Synthesis of Boryldiazenido Complexes from Tungsten Dinitrogen Complexes[1]

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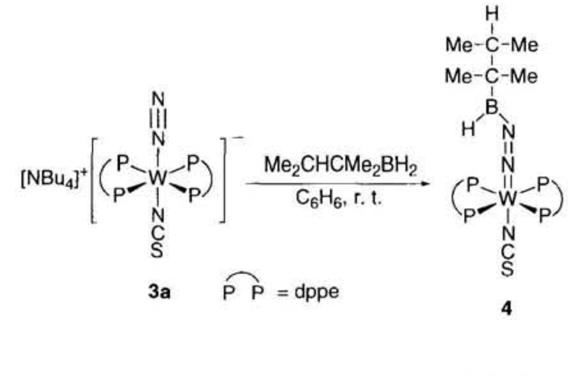
The anionic tungsten dinitrogen complex *trans*-[NBu_4][W(NCS)(N_2)(dppe)$_2$] reacted with primary and secondary boranes to give the corresponding boryldiazenido complexes, among which *trans*-[W(NCS)(N=NBHCMe_2CHMe_2)(dppe)$_2$] was structurally determined. A related boryldiazenido complex was also obtained by the reaction of *trans*-[W(N_2)$_2$(dppe)$_2$] with 9-borabicyclo[3.3.1]nonyl trifluoromethanesulfonate. These reactions provide the first examples of boration of coordinated dinitrogen.

Activation of molecular nitrogen on transition metal complexes has continuously been attracting considerable attention from the viewpoint of nitrogen fixation under mild conditions.[2] We have previously shown that the coordinated dinitrogen in *trans*-[M(N_2)$_2$(dppe)$_2$] (**1a**, M = W; **1b**, M = Mo; dppe = $Ph_2PCH_2CH_2PPh_2$) and *cis*-[M(N_2)$_2$(PMe_2Ph)$_4$] (**2a**, M = W; **2b**, M = Mo) undergoes electrophilic attack by various electrophiles including silyl and germyl iodides and transition metal Lewis acids to give silyldiazenido,[3,4] germyldiazenido,[4] disilylhydrazido,[5] and some other μ-dinitrogen complexes.[6,7] In spite of the high bond energy of a B–N bond[8] and the well-known electrophilic reactivity of boranes, there has so far been no report on the direct boration of coordinated dinitrogen.[9] However, intriguing reactivities of boranes toward carbon monoxide,[10] an isoelectronic molecule with dinitrogen, prompted us to investigate reactions of boranes with dinitrogen complexes. Here we describe the first direct boration of ligating dinitrogen in tungsten complexes to afford boryldiazenido complexes.

Although dinitrogen complexes **1a**, **2a**, and *trans*-[NBu_4][Mo(NCS)(N_2)(dppe)$_2$] (**3b**) did not react with thexylborane (1,1,2-trimethylpropylborane), the anionic tungsten dinitrogen complex *trans*-[NBu_4][W(NCS)(N_2)(dppe)$_2$] (**3a**) smoothly reacted with this borane (3 equiv.) in benzene at room temperature to give the boryldiazenido complex *trans*-[W(NCS)(N=NBHCMe_2CHMe_2)(dppe)$_2$] (**4**),[11] which was isolated as red crystals in 64% yield by recrystallization from benzene/hexane (eq 1). The high reactivity of **3a** is attributed to the effective π-back donation of electrons from the anionic tungsten center to the dinitrogen ligand, which is reflected in the low $\nu_{N\equiv N}$ value of complex **3a** (1860 cm^{-1}) in comparison with those of **1a**, **2a** and **3b** (1970–1890 cm^{-1}).[12] The reaction is assumed to accompany the formation of the salt [NBu_4][$H_3BCMe_2CHMe_2$], but IR and ^1H NMR analysis of the crude reaction mixture failed to confirm the presence of this borate salt.



(1)

3a $\widehat{P\ P}$ = dppe **4**

The IR spectrum of **4** showed a weak absorption at 2400 cm^{-1} and a strong absorption at 1495 cm^{-1} attributable to the ν_{BH} and $\nu_{N=N}$ bands, respectively. The ^1H NMR spectrum exhibited a set of CH and Me signals due to the thexyl group (δ 1.64 (sep), 0.89 (s), 0.82 (d)) in addition to those of the dppe protons. Unfortunately, we could not find any signal assignable to the B–H proton in the ^1H NMR spectrum. The $^{31}P\{^1H\}$NMR spectrum showed a singlet at δ 43.3 with tungsten satellites (J_{WP} = 292 Hz), indicating the trans configuration. The molecular structure of **4**·1.5(C_7H_8) was further confirmed by X-ray diffraction study (Figure 1).[13]

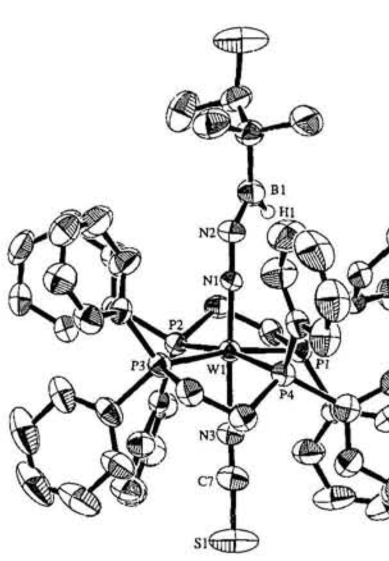


Figure 1. Molecular structure of **4**. Selected bond distances (Å) and angles (deg): W(1)–N(1), 1.804(4); N(1)–N(2), 1.262(7); N(2)–B(1), 1.374(9); W(1)–N(1)–N(2), 176.1(5); N(1)–N(2)–B(1), 133.6(6).

In agreement with the spectral data, complex **4** has an octahedral coordination structure with mutually trans boryldiazenido and isothiocyanato ligands. The W–N–N linkage is almost linear (176.1(5)°), and the N–N–B bond angle is 133.6(6)°. The N–N bond distance (1.262(7) Å) corresponds to the bond order of ca. 2, while the B–N bond distance at 1.374(9) Å is relatively short compared with a B–N bond in aminoboranes (typically 1.41 Å).[14] The B(1), N(2), C(1), and H(1) atoms are essentially coplanar. These structural features demonstrate a significant contribution of the hydrazido-type resonance structure **4B** with a B=N double bond character, in addition to **4A**.

4A **4B**

[W] = W(NCS)(dppe)$_2$

R = CMe$_2$CHMe$_2$

Reactions of **3a** with secondary boranes such as Cy$_2$BH (Cy = cyclohexyl) and 9-borabicyclo[3.3.1]nonane were sluggish at room temperature, and a higher temperature (50 °C) was necessary to allow the reactions to go to completion. The N-boration products with these secondary boranes *trans*-[W(NCS)(N=NBCy$_2$)(dppe)$_2$] (**5**) and *trans*-[W(NCS)(N=NBC$_8$H$_{14}$)(dppe)$_2$] (**6**)[11] showed a strong $\nu_{N=N}$ absorption at 1545 cm^{-1} and 1582 cm^{-1}, respectively, in the IR spectra. These values are higher by 50–90 cm^{-1} than that of **4**. This is probably because introduction of electron donating alkyl groups onto the boron atom diminishes contribution of the hydrazido-type resonance structure. BEt$_3$, a tertiary borane, failed to react with **3a**, while BH$_3$·THF gave a complex mixture.

Finally, the reaction of complex **1a** with 9-borabicyclo[3.3.1]nonyl trifluoromethanesulfonate was also found to afford the boryldiazenido complex *trans*-[W(OTf)(N=NBC$_8$H$_{14}$)(dppe)$_2$] (**7**, OTf = OSO$_2$CF$_3$).[11] This complex showed a $\nu_{N=N}$ absorption at 1705 cm^{-1}, which is significantly higher than those of **4**–**6**. The molecular structure of **7** was unambiguously determined crystallographically (Figure 2).[15]

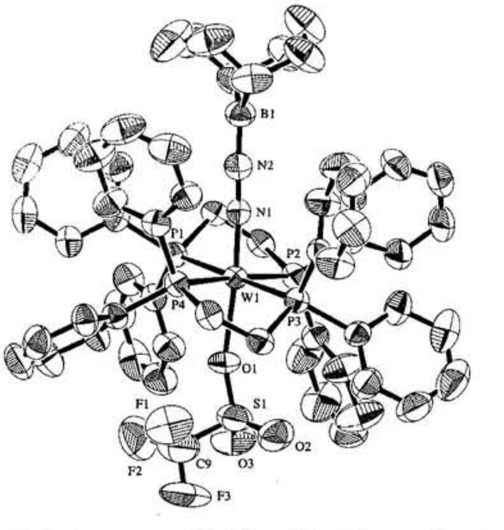


Figure 2. Molecular structure of **7**. Selected bond distances(Å) and angles (deg): W(1)–N(1), 1.777(5); N(1)–N(2), 1.235(6); N(2)–B(1), 1.398(9); W(1)–N(1)–N(2), 176.1(5); N(1)–N(2)–B(1), 168.3(7).

In contrast to the singly bent diazenido structure found for complex **4**, the W–N–N–B array in **7** is essentially linear, while the W–N, N–N, and N–B bond distances are comparable to the values for **4**. Although this type of linear structure is ubiquitous in complexes with a μ-N$_2$ ligand bridging two transition metal centers,[16] examples of linear μ-N$_2$ ligands between transition metals and main group metals are much fewer in number.[9a,17] It would be interesting to note that the anionic ligand on the tungsten atom controls the geometry around the nitrogen atom bonded to the boron. Studies on the reactivities of boryldiazenido complexes **4**–**7** are now under way.

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11 Satisfactory analytical data were obtained for complexes **4**–**7**.
4: yield 64%; ^{1}H NMR (C$_6$D$_6$) δ 0.82 (d, 6 H, J = 6.9 Hz), 0.89 (s, 6 H), 1.64 (sep, 1 H), 2.42–2.65 (m, 8 H), 6.85–7.95 (m, 40 H); ^{31}P{^{1}H} NMR (C$_6$D$_6$) δ 43.3 (s, J_{WP} = 292 Hz); IR (KBr) 2400 (w), 2054 (s), 1495 (s) cm^{-1}.
5: yield 33%; ^{1}H NMR (C$_6$D$_6$) δ 0.87–1.87 (m, 22 H), 2.23–2.32 (m, 4 H), 2.67–2.72 (m, 4 H), 6.76–7.96 (m, 40 H); ^{31}P{^{1}H} NMR (C$_6$D$_6$) δ 43.0 (s, J_{WP} = 294 Hz); IR (KBr) 2056 (s), 1549 (s) cm^{-1}.
6: yield 50%; ^{1}H NMR (CD$_2$Cl$_2$) δ 1.25–1.84 (m, 14 H), 2.23–2.32 (m, 4 H), 2.67–2.72 (m, 4 H), 6.68–7.54 (m, 40 H); ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$) δ 43.0 (s, J_{WP} = 292 Hz); IR (KBr) 2058 (s), 1582 (s) cm^{-1}.
7: yield 50%; ^{1}H NMR (C$_6$D$_6$) δ 1.24–1.88 (m, 14 H), 2.42–2.44 (m, 4 H), 2.96–2.98 (m, 4 H), 7.03–7.57 (m, 40 H); ^{31}P{^{1}H} NMR (C$_6$D$_6$) δ 48.2 (s, J_{WP} = 305 Hz); IR (KBr) 1705 (s) cm^{-1}.

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13 Crystals suitable for X-ray diffraction study were obtained by recrystallization from toluene/hexane. Crystal data: C$_{69.5}$H$_{74}$BN$_3$P$_4$SW, M = 1301.98, triclinic, space group $P\bar{1}$, a = 12.667(5) Å, b = 13.817(4) Å, c = 19.960(4) Å, α = 85.52(2)°, β = 76.39(2)°, γ = 68.68(3)°, V = 3162(1) Å^3, Z = 2, D_{calcd} = 1.367 gcm^{-3}, F(000) = 1334.00, μ(Mo Kα) = 20.06 cm^{-1}, R = 0.036, R_W = 0.049 for 6788 reflections with $I > 3\sigma(I)$. The BH hydrogen (H(1)) was found in the final difference Fourier map.

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15 Crystal data: C$_{61}$H$_{62}$BF$_3$N$_2$O$_3$P$_4$SW, M = 1278.78, monoclinic, space group $P2_1/n$, a = 10.015(3) Å, b = 24.026(4) Å, c = 23.711(4) Å, β = 94.96(3)°, V = 5684(2) Å^3, Z = 4, D_{calcd} = 1.494 gcm^{-3}, F(000) = 2592.00, μ(Mo Kα) = 22.41 cm^{-1}, R = 0.039, R_W = 0.035 for 6960 reflections with $I > 3\sigma(I)$.

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