Letters to the Editor

Synthesis of the first bromide complexes of the triple-decker type

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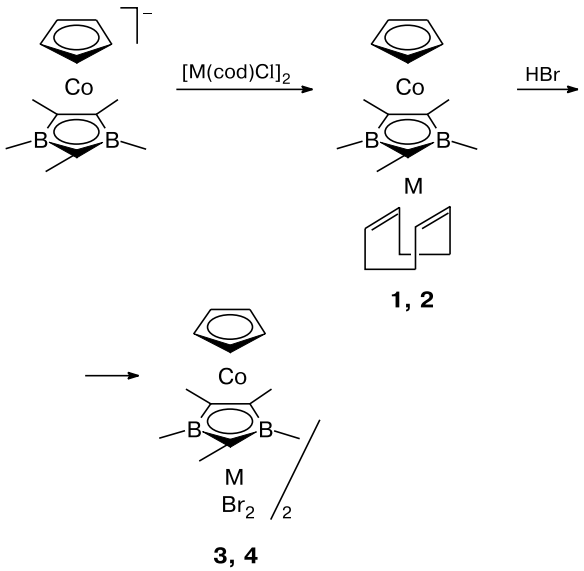
(Cyclopentadienyl)halide complexes of rhodium and iridium $[Cp^*MX_2]_2$ (M = Rh and Ir) are key compounds in the synthesis of various Cp*M-containing derivatives (see Ref. 1). They are also efficient catalysts for homogeneous hydrogenation.[2] Earlier, metallacarborane analogs of these compounds $[(\eta\text{-}9\text{-}SMe_2\text{-}7,8\text{-}C_2B_9H_{10})MX_2]_2$ (M = Rh and Ir; X = Cl, Br, and I) have been synthesized[3,4] and used as synthons of the fragments $(\eta\text{-}9\text{-}SMe_2\text{-}7,8\text{-}C_2B_9H_{10})M$ (see Ref. 5). In the present work, we obtained first dihalide complexes of the triple-decker type.

Recently, we have found that the diborolyl sandwich anion $[CpCo(C_3B_2Me_5)]^-$ is close to the cyclopentadienide anion in the ability to coordinate with transition metals.[6] Electrophilic stacking of this anion with chlorides $[(cod)MCl]_2$ (cod is 1,5-cyclooctadiene; M = Rh and Ir) gave triple-decker complexes $CpCo(C_3B_2Me_5)M(cod)$ (**1**, **2**) (Scheme 1). Subsequent reactions of these compounds with HBr produced dibromides $[CpCo(C_3B_2Me_5)MBr_2]_2$ (**3**, **4**). Compounds **3** and **4** were synthesized as described for $[(\eta\text{-}9\text{-}SMe_2\text{-}7,8\text{-}C_2B_9H_{10})MX_2]_2$ in Refs 3 and 4.

Scheme 1



M = Rh (**1**, **3**), Ir (**2**, **4**).

Compounds **3** and **4** are air-stable black solids that are poorly soluble in CH_2Cl_2 and acetone but well soluble in

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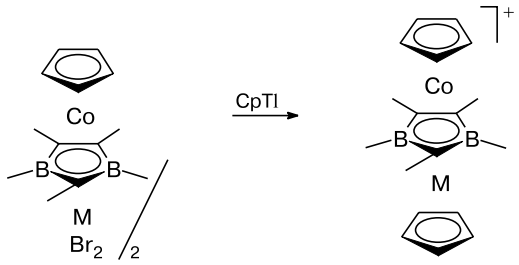
strongly coordinating solvents such as MeCN and DMSO. Bromides **3** and **4** were characterized by elemental analysis and ^{1}H and ^{11}B NMR spectroscopy. Based on the 18-electron rule and by analogy with the complexes $[Cp^*MBr_2]_2$ (M = Rh and Ir), the structures of which were proven by X-ray diffraction analysis,[7] one can formulate compounds **3** and **4** as dimers. The good solubilities of bromides **3** and **4** in strongly coordinating solvents are also evidence for their dimeric structures that break down *via* cleavage of the bromide bridges to give solvate complexes of the type $CpCo(C_3B_2Me_5)M(Solv)Br_2$.

An analogy with the complex $[Cp^*MX_2]_2$ (M = Rh and Ir) allows complexes **3** and **4** to be regarded as synthons of the triple-decker species $CpCo(C_3B_2Me_5)M$ (M = Rh and Ir). Indeed, the corresponding cyclopentadienyl triple-decker complexes **5** and **6** were obtained by reactions with CpTl (Scheme 2).

Scheme 2



3, 4 **5, 6**

M = Rh (**5**), Ir (**6**)

The reactions were carried out under argon in dry solvents dehydrated in standard ways. Manipulations for isolation of products were performed in air. The starting compounds $CpCo(1,3\text{-}C_3B_2Me_5H)$,[8] $[(cod)RhCl]_2$,[9] and $[(cod)IrCl]_2$[10] were prepared according to known procedures. ^{1}H and ^{11}B NMR spectra were recorded on a Bruker AMX-400 instrument (400.13 (^{1}H) and 128.38 MHz (^{11}B)) with reference to residual protons of the solvent.

(μ-η:η-Pentamethyldiborolyl)[(η-cyclopentadienyl)cobalt]-[(η-cyclooctadiene)rhodium], $CpCo(1,3\text{-}C_3B_2Me_5)Rh(cod)$ (1). A solution of $K[CpCo(1,3\text{-}C_3B_2Me_5)]$ prepared by stirring of $CpCo(1,3\text{-}C_3B_2Me_5H)$ (305 mg, 1.18 mmol) with the alloy $Na/K_{3.0}$ (0.2 mL) in THF (4 mL) for 1 h was filtered through a thick glass filter into a suspension of $[(cod)RhCl]_2$ (292 mg, 0.59 mmol) in THF (5 mL) at −78 °C. The resulting mixture was stirred at −78 °C for 1 h, slowly warmed to room temperature, and stirred for an additional 12 h. The reaction mixture was concentrated in water aspirator vacuum with a small amount of silica gel. The silica gel was transferred to a column (7×1.5 cm) packed with silica gel. The brown band was eluted with light petroleum and concentrated. Compound **1** was obtained as a brown oil that crystallized in prolonged storage *in vacuo*. The product was pure enough for use in subsequent reactions. An analytically pure sample was obtained by recrystallization from ethanol. The yield was 426 mg (71%). Found (%): C, 54.20; H, 7.03; B, 4.54. $C_{21}H_{32}B_2CoRh$. Calculated (%): C, 53.90; H, 6.89; B, 4.62. ^{1}H NMR ($CDCl_3$), δ: 4.28 (s, 5 H, Cp); 3.18 (m, 4 H, CH, cod); 2.03 (m, 4 H, CH_2, cod); 1.85 (s, 6 H, CMe); 1.55 (m, 4 H, CH_2, cod); 1.34 (s, 3 H, CMe); 0.89 (s, 6 H, BMe). ^{11}B NMR ($CDCl_3$), δ: 14.24 (s).

(μ-η:η-Pentamethyldiborolyl)[(η-cyclopentadienyl)cobalt]-[(η-cyclooctadiene)iridium], $CpCo(1,3\text{-}C_3B_2Me_5)Ir(cod)$ (2), was obtained analogously from $[(cod)IrCl]_2$ (396 mg, 0.59 mmol). Recrystallization from ethanol gave dark brown crystals. The yield was 370 mg (74%). Found (%): C, 45.68; H, 5.90; B, 3.88. $C_{21}H_{32}B_2CoIr$. Calculated (%): C, 45.26; H 5.79; B, 3.88. ^{1}H NMR ($CDCl_3$), δ: 4.37 (s, 5 H, Cp); 2.83 (m, 4 H, CH, cod); 1.91 (s, 6 H, CMe); 1.87 (m, 4 H, CH_2, cod); 1.40 (m, 4 H, CH_2, cod); 1.35 (s, 3 H, CMe); 1.15 (s, 6 H, BMe). ^{11}B NMR ($CDCl_3$), δ: 14.15 (s).

Bis{dibromo(μ-η:η-pentamethyldiborolyl)[(η-cyclopentadienyl)cobalt]rhodium}, $[CpCo(1,3\text{-}C_3B_2Me_5)RhBr_2]_2$ (3). A concentrated aqueous solution of HBr (6 mL) was added dropwise at 0 °C to a solution of complex **1** (467 mg, 1 mmol) in acetic anhydride—acetone (2 : 1, 25 mL). The reaction was accompanied by strong self-heating and the formation of a black precipitate. The product was centrifuged and washed with ethanol and ether. The yield was 482 mg (93%), a black powder. Found (%): C, 30.18; H, 4.01; B, 4.24; Br, 30.43. $C_{26}H_{40}B_4Br_4Co_2Rh_2$. Calculated (%): C, 30.05; H, 3.88; B, 4.16; Br, 30.76. ^{1}H NMR (DMSO-d_6), δ: 5.28 (s, 5 H, Cp); 2.32 (s, 6 H, CMe); 1.51 (s, 6 H, BMe); 1.48 (s, 3 H, CMe). ^{11}B NMR (DMSO-d_6), δ: 21.98 (s).

Bis{dibromo(μ-η:η-pentamethyldiborolyl)[(η-cyclopentadienyl)cobalt]iridium}, $[CpCo(1,3\text{-}C_3B_2Me_5)IrBr_2]_2$ (4), was obtained analogously from compound **2** (279 mg, 0.5 mmol). The yield was 292 mg (96%), a black powder. Found (%): C, 25.42; H, 3.23; B, 3.56; Br, 25.91. $C_{26}H_{40}B_4Br_4Co_2Ir_2$. Calculated (%): C, 25.64; H, 3.31; B, 3.55; Br, 26.25. ^{1}H NMR (DMSO-d_6), δ: 5.27 (s, 5 H, Cp); 2.41 (s, 6 H, CMe); 1.61 (s, 3 H, CMe); 1.53 (s, 6 H, BMe). ^{11}B NMR (DMSO-d_6), δ: 16.18 (s).

(μ-η:η-Pentamethyldiborolyl)[(η-cyclopentadienyl)cobalt]-[(η-cyclopentadienyl)rhodium] hexafluorophosphate, $[CpCo(1,3\text{-}C_3B_2Me_5)RhCp]PF_6$ (5). Cyclopentadienylthallium (56 mg, 0.21 mmol) was added to a green solution of complex **3** (104 mg, 0.1 mmol) in acetonitrile (4 mL). The reaction mixture turned bright red after 16-h stirring. The solvent was removed and the product was extracted with water. An aqueous solution of an excess of NH_4PF_6 was added to the resulting red solution. The red precipitate that formed was filtered off, washed with water, and reprecipitated with ether from acetone. The yield was 90 mg (77%). Found (%): C, 38.05; H, 4.00; B, 4.13. $C_{18}H_{25}B_2CoF_6RhP$. Calculated (%): C, 37.94; H, 4.42; B, 3.79. ^{1}H NMR (acetone-d_6), δ: 5.43 (d, 5 H, CpRh, J = 0.5 Hz); 5.21 (s, 5 H, CpCo); 2.64 (s, 6 H, CMe); 2.15 (s, 3 H, CMe); 1.41 (s, 6 H, BMe). ^{11}B NMR (acetone-d_6), δ: 15.16 (s).

(μ-η:η-Pentamethyldiborolyl)[(η-cyclopentadienyl)cobalt]-[(η-cyclopentadienyl)iridium] hexafluorophosphate, $[CpCo(1,3\text{-}C_3B_2Me_5)IrCp]PF_6$ (6), was obtained analogously from complex **4** (122 mg, 0.1 mmol). The yield was 55 mg (51%), an orange fine crystalline solid. Found (%): C, 32.84; H, 3.74; B, 3.29. $C_{18}H_{25}B_2CoF_6IrP$. Calculated (%): C, 32.80; H, 3.82; B, 3.28. ^{1}H NMR (acetone-d_6), δ: 5.48 (s, 5 H, CpIr); 5.26 (s,

5 H, CpCo); 2.77 (s, 6 H, CMe); 2.30 (s, 3 H, CMe); 1.54 (s, 6 H, BMe). ^{11}B NMR (acetone-d_6), δ: 8.83 (s).

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