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The first triple-decker complex with the $PtMe_3$ fragment: $CpCo(\mu\text{-}1,3\text{-}C_3B_2Me_5)PtMe_3$

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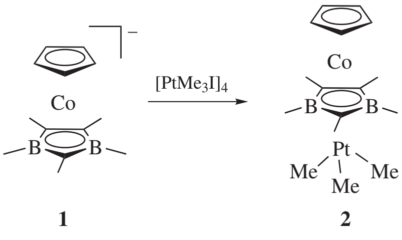
The μ-diborolyl triple-decker complex $CpCo(\mu\text{-}1,3\text{-}C_3B_2Me_5)PtMe_3$ was prepared by reaction of the sandwich anion $[CpCo(1,3\text{-}C_3B_2Me_5)]^-$ with $[PtMe_3I]_4$; according to energy decomposition analysis, attractive interactions between the $[CpCo(1,3\text{-}C_3B_2Me_5)]^-$ and $[PtMe_3]^+$ fragments are ~64% electrostatic and 36% covalent.

Only a few platinum-containing multidecker complexes are known. The triple- and tetra-decker complexes $CpM(\mu\text{-}C_3B_2MeEt_4)Pt(C_3B_2MeEt_4)$ (M = Co, Ni) and $[CpM(\mu\text{-}C_3B_2MeEt_4)]_2Pt$ (M = Fe, Ni) have been synthesized starting from $Pt(C_3B_2MeEt_4)_2$.[1] The hexa-decker complex $[Cp^*Co(\mu\text{-}C_2B_3H_2MeEt_2)Co(\mu\text{-}C_2B_3H_3Et_2)]_2Pt$ has been prepared by the reaction of the dianion $[Cp^*Co(\mu\text{-}C_2B_3H_2MeEt_2)Co(\mu\text{-}C_2B_3H_3Et_2)]^{2-}$ with $PtBr_2$.[2] The formation of the labile triple-decker cation $[Cp^*Fe(\mu\text{-}Cp)Pt(C_4Me_4)]^{2+}$ in nitromethane solution has been detected by ^1H NMR spectroscopy.[3] However, multidecker complexes with the $PtMe_3$ fragment remained unknown.

We prepared the first complex of this type, $CpCo(1,3\text{-}C_3B_2Me_5)PtMe_3$ **2**, by the reaction of sandwich anion $[CpCo(1,3\text{-}C_3B_2Me_5)]^-$ **1** with $[PtMe_3I]_4$ (Scheme 1).† μ-Diborolyl triple-decker complex **2** was isolated in 72% yield as an air-stable red-brown solid, which is highly soluble in aliphatic, aromatic and chlorinated solvents. Similar reactions of $[C_5R_5]^-$ anions with $[PtMe_3I]_4$ have been used earlier for the preparation of the (cyclopentadienyl)platinum derivatives $CpPtMe_3$[4] and Cp^*PtMe_3.[5]

The ^1H NMR spectrum of **2** exhibits one signal for the Cp protons and four signals for the Me group protons. The latter are coupled to ^{195}Pt (I = 1/2; natural abundance 33%; Pt–Me J_{PtH} 73.6 Hz; Pt–$Me_{C_3B_2}$ J_{PtH} = 12.0 Hz). These couplings are close to those for Cp^*PtMe_3 (Pt–Me J_{PtH} 79.0 Hz, Pt–Me_{Cp^*} J_{PtH} 8.0 Hz).[6] The signal of the Me(Pt) groups in **2** (0.96 ppm) is deshielded as compared to those in $CpPtMe_3$ (0.92 ppm),[4] $(C_5H_4Me)PtMe_3$ (0.83 ppm)[7] and Cp^*PtMe_3 (0.35 ppm).[6]



Scheme 1

The structure of **2** was determined by X-ray diffraction (Figure 1).‡ It crystallizes with four independent molecules in the unit cell, which differ by torsion angles between the C_5 and C_3B_2 rings [17.7(7), 19.7(7), 25.1(7) or 35.0(8)°]. The orientation of the Me(Pt) groups is similar for all independent molecules; *i.e.*, one Me(Pt) group occupies a *trans*-position to the C(6) atom, whereas two others are in a *cis*-position to B(1) or B(2).

The ring ligands are almost parallel (the C_3B_2/Cp dihedral angles 0.5–2.1°, av. 1.4°). The C_3B_2 ring is slightly folded along the B···B line (1.6–2.3°, av. 2.1°) with the C(6) atom deviated toward the Co atom. The Pt atom in **2** is less shifted with respect to the ring centroid (by 0.06 Å) than in the related cyclopentadienyl derivative $(C_5H_4Me)PtMe_3$ (by 0.30 Å); accordingly, the Pt–C(C_3B_2) bond lengths for **2** lie in a narrower range [2.296(5)–2.320(5) Å)] than for $(C_5H_4Me)PtMe_3$ [2.262(5)–2.356(5) Å].[7] Similarly, the Pt–C(Me) bond lengths for **2** are more equalized [2.043(6)–2.061(7) Å] than for $(C_5H_4Me)PtMe_3$ (1.990–2.141 Å).

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† A solution of $CpCo(1,3\text{-}C_3B_2Me_5H)$ (190 mg, 0.74 mmol) in THF (5 ml) was stirred with 0.2 ml of $Na/K_{3.0}$ alloy for 1 h. The resulting green solution was taken off with a syringe and added to a freezed (–196 °C) suspension of $[PtMe_3I]_4$ (202 mg, 0.18 mmol) in THF (10 ml). The mixture was stirred for 1 h at –78 °C and for 2 h at –30 °C, then warmed to room temperature and stirred overnight. The solvent was removed *in vacuo*. Chromatography of the residue with hexane on an alumina column (2 × 15 cm) afforded a brown band. Evaporation of the solvent gave red-brown complex **2**. Yield, 264 mg (72%). ^1H NMR ($CDCl_3$) δ: 4.03 (s, 5H, Cp), 1.88 (s, 6H, 4,5-Me, ^{195}Pt–$Me_{C_3B_2}$ J_{PtH} 12.0 Hz), 1.74 (s, 3H, 2-Me, ^{195}Pt–$Me_{C_3B_2}$ J_{PtH} 12.0 Hz), 1.09 (s, 6H, 1,3-Me), 0.96 (s, 9H, Pt–Me J_{PtH} 73.6 Hz). $^{11}B\{^1H\}$ NMR ($CDCl_3$) δ: 15.55 (s). Found (%): C, 39.11; H, 6.25; B, 4.20. Calc. for $C_{16}H_{29}B_2CoPt$ (%): C, 38.66; H, 5.88; B, 4.35.

‡ Crystals of complex **2** were grown up by the slow evaporation of hexane solution.

Crystal data for **2**: $C_{16}H_{29}B_2CoPt$, monoclinic, space group $P2_1/c$, a = 15.752(1), b = 28.646(2) and c = 16.187(1) Å, β = 100.992(4), V = 7170.6(11) Å^3, Z = 16, d_{calc} = 1.842 g cm^{-3}, μ = 8.708 mm^{-1}, crystal size 0.22 × 0.17 × 0.11 mm, $F(000)$ = 3840, T_{min}/T_{max} = 0.4476/0.2503, R_1 = 0.0271 [from 14135 unique reflections with $I > 2\sigma(I)$] and wR_2 = 0.0572 (from all 17307 unique reflections), GOF = 1.003. X-ray diffraction experiment was carried out with a Bruker SMART APEX2 CCD area detector at 100 K, using graphite monochromated MoKα radiation (λ = 0.71073 Å). The absorption correction was applied semi-empirically using the SADABS program. The structure was solved by a direct method and refined by the full-matrix least-squares technique against F^2 in anisotropic approximation for non-hydrogen atoms. All hydrogen atom positions were refined in isotropic approximation in riding model with the U_{iso}(H) parameters equal to 1.2 $U_{eq}(C_i)$, for methyl groups equal to 1.5 $U_{eq}(C_{ii})$, where $U(C_i)$ and $U(C_{ii})$ are respectively the equivalent thermal parameters of the carbon atoms to which the corresponding H atoms are bonded.

CCDC 822964 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2012.

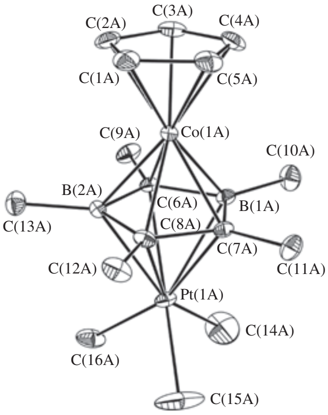

Figure 1 Structure of the independent molecule A of complex **2**. Selected bond lengths (Å): Co(1A)–C(1A) 2.051(5), Co(1A)–C(2A) 2.038(5), Co(1A)–C(3A) 2.034(5), Co(1A)–C(4A) 2.049(5), Co(1A)–C(5A) 2.057(5), Co(1A)–C(6A) 2.034(5), Co(1A)–C(7A) 2.028(5), Co(1A)–C(8A) 2.043(5), Co(1A)–B(1A) 2.095(5), Co(1A)–B(2A) 2.061(5), Pt(1A)–C(6A) 2.296(5), Pt(1A)– C(7A) 2.320(5), Pt(1A)–C(8A) 2.307(5), Pt(1A)–C(14A) 2.061(7), Pt(1A)–C(15A) 2.043(6), Pt(1A)–C(16A) 2.054(6), Pt(1A)–B(1A) 2.311(6), Pt(1A)–B(2A) 2.301(5). Ellipsoids are shown at the 50% level. Hydrogen atoms are omitted for clarity.

We have shown earlier that the sandwich anions [CpCo(1,3-$C_3B_2R_5$)]$^-$ (R = H, Me) are similar to the cyclopentadienide anions [C_5R_5]$^-$ in bonding properties toward transition metals,[8] making μ-diborolyl triple-decker complexes CpCo(1,3-$C_3B_2R_5$)-ML_n analogous to mononuclear compounds (C_5R_5)ML_n. To compare metal–ligand bonding in complex **2** with that in Cp*$PtMe_3$, we carried out the energy decomposition analysis (EDA)[9,§] in terms of interactions of the cation [$PtMe_3$]$^+$ with anions **1** and [Cp*]$^-$ (Table 1).[¶] For the anion [Cp*]$^-$, the attractive interactions are ~61% electrostatic and 39% covalent. In the case of anion **1**, the electrostatic attraction ΔE_{elstat} is stronger (by 11 kcal mol^{-1}), while the attractive orbital interaction ΔE_{orb} is weaker (by 8 kcal mol^{-1}) resulting in an increase of the electrostatic contribution (64%). The Pauli repulsion ΔE_{Pauli} is much stronger (by 20 kcal mol^{-1}), making the bonding of anion **1** much weaker (by 17 kcal mol^{-1}), as compared to [Cp*]$^-$.

Table 1 Results of EDA (energy values in kcal mol^{-1}) for (L)$PtMe_3$ and (L)RuCp complexes using L$^-$ and [$PtMe_3$]$^+$/[RuCp]$^+$ as interacting fragments at BP86/TZ2P.

L	(L)$PtMe_3$		(L)RuCp	
	1	Cp*	**1**	Cp*
ΔE_{int}	–173.05	–190.35	–206.92	–236.93
ΔE_{Pauli}	261.58	241.23	256.35	245.88
ΔE_{elstat}[a]	–276.26 (63.56%)	–265.32 (61.48%)	–275.37 (59.44%)	–272.80 (56.50%)
ΔE_{orb}[a]	–158.37 (36.44%)	–166.27 (38.52%)	–187.90 (40.56%)	–210.02 (43.50%)

[a] The values in parentheses give the percentage contribution to the total attractive interactions.

Interestingly, the bonding of the [$PtMe_3$]$^+$ fragment with anions **1** and [Cp*]$^-$ is much weaker, as compared to [RuCp]$^+$ (by 34 and 47 kcal mol^{-1}, respectively[8]), which is mainly caused by a decrease of the attractive orbital interactions for the Pt-containing fragment (by 30 and 44 kcal mol^{-1}). It is explained by poorer matching of the frontier orbitals of the [$PtMe_3$]$^+$ fragment with those of anions **1** and [Cp*]$^-$. The electrostatic attraction changes to a lesser extent, making the bonding of [$PtMe_3$]$^+$ with the anionic ligands considerably more ionic, as compared to [RuCp]$^+$.

As a result of this work, the first triple-decker complex with the $PtMe_3$ moiety, CpCo(μ-1,3-$C_3B_2Me_5$)$PtMe_3$, was synthesized. The EDA data suggest that the Pt–diborolyl bond is much weaker and considerably more ionic than Ru–diborolyl in the related complex CpCo(μ-1,3-$C_3B_2Me_5$)RuCp.

Online Supplementary Materials

Supplementary data associated with this article [atomic coordinates for optimized geometry and energy data for complexes **2**, CpCo(μ-1,3-$C_3B_2Me_5$)RuCp, Cp*$PtMe_3$ and Cp*RuCp] can be found in the online version at doi: 10.1016/j.mencom.2012.01.004.

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[§] According to the EDA method, the interaction energy between the bonding fragments ΔE_{int} can be divided into three main components:

$$\Delta E_{\text{int}} = \Delta E_{\text{elstat}} + \Delta E_{\text{Pauli}} + \Delta E_{\text{orb}}.$$

ΔE_{elstat} is the electrostatic interaction energy between the fragments with a frozen electron density distribution, ΔE_{Pauli} presents the repulsive four-electron interactions between occupied orbitals (Pauli repulsion), and ΔE_{orb} – the stabilizing orbital interactions. The ratio $\Delta E_{\text{elstat}}/\Delta E_{\text{orb}}$ indicates the electrostatic/covalent character of the bond.

[¶] Geometry optimizations were performed without constraints using the PBE exchange-correlation functional,[10] the scalar-relativistic Hamiltonian,[11] atomic basis sets of generally-contracted Gaussian functions[12] and a density-fitting technique,[13] as implemented in a recent version of the Priroda code.[14] The all-electron triple-ζ basis set L2 augmented by two polarization functions was used.[15] The optimized geometry of complex **2** is in a good agreement with X-ray diffraction data (deviations from average values for four independent molecules: Co···C_3B_2 0.003, Pt···C_3B_2 0.028 Å), confirming the reliability of the computational results.

The bonding interactions were studied by the Morokuma–Ziegler energy decomposition analysis as implemented in the ADF 2006.01 program package.[16] The calculations were performed using the exchange functional of Becke[17] and the correlation functional of Perdew[18] (BP86). Scalar relativistic effects were considered using the zero-order regular approximation (ZORA).[19] All-electron ZORA relativistic triple-ζ basis set augmented by two polarization functions TZ2P was used.