Synthesis and Molecular Structure of Tetranuclear Tungsten-Gallium Complexes with Bridging Dinitrogen Ligands[1]

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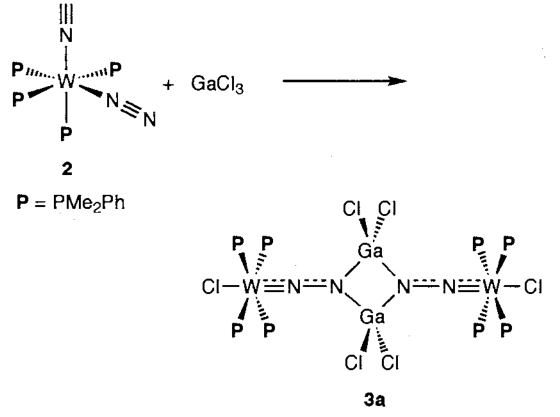
The dinitrogen complex *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ reacted with Ga_2Cl_4 or GaX_3 (X = Cl, Br) to form tetranuclear tungsten-gallium complexes with μ_3-η^1:η^1:η^1-N_2 ligands, *trans,trans*-$[\{WX(PMe_2Ph)_4(\mu_3\text{-}N_2)\}_2(GaX_2)_2]$ (**3**). The molecular structure of complex **3a** (X = Cl) has been determined by X-ray diffraction study.

Since the Fe-Mo multinuclear active site of nitrogenase was revealed by X-ray analysis,[2] binding and chemical transformation of molecular nitrogen at multimetallic centers have been attracting intense attention.[3,4] Various types of multinuclear bridging dinitrogen complexes have been prepared up to date, which exhibit intriguing reactivities.[4b-e] However, examples of heterobimetallic dinitrogen complexes are still limited in number.[4d,5-8] In the course of our continuous study on syntheses and reactivities of dinitrogen complexes, we previously reported several heterobimetallic complexes with μ-N_2 ligands such as the W-Al complex $[\{WCl(py)(PMe_2Ph)_3(\mu_3\text{-}N_2)\}_2(AlCl_2)_2]$ (**1**; py = pyridine),[5] which demonstrated the first example of a μ_3-η^1:η^1:η^1-N_2 ligand, and the W-Zr complex $[WCl(py)(PMe_2Ph)_3(\mu\text{-}N_2)ZrCp_2Cl]$ (Cp = η^5-C_5H_5)[6] with a μ_2-η^1:η^1-N_2 ligand. We describe here the synthesis and characterization of tetranuclear W-Ga complexes with μ_3-η^1:η^1:η^1-N_2 ligands, which provide hitherto unknown examples of dinitrogen complexes containing gallium.

When the dinitrogen complex *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ (**2**) was allowed to react with $GaCl_3$ (1 equiv.) in benzene at room temperature, evolution of N_2 gas (0.92 mol per tungsten atom) was observed. Recrystallization of the crude product from toluene-hexane gave orange crystals of *trans,trans*-$[\{WCl(PMe_2Ph)_4(\mu_3\text{-}N_2)\}_2(GaCl_2)_2]$ (**3a**)[9] in 46% yield (eq 1). A similar reaction of complex **2** with $GaBr_3$ afforded the bromo analog *trans,trans*-$[\{WBr(PMe_2Ph)_4(\mu_3\text{-}N_2)\}_2(GaBr_2)_2]\cdot THF$ (**3b**·THF) in 41% yield.[9] Complex **3a** exhibited a strong IR absorption at 1336 cm^{-1} attributable to the $\nu_{N\text{-}N}$ band. The ^1H and $^{31}P\{^1H\}$ NMR spectra showed a broad Me singlet at δ 1.85 and a singlet at δ −23.6 with ^{183}W satellites (J_{WP} = 284 Hz), respectively, indicating the *trans* configuration around the tungsten centers. These spectroscopic data are in agreement with the formulation.



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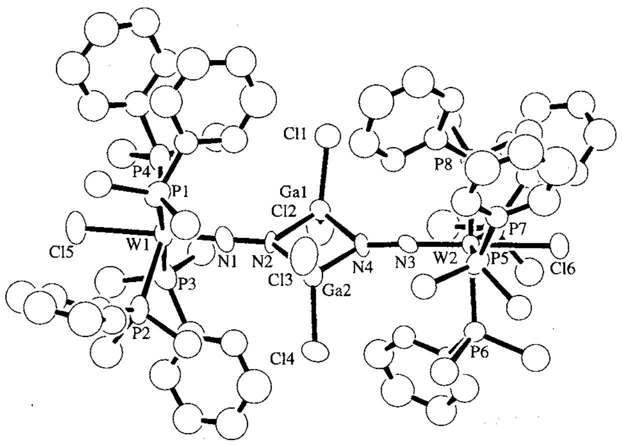
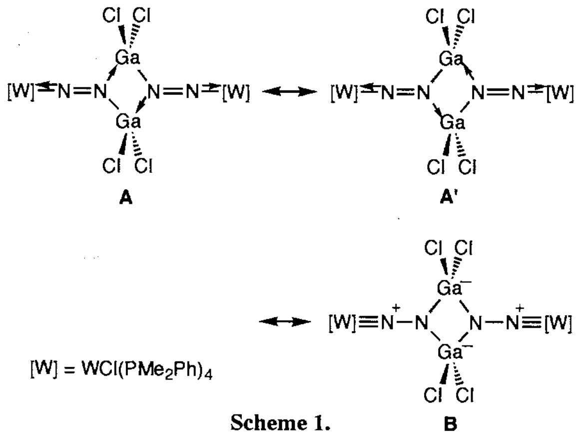


Figure 1. Molecular structure of **3a**. Selected bond distances (Å) and angles (deg): W(1)-N(1), 1.77(2); W(2)-N(3), 1.79(2); Ga(1)-N(2), 1.94(2); Ga(1)-N(4), 1.93(2); Ga(2)-N(2), 1.91(2); Ga(2)-N(4), 1.92(2); N(1)-N(2), 1.32(2); N(3)-N(4), 1.31(2); W(1)-N(1)-N(2), 176(1); W(2)-N(3)-N(4), 175(1); N(2)-Ga(1)-N(4), 84.8(8); N(2)-Ga(2)-N(4), 85.8(8); Ga(1)-N(2)-Ga(2), 94.6(8); Ga(1)-N(4)-Ga(2), 94.8(9); Ga(1)-N(2)-N(1), 132(1); Ga(1)-N(4)-N(3), 128(1); Ga(2)-N(2)-N(1), 132(1); Ga(2)-N(4)-N(3), 137(1).

The molecular structure of complex **3a** was unambiguously determined by X-ray diffraction study.[10] Single crystals of **3a**·$2.5(C_4H_8O_2)$ suitable for X-ray analysis were obtained by recrystallization from dioxane/hexane. As shown in Figure 1, complex **3a** has a tetranuclear structure with two μ_3-η^1:η^1:η^1-N_2 ligands, each of which bridges one tungsten and two gallium atoms. Thus, the two gallium atoms and two of the four nitrogen atoms constitute a four-membered ring. The $W(\mu_3\text{-}N_2)Ga_2(\mu_3\text{-}N_2)W$ core is essentially planar, and the W-N-N linkages are almost linear. Analogous tetranuclear cores with two μ_3-η^1:η^1:η^1-N_2 ligands have so far been found in or proposed for a few complexes including complex **1**, $[\{Co(PMe_3)_3(\mu_3\text{-}N_2)\}_2(AlR_2)_2]$ (R = Me, Et, $CH_2{}^i Pr$),[7a] $[\{Co(PMe_3)_3(\mu_3\text{-}N_2)\}_2\{MgR(OEt_2)\}_2]$ (R = Me, $CH_2{}^i Pr$, $^t Bu$, Ph),[7b] and $[\{W(\eta^5\text{-}C_5Me_5)Me_3(\mu_3\text{-}N_2)\}_2\{Mg(Me_2NCH_2CH_2NMe_2)\}_2]$.[7c] The structure of complex **3a** is essentially the same as that of complex **1**. However, bond distances in complex **1** could not be determined accurately due to the poor quality of the crystals. It is noteworthy that the N-N bond distances observed for complex **3a** (1.32(2), 1.31(2) Å) are significantly longer than those reported for the above-mentioned Co-Al (R = Me, 1.256(6) Å) and Co-Mg (R = ^{t}Bu, 1.211(4) Å) μ_3-η^1:η^1:η^1-N_2 complexes. The Ga-N bond distances at 1.91(2)-1.94(2) Å fall within the range of reported covalent Ga-N single bonds, but are considerably shorter than the values found for complexes with a Ga_2N_2 core such as $[Cl_2Ga(\mu\text{-}NHSiMe_3)]_2$ (1.974(4) Å),[11] $[Cl_2Ga(\mu\text{-}NMeSiMe_3)]_2$ (1.983(5)-1.985(5) Å),[11] $[Br_2Ga(\mu\text{-}NHSiMe_3)]_2$ (1.99(2)-2.00(2) Å),[12] $[H_2Ga(\mu\text{-}NMe_2)]_2$ (2.027(4) Å),[13] and $[Et_2Ga(\mu\text{-}NHNPh_2)]_2$ (2.042(7)-2.070(7) Å).[14]

On the basis of the molecular structure and spectral features, complex **3a** can be described as a resonance hybrid of the canonical structures depicted in Scheme 1. Structures **A** and **A'** may be regarded as the dimer of a hypothetical singly bent diazenido(2-) ($(N_2)^{2-}$) complex $[WCl(N{=}NGaCl_2)(PMe_2Ph)_4]$, while structure **B** represents the hydrazido(4-) ($(N_2)^{4-}$) complex. A significant contribution of the latter resonance structure is substantiated by the relatively long N-N and short Ga-N bond distances.



Scheme 1.

Complex **3a** was also obtained by the reaction of **2** with Ga_2Cl_4 (Ga:W = 2:1) in 40% yield. Further, the reaction of the dinitrogen complex *trans*-$[W(N_2)_2(depe)_2]$ (depe = $Et_2PCH_2CH_2PEt_2$) with Ga_2Cl_4 or $GaCl_3$ produced the corresponding W-Ga μ_3-η^1:η^1:η^1-N_2 complex *trans,trans*-$[\{WCl(depe)_2(\mu_3\text{-}N_2)\}_2(GaCl_2)_2]$ (**4**) in ca. 40% yield.[15,16] Studies on the reactivities of the W-Ga μ-N_2 complexes **3** and **4** are under way.

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9 **3a**: ^1H NMR (C_6D_6) δ 1.85 (br s, 48H, Me), 6.98 (t, 8H, *p*-PMe$_2$*Ph*), 7.18 (t, 16H, *m*-PMe$_2$*Ph*), 7.63 (br, 16H, *o*-PMe$_2$*Ph*); $^{31}P\{^1H\}$ NMR (C_6D_6) δ –23.6 (s, J_{WP} = 284 Hz); IR (KBr) 1336 cm^{-1}. Anal. Found: C, 41.21; H, 4.67; N, 2.94%. Calcd for $C_{64}H_{88}Cl_6Ga_2N_4P_8W_2$: C, 40.87; H, 4.36; N, 2.98%.
3b·THF: orange crystals, ^1H NMR (C_6D_6) δ 1.96 (br s, 48H, Me), 7.02 (t, 8H, *p*-PMe$_2$*Ph*), 7.17 (t, 16H, *m*-PMe$_2$*Ph*), 7.69 (br, 16H, *o*-PMe$_2$*Ph*); $^{31}P\{^1H\}$ NMR (C_6D_6) δ –29.5 (s, J_{WP} = 284 Hz); IR (KBr) 1323 cm^{-1}. Anal. Found: C, 36.57; H, 4.57; N, 2.37%. Calcd for $C_{68}H_{96}Br_6Ga_2N_4OP_8W_2$: C, 36.79; H, 4.36; N, 2.52%.

10 Crystallographic data for **3a**·2.5($C_4H_8O_2$): $C_{74}H_{108}Cl_6Ga_2N_4O_5P_8W_2$, M = 2101.34, monoclinic, space group $P2_1/c$, Z = 4, a = 20.493(4), b = 22.676(5), c = 20.808(3) Å, β = 114.82(1)°, V = 8776(2) Å^3, D_{calcd} = 1.509 gcm^{-3}, $\mu(MoK_\alpha)$ = 35.99 cm^{-1}, $F(000)$ = 4208.00, R = 0.055, R_w = 0.046 for 3337 unique reflections with $I > 3\sigma(I)$. The W, Ga, Cl, P, and N atoms were refined with anisotropic thermal parameters, while the C and O atoms were refined isotropically. The hydrogen atoms except for those of the dioxane molecules were included in the final stage of refinement with fixed isotropic parameters.

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15 **4**: orange crystals, ^1H NMR (C_6D_6) δ 1.00 (m, 24H, Me), 1.36 (m, 24H, Me), 1.5-2.5 (m, 48H, CH_2); $^{31}P\{^1H\}$ NMR (C_6D_6) δ 33.0 (s, J_{WP} = 279 Hz); IR (KBr) 1360 cm^{-1}, Anal. Found: C, 29.93; H, 6.14; N. 3.30%. Calcd for $C_{40}H_{96}Cl_6Ga_2N_4P_8W_2$: C, 30.01; H, 6.04; N, 3.50%.

16 Other dinitrogen complexes of tungsten and molybdenum such as *trans*-$[M(N_2)_2(dppe)_2]$ (M = W, Mo) and *trans*-$[W(N_2)_2(PMePh_2)_4]$ failed to give similar μ-N_2 complexes including gallium.