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(Methoxyborole)cobalt Complexes – Synthesis, Structures and Bonding

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Heating (η-C_4H_4BCy)$Co(CO)_2I$ (Cy = cyclohexyl) in benzene in the presence of $AlCl_3$ and subsequent methanolysis affords the cationic benzene complex [(η-C_4H_4BOMe)Co(η-C_6H_6)]$^+$ (**1**). Under visible-light irradiation, **1** reacts with MeCN and *t*BuNC to give the tris(ligand) complexes [(η-C_4H_4BOMe)$Co(L)_3$]$^+$ [L = MeCN (**2**), *t*BuNC (**4**)]. A similar reaction with $P(OMe)_3$ in MeCN affords [(η-C_4H_4BOMe)-$Co(MeCN)\{P(OMe)_3\}_2$]$^+$ (**5**). Cation **2** reacts with BPh_4^- in CH_2Cl_2 to give the zwitterionic arene complex (η-C_4H_4BOMe)Co(η-$C_6H_5BPh_3$) (**3**). Reactions of **2** with TlCp and Tl(η-9-SMe_2-7,8-$C_2B_9H_{10}$) afford the sandwich compounds (η-C_4H_4BOMe)CoCp (**6**) and (η-C_4H_4BOMe)Co(η-9-SMe_2-7,8-$C_2B_9H_{10}$) (**7**). The structures of **3** and **7** were determined by X-ray diffraction. The bonding in the borole complexes [(C_4H_4BR)$Co(C_6H_6)$]$^+$ and (C_4H_4BR)CoCp (R = H, OMe) was compared with that in the cyclobutadiene analogues [(C_4R_4)$Co(C_6H_6)$]$^+$ and (C_4R_4)CoCp (R = H, Me) using energy decomposition analysis.

Introduction

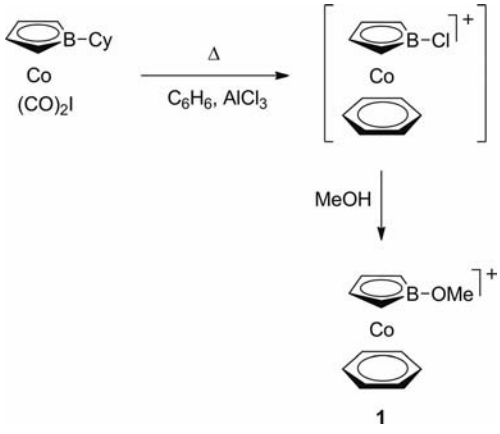
The benzene complexes [(ring)M(η-C_6H_6)]$^+$ [(ring)M = CpFe, (η-C_4Me_4)Co, (η^5-cyclohexadienyl)Fe] are known to be useful synthons for cationic [(ring)M]$^+$ fragments.[1,2,3] In particular, visible-light irradiation of these complexes causes the replacement of benzene by MeCN and arenes to give [(ring)M$(MeCN)_3$]$^+$ and [(ring)M(arene)]$^+$.[4,5,6] The (borole)cobalt fragments [(η-C_4H_4BR)Co]$^+$ are isolobal with [CpFe]$^+$, [(η-C_4Me_4)Co]$^+$ and [(η^5-cyclohexadienyl)-Fe]$^+$, which suggests the photochemical lability of [(η-C_4H_4BR)$Co(C_6H_6)$]$^+$.

We have recently synthesized the *B*-oxyborole complex [(η-C_4H_4BOH)Co(η-C_6H_6)]$^+$ by heating (η-C_4H_4BCy)-$Co(CO)_2I$ (Cy = cyclohexyl) in benzene in the presence of $AlCl_3$ with subsequent hydrolysis.[7] Herein we report the synthesis of the methoxy derivative [(η-C_4H_4BOMe)Co(η-C_6H_6)]$^+$ (**1**) and demonstrate its usefulness as a synthon of the [(η-C_4H_4BOMe)Co]$^+$ fragment.[8] The structural and bonding features of the complexes prepared are also described.

Results and Discussion

Synthesis and Reactivity

We found that heating (η-C_4H_4BCy)$Co(CO)_2I$ in benzene in the presence of $AlCl_3$ with subsequent methanolysis gave **1** (Scheme 1; all the cationic complexes described here were isolated as salts with the BPh_4^- anion). The benzene coordination was apparently accompanied by Cy/Cl exchange with the formation of the chlorine derivative [(η-C_4H_4BCl)$Co(C_6H_6)$]$^+$, which reacted further with MeOH to give **1**. A similar exchange of substituents at the boron atom in neutral borole and boratabenzene complexes has been described by Herberich et al.[9] Salt **1**BPh_4 is air stable in the solid state, whereas in solution it was readily hydrolyzed by traces of water to give the hydroxy derivative [(η-C_4H_4BOH)Co(η-C_6H_6)]$^+$.



Scheme 1. Synthesis of **1**.

Similar to the cyclobutadiene analogue [(η-C_4Me_4)Co(η-C_6H_6)]$^+$, complex **1** underwent benzene replacement by acetonitrile under visible-light irradiation to give the tris-(acetonitrile) derivative [(η-C_4H_4BOMe)$Co(MeCN)_3$]$^+$ (**2**, Scheme 2). Salt **2**BPh_4 is stable in the solid state and in acetonitrile solution at room temperature. However, in

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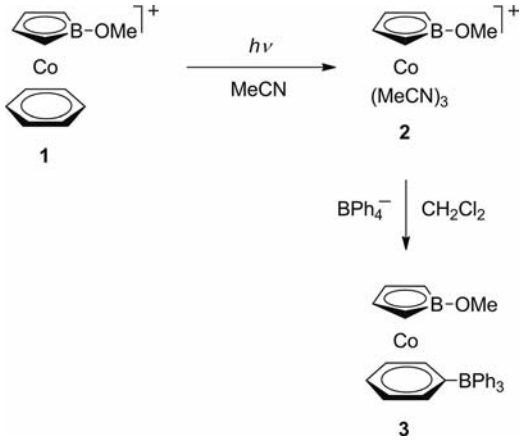
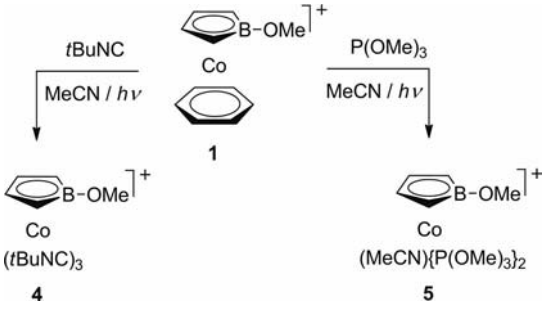
CH_2Cl_2, **2** reacted with BPh_4^- to give the zwitterionic arene complex (η-C_4H_4BOMe)Co(η-$C_6H_5BPh_3$) (**3**). Numerous related complexes with the η^6-coordinated tetraphenylborate anion have been described previously.[10]



Scheme 2. Synthesis of **3**.

The photochemical reaction of **1** with *t*BuNC in acetonitrile resulted in the tris(isocyanide) complex [(η-C_4H_4BOMe)Co(*t*BuNC)$_3$]$^+$ (**4**, Scheme 3). A similar reaction with $P(OMe)_3$ led to [(η-C_4H_4BOMe)Co(MeCN){$P(OMe)_3$}$_2$]$^+$ (**5**), which contains only two phosphite ligands, apparently owing to steric hinderance.

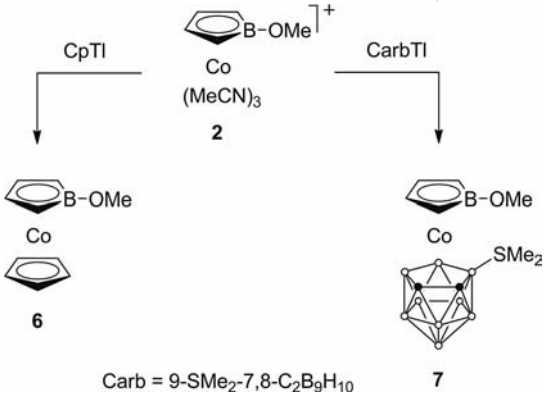


Scheme 3. Reactions of **1** with *t*BuNC and $P(OMe)_3$.

Complex **2** reacted with TlCp and Tl(η-9-SMe_2-7,8-$C_2B_9H_{10}$) to give the sandwich compounds (η-C_4H_4BOMe)CoCp (**6**) and (η-C_4H_4BOMe)Co(η-9-SMe_2-7,8-$C_2B_9H_{10}$) (**7**, Scheme 4). The use of much more reactive sodium salts instead of the thallium derivatives did not lead to the formation of **6** and **7**, presumably owing to the nucleophilic attack at the borole ring.

NMR Spectroscopy

In the ^{1}H NMR spectra of **1**–**7**, the signals of the borole ring protons are observed as two multiplets (α- and β-C_4H_4B) where the signals of the α protons are shifted further upfield than those of the β protons by 1.5–3.3 ppm. There are four different borole ring proton signals for **7**, which can be explained by its C_1 symmetry.[8d,11] It is interesting that the borole and benzene proton signals for **1** are very close to those for the hydroxy derivative [(η-C_4H_4BOH)Co(η-C_6H_6)]$^+$.[7a] The cyclopentadienyl proton signals for **6** and the cage CH protons for **7** are shifted downfield by 0.4–1.2 ppm from the corresponding signals for the related cyclobutadiene complexes (η-C_4Me_4)CoCp[12] and (η-C_4Me_4)Co(η-9-SMe_2-7,8-$C_2B_9H_{10}$),[13] which is in accordance with the weaker donor ability of C_4H_4BOMe vs. C_4Me_4 (vide infra).



Scheme 4. Reactions of **2** with anionic ligands.

In the ^{11}B NMR spectra of **1**–**7**, the signals of the boron atoms of the borole ligand are observed as broad singlets between 25.1 and 30.5 ppm.

X-Ray Diffraction Study

The structures of **3** and **7** are shown in Figures 1 and 2, respectively. The crystallographic cell of **7** contains two independent molecules. The borole rings in **3** and **7** are folded along the C(1)–C(4) line (9.0 and 6.7/8.9°, respectively) with the boron atom deviated away from the cobalt atom. This folding is typical for borole complexes,[14] which may be explained by the larger covalent radius of boron

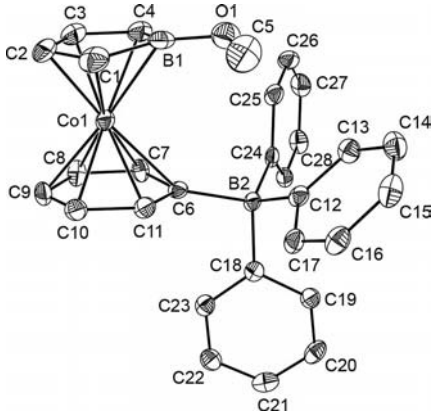


Figure 1. Structure of **3**. Atoms are represented by 50% thermal ellipsoids. Hydrogen atoms are not depicted for clarity. Selected bond lengths [Å] and angles [°]: Co1–C1 2.062(3), Co1–C2 2.010(3), Co1–C3 2.022(3), Co1–C4 2.072(3), Co1–B1 2.245(4), Co1–C6 2.207(3), Co1–C7 2.078(3), Co1–C8 2.081(3), Co1–C9 2.103(3), Co1–C10 2.070(3), Co1–C11 2.102(3), C1–C2 1.412(5), C2–C3 1.431(4), C3–C4 1.417(4), C1–B1 1.553(5), C4–B1 1.542(5), B1–O1 1.370(4), C1–C2–C3 110.7(3), C2–C3–C4 109.5(3), B1–C1–C2 108.2(3), C1–B1–C4 101.8(3), B1–C4–C3 109.0(3).

than carbon,[15] and is increased by B–N or B–O conjugation.[7b,16] The presence of B–O conjugation is confirmed by a small deviation of the methyl carbon atom from the BC(1)C(4) plane (0.231 Å for **3** and 0.159/0.224 Å for **7**).

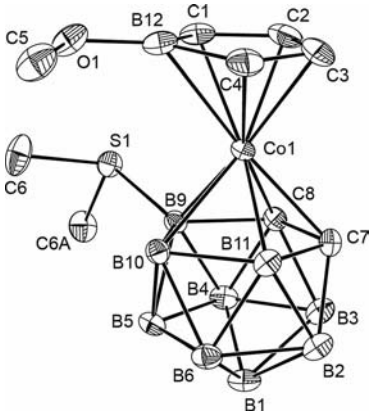


Figure 2. Structure of **7**. Atoms are represented by 50% thermal ellipsoids. Hydrogen atoms are not depicted for clarity. Selected bond lengths [Å] and angles [°]: Co1–C1 2.086(2)/2.081(2), Co1–C2 2.026(2)/2.013(2), Co1–C3 2.021(2)/2.006(2), Co1–C4 2.080(2)/2.073(2), Co1–B12 2.232(2)/2.255(2), Co1–C7 2.042(2)/2.026(2), Co1–C8 2.027(2)/2.021(2), Co1–B9 2.050(2)/2.052(2), Co1–B10 2.116(2)/2.113(2), Co1–B11 2.066(2)/2.059(2), C1–C2 1.418(3)/1.419(2), C2–C3 1.431(3)/1.420(3), C3–C4 1.421(3)/1.425(2), C1–B12 1.542(2)/1.544(2), C4–B12 1.540(3)/1.535(2), B12–O1 1.386(2)/1.383(2), C7–C8 1.606(2)/1.613(2), C7–B11 1.711(2)/1.708(3), C8–B9 1.699(2)/1.708(2), B9–B10 1.782(2)/1.780(2), B10–B11 1.803(2)/1.806(3), B9–S1 1.911(2)/1.900(2), C1–C2–C3 110.0(2)/110.3(2), C2–C3–C4 110.1(2)/110.1(2), C3–C4–B12 108.5(2)/108.2(2), C2–C1–B12 108.6(2)/108.0(2), C1–B12–C4 102.5(2)/102.6(1), C7–C8–B9 110.4(1)/110.3(1), C8–B9–B10 107.8(1)/107.6(1), B9–B10–B11 104.0(1)/104.4(1), B10–B11–C7 106.2(1)/106.1(1), B11–C7–C8 111.5(1)/111.6(1).

The coordinated five- and six-membered rings in **3** are almost parallel with a dihedral angle of 4.6°. The Co···C_6 distance in **3** (1.565 Å) is very close to that in [(η-C_4Me_4)-Co(C_6H_6)]$^+$ (1.561 Å).[2b] The position of the substituents on the rings is close to eclipsed. The methyl group is situated near the C(12)C(13)C(14)C(15)C(16)C(17) phenyl ring; the shortest distance between the closest methyl hydrogen atom and the Ph mean plane is 2.97 Å, which suggests that the eclipsed conformation is stabilized by weak C–H···π intramolecular interactions.

The C_4B and C_2B_3 rings in **7** are staggered in one independent molecule and eclipsed in the other. The angle between the rings is equal to 5.2/3.1° and the Co···C_4B and Co···C_2B_3 distances are 1.670/1.666 and 1.451/1.440 Å. The latter is close to the corresponding distance in the related cyclobutadiene complex (η-C_4Me_4)Co(η-9-SMe_2-7,8-$C_2B_9H_{10}$) (1.457 Å).[13] In both independent molecules, the OMe and SMe_2 groups are situated very close to each other, which results in the formation of weak intramolecular C(6)–H···O(1) contact [*d*(C–O) = 3.29/3.25 Å, ∠(C–H–O) = 170/160°].

Energy Decomposition Analysis

The bonding in the borole complexes was compared with that in the cyclobutadiene analogues by energy decomposition analysis (EDA).[17] According to the EDA method, the interaction energy between the bonding fragments (ΔE_{int}) can be divided into three main components, see Equation (1).

$$\Delta E_{int} = \Delta E_{elstat} + \Delta E_{Pauli} + \Delta E_{orb} \quad (1)$$

where 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} refers to the stabilizing orbital interactions. The ratio ΔE_{elstat}/ΔE_{orb} indicates the electrostatic/covalent character of the bond. The bond dissociation energy (D_e) is the negative value of the sum of two components, see Equation (2).

$$D_e = -(\Delta E_{int} + \Delta E_{prep}) \quad (2)$$

where ΔE_{prep} (the fragment preparation energy) is the energy necessary to promote the fragments from their equilibrium geometry and electronic ground state to the geometry and electronic state that they have in the optimized structure. This method has already proven its usefulness for the analysis of the nature of the metal–ligand bonding in ferrocene and other sandwich compounds.[3e,18]

The EDA data for the cationic benzene complexes [(L)Co(C_6H_6)]$^+$ (L = C_4H_4BH, C_4H_4BOMe, C_4H_4 and C_4Me_4) in terms of [Co(L)]$^+$ + C_6H_6 or [Co(C_6H_6)]$^{3+}$ + [L]$^{2-}$ are given in Table 1.

We begin with the analysis of the interaction between the [Co(L)]$^+$ and C_6H_6 fragments. In the parent borole complex, [(C_4H_4BH)Co(C_6H_6)]$^+$, all the contributions (ΔE_{Pauli}, ΔE_{elstat} and ΔE_{orb}) are higher (absolute magnitude) than those of the cyclobutadiene analogue [(C_4H_4)Co(C_6H_6)]$^+$. However, the attractive contributions (ΔE_{elstat} and ΔE_{orb}) increase by a greater extent than ΔE_{Pauli}, which results in the increased strength of the Co–C_6H_6 bond by 3 kcal mol^{-1}.

The introduction of donor substituents (MeO or Me) in the borole and cyclobutadiene rings leads to a slight increase of ΔE_{elstat}, which is, however, overruled by the destabilizing effect caused by the decrease of ΔE_{orb} and increase of ΔE_{Pauli}. As a result, for the substituted complexes **1** and [(C_4Me_4)Co(C_6H_6)]$^+$, the Co–C_6H_6 bond is weaker by 7–11 kcal mol^{-1} than for the parent analogues. Notably, this bond in **1** is stronger by 7 kcal mol^{-1} than in [(C_4Me_4)-Co(C_6H_6)]$^+$. The same differences are observed for D_e as ΔE_{prep} are similar in all cases (ca. 3 kcal mol^{-1}). The ΔE_{int} and D_e values correlate well with the Co···C_6H_6 distances.

The strengthening of the Co–C_6H_6 bond for the borole complexes compared to the cyclobutadiene analogues is in accordance with weaker bonding of the borole ligand vs. cyclobutadiene. Comparison of the parent complexes indicates that the weaker Co–C_4H_4BH bonding (by 77 kcal mol^{-1}) results from the decrease of both ΔE_{elstat} and ΔE_{orb}, whereas ΔE_{Pauli} remains almost unchanged. Interestingly, the D_e value for the Co–C_4H_4BH bond is weaker by only 9 kcal mol^{-1} compared to that of Co–C_4H_4, which is caused by a large ΔE_{prep} value for the cyclobutadiene complex. This is explained by the considerably different geome-

Table 1. Results of EDA [energy values in kcal mol^{-1}] for $[(L)Co(C_6H_6)]^+$ with $[Co(L)]^+ + C_6H_6$ or $[Co(C_6H_6)]^{3+} + [L]^{2-}$ as interacting fragments at BP86/TZ2P//PBE/L2.

	$[Co(L)]^+ + C_6H_6$				$[Co(C_6H_6)]^{3+} + [L]^{2-}$			
Complex	C_4H_4BH	C_4H_4BOMe	C_4H_4	C_4Me_4	C_4H_4BH	C_4H_4BOMe	C_4H_4	C_4Me_4
ΔE_{int}	–93.6	–86.0	–90.8	–79.2	–958.6	–972.6	–1036.0	–1067.6
ΔE_{Pauli}	163.1	168.0	151.1	160.4	198.6	181.9	200.9	225.4
ΔE_{elstat}[a]	–106.8 (41.6%)	–109.1 (43.0%)	–100.7 (41.6%)	–105.2 (43.9%)	–710.5 (61.4%)	–645.9 (55.9%)	–754.3 (61.0%)	–591.8 (45.8%)
ΔE_{orb}[a]	–149.9 (58.4%)	–144.9 (57.1%)	–141.1 (58.4%)	–134.5 (56.1%)	–446.7 (38.6%)	–508.6 (44.1%)	–482.6 (39.0%)	–701.3 (54.2%)
ΔE_{prep}	3.7	3. 9	3.0	3.2	5.9	12.4	74.1	56.9
D_e	89.9	82.1	87.8	76.0	952.8	960.2	961.9	1010.8
Co···C_6H_6 [Å]	1.552[b]	1.559[b]	1.553[b]	1.561[b], 1.561[c]				

[a] The values in parentheses give the percentage contribution to the total attractive interactions. [b] Calculated. [c] From XRD.

Table 2. Results of EDA [energy values in kcal mol^{-1}] for (L)CoCp with $[Co(L)]^+ + Cp^-$ or $[CoCp]^{2+} + [L]^{2-}$ as interacting fragments at BP86/TZ2P//PBE/L2.

	$[Co(L)]^+ + Cp^-$				$[CoCp]^{2+} + [L]^{2-}$			
Complex	C_4H_4BH	C_4H_4BOMe	C_4H_4	C_4Me_4	C_4H_4BH	C_4H_4BOMe	C_4H_4	C_4Me_4
ΔE_{int}	–243.8	–231.7	–228.1	–204.2	–657.2	–660.0	–722.5	–709.2
ΔE_{Pauli}	187.5	190.3	168.8	171.4	201.2	194.7	211.4	209.5
ΔE_{elstat}[a]	–252.1 (58.5%)	–248.0 (58.8%)	–238.2 (60.0%)	–227.1 (60.5%)	–543.3 (63.3%)	–527.0 (61.7%)	–583.1 (62.4%)	–477.3 (52.0%)
ΔE_{orb}[a]	–179.2 (41.5%)	–174.0 (41.2%)	–158.7 (40.0%)	–148.4 (39.5%)	–315.1 (36.7%)	–327.7 (38.3%)	–350.7 (37.6%)	–441.4 (48.1%)
ΔE_{prep}	2.2	4.3	1.4	1.7	2.5	4.1	15.1	20.0
D_e	–241.6	–227.4	–226.8	–202.5	–654.7	–655.9	–707.4	–689.2
Co···Cp [Å]	1.636[b]	1.642[b]	1.645[b]	1.659[b]				

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

try of the $[C_4H_4]^{2-}$ anion in the equilibrium ground state and in the optimized structure of $[(C_4H_4)Co(C_6H_6)]^+$ (Figure 3).

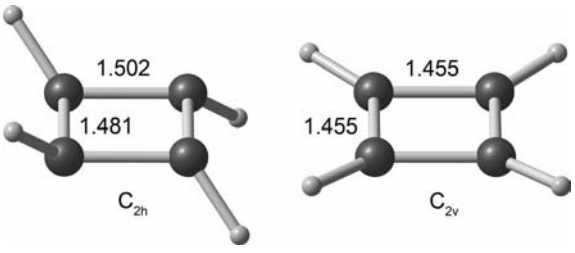


Figure 3. Geometries and bond lengths [Å] for the $[C_4H_4]^{2-}$ anion in the equilibrium ground state (left) and in the optimized structure of $[(C_4H_4)Co(C_6H_6)]^+$ (right).

Table 2 summarizes the EDA data for the cyclopentadienyl complexes (L)CoCp (L = C_4H_4BH, C_4H_4BOMe, C_4H_4 and C_4Me_4) in terms of $[Co(L)]^+ + Cp^-$ or $[CoCp]^{2+} + [L]^{2-}$.

The Co–Cp bond is stronger for the borole complexes compared to the cyclobutadiene analogues, which is similar to the Co–C_6H_6 bond in $[(L)Co(C_6H_6)]^+$. Interestingly, strengthening (by 15 kcal mol^{-1} for the parent compounds) is considerably higher than for the Co–C_6H_6 bond (by 3 kcal mol^{-1}) due to the greater increase of the attractive contributions. For substituted **6** and $(C_4Me_4)CoCp$, the Co–Cp bond is weaker by 12–24 kcal mol^{-1} than for the parent analogues. In this case the ΔE_{int} and D_e values also correlate with the Co···Cp distances. Similar to the benzene complexes, the Co–C_4H_4BH bond is weaker than Co–C_4H_4, which explains the stronger Co–Cp bond in the borole complexes.

Finally, energy partitioning suggests that the attractive interactions between the $[Co(L)]^+$ and C_6H_6 fragments are ca. 57% covalent and 43% electrostatic. The bonding of the same cations with the Cp^- anion is predominatly electostatic (58–60%) and slightly less electrostatic for the borole complexes.

Electrostatic Potentials at the Nuclei

The electrostatic potentials at the metal and carbon nuclei (E_{nuclei}) have been shown to be useful criteria for the estimation of donor–acceptor properties of ligands in metal complexes.[3e,18h] As expected, the E_{Co} and $E_{C(ring)}$ (ring = C_6H_6 or Cp) values for the tetramethylcyclobutadiene complexes $[(C_4Me_4)Co(C_6H_6)]^+$ and $(C_4Me_4)CoCp$ are higher (absolute magnitude) than those for the parent analogues, which is in accordance with the strong donor effect of the methyl groups (Table 3). Similarly, the methoxy-substituted borole ligand C_4H_4BOMe is a stronger donor than C_4H_4BH. Finally, the corresponding electrostatic potentials for the borole complexes are lower than those for the cyclobutadiene derivatives, which indicates the weaker donor

ability of borole ligands C_4H_4BR (R = H, OMe) compared with cyclobutadienes C_4R_4 in accordance with the π-acceptor character of the boron atom.

Table 3. Electrostatic potentials at the nuclei [a.u.] for $[(L)Co(C_6H_6)]^+$ and (L)CoCp.[a]

Complex	E_{Co}	$E_{C(C_6H_6)}$ av.	$E_{C(Cp)}$ av.
$[(C_4H_4BH)Co(C_6H_6)]^+$	–121.8936	–14.5684	
	–123.9592	*–14.5858*	
1	–121.9106	–14.5802	
	–123.9769	*–14.5983*	
$[(C_4H_4)Co(C_6H_6)]^+$	–121.9108	–14.5809	
	–123.9767	*–14.5982*	
$[(C_4Me_4)Co(C_6H_6)]^+$	–121.9427	–14.6031	
	–124.0118	*–14.6234*	
$(C_4H_4BH)CoCp$	–122.0840		–14.7499
	–124.1507		*–14.7689*
6	–122.0919		–14.7554
	–124.1603		*–14.7748*
$(C_4H_4)CoCp$	–122.1081		–14.7684
	–124.1762		*–14.7874*
$(C_4Me_4)CoCp$	–122.1221		–14.7790
	–124.1906		*–14.8007*

[a] Values at BP86/def2-TZVPP//BP86/TZ2P are shown in normal type and those at BP86/TZ2P in italics.

Notably for methoxy-substituted **1** and **6**, the folding angles of the borole ring (13.4 and 8.0°, respectively) are greater than those of the parent analogues (5.0 and 2.9°). The molecular orbitals of complexes **1** (HOMO-5) and **6** (HOMO-6), shown in Figure 4, clearly demonstrate that it is caused by B–O conjugation (vide supra).

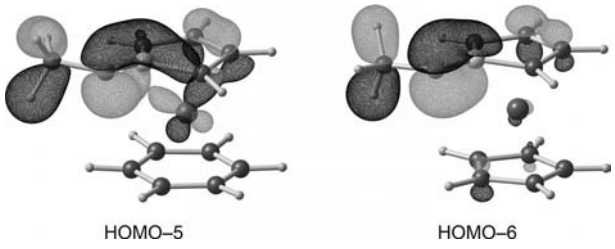


Figure 4. Molecular orbitals of **1** (left) and **6** (right) responsible for B–O conjugation. MO isodensity surface 0.05.

Conclusions

The benzene and acetonitrile complexes $[(\eta\text{-}C_4H_4BOMe)CoL]^+$ [L = C_6H_6 (**1**), 3MeCN (**2**)], which were easily accessed from $[(\eta\text{-}C_4H_4BCy)Co(CO)_2]_2$, were shown to be useful synthons of the (methoxyborole)cobalt fragment $[(\eta\text{-}C_4H_4BOMe)Co]^+$. In particular, photochemical reactions of **1** with 2-electron ligands gave tris(ligand) complexes. The interaction of **2** with cyclopentadienyl and carborane anions afforded sandwich complexes. An X-ray diffraction study and DFT calculations suggest strong B–O conjugation in the methoxy-substituted borole complexes.

According to EDA, the attractive interactions between the $[(\eta\text{-}C_4H_4BOMe)Co]^+$ and C_6H_6 fragments are ca. 57% covalent and 43% electrostatic. The bonding of the same cation with the Cp^- anion is much more electostatic (59%).

Comparison of the electrostatic potentials at Co and C(ring) (ring: C_6H_6 or Cp) nuclei indicate a weaker donor effect of the borole ligands C_4H_4BR (R = H, OMe) than that of cyclobutadienes C_4R_4 (R = H, Me), which is in accordance with the π-acceptor character of the boron atom.

Experimental Section

General: The reactions were carried out under an inert atmosphere in dry solvents. The isolation of products was conducted in air. $[(\eta\text{-}C_4H_4BCy)Co(CO)_2]_2$[19] and $Tl[9\text{-}SMe_2\text{-}7,8\text{-}C_2B_9H_{10}]$[20] were prepared as described in the literature. Irradiation was conducted in a Schlenk tube using a high-pressure mercury vapor lamp with a phosphor-coated bulb (400 W). Both the tube and the lamp were placed into a vessel of appropriate volume covered with aluminum foil, and cooling was accomplished with running water. ^1H, $^{11}B\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra (δ in ppm) were recorded with a Bruker Avance-400 spectrometer operating at 400.13, 128.38 and 161.98 MHz, respectively.

$[(\eta\text{-}C_4H_4BOMe)Co(\eta\text{-}C_6H_6)]BPh_4$ (1BPh$_4$): A solution of I_2 (127 mg, 0.5 mmol) in CH_2Cl_2 (10 mL) was slowly added to a stirring solution of $[(\eta\text{-}C_4H_4BCy)Co(CO)_2]_2$ (261 mg, 0.5 mmol) in CH_2Cl_2 (5 mL) at –60 °C. The reaction mixture was warmed to room temperature, the solvent was removed in vacuo, and the residue was extracted into light petroleum. Solvent evaporation gave $(\eta\text{-}C_4H_4BCy)Co(CO)_2I$ as a black oil, which was dissolved in benzene (10 mL) and $AlCl_3$ (1 g) was added. The reaction mixture was stirred for 12 h at room temperature and for 3 h under reflux. After cooling with ice, MeOH (10 mL) was added. The solvents were removed in vacuo, the residue dissolved in MeOH (5 mL), and an excess of $NaBPh_4$ solution in MeOH was added. The yellow precipitate was collected by filtration, washed with MeOH and Et_2O and dried in vacuo. Yield 240 mg (44%). Complex **1**BPh_4 is sensitive to water and therefore the methanol was dried carefully. $C_{35}H_{33}B_2CoO$ (550.20): calcd. C 76.43, H 6.00; found C 76.08, H 5.89. ^1H NMR ([D$_6$]acetone): δ = 3.76 (s, 3 H, OMe), 4.27 (m, 2 H, α-C_4H_4B), 6.08 (m, 2 H, β-C_4H_4B), 6.78 (s, 6 H, C_6H_6), 7.05 (m, 8 H, BPh_4), 7.35 (m, 12 H, BPh_4) ppm. $^{11}B\{^1H\}$ NMR ([D$_6$]acetone): δ = 27.6 (s, 1 B), –6.5 (s, 1 B, BPh_4) ppm.

$[(\eta\text{-}C_4H_4BOMe)Co(MeCN)_3]BPh_4$ (2BPh$_4$): Complex **1**BPh_4 (100 mg, 0.18 mmol) was irradiated for 6 h in MeCN (10 mL). The solvent was removed in vacuo to give **2**BPh_4 as a red solid (102 mg, 95%). $C_{35}H_{36}B_2CoN_3O$ (595.24): calcd. C 70.65, H 6.05, N 7.06; found C 69.29, H 6.05, N 6.64. ^1H NMR (CD_3CN): δ = 2.70 (m, 2 H, α-C_4H_4B), 3.68 (s, 3 H, OMe), 6.02 (m, 2 H, β-C_4H_4B), 7.03 (m, 8 H, BPh_4), 7.31 (m, 12 H, BPh_4) ppm. $^{11}B\{^1H\}$ NMR (CD_3CN): δ = 29.3 (s, 1 B), –6.6 (s, 1 B, BPh_4) ppm.

$(\eta\text{-}C_4H_4BOMe)Co(\eta\text{-}C_6H_5BPh_3)$ (3): Complex **2**BPh_4 (52 mg, 0.09 mmol) was stirred in CH_2Cl_2 for 5 h. Ether was added to precipitate **3** (22 mg, 53%) as a yellow solid. $C_{29}H_{27}B_2CoO{\cdot}0.25CH_2Cl_2$ (493.37): calcd. C 71.23, H 5.58; found C 71.68, H 5.68. ^1H NMR ($CDCl_3$): δ = 3.57 (s, 3 H, OMe), 3.65 (m, 2 H, α-C_4H_4B), 5.13 (m, 2 H, β-C_4H_4B), 6.32 (m, 2 H, C_6H_5), 6.48 (m, 1 H, C_6H_5), 6.83 (m, 2 H, C_6H_5), 7.07 (m, 6 H, BPh_3), 7.31 (m, 9 H, BPh_3) ppm. $^{11}B\{^1H\}$ NMR ($CDCl_3$): δ = 26.9 (s, 1 B), –7.6 (s, 1 B, BPh_4) ppm.

$[(\eta\text{-}C_4H_4BOMe)Co(t\text{BuNC})_3]BPh_4$ (4BPh$_4$): A solution of complex **1**BPh_4 (100 mg, 0.18 mmol) and *t*BuNC (0.2 mL) in MeCN (10 mL) was irradiated for 6 h. The solvent was removed in vacuo and the residue was eluted through a silica gel column (10 × 1 cm) with CH_2Cl_2. A yellow band was collected and an excess of Et_2O

was added to obtain **4**BPh_4 (79 mg, 60%) as a yellow solid. $C_{44}H_{54}B_2CoN_3O$ (721.48): calcd. C 73.28, H 7.43, N 5.82; found C 73.21, H 7.59, N 5.81. ^1H NMR ([D$_6$]acetone): δ = 1.59 (s, 27 H, *t*BuNC), 3.18 (m, 2 H, α-C_4H_4B), 3.63 (s, 3 H, OMe), 5.83 (m, 2 H, β-C_4H_4B), 6.92 (m, 8 H, BPh_4), 7.34 (m, 12 H, BPh_4) ppm. $^{11}B\{^1H\}$ NMR ([D$_6$]acetone): δ = 28.7 (s, 1 B), –6.5 (s, 1 B, BPh_4) ppm.

[(η-C_4H_4BOMe)Co(MeCN){P(OMe)$_3$}$_2$]BPh_4 (5BPh_4): A solution of **1**BPh_4 (50 mg, 0.09 mmol) and P(OMe)$_3$ (0.1 mL) in MeCN (10 mL) was irradiated for 6 h. The solvent was removed in vacuo and the residue was dissolved in CH_2Cl_2. Ether was added to precipitate **5**BPh_4 (57 mg, 76%) as a yellow solid. $C_{37}H_{48}B_2CoNO_7P_2$ (761.29): calcd. C 57.93, H 6.26; found C 57.99, H 6.44. ^1H NMR ([D$_6$]acetone): δ = 2.60 (s, 3 H, MeCN), 3.31 (m, 2 H, α-C_4H_4B), 3.66 (s, 3 H, OMe), 3.83 [s, 18 H, P(OMe)$_3$], 5.38 (m, 2 H, β-C_4H_4B), 6.92 (m, 8 H, BPh_4), 7.34 (m, 12 H, BPh_4) ppm. $^{11}B\{^1H\}$ NMR ([D$_6$]acetone): δ = 30.5 (s, 1 B), –6.5 (s, 1 B, BPh_4) ppm. ^{31}P NMR ([D$_6$]acetone): δ = 149.9 ppm.

(η-C_4H_4BOMe)CoCp (6): A solution of **1**BPh_4 (100 mg, 0.18 mmol) in MeCN (10 mL) was irradiated for 6 h. CpTl (54 mg, 0.2 mmol) was added, and the reaction mixture was stirred for 12 h. The solvent was removed in vacuo, and the residue was eluted through a silica gel column (10 × 1 cm) with CH_2Cl_2. A yellow band was collected, solvent was removed in vacuo, and the residue was dissolved in hexane. After standing overnight at –78 °C, **6** (38 mg, 95%) was obtained as an orange crystalline product. $C_{10}H_{12}BCoO{\cdot}0.25C_6H_{14}$: calcd. C 57.69, H 6.48; found C 57.24, H 6.62. ^1H NMR ($CDCl_3$): δ = 3.18 (m, 2 H, α-C_4H_4B), 3.62 (s, 3 H, OMe), 4.90 (s, 5 H, C_5H_5), 4.86 (m, 2 H, β-C_4H_4B) ppm. $^{11}B\{^1H\}$ NMR ($CDCl_3$): δ = 25.1 (s, 1 B) ppm.

(η-C_4H_4BOMe)Co(η-9-SMe_2-7,8-$C_2B_9H_{10}$) (7): A solution of **1**BPh_4 (100 mg, 0.18 mmol) in MeCN (10 mL) was irradiated for 6 h. [9-SMe_2-7,8-$C_2B_9H_{10}$]Tl (72 mg, 0.18 mmol) was added, and the reaction mixture was stirred for 12 h. The solvent was removed in vacuo, and the residue was eluted through a silica gel column (10 × 1 cm) with CH_2Cl_2. A yellow band was collected, and an excess of light petroleum was added. Complex **7**, as an orange precipitate, was collected, washed with a small amount of MeOH and dried in vacuo. Yield 60 mg (96%). $C_9H_{24}B_{10}CoOS$ (347.38): calcd. C 31.13, H 6.92, B 31.13; found C 31.54, H 6.89, B 30.96. ^1H NMR ($CDCl_3$): δ = 2.44 (s, 3 H, SMe_2), 2.92 (s, 3 H, SMe_2), 3.43 (m, 1 H, α-C_4H_4B), 3.47 (m, 1 H, α-C_4H_4B), 3.50 (s, 1 H, cage CH), 3.75 (s, 1 H, cage CH), 3.79 (s, 3 H, OMe), 5.06 (m, 1 H, β-C_4H_4B), 5.20 (m, 1 H, β-C_4H_4B) ppm. $^{11}B\{^1H\}$ NMR ($CDCl_3$): δ = 27.4 (1 B, C_4H_4B), –2.3 (1 B), –5.7 (1 B), –8.3 (1 B), –10.3 (1 B), –11.6 (1 B), –13.9 (1 B), –21.4 (1 B), –23.9 (1 B), –26.1 (1 B) ppm.

Hydrolysis of 1 (NMR tube experiment): Complex **1**BPh_4 (15 mg) was dissolved in [D$_6$]acetone (0.5 mL) in an NMR tube and water (0.05 mL) was added. The ^1H NMR measurements showed that the signals of the hydroxy derivative $[(\eta\text{-}C_4H_4BOH)Co(\eta\text{-}C_6H_6)]^+$ appeared within 10 min. After 24 h the degree of conversion was ca. 80%.

X-Ray Crystallography: Crystals of **3** and **7** were grown by slow diffusion in a two-layer system of Et_2O with a solution of the complex in CH_2Cl_2. The principal crystallographic data, procedures for collecting data and characteristics of structure refinement are listed in Table 4. Single-crystal X-ray diffraction experiments were carried out with a Bruker SMART APEX2 CCD area detector, using graphite monochromated Mo-K_α radiation (λ = 0.71073 Å). The structures were solved by direct methods and refined by full-matrix least-squares against F^2 in anisotropic approximation (for non-hydrogen atoms). Positions of hydrogen atoms in the carborane fragment were found from difference Fourier maps. All hydrogen atoms were refined in isotropic approximation in riding model with the U_{iso}(H) parameters equal to 1.5 $U_{eq}(C_i)$ for methyl groups and 1.2 $U_{eq}(C_{ii})$ for other atoms, where $U(C_i)$ and $U(C_{ii})$ are the equivalent thermal parameters of the atoms to which the H atoms are bonded. All calculations were performed using the SHELXTL software.[21]

Table 4. Crystallographic data and structure refinement parameters for **3** and **7**.

	3	**7**
Empirical formula	$C_{29}H_{27}B_2CoO$	$C_9H_{23}B_{10}CoOS$
Molecular weight	472.06	346.36
Crystal colour and habit	brown prism	red needle
Crystal size [mm]	0.21 × 0.13 × 0.08	0.37 × 0.18 × 0.16
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a [Å]	9.3351(6)	19.4078(5)
b [Å]	11.6967(7)	10.8102(3)
c [Å]	20.9284(13)	17.5792(5)
α [°]	90	90
β [°]	94.2800(10)	115.7850(10)
γ [°]	90	90
V [Å^3]	2278.8(2)	3320.93(16)
Z	4	8
$D_{calcd.}$ [g cm^{-3}]	1.376	1.386
T [K]	100	100
θ range [°]	1.95–28.00	3–33
μ [cm^{-3}]	7.73	11.46
Absorption correction	multiscan	multiscan
$T_{max.}/T_{min.}$	0.943/0.889	0.820/0.775
Collected reflections	25396	52392
Independent reflections	5501 (R_{int} = 0.0864)	12926 (R_{int} = 0.0443)
Observed reflections [$I > 2\sigma(I)$]	3707	9915
Parameters	299	477
R_1 (on *F* for observed reflections)	0.0500	0.0374
wR_2 (on F^2 for all reflections)	0.1038	0.1003
Weighting scheme	$w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, where $P = 1/3(F_o^2 + 2F_c^2)$	
a	0.0200	0.0527
b	3.8000	0.8891
F(000)	984	1424
Goodness-of-fit	1.005	0.997
Largest diff. peak and hole [e Å^{-3}]	0.661 and –0.554	0.910 and –0.367

CCDC-691336 (for **3**) and CCDC -691337 (for **7**) contain 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.

Computational Details: Geometry optimizations were performed without constraints using the PBE exchange-correlation functional,[22] the scalar-relativistic Hamiltonian,[23] atomic basis sets of generally-contracted Gaussian functions[24] and a density-fitting technique[25] as implemented in a recent version of Priroda.[26] The all-electron triple-ζ basis set L2 augmented by two polarization functions was used.[27] The calculated Co–C_6H_6 distance for $[(C_4Me_4)Co(C_6H_6)]^+$ (1.561 Å) coincides with that determined by X-ray diffraction, which confirmed the reliability of the computational results. Frequency calculations were performed to confirm the nature of the stationary points.

The bonding interactions were studied by Morokuma–Ziegler EDA as implemented in the ADF 2006.01 program package.[28] The calculations were performed using the exchange functional of Becke[29]

and the correlation functional of Perdew[30] (BP86). Scalar relativistic effects were considered using the zero-order regular approximation (ZORA).[31] The all-electron ZORA relativistic triple-ζ basis set augmented by two polarization functions TZ2P was used. The ChemCraft program[32] was used for molecular modelling and visualization.

Supporting Information (see footnote on the first page of this article): Details of DFT calculations for $[(L)Co(C_6H_6)]^+$ and (L)CoCp (L = C_4H_4BH, C_4H_4BOMe, C_4H_4, C_4Me_4), atomic coordinates for optimized geometry and energy data.

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