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Synthesis and Structure of (OC)$_5$W(η^1-GaH$_3$·(quinuclidine)): The First Gallane-Coordinated Transition-Metal Complex

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Summary: The first gallane-coordinated metal complex, (OC)$_5$W(η^1-GaH$_3$·(quinuclidine)) (2), was synthesized by photolysis of a ca. 1:1 mixture of W(CO)$_6$ and quinuclidine-coordinated gallane, H$_3$Ga·(quinuclidine) (1), in toluene and by the reaction of (OC)$_5$W(THF) with 1 equiv of gallane 1 in THF. X-ray crystal structure analysis of 2 revealed that gallane 1 is bound to the tungsten fragment via a W$-$H$-$Ga three-center$-$two-electron bond.

Reactions of boranes with transition-metal complexes have been investigated extensively.[1] It is now known that boranes can react with coordinatively unsaturated transition-metal fragments to give borane-coordinated metal complexes. For example, photolysis of M(CO)$_6$ (M = W, Mo, Cr) in the presence of the donor-coordinated borane BH$_3$·L (L = PMe$_3$, PPh$_3$, NMe$_3$, NC$_5$H$_5$) afforded the borane-coordinated complex [M(CO)$_5$(η^1-BH$_3$·L)], containing an M$-$H$-$B three-center$-$two-electron (3c$-$2e) bond.[1g] In contrast to borane-coordinated complexes, complexes containing heavier analogues of boranes, such as gallanes, have not been reported so far. Here we report the synthesis and structure of the first gallane-coordinated transition-metal complex.

Irradiation of a ca. 1:1 mixture of W(CO)$_6$ and quinuclidine-coordinated gallane, H$_3$Ga·quinuclidine (1),[2] in toluene-d_8 with a 450 W medium-pressure Hg lamp with stirring afforded the gallane-coordinated complex (OC)$_5$W(η^1-GaH$_3$·(quinuclidine)) (2)[3] in ca. 60% yield (by NMR). During the photolysis, evolution of CO gas was observed and the colorless solution turned yellow. Removal of the solvent and subsequent recrystallization of the residue with hexane afforded pale yellow crystals of complex 2 in 9% yield (eq 1). Complex 2 was also synthesized by the thermal reaction of

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(2) Atwood, J. L.; Bott, S. G.; Elms, F. M.; Jones, C.; Raston, C. L. *Inorg. Chem.* **1991**, *30*, 3792.

(3) Data for **2**: ^{1}H NMR (300 MHz, C$_6$D$_6$; δ/ppm): −7.32 (t, 1H, W$-$H$-$Ga, $^1J_{WH}$ = 48 Hz, $^2J_{HH}$ = 12 Hz), 0.75 (dt, 6H, HCCH_2−), 0.97 (sept, 1H, HCCH$_2$−), 2.24 (t, 6H, NCH_2−), 5.51 (br, 2H, GaH$_2$). ^{13}C NMR (75.5 MHz, C$_6$D$_6$; δ/ppm): 19.0 (HCCH_2−), 24.5 (HCCH$_2$−), 48.5 (NCH$_2$−), 196.9 (*cis*-CO), 200.0 (*trans*-CO). IR (hexane solution; cm^{-1}): 2087 (vw), 2077 (m), 1998 (vw), 1948 (vs, br). MS (EI, 70 eV; *m/z*): 507 (M$^+$, 32), 479 (M$^+$ − CO, 59), 477 (M$^+$ − CO − H$_2$, 46), 449 (M$^+$ − 2CO − H$_2$, 27), 421 (M$^+$ − 3CO − H$_2$, 45), 310 ((OC)$_2$WHGa$^+$, 14), 180 (Ga(quinuclidine)$^+$, 100), 111 (quinuclidine$^+$, 92). Exact MS: calcd for C$_{12}$H$_{16}$GaNO$_5$W (M$^+$) 506.9794, found 506.9799. Anal. Calcd for C$_{12}$H$_{16}$GaNO$_5$W: C, 28.38; H, 3.18; N, 2.76. Found: C, 28.29; H, 2.87; N, 3.30.
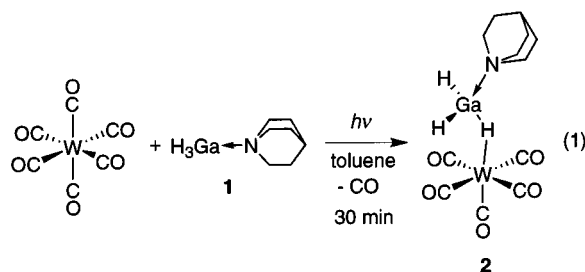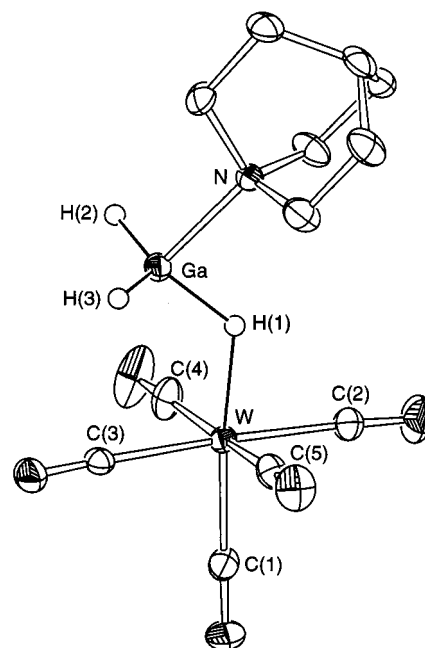
$(OC)_5W(THF)$ with 1 equiv of gallane **1** in THF in 38% yield (eq 2).[4] The low isolation yields of **2** in both cases
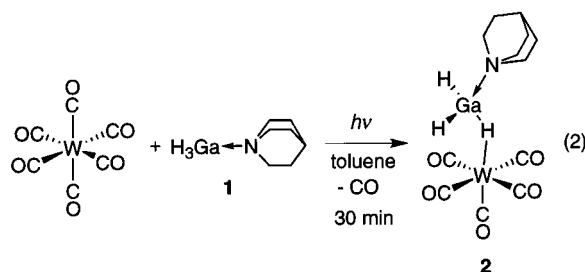
are attributable to the thermal instability of complex **2** (vide infra). Complex **2** was fully characterized by NMR, IR, and mass spectroscopy, elemental analysis, and X-ray structure analysis.

An X-ray crystal structure analysis of **2** (Figure 1) revealed that the tungsten atom has a six-coordinate octahedral geometry with five terminal CO ligands and gallane **1**, which is bound to the tungsten fragment via a W−H−Ga 3c−2e bond.[5] The W−Ga interatomic distance (3.0194(5) Å) is much longer than those of the known W−Ga single bonds (2.71−2.76 Å).[6] The Ga−N bond length (2.070(3) Å) is almost identical with that reported for gallane **1** (2.063(4) Å).[2] The bond length between tungsten and the carbonyl carbon atom trans to the gallane ligand (W−C(1) = 2.000(5) Å) is slightly shorter than those of W−C(cis) bonds (2.047(4)−2.071(5) Å). This result indicates that the trans influence of the gallane ligand **1** is weaker than that of CO.

The proton NMR spectrum of **2** showed signals assignable to the terminal and the bridging Ga−H at 5.51 and −7.32 ppm, respectively, in addition to those assignable to the quinuclidine moiety at 2.24, 0.97, and 0.75 ppm. The terminal Ga−H signal appeared as a very broad singlet, probably due to the quadrupolar effect of

(4) A THF solution of $(OC)_5W(THF)$ prepared by photolysis of $W(CO)_6$ (0.177 g, 0.50 mmol) in THF (20 mL) was slowly added to a THF (10 mL) solution of $H_3Ga·(quinuclidine)$ (**1**; 0.131 g, 0.71 mmol) at −46 °C with vigorous stirring. The mixture was stirred for 40 min at −46 °C and then for 1 h at room temperature. Volatiles were removed from the reaction mixture under reduced pressure. The residue was extracted with 30 mL of hexane. The extract was filtered through a membrane filter, concentrated to 15 mL, and cooled to −30 °C. Pale yellow crystals of **2** were obtained in 38% yield (0.098 g, 0.19 mmol).

(5) Crystallographic data for **2**: crystal dimensions 0.15 × 0.15 × 0.10 mm³, triclinic, space group $P\bar{1}$, $a = 6.9682(6)$ Å, $b = 10.4874(8)$ Å, $c = 11.6480(12)$ Å, $\alpha = 79.185(3)°$, $\beta = 84.411(5)°$, $\gamma = 74.069(4)°$, $V = 803.04(12)$ Å³, $T = 150(2)$ K, $\rho_{calcd} = 2.100$ g cm⁻³. The structure was solved by Patterson and Fourier transform methods (SHELXS-97) and refined by full-matrix least-squares techniques on all F^2 data (SHELXL-97).[9] All hydrogens were found in the difference Fourier map and refined with isotropic temperature factors. R1 = 0.0276 and wR2 = 0.0702 for 3548 refractions with $I > 2\sigma(I)$.

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Figure 1. ORTEP drawing (50% probability level) of $(OC)_5W(\eta^1\text{-}GaH_3·(quinuclidine))$ (**2**). Hydrogen atoms of quinuclidine are omitted for clarity. Selected interatomic distances (Å) and angles (deg): W−Ga = 3.0194(5), W−H(1) = 1.80(6), Ga−H(1) = 1.60(7), Ga−H(2) = 1.45(8), Ga−H(3) = 1.53(7), Ga−N = 2.070(3); Ga−W−H(1) = 26(2), W−H(1)− Ga = 125(4), W−Ga−H(1) = 29(2), Ga−W−C(1) = 160.69- (13), H(1)−W−C(1) = 173(2), N−Ga−W = 118.30(10), N−Ga−H(1) = 91(2).

the gallium atom, while the bridging W−H−Ga signal was observed as a relatively sharp triplet coupled with the two terminal Ga−H atoms ($^2J_{HH} = 12$ Hz) with tungsten satellites ($^1J_{WH} = 48$ Hz). The carbon-13 NMR spectrum of **2** showed two carbonyl signals at 196.9 and 200.0 ppm with an approximate intensity ratio of 4:1. These signals are assignable to cis and trans CO, respectively.

The terminal and bridging hydrides have been reported to exchange rapidly in the GaH_4^--coordinated complexes $[Zn(\eta^1\text{-}GaH_4)Cl(pmdeta)]$ (pmdeta = N,N,N,N',N'-pentamethyldiethylenetriamine) and [Zn- $(\eta^2\text{-}GaH_4)Cl(tmen)]$ (tmen = N,N,N,N-tetramethylethylenediamine).[7] Rapid exchange between the terminal and bridging hydrides similar to this has been also reported for the borane-coordinated complexes $(OC)_5M$- $(\eta^1\text{-}BH_3·L)$ (M = Cr, Mo, W; L = NMe₃, PMe₃, PPh₃, NC_5H_5).[1g] However, neither broadening nor coalescence of Ga−H signals was observed up to 40 °C for **2** by VT ¹H NMR (300 MHz). This indicates that hydride exchange does not take place or is much slower than the NMR time scale. The $\Delta G^\ddagger$ value for the hydride exchange process of **2** was found to be larger than 53 kJ mol⁻¹ at 313 K from the NMR data, which is much larger than that of the borane-coordinated complex $(OC)_5Cr(\eta^1\text{-}BH_3·PMe_3)$ ($\Delta G^\ddagger < 30$ kJ mol⁻¹ at 193 K).[1g]
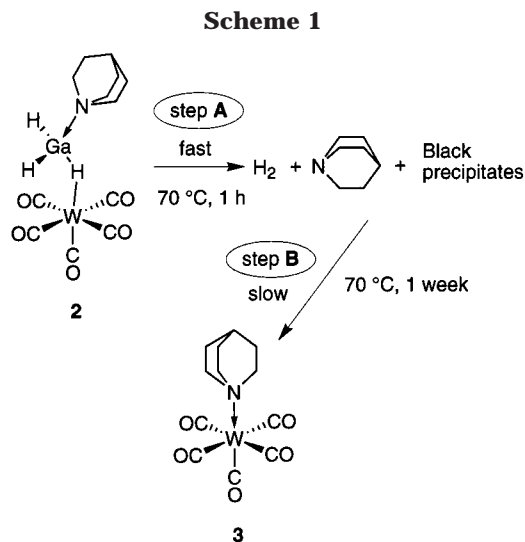
Complex **2** is thermally unstable and decomposes gradually at room temperature. Heating a toluene-d_8 solution of **2** in a sealed NMR sample tube at 70 °C for 1 h resulted in complete decomposition to form H_2, free

(7) Koutsantonis, G. A.; Lee, F. C.; Raston, C. L. *J. Chem. Soc., Chem. Commun.* **1994**, 1975.

Scheme 1

quinuclidine, and black precipitates of unidentified products (step **A** in Scheme 1). The decomposition reaction was followed by a slow reaction to give the known quinuclidine-coordinated tungsten complex $(OC)_5W$-(quinuclidine) (**3**)[8] (step **B** in Scheme 1). The latter reaction reached completion after 1 week under the experimental conditions. The free quinuclidine gener-

ated in step **A** was consumed completely, and complex **3** was formed almost quantitatively based on complex **2**.

During the course of the decomposition reaction of **2**, free gallane **1** was not observed at all. No gallane **1** was also detected in the reaction of complex **2** with PPh_3 at room temperature, which proceeded very slowly to give H_2, free quinuclidine, and $(OC)_5W(PPh_3)$. These facts indicate that the gallane ligand is inert toward direct substitution reactions and complex **2** decomposes without releasing free gallane **1**.

Supporting Information Available: Tables giving crystal structure data for **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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