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Preparation and properties of molybdenum and tungsten dinitrogen complexes

XLI *. Silylation and germylation of a coordinated dinitrogen in *cis*-$[M(N_2)_2(PMe_2Ph)_4]$ (M = Mo, W) using R_3ECl/NaI and R_3ECl/Na mixtures (E = Si, Ge). X-ray structure of *trans*-$[WI(NNGePh_3)(PMe_2Ph)_4] \cdot C_6H_6$

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Abstract

Treatment of *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ (**1**) with R_3SiCl and excess NaI in benzene afforded a series of silyldiazenido complexes *trans*-$[WI(NNSiR_3)(PMe_2Ph)_4]$ ($R_3 = Me_3$, $EtMe_2$, Et_3, $Me_{3-n}Ph_n$ (n = 1–3), $(MeO)Me_2$, $(MeO)_2Me$), while a dinuclear complex with bridging silyldiazenido ligand $[(PhMe_2P)_4IW(NNSiMe_2$-*p*-$C_6H_4SiMe_2NN)WI(PMe_2Ph)_4]$ was obtained from the reaction of **1** with *p*-$ClMe_2SiC_6H_4SiMe_2Cl$ and NaI. Analogous treatment of **1** with a mixture of R_3GeCl and excess NaI gave novel germylated dinitrogen complexes *trans*-$[WI(NNGeR_3)(PMe_2Ph)_4]$ (R = Me, Ph (**13**)). The molecular structure of **13** · C_6H_6 was determined by an X-ray analysis. Crystal data for **13** · C_6H_6: triclinic, space group $P\bar{1}$ with $a = 13.533(3)$, $b = 19.629(7)$, $c = 11.941(6)$ Å, $\alpha = 103.59(3)$, $\beta = 116.11(3)$, $\gamma = 81.12(2)°$, $V = 2763.7(16)$ Å^3, $Z = 2$ and $R = 0.042$ for 7476 reflections. On the other hand, when a variety of chlorosilanes or Me_3GeCl was reacted with one equiv of Na in THF under nitrogen in the presence of a catalytic amount of *cis*-$[Mo(N_2)_2(PMe_2Ph)_4]$, molecular nitrogen was converted into the N_1 products, whose yields, detected as NH_3 after hydrolysis, varied from 0.2 to 7.5 mol/Mo atom depending on the substituent in R_3ECl (E = Si, Ge).

1. Introduction

The continuing evolution of the chemistry of dinitrogen complexes $[M(N_2)_2(L)_4]$ (M = Mo, W; L = tertiary phosphine) has resulted in the exploitation of various potential methods to form N–H and N–C bonds at a coordinated dinitrogen. Among these are several reaction systems that lead ultimately to the formation of ammonia, hydrazine, amines, and azines under ambient conditions. However, few examples are known in which transformation of molecular nitrogen into nitrogenous compounds proceeds catalytically by the use of these and other well-characterized dinitrogen complexes [2].

The formation of $N(SiMe_3)_3$ and $HN(SiMe_3)_2$ from the reaction of Me_3SiCl and Na under N_2 in the presence of $[M(N_2)_2(P)_4]$ (P = PMe_2Ph, 1/2 dpe; dpe = $Ph_2PCH_2CH_2PPh_2$), reported previously from this laboratory, constitutes one of the quite rare examples of catalytic N_2-fixing systems promoted by transition metal complexes (eqn. (1)) [3].

$$Me_3SiCl + Na + N_2 \xrightarrow[\text{THF, 30°C, 4 h}]{[Mo(N_2)_2(PMe_2Ph)_4]} N(SiMe_3)_3 + HN(SiMe_3)_2 \quad (1)$$

In relevance to this unique reaction, we have also reported isolation of trimethylsilylated dinitrogen complexes *trans*-$[MX(NNSiMe_3)(P)_4]$ from the reactions of

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a series of $[M(N_2)_2(P)_4]$ and Me_3SiX ($X = I, CF_3SO_3$) (eqn. (2)) [4].

$$[M(N_2)_2(P)_4] + Me_3SiX \longrightarrow trans\text{-}[MX(NNSiMe_3)(P)_4] \quad (2)$$

We have now found that a variety of silyldiazenido complexes *trans*-$[WI(NNSiR_3)(PMe_2Ph)_4]$ can be prepared easily by treatment of *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ (**1**) with various R_3SiCl compounds in the presence of excess NaI. Furthermore, analogous treatment of **1** with R_3GeCl/NaI mixtures has resulted in the formation of novel germylated dinitrogen complexes [5]. We wish to describe here the details of these silylation and germylation reactions of coordinated dinitrogen together with the catalytic formation of amines resulting from replacing Me_3SiCl with various chlorosilanes and with Me_3GeCl in eqn. (1).

2. Experimental section

2.1. General

All experiments were carried out under dry nitrogen with thoroughly dried glassware. Complexes **1** and **10** were prepared according to literature methods [4c,6]. Solvents were distilled from Na-benzophenone and degassed just before use. All chlorosilanes and Ph_3GeCl were commercially obtained. Me_3GeCl was supplied by Professor K. Mochida. NaI was dried and stored under nitrogen. Na microdispersion (8–10 μm diameter) was obtained from Nihon Soda Co. IR spectra were recorded on a Shimadzu IR-400 or FT-8100M spectrometer and ^1H NMR spectra were measured on a JEOL JMN-GX-400 spectrometer. GLC analyses were carried out on a Shimadzu GC-14A Gas Chromatograph equipped with 0.2 mm × 25 m CBP-1 or CBP-10 capillary column, while GC-MS (70 eV) analyses were undertaken on a Shimadzu GC-MS QP-1000 spectrometer. Elemental analyses were performed at the Elemental Analysis Laboratory, Department of Chemistry, Faculty of Science, University of Tokyo.

2.2. Preparation of *trans*-$[WI(NNSiMe_3)(PMe_2Ph)_4]$ (2)

A previous method [4b] was modified as follows. A mixture of Me_3SiCl (1.0 ml, 7.9 mmol) and NaI (4.94 g, 33.0 mmol) in benzene (22.5 ml) was carefully degassed by freeze (at −40 to −50°C)-pump-thaw cycles, and then **1** (3.13 g, 3.95 mmol) was added. After stirring of the suspension 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 a yellow solid, which was filtered off, washed with hexane, and dried *in vacuo* (2.96 g, 78% yield).

Other silyldiazenido complexes *trans*-$[WI(NNSiR_3)(PMe_2Ph)_4]$ ($R_3 = EtMe_2$ (**3**), Et_3 (**4**), $PhMe_2$ (**5**), Ph_2Me (**6**), Ph_3 (**7**), $Me_2(OMe)$ (**8**), $Me(OMe)_2$ (**9**)) were prepared analogously.

3: yield 72%. Anal. Found: C, 43.37; H, 5.69; N, 2.74. $C_{36}H_{55}N_2SiP_4IW$ calc.: C, 44.18; H, 5.66; N, 2.86%.

4: yield 54%. Anal. Found: C, 45.26; H, 5.87; N, 2.88. $C_{38}H_{59}N_2SiP_4IW$ calc.: C, 45.34; H, 5.91; N, 2.78%.

5: yield 67%. Anal. Found: C, 46.03; H, 5.33; N, 2.81. $C_{40}H_{55}N_2SiP_4IW$ calc.: C, 46.80; H, 5.40; N, 2.73%.

6: yield 65%. Anal. Found: C, 50.19; H, 5.54; N, 2.55. $C_{45}H_{57}N_2SiP_4IW$ calc.: C, 49.65; H, 5.28; N, 2.57%.

7: yield 72%. Anal. Found: C, 53.16; H, 5.36; N, 2.42. $C_{50}H_{59}N_2SiP_4IW$ calc.: C, 52.19; H, 5.17; N, 2.43%.

8: yield 29%. Anal. Found: C, 42.11; H, 5.37; N, 2.86. $C_{35}H_{53}N_2OSiP_4IW$ calc.: C, 42.87; H, 5.45; N, 2.86%.

9: yield 35%. Anal. Found: C, 41.38; H, 5.27; N, 2.63. $C_{35}H_{53}N_2O_2SiP_4IW$ calc.: C, 42.18; H, 5.36; N, 2.81%.

2.3. Preparation of $[(PhMe_2P)_4IW(NNSiMe_2\text{-}p\text{-}C_6H_4SiMe_2NN)WI(PMe_2Ph)_4]$ (11)

To a suspension of *p*-$ClMe_2SiC_6H_4SiMe_2Cl$ (81.6 mg, 0.310 mmol) and NaI (571 mg, 3.81 mmol) in benzene (6.0 ml) was added **1** (490 mg, 0.618 mmol). After the suspension was stirred for 70 h at 50°C in the dark, the reaction mixture was filtered. Addition of hexane to the filtrate gave a yellow powder, which was filtered off, washed with hexane, and dried *in vacuo* (348 mg, 57% yield). Anal. Found: C, 44.57; H, 5.62; N, 2.77. $C_{74}H_{104}N_4Si_2P_8I_2W_2$ calc.: C, 45.00; H, 5.31; N, 2.84%.

2.4. Preparation of *trans*-$[WI(NNGeMe_3)(PMe_2Ph)_4]$ (12a) and *mer*-$[WI_2(NNHGeMe_3)(PMe_2Ph)_3]$ (12b)

Benzene (*ca.* 5 ml) was condensed by the trap to trap method into a Schlenk tube charged with NaI (502 mg, 3.35 mmol), and then Me_3GeCl (138 μl, 1.12 mmol) added. The mixture was carefully degassed by freeze (at −40 to −50°C)-pump-thaw cycles, and **1** (440 mg, 0.555 mmol) was added. After the mixture had been stirred at 50°C for 70 h in the dark, the dark brown product solution was separated by filtration. Addition of hexane by trap to trap condensation to the filtrate concentrated *in vacuo* gave orange crystals of **12a** (124 mg, 22.8%). Anal. Found: C, 40.88; H, 5.18; N, 2.53. $C_{35}H_{53}N_2P_4GeIW$ (**12a**) calc.: C, 41.66; H, 5.34; N, 2.78%. A small amount of a dark brown crystalline solid byproduct, **12b**, was isolated when the reaction was carried out in benzene that had been freshly distilled but not degassed, the reactant and solvent having been transferred into a reaction vessel by syringe. However, the yields of **12b** from several runs were not reproducible. Anal. Found: C, 33.40; H, 4.37; N, 2.85. $C_{27}H_{43}N_2P_3GeI_2W$ (**12b**) calc.: C, 32.47; H, 4.34; N, 2.80%.

2.5. *Preparation of trans-[WI(NNGePh$_3$)(PMe$_2$Ph)$_4$]·C$_6$H$_6$(13·C$_6$H$_6$)*

Complex **13** was obtained as an orange crystalline solid by an analogous procedure, treatment of Ph_3GeCl and excess NaI with **1** for 45 h (56% yield). Formation of germylhydrazido(2 –) complex was not observed under the conditions which had given a mixture of **12a** and **12b**. Anal. Found: C, 51.34; H, 5.47; N, 2.13. $C_{50}H_{59}N_2P_4GeIW \cdot C_6H_6$ calc.: C, 52.82; H, 5.15; N, 2.20%. Although three separate combustion analyses were performed for **13**, satisfactory carbon analyses were not obtained. Difficulty of this kind in getting good carbon analyses has been observed for several silyl-metal complexes, and ascribed to the formation of silicon carbide during combustion [1,7].

2.6. *Catalytic conversion of N$_2$ gas into silylamines using cis-[Mo(N$_2$)$_2$(PMe$_2$Ph)$_4$] (10)*

A typical procedure was as follows. To a mixture of Na microdispersion (10 mmol) and R_3SiCl (10 mmol) in THF (6.5 ml) degassed by freeze (–78°C)-pump-thaw cycles, **10** (0.1 mmol) was added. After stirring of the mixture at 30°C for 4 h under N_2 (1 atm), the aliquots were analyzed by GLC and GC-MS. Aqueous KOH solution (10 ml, 40%) was then added and the mixture distilled into aqueous H_2SO_4 solution (10 ml, 0.1 N), which was then diluted to a known volume with water. Yields of NH_3 were determined using indophenol reagent.

2.7. *X-ray crystallographic analysis of trans-[WI(NNGePh$_3$)(PMe$_2$Ph)$_4$]·C$_6$H$_6$ (13·C$_6$H$_6$)*

An X-ray diffraction study was carried out at room temperature by using a single crystal sealed in a glass capillary under Ar. The orientation matrices and unit cell parameters were derived from a least-squares fit of 20 machine-centered reflections with 2θ values between 20 and 25°. No significant decay in intensities of three standard reflections was observed 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 $\mathbf{13} \cdot C_6H_6$ are summarized in Table 1. Tables of bond distances and angles, anisotropic thermal parameters, positional parameters for the hydrogen atoms, and listing of observed and calculated structure factors for $\mathbf{13} \cdot C_6H_6$ are available from the authors. Positional parameters of the non-hydrogen atoms are listed in Table 2. Structure solution and refinements were performed at the Computer Center of the University of Tokyo, using the UNIX-III program package. The W atom was found by the direct method program MULTAN 78. Subsequent cycles of difference Fourier syntheses and block-diagonal least-squares refinements revealed all non-hydrogen atoms in **13** as well as the carbon atoms in the solvating benzene (C(81)–C(86)), 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. 8.

TABLE 1. Details of X-ray crystallography for *trans*-[WI(NNGePh$_3$)(PMe$_2$Ph)$_4$]·C$_6$H$_6$ (**13**·C$_6$H$_6$)

(a) Crystal data	
Formula	$C_{56}H_{65}N_2P_4GeIW$
Molecular weight	1273.3
Crystal dimensions, mm	0.43×0.37×0.25
Space group (crystal system)	$P\bar{1}$ (triclinic)
a, Å	13.533(3)
b, Å	19.629(7)
c, Å	11.941(6)
α, deg	103.59(3)
β, deg	116.11(3)
γ, deg	81.12(2)
V, Å^3	2763.7(16)
Z	2
D_{calcd}, g cm^{-3}	1.530
$F(000)$, electrons	624
μ_{calcd}, cm^{-1}	33.63
(b) Data collection and reduction	
Diffractometer	MAC MXC-18
Monochromator	graphite
Radiation (λ/Å)	Mo Kα (0.7107)
2θ range, deg	$3 < 2\theta < 50$
Scan method	$\omega - 2\theta$
Scan speed, deg min^{-1}	16
Absorption correction	Gaussian integration method
Transmission factor	0.278–0.470
Reflections measured	$\pm h, \pm k, +l$
No. of unique data	8714
No. of data used	7476 ($\|F_o\| > 3\sigma(\|F_o\|)$)
(c) Solution and refinement	
No. of parameters refined	727
R	0.042
R_w	0.050
Max residuals, e Å^{-3}	1.25 (around W atom)

TABLE 2. Positional parameters ($\times 10^4$) and equivalent temperature factors for *trans*-[WI(NNGePh$_3$)(PMe$_2$Ph)$_4$]·C$_6$H$_6$ (**13**·C$_6$H$_6$)

Atom	x	y	z	B_{eq}
W	5650.6(3)	2493.7(2)	6775.5(3)	2.4
I	4244.2(5)	3057.2(3)	4494.1(5)	4.2
Ge	7992.4(7)	1813.1(5)	10604.7(8)	3.3
P(1)	7333(2)	3028(1)	7071(2)	3.2
P(2)	5912(2)	1509(1)	5114(2)	3.1
P(3)	4048(2)	1945(1)	6657(2)	3.4
P(4)	5056(2)	3615(1)	7904(2)	3.3
N(1)	6490(5)	2079(3)	8126(6)	3.0
N(2)	6967(7)	1684(4)	8913(7)	5.0
C(1)	8190(7)	3344(5)	8761(8)	4.5
C(2)	7189(8)	3798(5)	6383(10)	4.8
C(3)	6334(8)	1755(5)	3996(9)	4.5
C(4)	4722(8)	1021(5)	3905(8)	4.4
C(5)	2716(7)	2004(6)	5312(9)	5.0
C(6)	4218(9)	985(5)	6638(10)	4.8
C(7)	3563(8)	3878(5)	7321(10)	4.8
C(8)	5412(8)	3629(5)	9576(8)	4.4
C(11)	8420(6)	2495(4)	6684(7)	3.2
C(12)	8766(8)	2613(5)	5814(9)	4.6
C(13)	9593(9)	2194(6)	5546(10)	5.6
C(14)	10111(8)	1656(6)	6203(11)	6.0
C(15)	9787(9)	1519(6)	7069(11)	5.7
C(16)	8939(8)	1929(5)	7301(9)	4.4
C(21)	6911(7)	786(4)	5716(8)	3.6
C(22)	6906(7)	531(5)	6694(8)	3.8
C(23)	7632(8)	−15(5)	7159(9)	4.9
C(24)	8393(9)	−304(6)	6682(11)	6.0
C(25)	8405(9)	−57(6)	5716(11)	6.1
C(26)	7676(8)	480(5)	5230(9)	4.9
C(31)	3664(7)	2176(5)	8006(9)	4.1
C(32)	2608(9)	2461(6)	7892(11)	5.8
C(33)	2338(10)	2580(6)	8945(13)	7.0
C(34)	3101(12)	2443(7)	10076(11)	7.5
C(35)	4159(11)	2135(8)	10200(11)	7.7
C(36)	4436(9)	2022(6)	9171(9)	5.2
C(41)	5534(7)	4466(4)	7998(9)	4.0
C(42)	6349(9)	4823(5)	9092(9)	4.9
C(43)	6689(10)	5450(6)	9101(11)	6.1
C(44)	6236(10)	5735(6)	8018(12)	6.4
C(45)	5441(10)	5392(5)	6920(11)	5.5
C(46)	5061(8)	4776(5)	6903(9)	4.6
C(51)	9512(7)	1667(5)	10756(8)	4.0
C(52)	10352(8)	2084(5)	11626(9)	4.9
C(53)	11426(8)	1932(6)	11690(10)	5.5
C(54)	11635(8)	1360(6)	10910(11)	5.4
C(55)	10824(9)	925(6)	10075(10)	5.7
C(56)	9765(8)	1086(5)	10002(9)	4.6
C(61)	7703(7)	996(5)	11081(9)	4.1
C(62)	8430(9)	802(5)	12219(9)	5.0
C(63)	8300(11)	189(6)	12525(11)	6.4
C(64)	7436(11)	−218(7)	11722(14)	7.4
C(65)	6700(10)	−33(6)	10594(14)	7.0
C(66)	6843(9)	582(6)	10280(11)	5.7
C(71)	7778(7)	2689(5)	11671(8)	4.0
C(72)	8245(8)	3298(5)	11871(9)	4.6
C(73)	7989(10)	3915(6)	12594(10)	5.8
C(74)	7206(10)	3922(6)	13043(10)	6.2
C(75)	6716(10)	3313(6)	12835(10)	5.7
C(76)	6981(8)	2694(5)	12163(9)	4.4
C(81)	1052(16)	4788(11)	3948(18)	12.5
C(82)	1172(15)	4291(11)	3014(20)	12.6
C(83)	539(16)	4397(12)	1776(18)	13.6
C(84)	−169(14)	4946(11)	1536(16)	11.6
C(85)	−332(16)	5474(11)	2523(19)	13.6
C(86)	306(15)	5390(10)	3750(16)	11.7

3. Results and discussion

3.1. Preparation of silyldiazenido complexes using a mixture of R_3SiCl and NaI

Treatment of *cis*-[W(N$_2$)$_2$(PMe$_2$Ph)$_4$] (**1**) with 2 equiv of Me$_3$SiCl in the presence of excess NaI at 50°C in benzene gave *trans*-[WI(NNSiMe$_3$)(PMe$_2$Ph)$_4$] (**2**) in 78% yield. The isolated yield of **2** prepared by this method was slightly higher than that from the reaction of **1** with Me$_3$SiI (*ca.* 70%) [4b]. Since a variety of chlorosilanes is readily available from commercial sources, this reaction system provides a quite convenient method to prepare numerous silylated dinitrogen complexes. Thus the analogous reaction of **1** with a mixture of R$_3$SiCl and excess NaI afforded a series of new silyldiazenido complexes *trans*-[WI(NNSiR$_3$)(PMe$_2$Ph)$_4$] (R$_3$ = Me$_2$Et (**3**), Et$_3$ (**4**), Me$_2$Ph (**5**), MePh$_2$ (**6**), Ph$_3$ (**7**), (MeO)Me$_2$ (**8**), (MeO)$_2$Me (**9**)) in *ca.* 30–70% yields (eqn. (3)).

$$\underset{\mathbf{1}}{cis\text{-}[\mathrm{W(N_2)_2(PMe_2Ph)_4}]} + \mathrm{R_3SiCl} + \text{excess NaI} \longrightarrow \underset{\mathbf{3\text{–}9}}{trans\text{-}[\mathrm{WI(NNSiR_3)(PMe_2Ph)_4}]} \qquad (3)$$

Despite the presence of a more than stoichiometric amount of silyl compounds, none of these reactions gave the disilylated products. The other silylation reactions using Me$_3$SiX (X = I, CF$_3$SO$_3$) [4] or R$_3$SiCo(CO)$_4$ [9] reported previously also afford uniquely the monosilylated complexes. It is to be noted that the disilylation of a coordinated dinitrogen has been observed only in the reactions of **1** and *cis*-[Mo(N$_2$)$_2$(PMe$_2$Ph)$_4$] (**10**) with a ClMe$_2$SiCH$_2$CH$_2$SiMe$_2$Cl/NaI mixture as described elsewhere, which resulted in the formation of disilylhydrazido(2 −) complexes *mer*-[MI$_2$(N$\overline{\mathrm{NSiMe_2CH_2CH_2Si}}Me_2$)(PMe$_2$Ph)$_3$] (M = Mo, W) [1,5].

On the other hand, when 2 equiv of **1** was allowed to react with *p*-ClMe$_2$SiC$_6$H$_4$SiMe$_2$Cl and excess NaI, a dinuclear complex with bridging silyldiazenido ligand [(PhMe$_2$P)$_4$IW(NNSiMe$_2$-*p*-C$_6$H$_4$SiMe$_2$NN)WI(PMe$_2$Ph)$_4$] (**11**) was obtained in 57% yield.

Since **1** does not react with R_3SiCl in the absence of NaI, the silylation reactions reported here presumably proceed via an initial formation of R_3SiI *in situ*. Subsequent electrophilic attack of R_3SiI at the terminal nitrogen atom might afford the silyldiazenido complexes [1]. Isolated yields of methoxysilyldiazenido complexes **8** and **9** were considerably lower than those of **2–7** and **11**. This may be ascribed at least in part to the low stability of the silyldiazenido ligands in **8** and **9**, since it has been reported that the electronegative groups on a Si atom decrease the thermostability of silyldiazenes $R_3SiN{=}NSiR'_3$ [10].

Spectroscopic data for **2–9** and **11** are summarized in Table 3. Two characteristic IR bands assignable to ν(N=N) and ν(SiN) are observed for all complexes, whose values vary substantially depending upon the nature of the substituents on the Si atoms. In their ^{1}H NMR spectra, the methyl protons of PMe_2Ph ligands appear as a broad singlet, which suggests that all PMe_2Ph ligands occupy equivalent positions and the silyldiazenido and iodide ligands are sited in the *trans* positions as confirmed previously for **2** by X-ray analysis [4b].

Dichlorosilanes R_2SiCl_2 (R = Me, Et, Ph) and hy-

TABLE 3. IR and ^{1}H NMR data for silylated and germylated dinitrogen complexes *trans*-[WI(NNER$_3$)(PMe$_2$Ph)$_4$] (E = Si (**2–9**), Ge (**12a**, **13**)), [(PMe$_2$Ph)$_4$IW(NNSiMe$_2$-*p*-C$_6$H$_4$SiMe$_2$NN)WI(PMe$_2$Ph)$_4$] (**11**) and *mer*-[WI$_2$(NNHER$_3$)(PMe$_2$Ph)$_3$] (E = Si, Ge (**12b**))

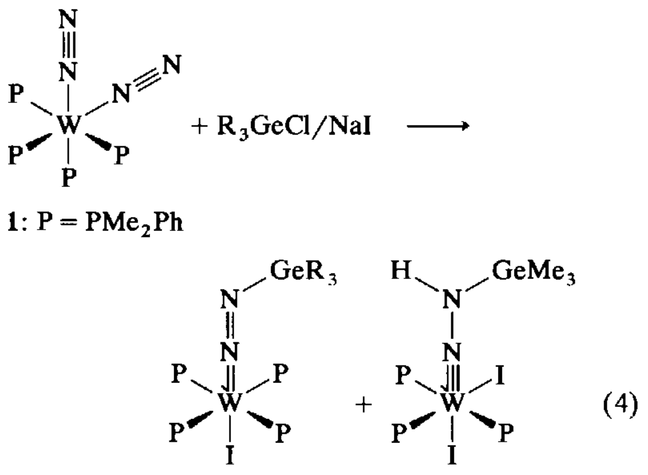
	ER$_3$	IR[a]		^{1}H NMR[b]	
(a) Diazenido complexes					
2	SiMe$_3$ [c]	1580	ν(NN)	0.47	(s, 9H, Si-*Me*)
		1246	δ(SiMe)	1.73	(broad s 24H, P-*Me*)
		873	ν(SiN)		
3	SiMe$_2$Et	1575	ν(NN)	0.50	(s, 6H, Si-*Me*)
		1240	δ(SiMe)	0.91	(q, 2H, Si-C*H*$_2$)
		863	ν(SiN)	1.29	(t, 3H, CH$_2$-*Me*)
				1.77	(broad s, 24H, P-*Me*)
4	SiEt$_3$	1570	ν(NN)	0.98	(q, 6H, Si-C*H*$_2$)
		855	ν(SiN)	1.25	(t, 9H, CH$_2$-*Me*)
				1.73	(broad s, 24H, P-*Me*)
5	SiMe$_2$Ph	1560	ν(NN)	0.70	(s, 6H, Si-*Me*)
		1240	δ(SiMe)	1.70	(broad s, 24H, P-*Me*)
		880	ν(SiN)		
6	SiMePh$_2$	1545	ν(NN)	0.99	(s, 3H, Si-*Me*)
		1245	δ(SiMe)	1.66	(broad s, 24 H, P-*Me*)
		865	ν(SiN)		
7	SiPh$_3$	1545	ν(NN)	1.63	(broad s, 24H, P-*Me*)
		860	ν(SiN)		
8	SiMe$_2$(OMe)	1555	ν(NN)	0.46	(s, 6H, Si-*Me*)
		1248	δ(SiMe)	1.74	(broad s, 24H, P-*Me*)
		875	ν(SiN)	3.66	(s, 3H, O-*Me*)
9	SiMe(OMe)$_2$	1525	ν(NN)	0.48	(s, 3H, Si-*Me*)
		1250	δ(SiMe)	1.76	(broad s, 24H, P-*Me*)
		885 [d]	ν(SiN)	3.67	(s, 6H, O-*Me*)
11		1541	ν(NN)	0.81	(s, 12H, Si-*Me*)
		1244	δ(SiMe)	1.77	(broad s, 48H, P-*Me*)
		858	ν(SiN)		
12a	GeMe$_3$	1530	ν(NN)	0.36	(s, 9H, Ge-*Me*)
				1.74	(broad s, 24H, P-*Me*)
13	GePh$_3$	1510	ν(NN)	1.64	(broad s, 24H, P-*Me*)
(b) Hydrazido(2 –) complexes					
	SiMe$_3$ [c]	3250	ν(NH)	−0.07	(s, 9H, Si-*Me*)
		1360	ν(NN)	1.41	(d, 6H, P-*Me*)
		1254	δ(SiMe)	2.08	(s, 1H, N-*H*)
		842	ν(SiN)	2.24	(2t, 12H, P-*Me*)
12b	GeMe$_3$	3260	ν(NH)	0.20	(s, 9H, Ge-*Me*)
		1351	ν(NN)	1.55	(d, 6H, P-*Me*)
				2.30	(t, 6H, P-*Me*)
				2.36	(t, 6H, P-*Me*)
				2.88	(s, 1H, N-*H*)

[a] cm^{-1}; KBr disks. [b] δ; C$_6$D$_6$ solution; phenyl protons omitted. [c] Ref. 4b. [d] Obscured by the absorptions of the PMe$_2$Ph ligand.

dridochlorosilanes R_2HSiCl ($R_2 = Me_2$, MeCl, Ph_2, PhCl) also reacted with **1** under the analogous conditions, but no silylated dinitrogen complexes could be isolated from the reaction mixtures.

3.2. Preparation of germylated dinitrogen complexes

When **1** was treated with R_3GeCl in the presence of excess NaI at 50°C in benzene, novel germyldiazenido complexes *trans*-[$WI(NNGeR_3)(PMe_2Ph)_4$] (R = Me (**12a**), Ph (**13**)) were formed as orange crystals in *ca.* 20 and 55% yields, respectively (eqn. (4)).



1: P = PMe_2Ph

12a: R = Me
13: R = Ph
12b

As observed in Si–N bond formation described above, germylation did not occur in the absence of NaI. IR and ^1H NMR data for **12a** and **13** listed in Table 3 correspond well to those for the silyldiazenido complexes. In the IR spectra there appears a strong band characteristic of ν(N=N) at 1530 (**12a**) or 1510 cm^{-1} (**13**), respectively. The ν(N=N) values for **12a** and **13** are significantly lower than those for the silyl analogues **2** (1580 cm^{-1}) and **7** (1545 cm^{-1}). In their ^1H NMR spectra, the methyl protons of PMe_2Ph ligands appear as a broad singlet, indicating that the *trans* structure is plausible also for **12a** and **13**.

From the reaction using a mixture of Me_3GeCl/NaI, in addition to orange crystals of **12a** brown crystals were isolated in low yield. The IR and ^1H NMR data for the latter are diagnostic of the formulation of this byproduct as a trimethylgermylhydrazido(2 –) complex *mer*-[$WI_2(NNHGeMe_3)(PMe_2Ph)_3$] (**12b**), if compared with those for the trimethylsilylhydrazido-(2 –) complex *mer*-[$WI_2(NNHSiMe_3)(PMe_2Ph)_3$] (Table 3). Complex **12b** presumably results from the further reaction of **12a** with HI, which is generated *in situ* by the reaction of Me_3GeCl/NaI and adventitious moisture. Thus only **12a** could be isolated under the extremely dry reaction conditions. A similar mechanism has already been proposed for the concurrent formation of trimethylsilylhydrazido(2 –) complexes [$MX_2(NNHSiMe_3)(PMe_2Ph)_3$] or [$MX(NNHSiMe_3)(dpe)_2$]X with trimethylsilyldiazenido complexes [$MX(NNSiMe_3)(P)_4$] [4].

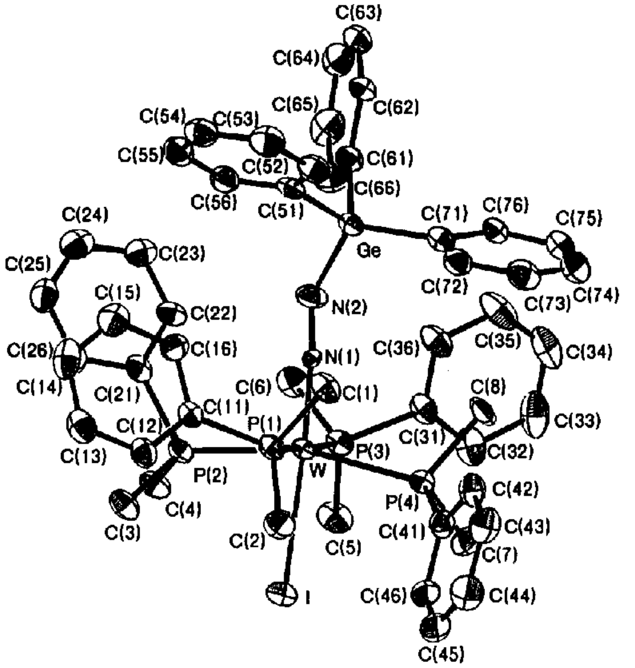


Fig. 1. ORTEP diagram of *trans*-[$WI(NNGePh_3)(PMe_2Ph)_4$]·C_6H_6 (**13**·C_6H_6), showing the atom-labeling scheme. The solvent molecule has been omitted.

Trimethylgermylated dinitrogen complexes **12** are much less stable than the silyl analogues, which resulted in their lower isolated yields and the failure in further purification of **12** by recrystallization from benzene/hexane. This accords with the stability of germyldiazenes $R_3GeN{=}NR'$ being lower than that of the corresponding silyldiazenes [10]. In contrast, **13** could be obtained in higher yield and recrystallized from benzene/hexane.

3.3. Structure of trans-[$WI(NNGePh_3)(PMe_2Ph)_4$]·C_6H_6 (13·C_6H_6)

X-ray crystallography of **13** was performed to confirm the structure of the germyldiazenido complexes [11*]. Figure 1 depicts the molecular structure of **13** and selected bond distances and angles are given in Table 4.

The crystal of **13** consists of two molecules of the W complex packed with two benzene molecules in the unit cell. The complex **13** has a slightly distorted octa-

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* Reference number with asterisk indicates a note in the list of references.

hedral geometry. Four PMe_2Ph ligands lie on the basal plane whereas triphenylgermyldiazenido and iodide ligands occupy the remaining sites in the *trans* positions. The W–N–N bond angle in the germyldiazenido ligand is essentially linear (168.2(6)°). The W–N distance (1.809(6) Å) is indicative of some multiple bond character and the N–N bond length of 1.248(10) Å is comparable to that of the common N–N double bond (*ca.* 1.24 Å) [12]. These structural features correspond well to those of the related silyldiazenido complexes **2** (W–N–N = 168(2)°; W–N = 1.82(2), N–N = 1.24(3) Å) [4b] and *trans*-[Mo(NNSiMePh$_2$)(dpe)$_2$](μ-OC)Co(CO)$_3$ (**14**) (Mo–N–N = 177(1)°; Mo–N = 1.801(9), N–N = 1.21(1) Å) [9]. The Ge–N bond length of 1.861(7) Å is within the range of common Ge–N single bond lengths (1.82–1.86 Å) and comparable to the values reported for germylamines such as $N(GeH_3)_3$ (1.836(5) Å [13]), $LiN(GeMe_3)_2$ (trimer *ca.* 1.81–1.88 Å [14]) and Mes_3GeNH_2 (1.854(3) Å [15]). These bond lengths observed in the germyldiazenido ligand in **13** are consistent with the description of this ligand as $W \overset{\Leftarrow}{=} N{=}N{-}GeR_3$. However, the N–N–Ge angle of 134.2(6)° is much larger than the 120° expected for the sp^2 hybridized terminal N atom. This might be attributable to the steric repulsion of the Ph_3Ge group against the PMe_2Ph ligands in *cis* positions. Such distortion in the diazenido ligands has also been demonstrated in the silyldiazenido complexes **2** [4b] and **14** [9] (N–N–Si = 152(2), 152(1)°) and in some alkyl or aryldiazenido complexes such as *trans*-[MoI(NNC$_6$H$_{11}$)(dpe)$_2$] [16] and *mer, trans*-[RuCl$_3$(NNC$_6$H$_4$CH$_3$-*p*)(PPh$_3$)$_2$]·(S) (S = CH_2Cl_2 [17], acetone [18]) (N–N–C = 132(1), 137.1(5), 136(1)°).

TABLE 4. Selected bond distances (Å) and angles (deg) in *trans*-[WI(NNGePh$_3$)(PMe$_2$Ph)$_4$]·C$_6$H$_6$ (**13**·C$_6$H$_6$)

(a) Bond distances			
W–I	2.910(2)	W–P(1)	2.503(3)
W–P(2)	2.530(2)	W–P(3)	2.503(3)
W–P(4)	2.514(2)	W–N(1)	1.809(6)
N(1)–N(2)	1.248(10)	Ge–N(2)	1.863(7)
Ge–C(51)	1.964(10)	Ge–C(61)	1.967(11)
Ge–C(71)	1.950(9)		
(b) Bond angles			
I–W–P(1)	93.54(6)	I–W–P(2)	80.13(6)
I–W–P(3)	90.81(6)	I–W–P(4)	84.24(6)
I–W–N(1)	175.7(2)	P(1)–W–P(2)	89.67(8)
P(1)–W–P(3)	175.48(7)	P(1)–W–P(4)	91.31(8)
P(1)–W–N(1)	89.0(3)	P(2)–W–P(3)	92.30(8)
P(2)–W–P(4)	164.37(7)	P(2)–W–N(1)	96.5(2)
P(3)–W–P(4)	87.89(8)	P(3)–W–N(1)	86.7(3)
P(4)–W–N(1)	99.2(2)	N(2)–Ge–C(51)	111.7(4)
N(2)–Ge–C(61)	98.9(4)	N(2)–Ge–C(71)	115.3(3)
C(51)–Ge–C(61)	106.7(4)	C(51)–Ge–C(71)	111.7(4)
C(61)–Ge–C(71)	111.6(5)	W–N(1)–N(2)	168.2(6)
Ge–N(2)–N(1)	134.2(6)		

TABLE 5. Conversion of N_2 gas into silylamines catalyzed by *cis*-[Mo(N$_2$)$_2$(PMe$_2$Ph)$_4$] (**10**) [a]

Chlorosilanes	Yield of silylamines [b] (mol/Mo atom)	Major byproduct [c]
$ClSiPhMe_2$	0.2	$PhMe_2SiSiMe_2Ph$
$ClSiEt_3$	3.0	$Et_3SiSiEt_3$
$ClSiMe_2H$ [d,e]	1.9	$HMe_2SiSiMe_2H$
$ClSiMe_2(OMe)$ [d]	7.0	$(MeO)_2SiMe_2$
$ClSiMe(OMe)_2$ [d]	3.1	$(MeO)_3SiMe$
$ClSiMe_2Cl$	1.5	$(Me_2Si)_n$ [f]
$(ClMe_2SiCH_2)_2$ [g]	1.9	
$ClGeMe_3$ [h]	0.6	$Me_3GeGeMe_3$
$ClSiMe_3$ [d,i]	7.5 [j]	$Me_3SiSiMe_3$
$ClSiEtMe_2$ [d,i]	4.4 [j]	$EtMe_2SiSiMe_2Et$

[a] Reaction conditions: chlorosilane, 10 mmol; Na microdispersion, 10 mmol; THF, 6.5 ml; complex **10**, 0.1 mmol; N_2, 1 atm; 30°C; 4 h. [b] Yields determined as NH_3 after hydrolysis. [c] Characterized by GLC and GC-MS. [d] $N(SiR_3)_3$ was formed. [e] 0°C; 15 h. [f] Characterized by IR; ref. 22. [g] Na microdispersion, 20 mmol. [h] $ClGeMe_3$, 5 mmol; Na microdispersion, 5 mmol; THF, 3.3 ml; complex **10**, 0.05 mmol. [i] Ref. 3. [j] Yield of $N(SiR_3)_3$ determined by GLC.

3.4. Catalytic conversion of N_2 gas into silylamines using cis-[Mo(N$_2$)$_2$(PMe$_2$Ph)$_4$] (10)

The catalytic reaction forming trimethylsilylamines shown in eqn. 1 has now been extended to the reaction systems involving various chlorosilanes and Me_3GeCl.

Reactions were carried out under the conditions which exhibited the highest catalytic activity with respect to the $N(SiMe_3)_3$ and $HN(SiMe_3)_2$ formation, *viz*, in THF at 30°C by using Na microdispersion as a reducing reagent and **10** as a catalyst. The total yield of silylated N_1 products was determined as the amount of NH_3 produced after hydrolysis of the reaction mixture. As summarized in Table 5, most reaction systems afforded significant amounts of NH_3. No hydrazine was detected after the workup of the reaction mixture from any run. The yield of NH_3 is much affected by the nature of the substituent attached to the Si atom and the increase in steric bulk apparently results in the decrease in the yield of NH_3 ($Me_3 > EtMe_2 > Et_3 \gg PhMe_2$). Formation of the trissilylamines in the resultant reaction mixtures was confirmed for several systems by GC-MS study (Table 5), while no $N(SiEt_3)_3$ was detected in the product solution from Et_3SiCl despite the formation of 3.0 mol NH_3/Mo atom after hydrolysis. This suggests that the N_1 products from those reactions which involve bulky chlorosilanes are formed predominantly as sodium amides such as $NaN(SiR_3)_2$ under these conditions. Degradation of trimethylsilyldiazenido complexes *trans*-[MoI(NNSiMe$_3$)(PMe$_2$Ph)$_4$] and **2** into sodium amides such as

$NaN(SiMe_3)_2$ and $NaNH(SiMe_3)$ upon reduction with Na has been clarified in detail already [4c].

In these reactions using monochlorosilanes, the major characterizable byproducts are disilanes, whose formation is also accelerated by **10**. Methoxy monosilanes, observed as the major byproduct from the reactions with methoxychlorosilanes, might be generated after successive disproportionation reactions of initially formed methoxydisilanes $(MeO)Me_2SiSiMe_2(OMe)$ and $(MeO)_2MeSiSiMe(OMe)_2$ in the presence of the Mo catalyst (eqns. (5), (6)). Similar base catalyzed or thermal redistribution reactions of methoxydisilanes to monosilanes have been reported previously [19–21].

$$(MeO)Me_2SiSiMe_2(OMe) \longrightarrow (MeO)_2Me_2Si + [Me_2Si:] \quad (5)$$

$$(MeO)_2MeSiSiMe(OMe)_2 \longrightarrow (MeO)_3MeSi + [(MeO)MeSi:] \quad (6)$$

We have also carried out a catalytic conversion of N_2 gas into germylamines using Me_3GeCl instead of R_3SiCl. However, a major reaction product was $Me_3GeGeMe_3$ and trisgermylamine $N(GeMe_3)_3$ was not detected in the reaction mixture from a GC-MS criteria, although 0.6 mol NH_3/Mo atom was obtained after hydrolysis.

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