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Unusual Organic Chemistry of a Metallaborane Substrate: Formation of a Tantalaborane Complex with a Bridging Acyl Group (μ-η^2)

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The addition of $LiBH_4 \cdot THF$ to Cp^*TaCl_4 (**1**; $Cp^* = \eta^5$-C_5Me_5) at −40 °C, followed by mild pyrolysis with excess $BH_3 \cdot THF$, results in the formation of the μ-acyl complex $(Cp^*Ta)_2B_4H_8(\mu$-η^2-$COCH_3)$ (**2**). The title compound represents a novel class of μ-acyl complexes in which the bicapped-tetrahedral unit $(Cp^*Ta)_2B_4H_8$ is bridged by a μ-η^2-$COCH_3$ acyl ligand.

Migratory CO insertion is one of the most studied reactions in organo-transition-metal chemistry, homogeneous catalysis, and organometallic applications in organic synthesis for C−C bond formation.[1] Migratory insertion of CO into the transition-metal−alkyl bonds, in general, generates η^1- or η^2-acyl derivatives, with the latter[2] most general with early transition metals, lanthanides, and actinides. Because metal acyl derivatives are important intermediates in many catalytic processes,[3] knowledge of the metal−acyl bonding model, in particular, becomes significant. Three different classes of metal acyl derivatives can be recognized: (a) C-bonded σ-acyl;[4,5] (b) η-acyls, C- and O-bonded to the same metal;[6] and (c) C- and O-bonded μ-acyls, bridging two metal centers[7] (Chart 1).

Most recently, the in situ generated reactive intermediate, produced in the reaction of **1** with $LiBH_4 \cdot THF$, provided a series of interesting low-boron-content tantalaboranes by pyrolysis with monoborane reagents.[8] As a result, prompted by the research work of Fehlner and co-workers, we were tempted to look at thermally driven borane cluster building on the metallaborane frameworks. In terms of systematic cluster expansion, the most versatile metal is rhenium, where known Re_2B_n frameworks run from $n = 4$ to 10.[9] Ruthenium offers, although fewer, interesting cluster compounds.[10] In most of the cases, yields are poor and selectivities are low, but these drawbacks are acceptable simply because the approach generates new cluster types. Although the objective of generating higher-nuclearity tantalaborane clusters was not achieved, revisiting the system utilizing different reaction conditions permits isolation of the μ-η^2-acyl complex $(Cp^*Ta)_2B_4H_8(\mu$-η^2-$COCH_3)$ (**2**; Scheme 1).[11] Complex **2** was isolated in ca. 19% yield by using freshly prepared $BH_3 \cdot THF$.[12] However, all of our attempts to raise this yield through changes in the solvents, temperature, and time did not meet with success. η^2-Acyl complexes of tantalum are relatively rare. The first

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(11) **1** (0.16 g, 0.35 mmol) was suspended in toluene (15 mL) and cooled to −40 °C; an excess of $LiBH_4 \cdot THF$ was added, and the resulting solution was warmed slowly over 1 h to room temperature. Volatiles were removed and extracted into hexane. The filtrate was concentrated, and a toluene solution (15 mL) of the intermediate was pyrolyzed in the presence of an excess of freshly prepared $BH_3 \cdot THF$ at 70 °C for 96 h. Volatiles were removed in vacuo, and the residue was extracted into hexane and filter through Celite. After removal of the solvent from the filtrate, the residue was subjected to chromatographic workup using silica gel TLC plates. Elution with a hexane/CH_2Cl_2 (9:1, v/v) mixture yielded a yellow **2** (0.05 g, 19%), along with other tantalaboranes reported earlier.[8] ^{11}B NMR (22 °C, 128 MHz, C_6D_6): δ 38.7 (s, 2B), −5.8 (s, 2B). ^1H NMR (22 °C, 400 MHz, C_6D_6): δ 5.18 [2H, partially collapsed quarted (pcq), BH_t], 3.75 (2H, pcq, BH_t), 3.22 (3H, s, $COCH_3$), 2.30 (15H, s, Cp*), 2.15 (15H, s, Cp*), −7.37 (2H, pcq, Ta−H−B), −11.28 (2H, pcq, Ta−H−B). ^{13}C NMR (22 °C, 100 MHz, C_6D_6): δ 263.9 ($\mathit{C}OCH_3$), 114.1 (C_5Me_5), 110.1 (C_5Me_5), 30.8 ($CO\mathit{C}H_3$), 14.1 ($C_5\mathit{Me}_5$), 13.8 ($C_5\mathit{Me}_5$). IR (hexane) ν/cm^{-1}: 2457 (BH_t), 1454 (CO), 865 (Ta−O−Ta). MS (FAB) P^+(max): *m*/*z* (%) 727. Elem anal. Calcd for $^{12}C_{22}{}^1H_{41}{}^{180}Ta_2{}^{11}B_4{}^{16}O_1$: C, 36.36; H, 5.69. Found: C, 36.79; H, 5.82.

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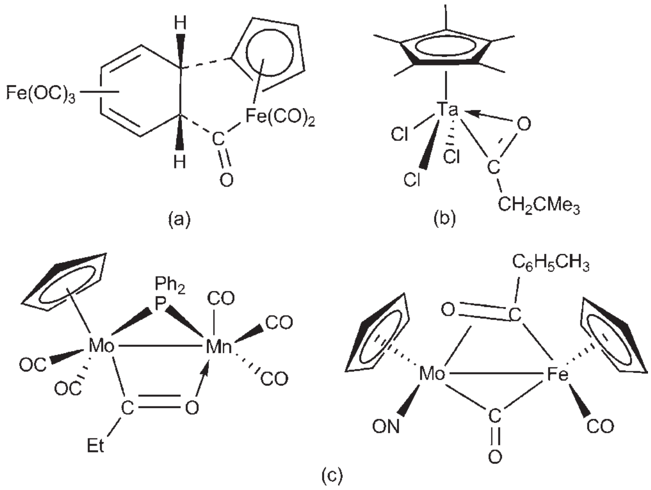
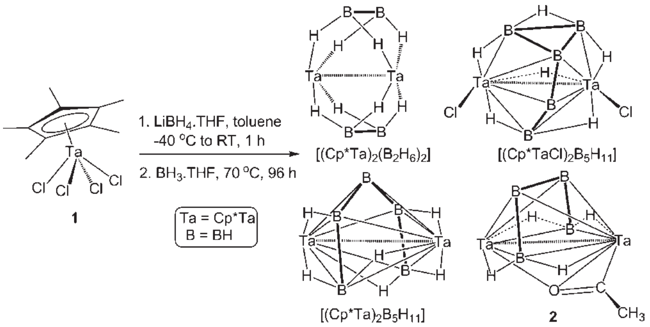
Chart 1



Scheme 1



compound of this type, dinuclear species $Cp^*Ta(C(O)CH_2EMe_3)Cl_3$ (E = Si, C), was prepared by Rocklage and Schrock[13] by carbonylation of the alkyl complexes $Cp^*Ta(CH_2EMe_3)Cl_3$. To the best of our knowledge, the homodinuclear μ-η^2-acyl complex **2** represents the first metallaborane complex with a bridging acyl group.

Following chromatographic separation of **2** from the other products using 9:1 hexane/CH_2Cl_2 in thin-layer chromatography (TLC), crystals suitable for X-ray diffraction analysis were grown by cooling a concentrated hexane solution to −10 °C. Single-crystal X-ray diffraction studies on **2** not only established the location of all atoms including hydrogens but also revealed the nature of the acyl moiety attached to tantalum atoms.[14] A solid-state structure of **2**, shown in Figure 1, shows the μ-η^2-acyl ligand coordinated to the bicapped-tetrahedral cage, $(Cp^*Ta)_2B_4H_8$, bonding via O1 to Ta1 and Ta2 and via C21 to Ta1. The observed Ta−Ta bond length of 2.8738(6) Å in **2**, comparable to that of $(Cp^*Ta)_2B_4H_{10}$,[8a] indicates a weak bridging property of the acyl group. Although the Ta2−O1 bond length of 2.003(11) Å is in the range for Ta−O single bonds,[15] the Ta1−O1 distance of 2.314(12) Å is much longer than a single bond. This notable difference in the bond length may be due to two different bonding modes of the acyl group to Ta1 and Ta2. In addition, a short C21−O1 bond length of 1.185(15) Å suggests significant shrinkage of this linkage; this is far closer to the 1.15−1.30 Å range of η^2-acyls[2] than to the C−O single bond distance.

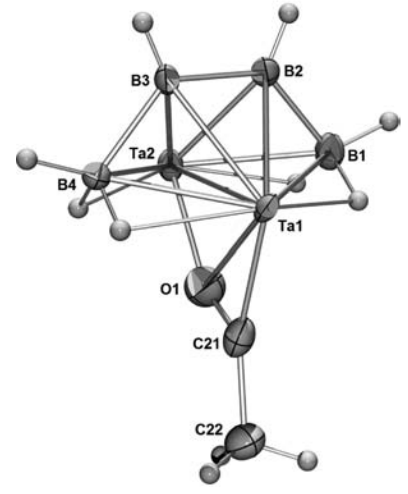


Figure 1. Molecular structure and labeling diagram for **2**. Cp* ligands are omitted for clarity. Relevant bond lengths (Å) and angles (deg): Ta1−Ta2 2.8738(6), Ta1−O1 2.314(12), Ta2−O1 2.003(11), Ta1−C21 2.157(12), Ta1−B1 2.472(13), Ta2−B2 2.288(13), B1−B2 1.74(2), B2−B3 1.644(17), C21−O1 1.185(15); O1−C21−Ta1 82.1(8), Ta2−O1−Ta1 83.1(4), Ta2−O1−C21 150.5(11).

Most of the X-ray studies on μ-acyl compounds[16−18] reveal the presence of an effectively planar M−O═C(R)−M′ moiety with a 180° M−O−C−R dihedral angle, representing a M−O σ bond pertaining to the oxygen lone pair and a nonbonding M−C distance that is normally very close to the M−M′ distance.[17] Although the observed dihedral angle of Ta1−O1−C21−CH_3 is 179°, the Ta1−C21 distance is 2.157(12) Å, much shorter than the Ta1−Ta2 bond length. The acyl fragment Ta1−[C21−O1]−Ta2, anchored to the bicapped-tetrahedral Ta_2B_4, has a "butterfly" geometry in which the Ta1−C21−O1 plane has been displaced by 0.48° from coplanarity with the Ta2−Ta1−O1 system. The bond angles and lengths of **2**, associated with the μ-acyl moiety, are in line with other μ-acyl compounds listed in Table 1. Furthermore, experimentally determined structural parameters of **2** are also reasonably comparable to the structurally characterized tantalum acyl complexes $TaCp^*Me\{\eta^2\text{-}C(CH_2CMe_2Ph){=}O\}\{N(2,6\text{-}Me_2C_6H_3)\}$[19] and $Cp^*Ta\ (C(O)CH_2CMe_3)Cl_3$.[6b]

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(14) Crystal data of **2**: $C_{22}H_{41}B_4OTa_2$, M_r = 726.69 g/mol, monoclinic, space group $P2_1/c$, a = 19.6992(6) Å, b = 8.8435(2) Å, c = 15.8348(5) Å, β = 112.9940(10)°, V = 2539.40(13) $Å^3$, Z = 4, ρ_{calcd} = 1.901 g/cm^3, final R indices [$I > 2\sigma(I)$] R1 = 0.0518 and wR2 = 0.1185, reflections collected 17 399, independent reflections 6249, R_{int} = 0.0357, GOF on F^2 = 1.093.

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Table 1. Selected Structural Parameters of **2** and Related Acyl Complexes

compound	type	*d*[M−M] [Å]	*d*[M−O] [Å]	*d*[M−C] [Å]	[M−O−C] [deg]	^{13}C NMR [ppm]	ref
$(Cp^*Ta)_2B_4H_8(\mu\text{-}\eta^2\text{-}COCH_3)$ (**2**)	μ-η^2	2.873	2.158[a]	2.157	108.9	263.9	this work
$Cp^*Ta(C(O)CH_2CMe_3)Cl_3$	η^2		2.108	2.07	70.8	315.4	6b
$(CpFeCO)(\mu\text{-}C(O)\text{-}p\text{-tolyl})(\mu\text{-}CO)(Mo(NO)Cp)$	μ-η^2	2.717	2.115	2.158[b]	85.7	265.0	7c
$WFe_2(\mu_3\text{-}OCCH_2C_6H_4Me\text{-}4)(PPh_2)_2(CO)_5Cp$	μ_3-η^2	2.683[c]	2.070[a]	2.034[b]	86.9[d]	258.5	16a
$CpMoMn\{\mu\text{-}C(O)C_6H_{11}\}(PPh_2)(CO)_5$	μ	2.963	2.027	2.200	109.3	300.8	7b
$Co(IMes)(CO)_3(COMe)$[e]	η^1			2.016		238.7	21a
$Mo(C(O)CH_3)(S_2C(PMe_3)OCH_2CF_3)CO(PMe_3)_2$	η^1			2.057		268.2	21c

[a] The average distance of M−O. [b] The average distance of M−C_{acyl}. [c] The average distance of M−M. [d] The average angle of M−O−C. [e] IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene.

Spectroscopic data are consistent with the solid-state structure of **2**. The IR spectrum of **2** exhibited broad medium-intensity absorption at 1454 cm^{-1}, which we assign to the η^2-acyl C−O stretch. In addition, a broad absorption band at 865 cm^{-1} has been assigned to the Ta−O−Ta stretching mode.[20] The ^{11}B NMR spectrum displays two resonances with equal intensities, and the presence of two pairs of Ta−H−B and two B−H terminal resonances is observed in ^{1}H NMR. The peak at δ = 3.22 ppm with an intensity of three has been assigned to the acetyl methyl protons (SI-Fig.-1 in the Supporting Information). The low-field acyl resonance in ^{13}C NMR at δ = 263.9 ppm is consistent with both η^1[21] and η^2 coordination (Table 1); however, the latter is more likely based on the absence of other coordinating ligands.

Mechanistic insight was provided by the treatment of $BH_3\cdot THF\text{-}d_8$ with the intermediate, generated from the reaction of Cp^*TaCl_4 (**1**) and $LiBH_4\cdot THF$, to yield $(Cp^*Ta)_2B_4H_8(\mu\text{-}\eta^2\text{-}COCD_3)$. The ^{2}H NMR spectrum revealed a single resonance at δ = 3.33 ppm (SI-Fig.-2 in the Supporting Information). The presence of the ^{2}H label in the acyl ligand of **2** demonstrates that formation of the acyl bridging must occur from the cleavage of THF,[22,23] which is coordinated to the metal center to form the acyl complex. To verify whether tantalaborane cleaves THF, a blank reaction was carried out under the same reaction conditions, with the exception that no **1** was added. We observed that the reaction mixture did not contain the acyl ligand, indicating that tantalaborane plays an important role in the cleavage of THF.

After pyridine had been shown to assist in enolization of the neopentyl η^2-acyl compound $Cp^*Ta(C(O)CH_2CMe_3)Cl_3$ at 22 °C,[13a] an investigation of a related system containing a similar type of acyl linkage became attractive. Thus, a number of experiments using pyridine and THF were surveyed on **2** by means of ^{1}H and ^{13}C NMR spectra. Unfortunately, in both the cases, no deinsertion and rearrangement to an enolate complex $(Cp^*Ta)_2B_4H_8$ $(OCH{=}CH_2)$ could be identified, even after several days at 80 °C.

In conclusion, thermolysis of **1** with monoborane reagents has been shown to lead to at least two possible outcomes: BH fragment growth leading to the formation of low-boron-content tantalaboranes and the Ta-η^2-acyl complex. The solid-state X-ray structure of **2** represents a new structural class of η^2-acyl complexes distinct from the common bis(cyclopentadienyl) early-transition-metal acyl complexes.

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Supporting Information Available: Experimental preparation, spectra, and an X-ray crystallographic file for **2** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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