC in benzene at 50 °C (eq 6). It is interesting to note that the reactions of *mer*-[WCl$_2$(NN=CMe$_2$)(PMe$_2$Ph)$_3$] or [WCl$_2$(NBu-*t*)(PPh$_2$Me)$_3$] with *t*-BuNC proceed analogously to those with CO and olefins to give the neutral complexes exclusively.[20,21] The IR spectrum of **6a** exhibits a strong band at 2122 cm^{-1} attributable to ν(N≡C) together with those characteristic of the disilylhydrazido(2–) ligand, while the ^{1}H NMR spectrum shows the presence of the three mutually meridional PMe$_2$Ph ligands. It has been previously reported that the reactions of the hydrazido(2–) complexes *mer*-[WBr$_2$(NNH$_2$)(PMe$_2$Ph)$_3$] or *mer*-[WCl$_2$(NNHCOCHPh$_2$)(PMe$_2$Ph)$_3$] with pyridines give the cationic hydrazido(2–) complexes *mer*-[WBr(NNH$_2$)(4-MePy)(PMe$_2$Ph)$_3$]Br[25] or *mer*-[WCl(NNHCOCHPh$_2$)(Py)(PMe$_2$Ph)$_3$]Cl,[26] respectively, and the X-ray analyses have unambiguously clarified the coordination of the pyridines to the cis site with respect to the hydrazido(2–) ligands in these products. This strongly suggests that the structure analogous to these pyridine adducts is also plausible for **6a** as shown in eq 5.



(6)

5c: R = *p*-MeC$_6$H$_4$
5d: R = *p*-MeCOC$_6$H$_4$

6b

Reactions of *mer*-[WI$_2$(NNSiMe$_2$CH$_2$CH$_2$SiMe$_2$)(PMe$_2$Ph)$_3$] (1) with CH$_2$X$_2$ (X = Cl, I) Affording Paramagnetic Disilylhydrazido(2–) Complexes [WX$_3$(NNSiMe$_2$CH$_2$CH$_2$SiMe$_2$)(PMe$_2$Ph)$_2$] (7). During the trials to purify **1** from various solvents, we have found that **1** reacts readily with CH$_2$Cl$_2$ to give a paramagnetic product. Thus, when **1** dissolved in CH$_2$Cl$_2$ was stirred for 2 h and hexane was added to the resultant solution, dark red crystals precipitated in moderate yield. Elemental analysis of the product suggested the formation of the unexpected W(V) complex [WCl$_3$(NNSiMe$_2$CH$_2$CH$_2$SiMe$_2$)(PMe$_2$Ph)$_2$] (**7a**), and an X-ray analysis was undertaken to characterize the structure of **7a** in detail. The ORTEP drawing for **7a** is shown in Figure 3, which unambiguously demonstrates the octahedral structure with three Cl and two PMe$_2$Ph ligands in mutually meridional and trans positions, respectively. Interestingly, not only one PMe$_2$Ph ligand but two iodide ligands in **1** are replaced by chloride ligands to give **7a**.

The bonding parameters in the disilylhydrazido(2–) ligand in **7a** (Table IX) correspond well to those in **1**, and this is consistent with the appearance of ν(NN) and ν(SiN) bands in its IR spectrum analogous to that of **1**, although the former of **7a** is significantly higher (1383 cm^{-1}) than that of **1** (1306 cm^{-1}). The paramagnetic feature of **7a** is confirmed by its ESR spectrum in solution, exhibiting a broad 1:2:1 triplet resonance coupled to two equivalent P atoms (g = 1.92, $A(^{31}P)$ = 3.10 mT).[27]

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(25) Chatt, J.; Pearman, A. J.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1978**, 1766.

(26) Aoshima, T.; Mizobe, Y.; Hidai, M.; Tsuchiya, J. *J. Organomet. Chem.* **1992**, *423*, 39.

(27) ESR spectra of structurally related W(V) imido complexes *mer,trans*-[Cl$_3$(**P**)$_2$W≡N-*o*-C$_6$H$_4$N≡WCl$_3$(**P**)$_2$] (**P** = PMe$_3$, PEt$_2$Ph) and *mer,trans*-[Cl$_3$(PhEt$_2$P)$_2$W≡N-*p*-C$_6$H$_4$N≡WCl$_3$(PEt$_2$Ph)$_2$] recently reported also show a triplet near g = 1.90 ($A(^{31}P)$ = ca. 3.1 mT) arising from the coupling of the unpaired electron on each W(V) center with two equivalent P nuclei: Liang, M.; Maatta, E. A. *Inorg. Chem.* **1992**, *31*, 953.

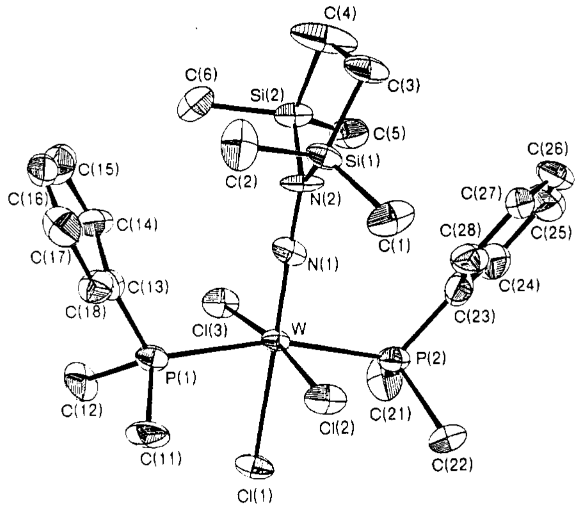

Figure 3. ORTEP diagram of [$WCl_3(NNSiMe_2CH_2CH_2SiMe_2)(PMe_2Ph)_2$] (**7a**), showing the atom-labeling scheme.

Table IX. Selected Bond Distances and Angles in 7a

	Bond Distances (Å)		
W-Cl(1)	2.497 (5)	W-Cl(2)	2.429 (5)
W-Cl(3)	2.432 (5)	W-P(1)	2.532 (5)
W-P(2)	2.541 (6)	W-N(1)	1.76 (1)
N(1)-N(2)	1.33 (2)	Si(1)-N(2)	1.79 (1)
Si(2)-N(2)	1.75 (1)		
	Bond Angles (deg)		
Cl(1)-W-Cl(2)	85.4 (2)	Cl(1)-W-Cl(3)	84.9 (2)
Cl(1)-W-P(1)	82.3 (2)	Cl(1)-W-P(2)	81.4 (2)
Cl(1)-W-N(1)	177.2 (4)	Cl(2)-W-Cl(3)	170.3 (2)
Cl(2)-W-P(1)	88.6 (2)	Cl(2)-W-P(2)	89.3 (2)
Cl(2)-W-N(1)	97.3 (4)	Cl(3)-W-P(1)	89.3 (2)
Cl(3)-W-P(2)	90.1 (2)	Cl(3)-W-N(1)	92.3 (4)
P(1)-W-P(2)	163.7 (2)	P(1)-W-N(1)	98.2 (6)
P(2)-W-N(1)	98.1 (6)	N(2)-Si(1)-C(3)	95.5 (9)
N(2)-Si(2)-C(4)	96.7 (10)	W-N(1)-N(2)	175.9 (14)
N(1)-N(2)-Si(1)	122.7 (11)	N(1)-N(2)-Si(2)	122.0 (10)

Although formation of chloro complexes after the cleavage of a C–Cl bond in CH_2Cl_2 on the transition metal sites is known for some late transition metal complexes such as Ru,[28] Co,[29] Rh,[30] and Pt,[31] it has been rarely reported for the high-valent early transition metal complexes like **1**. Complex **1** reacts analogously with CH_2I_2 in benzene to give a corresponding paramagnetic complex [$WI_3(NNSiMe_2CH_2CH_2SiMe_2)(PMe_2Ph)_2$] (**7b**). It is noteworthy that no halogen metathesis took place by treatment of **7b** with CH_2Cl_2. Other W(IV) complexes such as [$WI_2(NNH_2)(PMe_2Ph)_3$] and [$WI_2(NN{=}CMe_2)(PMe_2Ph)_3$] did not react with CH_2I_2 in CH_2Cl_2 solution at room temperature.[32] Related paramagnetic hydrazido(2–) complexes with the W(V) center *fac,cis*-[$WCl_3(NNH_2)(PMe_2Ph)_2$] and *mer,trans*-[$WCl_3(NNHPh)(PMe_2Ph)_2$] have already been reported, which are produced from the hydrido–hydrazido(2–) complexes with W(VI) centers [$WCl_3H(NNH_2)(PMe_2Ph)_2$] and [$WCl_3H(NNHPh)(PMe_2Ph)_2$] by the accidental loss of the hydrogen atom upon crystallization from CH_2Cl_2/THF/ether.[33] Since the GLC study of the reaction mixtures for preparing complexes **7** failed in the detection of any products derived from CH_2Cl_2 or CH_2I_2, the details of the formation of complexes **7** are not yet clear. Further study to clarify this as well as the reactivity of these paramagnetic disilylhydrazido(2–) complexes is now in progress and will be reported in subsequent papers.

Acknowledgment. We thank Dr. Akiko Kobayashi for the X-ray data collection of **1** and Dr. Junichi Tsuchiya for recording ESR spectra. The financial support by the Ministry of Education, Science, and Culture of Japan is greatly appreciated.

Supplementary Material Available: Tables giving bond distances and angles, anisotropic thermal parameters, and hydrogen positions (12 pages). Ordering information is given on any current masthead page.

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[32] Recently, we have found that treatment of CH_2X_2 (X = Br, I) with [$WX_2(NN{=}CMeR)(P)_3$] (P = PMe_2Ph; R = Me, Ph) in toluene at 80 °C affords W(V) diazoalkane complexes *mer,trans*-[$WX_3(NN{=}CMeR)(P)_2$] in moderate yields. The molecular structure of *mer,trans*-[$WBr_3(NN{=}CMePh)(P)_2$] was determined by an X-ray diffraction analysis. The details will be reported elsewhere.

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