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Reactivity of $[Cp_2Ti(CO)_2]$ and $B(C_6F_5)_3$: Formation of the Acylborane Complexes $[Cp_2Ti(CO)(\eta^2\text{-}OCB(C_6F_5)_3)]$ and $[Cp_2Ti(THF)(\eta^2\text{-}OCB(C_6F_5)_3)]$

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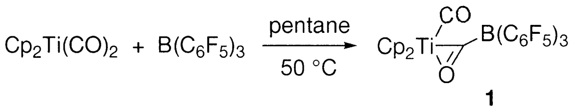
Summary: The reaction of $[Cp_2Ti(CO)_2]$ *with* $B(C_6F_5)_3$ *leads, surprisingly, as revealed by X-ray structure determination to the unexpected titana acylborane* $[Cp_2Ti(L)(\eta^2\text{-}OCB(C_6F_5)_3)]$ *(**1**, L = CO, "O-outside" configuration; **2**, L = THF, "O-inside" configuration) with the tris(perfluorophenyl)borane, as a Lewis acid, attached to the carbonyl carbon atom. The acylborane picture is strengthened by a theoretical calculation (ELF).*

The field of Lewis acid chemistry has given rise to a large organic and organometallic chemistry. From a significant amount of literature, it appears that the Lewis acid borane L = $B(C_6F_5)_3$ is especially suitable for the formation of cationic active species in Ziegler−Natta catalysts for olefin polymerization.[1] Recent works have been devoted to its Lewis acid properties toward organic substrates and organometallic complexes.[2−7]

We continue our investigations into the reactivity of L with other organometallic complexes, and another approach is its reactivity with early-transition-metal complexes containing carbonyl C≡O ligands. Several adducts of Lewis-type acids with different transition metals have been described in which the borane (or the Lewis acid) is either coordinated to the metal or interacts with the carbonyl oxygen atom.[8−11] In this report, a new aspect of this chemistry is observed between L and $Cp_2Ti(CO)_2$ where neither the formation of an adduct of L on the metal nor interaction with the oxygen atom of the carbonyl moiety occurred.

Scheme 1



Indeed, the reaction in pentane solution of $Cp_2Ti(CO)_2$ and L leads to the unexpected formation of the acylborane $[Cp_2Ti(CO)(\eta^2\text{-}OCB(C_6F_5)_3)]$ (**1**) (Scheme 1) with a rare O-outside structure (Figure 1).

The main feature of this structure is the attachment of the borane to the carbon of the carbonyl moiety. The Ti−C(1), Ti−O(1), and C(1)−O(1) bond lengths of the TiCO acyl fragment (2.187(4), 2.108(3), and 1.219(4) Å, respectively) are different from those observed in the acyl $[Cp_2TiCl(COMe)]$[12] (**A**) and the zwitterionic $[Cp_2Ti(CO\text{-}i\text{-}Pr)NCBPh_3]$[13] (**B**) complexes (**A**, 2.07(2), 2.194(14), 1.18(2) Å; **B**, 2.04(2), 2.17(1), 1.23(2) Å, respectively). There is a shortening of the Ti−O distance which could reflect a σ Ti−O bond (Ti−O distances for the Ti−μ-O(*i*-Pr)−Ti bridge are in the range of 1.96 to 2.10 Å[14]). The Ti−C(1) bond is elongated and could reflect a $C(sp^2)$ character (similar distances are observed in a Ti(II) diene complex[15]). As a consequence, the Ti−O−C angle is less acute in **1** (77.1(2)°) than in **A** and **B** (68.3(7) and 67.5(10)°, respectively). The Ti−C(2) and C(2)−O(2) bond lengths and Ti−C−O angle (2.081(5) and 1.134(5) Å, 177.3(4)°) of the Ti−CO unit are nearly similar to those of $[Cp_2Ti(CO)_2]$[16] (2.030(11) and 1.15(1) Å, 179.4°), and the C(2)−O(2) distance is similar to that observed in free CO (1.128 22(7) Å) and H_3B−CO (1.13(2) Å[17]). Atoms Ti, C(1), O(1), C(2),

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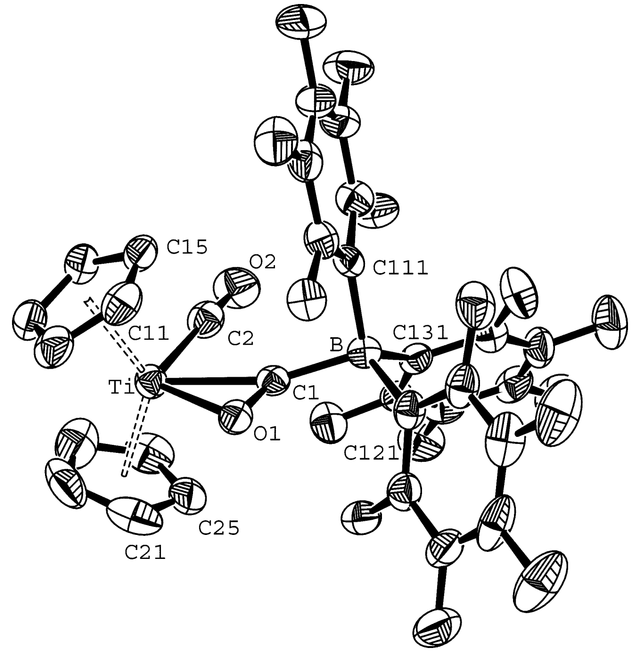
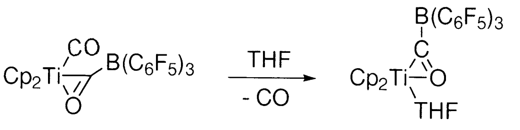


Figure 1. Molecular structure of **1.** Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ti(1)−C(2) = 2.081(5), Ti(1)−C(1) = 2.187(4), Ti(1)−O(1) = 2.108(3), C(1)−B(1) = 1.650(6), C(1)−O(1) = 1.219(4), Cp1−Ti = 2.057, Cp2−Ti = 2.051; Ti(1)−C(2)−O(2) = 177.3(4), Ti(1)−O(1)−C(1) = 77.1(2), Ti(1)−C(1)−O(1) = 70.0(2), Ti(1)−C(1)−B(1) = 161.6(3), Cp1−Ti−Cp2 = 132.99.

Scheme 2



1 **2**

and O(2) are contained in the same plane, whereas the boron atom is 0.287 Å out of the plane. This complex is insoluble in benzene and toluene, which precludes any spectroscopic NMR studies, and decomposes in CH_2Cl_2 to give Cp_2TiCl_2 as a red solid (controlled by ^1H NMR). The IR spectrum of **1** (KBr) shows two ν(CO) bands at 2072 and 1608 cm^{-1}, attributed to the terminal carbonyl CO and the acyl group, respectively. The ν(CO) band at 2072 cm^{-1} observed in **1** is higher than those observed in $Cp_2Ti(CO)_2$ (1977 and 1899 cm^{-1} in hexane), in agreement with the structural parameters of the Ti−CO moiety discussed above and consistent with a Ti(IV) species.

When a slurry of **1** in toluene is treated with THF, CO evolution occurred. The resulting yellow solution gives, after workup, crystalline $[Cp_2Ti(THF)(\eta^2\text{-}OCB(C_6F_5)_3)]$ (**2**) (Scheme 2), which was fully characterized by an X-ray structure determination (Figure 2). The structural data are nearly the same for the $[Cp_2Ti(\eta^2\text{-}OCB(C_6F_5)_3)]$ moiety as in **1**, except that **2** is a CO O-inside complex. The Ti−C(1) distance is ca. 0.06 Å shorter than the corresponding distance in **1** (the Ti−O(1)−C(1) angle is reduced to 72.30(17)°). The Ti−O(2) distance (2.266(2) Å) is 0.11 Å longer than the Ti−O distance in $[(C_5Me_5)_2TiMe(THF)]^+$, in which it was found that labile THF is easily displaced by donor molecules.[18] All atoms Ti, C(1), O(1), and B(1) are contained in the same plane, as well as the coordinated THF.

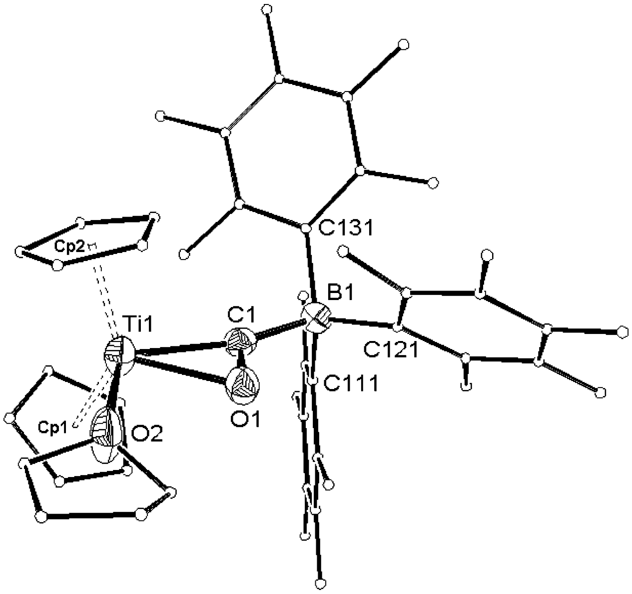


Figure 2. Molecular structure of **2**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ti(1)−C(1) = 2.129 (3), Ti(1)−O(1) = 2.109(2), Ti(1)−O(2) = 2.266(2), C(1)−B(1) = 1.672(5), C(1)−O(1) = 1.226(3), Cp1−Ti = 2.075, Cp2−Ti = 2.073; Ti(1)−C(1)−O(1) = 72.30(17), Ti(1)−O(1)−C(1) = 74.06(17), Ti(1)−C(1)−B(1) = 162.0(2), Cp1−Ti−Cp2 = 134.47.

The problem of the O-outside/O-inside configuration in early transition metals by insertion of CO into a metal−carbon bond has been extensively studied by synthetic, mechanistic, and theoretical points of view[19] and well described by Jordan and co-workers[20] on the first isolable terminal carbonyl acyl cationic complex, $[(C_5Me_5)_2Zr(CO)(\eta^2\text{-}COCH_3)]^+$. Here the solid-state transformation of the O-outside complex **1** suspended in pentane or toluene leading to the thermodynamically more stable structure, O-inside complex **2**, is in relation to the formation of a Ti−O π bonding upon CO substitution.

Compounds **1** and **2** can be viewed either as the Ti(IV) borato−acyl species $[Cp_2Ti^+(CO)\{\eta^2\text{-}C({=}O)\text{-}R\}]$ or as Ti(II) side-bound $OC{-}B(C_6F_5)_3$ analogous to $[Cp_2Ti(CO)\{\text{olefin}\}]$. To propose a coherent bonding picture, we analyzed the specroscopic (IR) and structural data, together with ELF studies, and compare them to those for the known η^2-acyl complex $[Cp_2TiCl(COMe)]$[12] (**A**) and η^1-acyl complex $[Cp_2TiCl(-C({=}O)(CH_2)_3O\text{-})]$[21] (**C**). The ELF analysis, the geometrical parameters (vide infra), and the IR data for **1** (ν(CO) 1608 cm^{-1}) and **A** (ν(CO) 1620 cm^{-1}) are therefore very similar and in agreement with η^2-acyl complexes including a dative Ti−O bond, with data very different from those of the

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η^1-acyl complex **C** (Ti−O = 3.116(4) Å, Ti−C = 2.218(3) Å, C−O = 1.211(3) Å).

One question remains unclear: why does the borane not simply attack at the more nucleophilic site, which is the O atom of the carbonyl ligand (as expected from the atomic charges (AIM or Mulliken) or the molecular electrostatic potential[22])? The attack of $B(C_6F_5)_3$ at the oxygen atom of CO has been investigated at the B3PW91/6-31G* level using BF_3 as a model. The pyramidal BF_3 moiety initially located at 1.350 Å from the oxygen atom of CO (the boron atom being aligned with the C and O atoms) is pushed away side-on at 2.461 Å from the oxygen atom of CO at the end of the geometry optimization, and a planar BF_3 moiety is recovered. This suggests that the coordination of BF_3 to the oxygen of CO would be very unfavorable. Although we have no explanation to assess this point, we could only state that the surprising electrophilic attack at the carbonyl carbon is possible in terms of frontier molecular orbital overlap, namely between the LUMO of $B(C_6F_5)_3$ and the HOMO of $Cp_2Ti(CO)_2$.

By taking these results into account, we can consider that **1** is the first example of an O-outside acylborane titanium complex and that **1** and **2** are trapped forms, via the titanocene, of the elusive carbonylborane $OCB(C_6F_5)_3$.[3a,23] With regard to this last aspect, **1** and **2** would then be regarded as models, as intermediate species, in the carbonylation reactions of organoboranes, well-known organic reactions.[24] Exploration of the reactivity of **1** and **2** toward nitrile,[25] isonitrile, and phosphine is in progress.

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Supporting Information Available: Full experimental details, theoretical studies, and crystallographic data for compounds **1** and **2**, including ORTEP diagrams and tables of crystal data and data collection parameters, atomic coordinates, anisotropic displacement parameters, and all bond lengths and bond angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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