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Silylation of Coordinated Dinitrogen by Silylcobalt Complexes. Preparation of a New Series of Silyldiazenido and Silylhydrazido(2-) Complexes of Molybdenum and Tungsten[1)]

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The silylcobalt complexes $[R_2R'SiCo(CO)_4]$ (R, R' = Ph, Me) reacted with dinitrogen complexes of the type $[M(N_2)_2(P)_4]$ (M = Mo, W; P = tertiary phosphine) to give new silyldiazenido complexes *trans*-$[M(NNSiR_2R')(P)_4][(\mu\text{-}OC)Co(CO)_3]$, which were further converted to silylhydrazido(2-) complexes such as *trans*-$[WX(NNHSiR_2R')(dpe)_2][Co(CO)_4]$ by treatment with HX (dpe = $Ph_2PCH_2CH_2PPh_2$; X = OH, OMe, Br).

Previously we reported that dinitrogen complexes of the type $[M(N_2)_2(P)_4]$ (M = Mo, W; P = tertiary phosphine) react with Me_3SiX (X = I,[2)] CF_3SO_3[3)]) to give trimethylsilyldiazenido complexes $[MX(NNSiMe_3)(P)_4]$. Detailed investigation of the reactivities of the silyldiazenido complexes has recently led to the discovery of the reaction system in which molecular nitrogen is converted into silylamines by treatment with Me_3SiCl and Na in the presence of molybdenum and tungsten dinitrogen complexes as catalyst.[4)] During the course of our extensive study on silylation of molecular nitrogen, we have now found the reaction of the dinitrogen complexes with silylcobalt complexes to give a new series of silyldiazenido complexes. This finding may provide some clue for further progress in catalytic silylation of molecular nitrogen.

When treated with some excess of $[Ph_2MeSiCo(CO)_4]$ prepared from Ph_2MeSiH and $Co_2(CO)_8$,[5)] *trans*-$[Mo(N_2)_2(dpe)_2]$ in benzene gave a novel silyldiazenido complex *trans*-$[Mo(NNSiPh_2Me)(dpe)_2][(\mu\text{-}OC)Co(CO)_3]$(**1**) in 35% yield[6)] at room temperature under rigorously dry conditions. The molecular structure determined by an X-ray crystallography by using reddish orange single crystals of **1** is shown in Fig. 1.[7)] Complex **1** has an octahedral structure around the Mo atom and the silyldiazenido and μ-isocarbonyl ligands occupy the mutually *trans* positions. The Mo-N(1)-N(2) linkage is essentially linear (177.1(10)°) and the N(1)-N(2)-Si bond is bent with the angle of 152.2(11)°. The N-N and N-Si bond lengths of 1.21(1) and 1.73(1) Å, respectively, are indicative of the bond orders between one and two. These bond lengths and angles

$$[M(N_2)_2(P)_4] + [R_2R'SiCo(CO)_4] \longrightarrow \textit{trans}\text{-}[M(NNSiR_2R')(P)_4][(\mu\text{-}OC)Co(CO)_3]$$

in **1** well correspond to those observed for *trans*-[WI(NNSiMe$_3$)(PMe$_2$Ph)$_4$] previously reported.[2)]

The structure of the [Co(CO)$_4$] anion is tetrahedral around the Co atom and one CO ligand bridges the Mo and Co atoms. The Mo–O(1) bond length (2.256(8) Å) is indicative of relatively weak coordination of the O(1) atom to the Mo atom. The Mo–O(1)–C(1)–Co linkage is almost linear (Mo–O(1)–C(1): 164.9(9)°; O(1)–C(1)–Co: 177.3(11)°) as observed in the μ-isocarbonyl complexes [(π-C$_5$Me$_5$)$_2$V][(μ-OC)V(CO)$_5$][8)] and [V(THF)$_4$][(μ-OC)V-(CO)$_5$]$_2$.[9)]. The C(1)–O(1) distance of the μ-isocarbonyl ligand (1.21(2) Å) is slightly longer than those of the other three terminal carbonyl ligands (1.15(3), 1.13(2), and 1.16(2) Å), whereas the Co–C(1) bond (1.70(1) Å) is shorter than the other Co–C bonds (1.76(2), 1.80(2), and 1.75(2) Å). This indicates that the back-donation of the electron density from the Co atom occurs to a larger extent into the μ-isocarbonyl ligand than into the terminal carbonyls. Such trends are also observed in the other μ-isocarbonyl complexes.[8,9)]

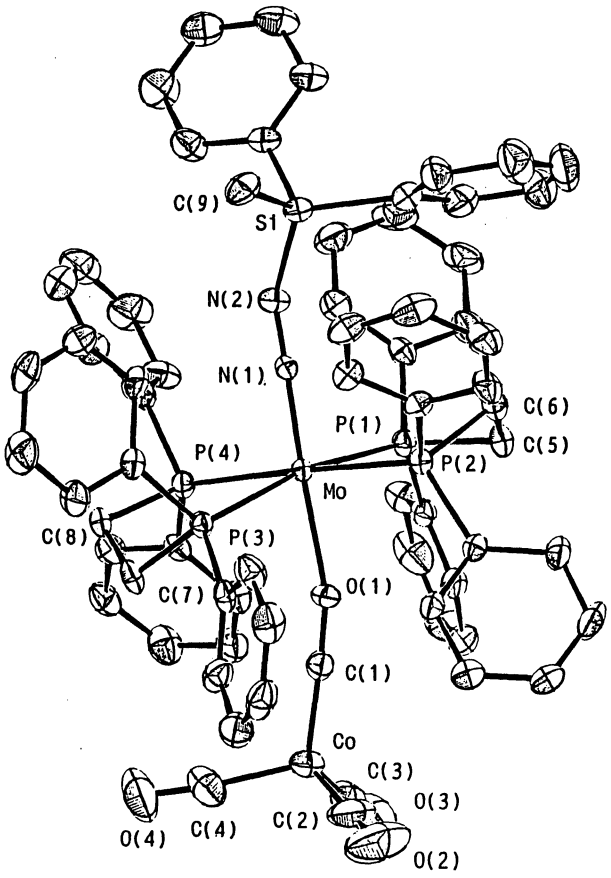

Fig. 1. The molecular structure of **1**.

A series of novel silyldiazenido complexes were prepared by the analogous treatment of the molybdenum and tungsten dinitrogen complexes with [Ph$_2$MeSiCo(CO)$_4$] and [Me$_2$PhSiCo(CO)$_4$], the spectroscopic data of which are summarized in Table 1. Silylcobalt complexes such as [Cl$_3$SiCo(CO)$_4$] and [(MeO)$_3$SiCo(CO)$_4$] also reacted with *trans*-[M(N$_2$)$_2$(dpe)$_2$] under the same reaction conditions, but no silyldiazenido complexes were isolated from these reaction mixtures.

Further treatment of the silyldiazenido complex *trans*-[W(NNSiPh$_2$Me)(dpe)$_2$][(μ-OC)Co(CO)$_3$](**2**) with one equiv of H$_2$O in benzene afforded the silylhydrazido(2–) complex *trans*-[W(OH)(NNHSiPh$_2$Me)-(dpe)$_2$][Co(CO)$_4$] (**3**) in 56% yield. An X-ray analysis performed by using yellow single crystals of **3** obtained

trans-[W(NNSiPh$_2$Me)(dpe)$_2$][(μ-OC)Co(CO)$_3$] + HX
⟶ _trans_-[WX(NNHSiPh$_2$Me)(dpe)$_2$][Co(CO)$_4$]
(X = OH, OMe, Br)

Table 1. Properties of trans-$[M(NNSiR_2R')(dpe)_2][(\mu\text{-}OC)Co(CO)_3]$

Cation	Yield	IR ν/cm^{-1} a)			^{1}H NMR δ/ppm b)
	%	ν(CO)	ν(NN)	ν(SiN)	
$[Mo(NNSiPh_2Me)(dpe)_2]$	35	2000m 1905vs 1775s	1660sh 1620s 1585sh 1570sh	835m	0.50 (s, 3H, SiMe) 1.99, 2.57 (br.m, 4H each, PCH_2)
$[W(NNSiPh_2Me)(dpe)_2]$	90	2050m 1920vs 1890vs 1765s	1610s 1590sh 1570sh	860m	0.55 (s, 3H, SiMe) 2.00, 2.65 (br.m, 4H each, PCH_2)
$[W(NNSiPh_2Me)(PMe_2Ph)_4]$	81	2010m 1920vs 1890s 1765s	1590m 1570m 1550s	860m	0.94 (s, 3H, SiMe) 1.41 (s, 24H, PMe)
$[W(NNSiMe_2Ph)(dpe)_2]$	81	2000m 1925sh 1910vs 1885sh 1755s	1640s 1585sh	855m	0.22 (s, 6H, SiMe) 2.10, 2.65 (br.m, 4H each, PCH_2)

a) KBr disk. b) In C_6D_6 solution. Phenyl protons are omitted.

from CH_2Cl_2/hexane disclosed the structure depicted in Fig. 2.[11] The cation in **3** has an octahedral structure and the *trans* position of the silylhydrazido(2–) ligand is occupied by the OH group. The $Co(CO)_4$ anion has a normal tetrahedral structure and there exists no bonding interaction between the cation and the anion. The almost linear W–N(1)–N(2) linkage (169.3(9)°) and the bent N(1)–N(2)–Si bond (131.8(9)°) as well as the N(1)–N(2) and N(2)–Si bond lengths of 1.36(2) and 1.76(1) Å, respectively, observed in **3** are essentially analogous to those in the other well characterized silylhydrazido(2–) complexes with PMe_2Ph ligands *mer*-$[WI_2(NNHSiMe_3)(PMe_2Ph)_3]$[2] and *mer*-$[WI_2(NN\overline{SiMe_2CH_2CH_2SiMe_2})(PMe_2Ph)_3]$,[12] indicating that the hydrazido proton is attached to the terminal nitrogen atom. Spectroscopic data observed for **3** are also diagnostic of this

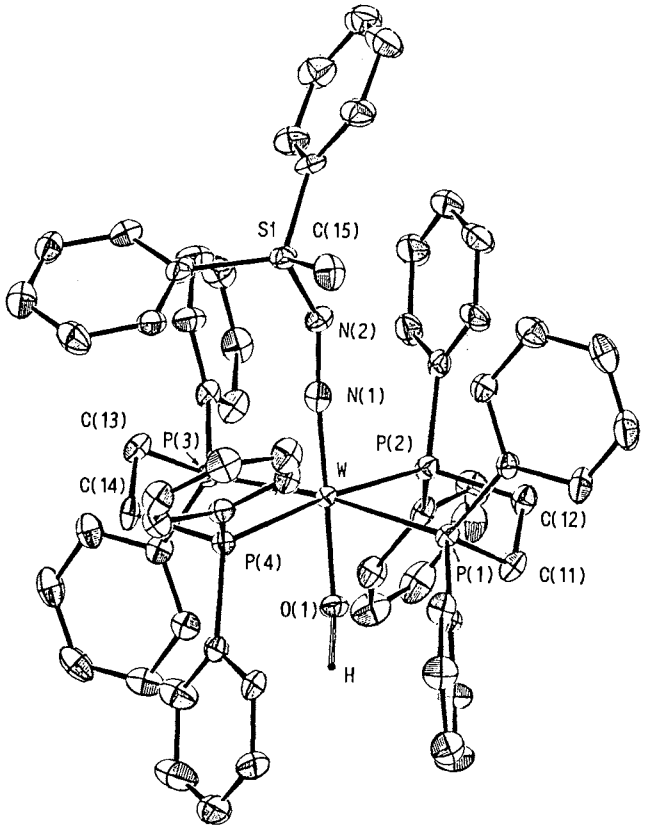

Fig. 2. The structure of the cation in **3**.

structure.[13] The reaction of **2** with HOMe or HBr gas proceeded analogously to give the silylhydrazido(2–) complexes *trans*-[WX(NNHSiPh$_2$Me)(dpe)$_2$][Co(CO)$_4$] (X = OMe,[14] Br[15]). It is to be noted that the reaction of [WI(NNSiMe$_3$)(P)$_4$] with H_2O or HOMe results in the facile cleavage of Si–N bonds and the expected silylhydrazido(2–) complexes are not formed.[3]

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6) Elemental analysis data are satisfactory for all new complexes reported here.

7) Crystallographic data for **1**: M = 1289.0, monoclinic, space group $P2_1/a$, a = 19.696(2), b = 28.060(4), c = 12.451(4) Å, β = 100.99(1)°, V = 6754.8 Å^3, Z = 4, D_{calcd} = 1.27 g cm^{-3}, μ(Mo Kα) = 5.81 cm^{-1}, R = 0.088, Rw = 0.12 for 8934 reflections (Fo > 5σ(Fo)).

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11) Crystallographic data for **3**: M = 1395.0, monoclinic, space group Pa, a = 23.703(10), b = 11.787(4), c = 11.306(7) Å, β= 95.29(5)°, V = 3145.3 Å^3, Z = 2, D_{calcd} = 1.47 g cm^{-3}, μ(Mo Kα) = 22.98 cm^{-1}, R = 0.048, Rw = 0.058 for 6738 reflections (Fo > 3σ(Fo)).

12) H. Oshita, Y. Mizobe, and M. Hidai, *Chem. Lett.*, **1990**, 1303.

13) IR (KBr disk, cm^{-1}): ν(NH) = 3240w, ν(NN) = 1320m, ν(SiN) = 800m, ν(C≡O) = 1880vs. ^{1}H NMR (CD_2Cl_2 solution, ppm): 0.22 (s, 3H, SiMe), 2.60 and 2.24 (br.m, 4H each, PCH_2), 4.08 (s, 1H, NH), –0.78 (quintet, J_{PH} = 4.6 Hz, 1H, OH), 7.6 – 6.8 (m, Ph).

14) IR (KBr disk, cm^{-1}): ν(NN) = 1315m, ν(SiN) = 800m, ν(C–O) = 1150m, ν(C≡O) = 1880vs. ^{1}H NMR (CD_2Cl_2 solution, ppm): 0.34 (s, 3H, SiMe), 2.54 and 2.21 (br.m, 4H each, PCH_2), 3.95 (s, 1H, NH), 1.83 (s, 3H, OMe), 7.5 – 6.5 (m, Ph).

15) IR (KBr disk, cm^{-1}): ν(NH) = 3240w, ν(SiN) = 820m, ν(C≡O) = 1880vs. ^{1}H NMR (C_6D_6 solution, ppm): 0.52 (s, 3H, SiMe), 2.57 and 2.34 (br.m, 4H each, PCH_2), 7.7 – 6.8 (m, Ph).

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