center-to-center distances were calculated from the computer-simulated structures, and the overlap integral, calculated from emission and absorption spectra, was assumed to contain 36 equal contributions. For more details, see V. Grosshenny, A. Harriman, M. Hissler, R. Ziessel, *J. Chem. Soc. Faraday Trans.* **1996**, *92*, 2223.

[12] The triplet energies of the ditopic ligands used to assemble complexes **RO3** and **RO4** were derived to be 21400 and 16700 cm^{-1}, respectively, from room-temperature emission spectra recorded in micellar media. The triplet energy for the ditopic ligand present in **RO1** was found to be 20270 cm^{-1} from phosphorescence spectra recorded at 77 K. Triplet energies for the bpy-based ditopic ligands relevant to **RO5** and **RO6** were measured to be 21970 and 16100 cm^{-1}, respectively, from room-temperature emission spectra recorded in micellar media.

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$[Ti(CO)_4(\eta^3\text{-}BH_4)]^-$ and $[Ti(CO)_4(\eta^5\text{-}C_4H_4N)]^-$: The First Zerovalent Metal Complexes Containing η^3-Borohydride and Pyrrolyl Ligands[**]

Paul J. Fischer, Victor G. Young, Jr., and John E. Ellis*

Dedicated to Professor Heinrich Nöth
on the occasion of his 70th birthday

Metal borohydrides are an important class of substances that are known for practically all metals throughout the periodic table. Most contain metals in positive formal oxidation states.[1] Indeed, only two well-defined examples of zerovalent metal borohydrides have been reported, and both of these contain bidentate borohydride ligands: $[Mo(CO)_4(\eta^2\text{-}BH_4)]^-$[2] and $[Cr(CO)_4(\eta^2\text{-}BH_4)]^-$.[3a] We now report on the new zerovalent metal borohydride $[Ti(CO)_4(\eta^3\text{-}BH_4)]^-$ (**1**), the first to contain titanium and a tridentate borohydride ligand.

The synthetic route to this borohydride complex also appears to be unprecedented, that is, the reaction of $BH_3 \cdot THF$ with a mononuclear metal carbonyl anion.[4a] Prior reactions of this type provided only $M-BH_3$[4b] or $M-\eta^2\text{-}B_2H_5$ complexes.[5] The above-mentioned Group 6 zerovalent metal carbonyl borohydride complexes were obtained as pure products by treatment of an appropriate metal carbonyl with borohydride salts.[2, 3a] Complex **1** is is a very labile species and appears to be the most reactive isolable synthon for neutral $\{Ti(CO)_4\}$, a highly unsaturated 12-electron fragment (see below).

Treatment of a slurry of $[K([15]crown\text{-}5)_2]_2[Ti(CO)_6]$[3b] with $BH_3 \cdot THF$ (10 equiv, unoptimized) in THF at $-60\,^{\circ}C$ provided a very air-sensitive red solution. After careful separation of non-carbonyl by-products, deep red, pure, solid $[K([15]crown\text{-}5)_2]$-**1** was isolated in 38% yield (see Experimental Section) as a thermally stable substance at room temperature. By an analogous procedure $[K([18]crown\text{-}6)]$-**1** was obtained in 15% yield as orange-red microcrystals.[6]

Spectroscopic properties of both salts are virtually identical for the anionic component and are described here in detail for the $[K([15]crown\text{-}5)_2]^+$ salt. The IR spectra in THF show two peaks (1945(m), 1811(s) cm^{-1}) in the $\nu(CO)$ region that have the same pattern as observed for other titanium tetracarbonyl complexes in THF, including $[Ti(CO)_4(\eta^5\text{-}C_5H_5)]^-$ (**2**; $\tilde{\nu}(CO) = 1921$ (m), 1779 cm^{-1} (s)).[7a] The $\nu(CO)$ values of **1** are the highest reported for any titanium tetracarbonyl complex and suggest that $[BH_4]^-$ is the weakest donor presently known to stabilize this Ti^0 unit. The IR spectra of Nujol mulls of **1** in the $\nu(BH)$ region show bands at 2495 (m), 2132 (vw), and 2058 cm^{-1} (w), which have a pattern diagnostic of tridentate borohydride ligands.[1a] The borohydride signals observed in the ^1H ($\delta_H = -3.60$, 1:1:1:1 quartet, $J_{B,H} = 85$ Hz) and ^{11}B NMR spectra ($\delta_B = -6.42$, binomial quintet, $J_{H,B} = 87$ Hz) at 23 °C are consistent with the presence of a highly fluxional BH_4 group, as expected on the basis of prior studies.[1a] As the temperature was lowered, the 1:1:1:1 quartet in the ^1H NMR spectrum broadened and coalesced at $-63 \pm 5\,^{\circ}C$. At $-95\,^{\circ}C$ the slow exchange limit was reached, and two broad singlets of relative intensity 3:1 were present at $\delta_H = -4.87$ and 0.044, respectively, the weighted average of which is in satisfactory agreement with the resonance position at 23 °C. This study corroborated the presence of a $\eta^3\text{-}BH_4$ ligand in **1** and allowed the free energy of activation of the bridging/terminal hydrogen (H_t/H_b) exchange process to be calculated as 8.8 ± 0.2 $kcal\,mol^{-1}$ by standard procedures.[7b] This barrier is somewhat lower than the corresponding $\Delta G^{\ominus}$ of 10.0 ± 0.2 $kcal\,mol^{-1}$ reported for $[Mo(CO)_4(\eta^2\text{-}BH_4)]^-$, the only other borohydride carbonyl complex for which this value is known.[2]

A single-crystal X-ray diffraction study on the [K(18-crown-6)]$^+$ salt confirmed the existence of **1** in the solid state.[8] Two independent anions with nearly identical structures were present in the unit cell, and that shown in Figure 1 will be described in some detail here. All hydrogen atoms of the borohydride ligand were visible in the difference map after the remaining anisotropic refinement was complete. The linear H_t-B-Ti skeleton (179(2)°), three short Ti–H distances (av 2.02(4) Å), and the associated short Ti–B distance (2.158(7) Å) are all indicative of a $\eta^3\text{-}BH_4\text{-}Ti$ interaction. Slightly longer Ti–B distances in tridentate borohydride Ti^{IV} complexes have been reported, including $[Ti(OAr)_3(\eta^3\text{-}BH_4)]$ ($Ar = 2,6\text{-}i Pr_2C_6H_3$; 2.20(1) Å[9a]), and $[Ti(BP)_2(\eta^3\text{-}BH_4)_2]$ (BP = a biphenoxo dianion; 2.19(1) Å[9b]). The coordinated borohydride ligand is essentially tetrahedral, with an average $B-H_b$ distance of 1.11(2) Å, which does not significantly differ

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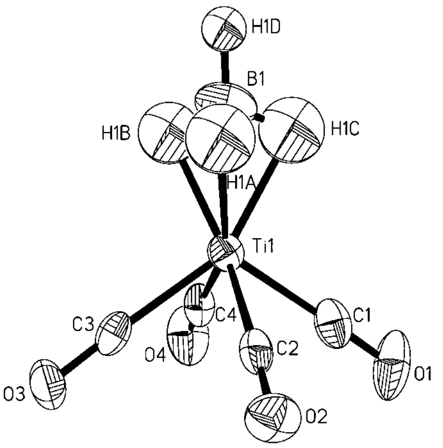

Figure 1. Molecular structure of **1** showing the labeling scheme (50% probability thermal ellipsoids; hydrogen atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Ti-C1 1.996(5), Ti-C2 1.997(5), Ti-C3 2.000(5), Ti-C4 2.016(6), C1-O1 1.173(5), C2-02 1.178(5), C3-O3 1.172(5), C4-O4 1.174(6), Ti-B 2.158(7), B-H1A 1.10(2), B-H1B 1.11(2), B-H1C 1.12(2), B-H1D 1.08(2), Ti-H1A 2.05(4), Ti-H1B 1.97(4), Ti-H1C 2.04(4); Ti-C1-O1 178.2(4), Ti-C2-O2 177.8(4), Ti-C3-O3 177.1, Ti-C4-O4 176.8(4).

from the B–H_t distance (1.08(2) Å). Also, all H-B-H angles are in the narrow range of 108(2) – 112(2)°, which is consistent with the presence of a relatively unperturbed tetrahedral borohydride group.

Interestingly, structures of the $Ti(CO)_4$ units in **1** and **2** are nearly superimposable, despite substantial electronic and structural differences in the donor ligands. For example, in **1** the average Ti–C and C–O distances (1.994(5) and 1.164(5) Å, respectively) as well as the *cis*- and *trans*-OC-Ti-CO angles (72(2) and 112.6(4)°, respectively) are experimentally indistinguishable from the corresponding values in **2** (Ti–C 2.00(1), C–O 1.174(5) Å; *cis*-OC-Ti-CO 72(1), *trans*-OC-Ti-CO 112.7(8)°).[7a] These structural data are consistent with the idea that the η^3-BH_4^- group is effectively isolobal with η^5-$C_5H_5^-$ in these complexes. Although the isolobal nature of η^3-BH_4^- and η^5-$C_5H_5^-$ was previously recognized in complexes containing a high-valent metal center, such as $[Sc(\eta^3\text{-}BH_4)_3]$ and $[Sc(\eta^5\text{-}C_5H_5)_3]$,[10] **1** and **2** are the first pair of metal carbonyl complexes that show this feature.

The asymmetric unit contains two [K([18]crown-6)] counterions that form infinite polymers with the anions through the carbonyl oxygen atoms, O1 and O3. The average K···O (carbonyl) and K···O (crown ether) distances of 2.80(4) and 2.80(3) Å, respectively, are essentially the same but are significantly longer than the average K···O (THF) distance of 2.69(4) Å in $[K([18]crown\text{-}6)(thf)_2]^+$;[11] this suggests that the K^+–$O_{carbonyl}$ interactions are weak at best. Indeed, the overall structure of the anion appears to be essentially unperturbed by this binding. For example, the formally "bridging" carbonyl ligands C1O1 and C3O3 are structurally identical to the other CO groups of **1**.

Treatment of **1** with a variety of nucleophiles at 20 °C in THF invariably results in rapid loss of $[BH_4]^-$ and quantitative formation of previously known zerovalent titanium carbonyl complexes [Eq. (1); L = $C_5H_5^-$, $C_5Me_5^-$,[7a] Ph_3C^-,[12a] $HBPz_3^-$,[12b] tacn, Me_3tacn[13]]. Although reactions of other transition metal borohydride complexes with nucleophiles often result in formation of the respective nucleophile – borane adducts and metal hydrides,[3a, 9, 14] no evidence for the generation of titanium hydrides was obtained in any of the reactions of **1** examined to date. The utility of **1** in the synthesis of new complexes was demonstrated by its facile reaction with the pyrrolyl anion to give the first (η^5-pyrrolyl)titanium complex $[Ti(CO)_4(\eta^5\text{-}C_4H_4N)]^-$ (**3**) [Eq. (2)].

$$[Ti(CO)_4(\eta^3\text{-}BH_4)]^- + L \xrightarrow{\text{THF, }20^\circ C} [Ti(CO)_4L] + BH_4^- \qquad (1)$$

$$[Ti(CO)_4(\eta^3\text{-}BH_4)]^- + KC_4H_4N \longrightarrow [Ti(CO)_4(\eta^5\text{-}C_4H_4N)]^- + KBH_4\downarrow \qquad (2)$$

Pure orange microcrystalline **3** was isolated in 52% yield as a thermally stable $[K([15]crown\text{-}5)_2]^+$ salt. Spectroscopic properties of **3** (see Experimental Section) are entirely consistent with the proposed formulation. Also, a single-crystal X-ray structural characterization of the corresponding bis(triphenylphosphane)iminium salt was carried out.[15] Although pyrrolyl complexes of metals in formally positive oxidation states are now fairly common,[16] including η^1-pyrrolyl complexes of Group 4 metals[17] and the long-known neutral $[Mn(CO)_3(\eta^5\text{-}C_4H_4N)]$, the only previous example of a half-sandwich metal carbonyl complex containing a pyrrolyl ligand,[18] **3** is presently the only known zerovalent metal complex to contain this ligand. Extensions of this research to other early transition metals and studies on the general reactivity patterns of **1** and **3** are in progress.

Experimental Section

$[K([15]crown\text{-}5)_2]$-**1**: A cold (−60 °C) solution of $BH_3 \cdot THF$ in THF (1.0 M, 20.0 mL, 20.0 mmol) was added to a finely divided suspension of $[K[15]crown\text{-}5)_2]_2[Ti(CO)_6] \cdot$pyridine (2.50 g, 2.00 mmol) in THF (95 mL), and the mixture was stirred under an atmosphere of argon while slowly being warmed to 10 °C over a period of 16 h. The mixture was then cooled to −60 °C and filtered at this temperature. Following removal of solvent in vacuo (temperature of solution should not exceed 10 °C), cold diethyl ether (0 °C, 150 mL) was added to precipitate the product. The latter was taken up in cold THF (−50 °C) containing 1 mL of [15]crown-5 and filtered again at −60 °C. All but about 4 mL of THF was removed. Slow addition of cold diethyl ether (0 °C, 100 mL) to the resulting concentrated filtrate (0 °C) provided a powdery solid. This was isolated by filtration, washed with cold diethyl ether (0 °C, 3 × 10 mL), and dried in vacuo at room temperature to give 0.494 g (38% yield) of a deep red powder, which provided satisfactory elemental analyses for unsolvated $[K([15]crown\text{-}5)_2]$-**1**. Elemental analysis calcd (%) for $C_{24}H_{44}O_{14}BKTi$: C 44.05, H 6.78; found: C 43.74, H 6.92; m.p. 115 – 118 °C (decomp); IR (CH_2Cl_2): $\tilde{\nu} = 1947$ (m), 1806 cm^{-1} (s) (CO); ^1H NMR (300 MHz, $[D_8]$THF, 0 °C, TMS): $\delta = 3.53$ (s, 40H, [15]crown-5), −3.60 (1:1:1:1 quartet, $J_{B,H} = 85$ Hz, 4H, BH_4); $^{13}C\{^1H\}$ NMR (75 MHz, $[D_8]$THF, 0 °C, TMS): $\delta = 291.7$ (s, CO), 69.2 (s, [15]crown-5); ^{11}B NMR (96.2 MHz, $[D_8]$THF, 0 °C, $BF_3 \cdot OEt_2$): $\delta = -6.42$ (quintet, $J_{H,B} = 87$ Hz; BH_4). Attempts to grow X-ray quality crystals of $[K([15]crown\text{-}5)_2]$-**1** were unsuccessful, but suitable red-violet needles of [K([18]crown-6)]-**1**, obtained by the procedure outlined above, were grown from THF/pentane at 4 °C over 7 d.

$[K([15]crown\text{-}5)_2]$-**3**: A solution of pyrrolylpotassium (0.153 g, 1.45 mmol) in THF (200 mL) was added to $[K([15]crown\text{-}5)_2]$-**1**, (0.306 g, 0.468 mmol) in cold THF (−50 °C, 10 mL) with stirring. The color of the reaction mixture immediately changed from red to orange. After 10 min the solution was cooled to −70 °C and filtered at −70 °C, and all but about 3 mL of solvent was removed in vacuo. Addition of cold diethyl ether (0 °C, 200 mL) resulted in formation of an orange solid. The latter was recrystallized from THF/diethyl ether to provide air-sensitive orange microcrystals

(0.170 g, 52% yield). Elemental analysis calcd (%) for $C_{28}H_{44}O_{14}NKTi$: C 47.66, H 6.28, N 1.99; found: C 47.43, H 6.27, N 2.06; m.p. 124–125 °C (decomp); IR (THF): $\tilde{\nu} = 1930$ (m), 1793 cm^{-1} (s) (CO); ^1H NMR (300 MHz, $[D_8]THF$, 0 °C, TMS): $\delta = 6.16$ (m, 2H, pyrrolyl), 5.40 (m, 2H, pyrrolyl), 3.62 (s, 40H, [15]crown-5); $^{13}C\{^1H\}$(75 MHz, $[D_8]THF$, 0 °C, TMS): $\delta = 289$ (s, CO), 114 (s, pyrrolyl), 99 (s, pyrrolyl), 69 (s, [15]crown-5).

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A Metamagnetic Two-Dimensional Molecular Material with Nickel(II) and Azide[**]

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Until a few years ago, the main aim of magnetochemical research was to show that molecular magnetism could lead to the development of new magnetic materials.[1] One strategy for the design of molecular-based magnets involves assembling transition metal ions in one-, two-, or three-dimensional networks. We are currently studying materials formed from the interaction of transition metal ions with the azido ligand. The azido bridge is a versatile and efficient magnetic coupler; it may transmit either antiferro- or ferromagnetic interactions. Working with Ni^{II} salts and diamines as blocking ligands, for a Ni/diamine ratio of 1/1 four positions in the coordination sphere of the nickel are free. These positions can be occupied by four azido bridges. The most remarkable species obtained to date are the neutral polymeric compounds $[Ni(\mu\text{-}N_3)_2\text{-}(diamine)]_n$: three one-dimensional systems showing global ferromagnetic behavior and metamagnetism at low temperature,[2] five one-dimensional complexes with alternating end-on (EO) and end-to-end (EE) azido bridges in different sequences showing global anti-ferromagnetic behavior,[3–6]

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