Binuclear half-sandwich cobalt(III) and rhodium(III) *ortho*-carboranedichalocogenolato complexes with ether chain-bridged bis(cyclopentadienyl) ligand

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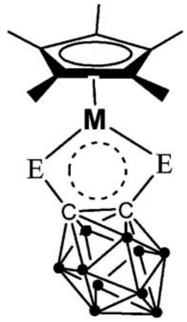
1, 1′-(3-Oxapentamethylene)dicyclopentadiene [$O(CH_2CH_2C_5H_5)_2$] (**1**), containing a flexible chain-bridged group, was synthesized by the reaction of sodium cyclopentadienide with bis(2-chloroethyl) ether through a slightly modified literature procedure. Furthermore, the binuclear cobalt(III) complex $O[CH_2CH_2(\eta^5\text{-}C_5H_4)Co(CO)I_2]_2$ (**3**) and insoluble polynuclear rhodium(III) complex $\{O[CH_2CH_2(\eta^5\text{-}C_5H_4)RhI_2]_2\}_n$ (**8**) were obtained from reactions of **1** with the corresponding metal fragments and they react easily with PPh_3 to give binuclear metal complexes, $O[CH_2CH_2(\eta^5\text{-}C_5H_4)Co(PPh_3)I_2]_2$ (**4**) and $O[CH_2CH_2(\eta^5\text{-}C_5H_4)Rh(PPh_3)I_2]_2$ (**9**), respectively. Complexes **3**, **4** and **9** react with bidentate dilithium dichalcogenolato *ortho*-carborane to give eight binuclear half-sandwich *ortho*-carboranedichalcogenolato cobalt(III) and rhodium(III) complexes $O[CH_2CH_2(\eta^5\text{-}C_5H_4)Co(PPh_3)(E_2C_2B_{10}H_{10})]_2$ (E = S (**5a**) and Se (**5b**)), $O[CH_2CH_2(\eta^5\text{-}C_5H_4)]_2Co_2(E_2C_2B_{10}H_{10})$ (E = S (**6a**) and Se (**6b**)), $O[CH_2CH_2(\eta^5\text{-}C_5H_4)Co(E_2C_2B_{10}H_{10})]_2$ (E = S (**7a**) and Se (**7b**)) and $O[CH_2CH_2(\eta^5\text{-}C_5H_4)Rh(PPh_3)(E_2C_2B_{10}H_{10})]_2$ (E = S (**10a**) and Se (**10b**)). All complexes have been characterized by elemental analyses, NMR spectra (^1H, ^{13}C, ^{31}P and ^{11}B NMR) and IR spectroscopy. The molecular structures of **3**, **5a**, **6a**, **6b**, **9** and **10b** were determined by X-ray diffractometry.

Introduction

Half-sandwich transition metal complexes possessing an ancillary dichalcogenolato-*ortho*-carboranyl ligand have received considerable attentions, due to their unique molecular structures and their wide-ranging potential applications.[1] The rigid geometries of the *ortho*, *meta* and *para* isomers of $C_2B_{10}H_{12}$, together with the relative ease of derivatisation at the carbon vertices make them excellent candidates for crystal engineering.[2] It is well-known that the coordinatively unsaturated Co,[3] Rh[4] or Ir[5] compounds (Fig. 1) bearing both 1,2-E_2-1,2-$C_2B_{10}H_{10}$ and cyclopentadienyl units could serve as excellent precursors to study the addition reactions at the metal atom, even to form the heterometallic clusters[6] or discrete supramolecular assemblies.[7]

We are interested in using functionalized cyclopentadienyl ligands to prepare half-sandwich *ortho*-carboranedichalcogenolato metal complexes and in studying the impact of flexible chains on the geometric structure of the complexes. Recently, we have described the syntheses and characterization of several S- and O-functionalized cyclopentadienyl half-sandwich cobalt complexes containing dichalcogenolato *ortho*-carboranyl ligands.[8] We find that the structures of these complexes are apparently influenced by the functionalized side-arm of cyclopentadienyl group. Herein, some binuclear half-sandwich *ortho*-carboranedichalcogenolato cobalt and rhodium complexes with ether chain-bridged bis(cyclopentadienyl) were obtained from 1,1′-(3-oxapentamethylene)dicyclopentadiene. Additionally, another efficient syntheses route for binuclear cobalt, iridium and ruthenium complexes, by introducing pyridyl-based organic linkers, is presented concurrently in this issue (preceding paper).[7]



M = Co, Rh, Ir;
E = S(**1a**), Se(**1b**)

Fig. 1 Half-sandwich complexes $Cp^*M(E_2C_2B_{10}H_{10})$.

Results and discussion

Binuclear cobalt complexes

1,1′-(3-Oxapentamethylene)dicyclopentadiene **1** was prepared by the reaction of sodium cyclopentadienide with bis(2-chloroethyl) ether in THF through a slightly modified literature procedure.[9]

1 reacted with $Co_2(CO)_8$ in refluxing CH_2Cl_2 solution to give an orange dicarbonyl complex **2** in moderate yield. The IR spectrum of **2** showed two typical strong terminal carbonyl absorptions at

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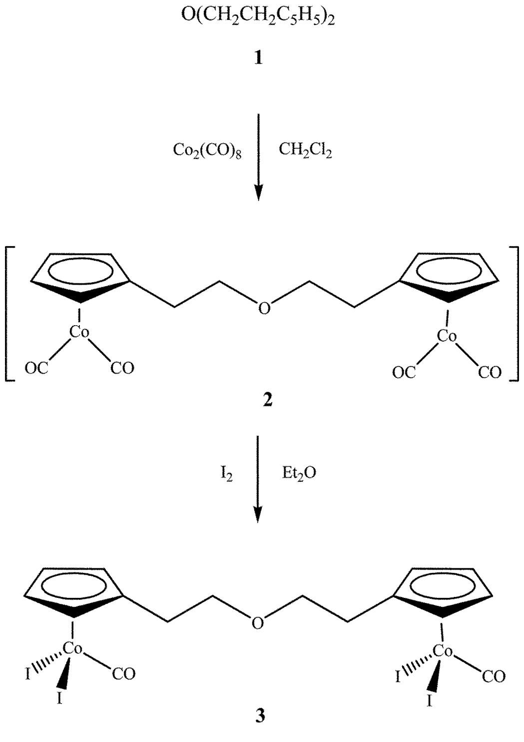
2023 and 1960 cm^{-1}, which was consistent with the previously reported analogous complexes.[10] Addition of elemental iodine to a diethyl ether solution of **2** caused oxidative addition to the cobalt center and gave the air-stable diiodocobalt(III) complex **3**,[11] according to the method of the preparation of $[CH_2(\eta^5\text{-}C_5H_4)_2][Co(CO)I_2]_2$[12] (Scheme 1). Complex **3** showed a strong carbonyl absorption at 2062 cm^{-1} in the typical region for terminal carbonyl groups, which was in agreement with the structure. In the ^1H NMR spectrum of **3** in $CDCl_3$, the mono-substituted cyclopentadienyl proton signals were observed at 5.65 and 5.42 ppm and the ether chain protons (OCH_2 and CH_2) appear at 3.92 and 3.12 ppm.



Scheme 1

Crystals of complex **3** was obtained by slow diffusion of hexane into a concentrated solution of the complex in dichloromethane at low temperature. As depicted in Fig. 2, the binuclear complex **3** possesses two three-legged half-sandwich CpM fragments, linked by a five-atom chain with a *cis*-configuration. In each fragment, the Co atom is η^5-bound to the cyclopentadienyl ring and δ-bound to two terminal-iodine atoms and to one carbonyl group. The two cyclopentadienyl rings lie in the same direction and the dihedral angle between the two Cp planes is 176°, indicating that the two cyclopentadienyl rings are almost parallel. The distance of two iodine atoms in two adjacent molecules is 3.817 Å, which is shorter than the diameter of the iodine atom, suggesting that there is a weak van der Waals attraction between different molecules.[13]

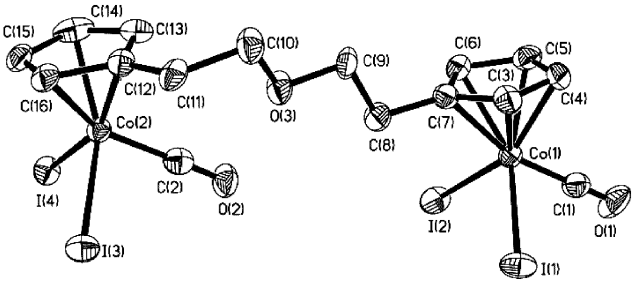
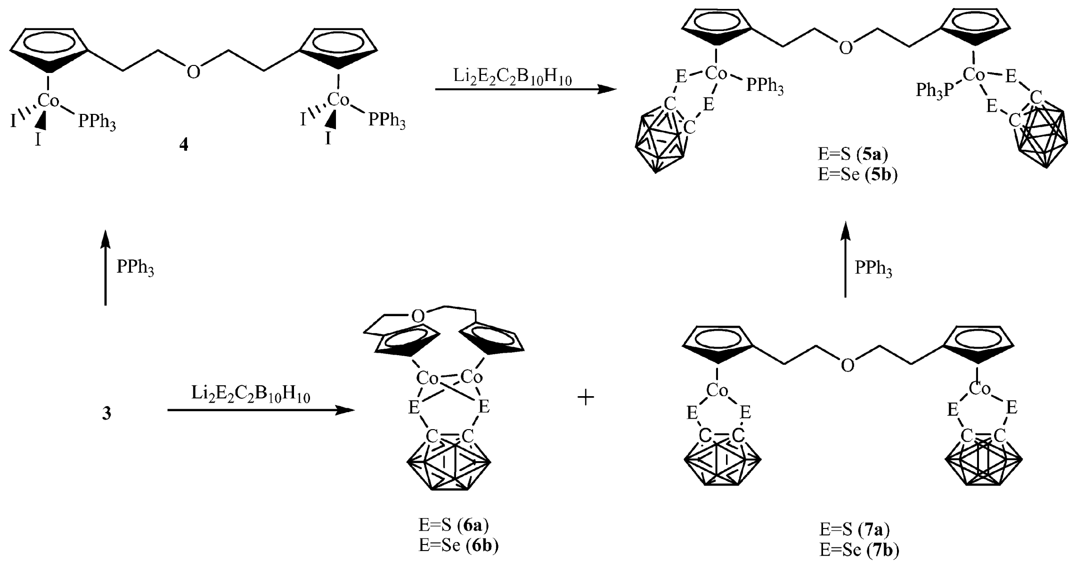


Fig. 2 Molecular structure of **3** with ellipsoids at the 30% probability level; H atoms are omitted for charity. Selected bond lengths (Å) and angles (°): Co(1)–C(1) 1.795(13), Co(1)–I(1) 2.5722(15), Co(1)–I(2) 2.5754(15), C(1)–O(1) 1.080(12), Co(2)–C(2) 1.788(13), Co(2)–I(3) 2.5693(15), Co(2)–I(4) 2.5803(14), C(2)–O(2) 1.105(12), Co(1)···Co(2) 8.385; C(1)–Co(1)–I(1) 87.6(3), C(2)–Co(2)–I(3) 88.0(3), C(1)–Co(1)–I(2) 89.4(4), C(2)–Co(2)–I(4) 88.9(3), I(1)–Co(1)–I(2) 95.11(5), I(3)–Co(2)–I(4) 95.37(5), O(1)–C(1)–Co(1) 178.9(11), O(2)–C(2)–Co(2) 178.5(10).

The carbonyl groups of complex **3** could be easily displaced by two PPh_3 in CH_2Cl_2 and a CO-free binuclear derivative **4** was obtained. Treatment of binuclear complex **4** with dilithium dichalcogenolato carborane gave binuclear dithiolate and diselenolate carborane complexes (**5a** and **5b**) as grass-green solids (Scheme 2). Complexes **4**, **5a** and **5b** have been characterized by ^1H, ^{31}P, ^{11}B NMR and IR spectroscopy.



Scheme 2

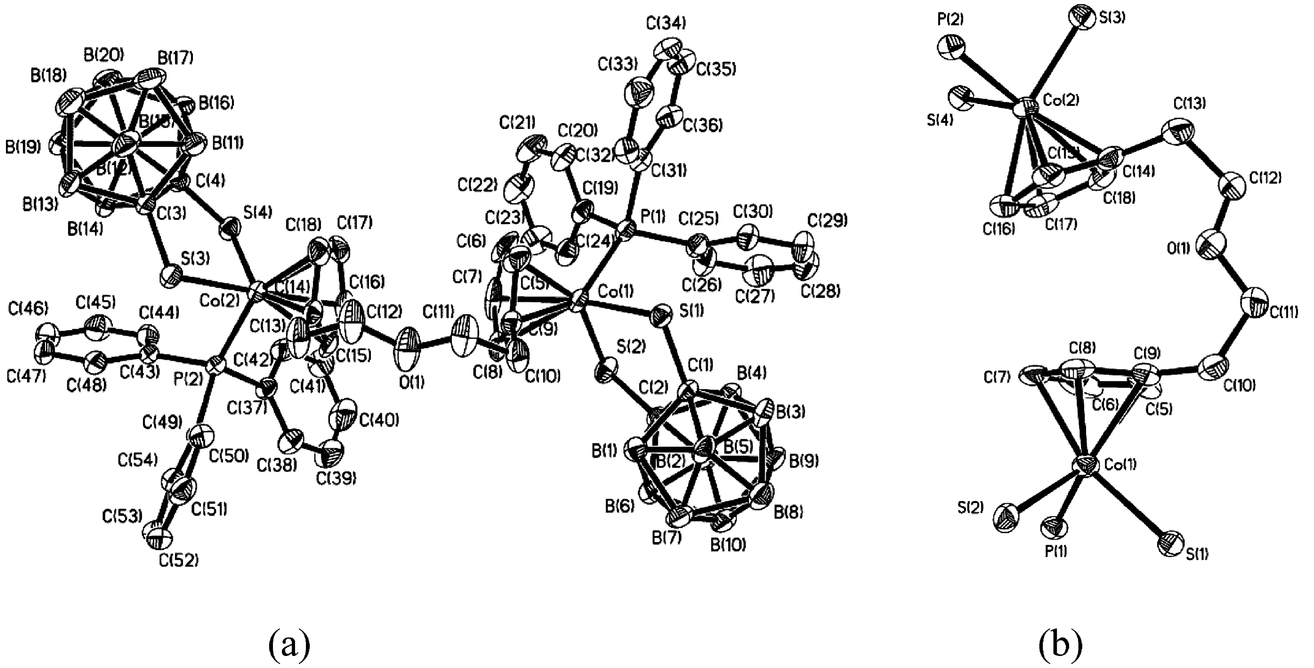


Fig. 3 Molecular structure of **5a** with ellipsoids at the 30% probability level; H atoms are omitted for charity. (a) Global view. (b) Side view (the phenyl groups and carboranyl groups have been omitted for clarity). Selected bond lengths (Å) and angles (°): Co(1)–P(1) 2.235(2), Co(1)–S(1) 2.241(2), Co(1)–S(2) 2.251(2), S(1)–C(1) 1.799(7), S(2)–C(2) 1.793(7), C(1)–C(2) 1.646(9), Co(1) · · · Co(1) 7.246, Co(2)–P(2) 2.236(2), Co(2)–S(3) 2.241(2), Co(2)–S(4) 2.257(2), S(3)–C(3) 1.780(7), S(4)–C(4) 1.765(7), C(3)–C(4) 1.665(10); P(1)–Co(1)–S(1) 90.82(8), P(1)–Co(1)–S(2) 93.54(8), S(1)–Co(1)–S(2) 92.36(7), P(2)–Co(2)–S(3) 91.44(8), P(2)–Co(2)–S(4) 92.12(8), S(3)–Co(2)–S(4) 92.08(8).

The molecular structure of **5a** is depicted in Fig. 3. Complex **5a** possesses basically two three-legged half-sandwich CpCo structures, in which the two CpCo fragments are linked by an ether bridge on the cyclopentadienyl rings. In each CpCo unit, the bidentate dichalcogenolate carborane group and PPh_3 are, respectively, coordinated to the cobalt atom. The two cyclopentadienyl rings of complex **5a** lie in an interesting position which is different from **3**. The two Cp rings face each other with their non-coordinated side and the dihedral angle is 25.4°, due to the repulsion of the bulky ligands and the flexibility of the five-membered chain.

However, complex **3** reacted directly with dilithium dichalcogenolate carborane $[Li_2E_2C_2(B_{10}H_{10}), E = S, Se]$ to give complexes **6a**, **7a** for dithiolate and complexes **6b**, **7b** for diselenolate.

As shown in Fig. 4, complexes **6a** and **6b** contain a pair of cobalt atoms linked by a single metal–metal bond, one chelated dichalcogenolato carborane ligand and the chain-bridged cyclopentadienyl groups. The two molecules both contain a mirror plane. The Co–Co distance is 2.4076(13) Å for **6a** and 2.4193(11) Å for **6b**, which is a little longer than the bond length of the analogous Cp complex $(CpCo)_2[S_2C_2(B_{10}H_{10})]$,[3a,b] due to the tension of the bridging bis(cyclopentadienyl) ligand. Thus complexes **6a** and **6b** are formally 18-electron complexes.

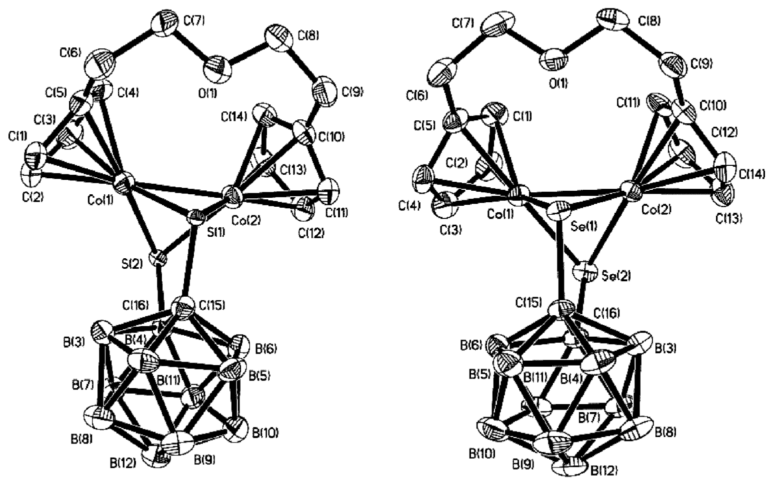
The red products **7a** and **7b** were characterized by elemental analyses and IR, NMR spectroscopy. The IR spectrum showed an intense B–H stretching of carborane (2579 cm^{-1} for **7a** and 2577 cm^{-1} for **7b**). The ^1H NMR spectrum indicated that both **7a** and **7b** contain the 1,1′-(3-oxapentamethylene)dicyclopentadienyl unit. We presumed that **7a** or **7b** were composed of two 16-electron *ortho*-carboranedichalocogenolato cobalt units linked by the ether chain. Their formulations have been confirmed by reaction with two-electron donor ligands such as PPh_3, which gave the 18-electron binuclear derivatives **5a** or **5b**, respectively.

Binuclear rhodium complexes

For comparison with binuclear cobalt complexes, a series of binuclear rhodium complexes with an ether chain-bridged bis(cyclopentadienyl) group have been synthesized. The 1,1′-(3-oxapentamethylene)dicyclopentadiene **1** reacted with NaH and then $[Rh(COD)Cl]_2$ in THF solution to gave the cyclooctadiene (COD) rhodium complex,[14] which, without isolation, was easily oxidized by elemental iodine in diethyl ether and gave the air-stable diiodo rhodium(III) complex **8** in good yield.

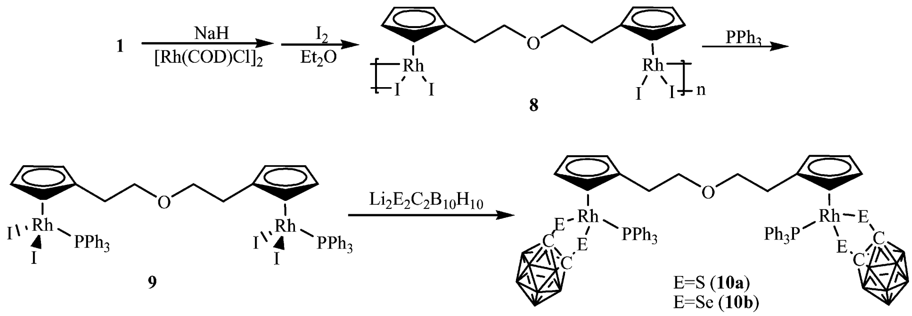
Complex **8** is a black–red, air-stable solid, insoluble in all organic solvents. The elemental analysis suggested that it should be an organometallic polymer, perhaps linked by Rh–I–Rh bridges as shown in Scheme 3.[15] Occasionally, we found that complex **8** could react with PPh_3 in CH_2Cl_2 and got a red soluble product. It is possible that PPh_3 could cleanly split the iodo-bridges to form the 18e binuclear complex **9**. Treatment of **9** with dilithium dichalcogenolato carborane gave the dithiolate and diselenolate carborane complexes **10a** and **10b** with similar structure to **5a** and **5b**.

The structures of **9** and **10b** have been characterized by X-ray analysis using single crystals grown from dichloromethane–hexane. The crystal structure of **9** reveals that the $RhI_2(PPh_3)$ fragments are positioned on the C_5H_4 faces of the bridging ligand so that inter-ring repulsions are minimized (Fig. 5). This results in a long interatomic separation of Rh(1) · · · Rh(2) (8.739 Å), which is a little longer than the similar cobalt complex **3**

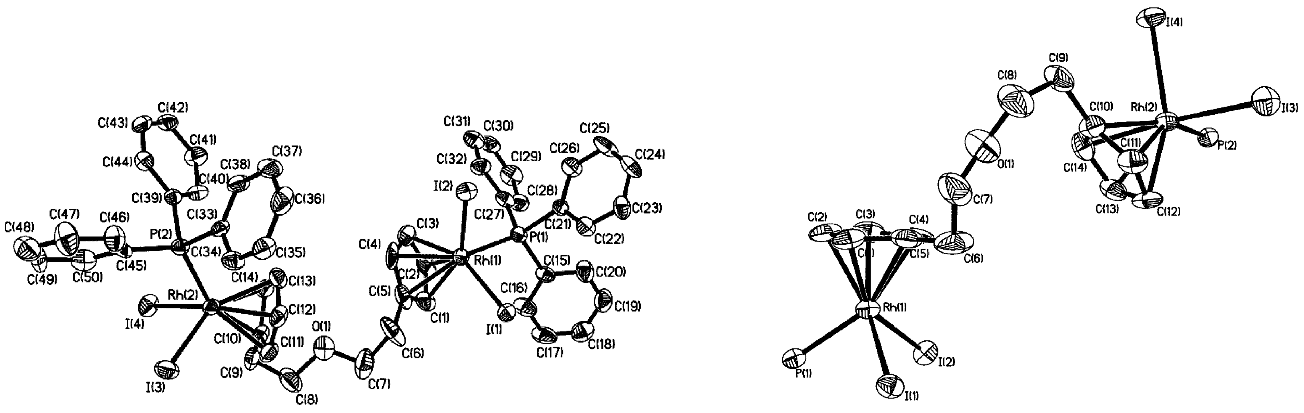


(a) (b)

Fig. 4 Molecular structures of **6a** (a) and **6b** (b) with ellipsoids at the 30% probability level. All hydrogen atoms are omitted for charity. Selected bond lengths (Å) and angles (°): **6a**: Co(1)–S(1) 2.2402(17), Co(1)–S(2) 2.2188(16), S(1)–C(15) 1.857(6), Co(2)–S(1) 2.2500(16), Co(2)–S(2) 2.2418(16), S(2)–C(16) 1.862(6), Co(1)–Co(2) 2.4076(13); S(2)–Co(1)–S(1) 86.66(5), S(2)–Co(1)–Co(2) 57.79(4), S(1)–Co(1)–Co(2) 57.77(4). **6b**: Se(1)–C(15) 1.978(5), Se(1)–Co(1) 2.3132(9), Se(1)–Co(2) 2.3175(9), Se(2)–C(16) 1.976(5), Se(2)–Co(2) 2.2982(9), Se(2)–Co(1) 2.3090(9), Co(1)–Co(2) 2.4193(11); C(15)–Se(1)–Co(1) 100.13(13), C(15)–Se(1)–Co(2) 100.40(13), C(16)–Se(2)–Co(2) 101.02(13), C(16)–Se(2)–Co(1) 100.55(13), Co(1)–Se(1)–Co(2) 62.99(3), Co(2)–Se(2)–Co(1) 63.35(3), Se(2)–Co(1)–Se(1) 87.32(3), Se(2)–Co(2)–Se(1) 87.48(3), Se(1)–Co(2)–Co(1) 58.42(2).



Scheme 3



(a) (b)

Fig. 5 Molecular structure of **9** with ellipsoids at the 30% probability level; H atoms are omitted for charity. (a) Global view. (b) Side view (the phenyl groups have been omitted for clarity). Selected bond lengths (Å) and angles (°): Rh(1)–P(1) 2.307(3), Rh(1)–I(1) 2.6872(14), Rh(1)–I(2) 2.6730(16), Rh(2)–P(2) 2.303(3), Rh(2)–I(3) 2.6672(16), Rh(2)–I(4) 2.6912(14), Rh(1)–Rh(2) 8.739; P(1)–Rh(1)–I(2) 90.46(8), P(1)–Rh(1)–I(1) 91.32(8), I(2)–Rh(1)–I(1) 96.40(4), P(2)–Rh(2)–I(3) 91.86(8), P(2)–Rh(2)–I(4) 93.84(8), I(3)–Rh(2)–I(4) 93.26(4).

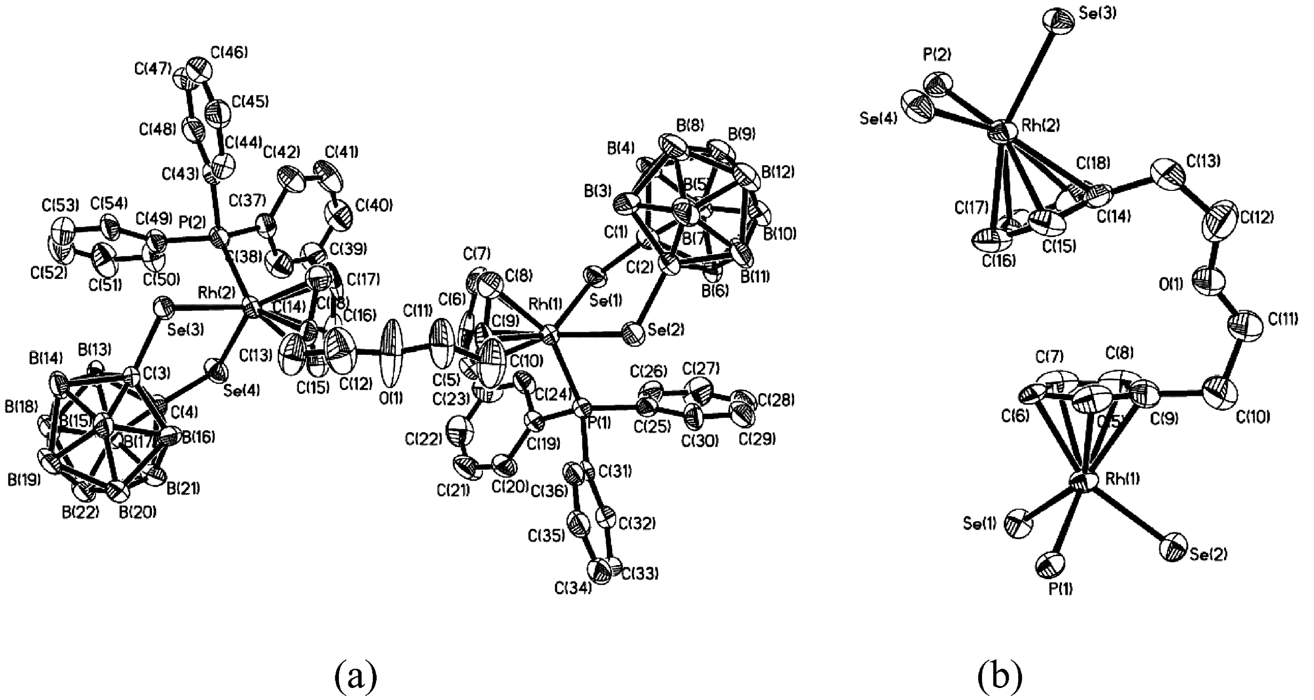


Fig. 6 Molecular structure of **10b** with ellipsoids at the 30% probability level. H atoms are omitted for charity. (a) Global view. (b) Side view (the phenyl groups and carboranyl groups have been omitted for clarity). Selected bond lengths (Å) and angles (°): Rh(1)–P(1) 2.290(3), Rh(2)–P(2) 2.286(3), Rh(1)–Se(2) 2.4520(13), Rh(1)–Se(1) 2.4557(13), Rh(2)–Se(3) 2.4569(13), Rh(2)–Se(4) 2.4514(14), Se(1)–C(1) 1.938(10), Se(2)–C(2) 1.949(10), C(1)–C(2) 1.641(13), C(53)–C(54) 1.586(12), Rh(1) ··· Rh(2) 7.403; P(1)–Rh(1)–Se(2) 90.04(8), P(1)–Rh(1)–Se(1) 91.05(8), P(2)–Rh(2)–Se(4) 93.03(8), P(2)–Rh(2)–Se(3) 88.50(8), Se(2)–Rh(1)–Se(1) 90.12(5), Se(4)–Rh(2)–Se(3) 91.13(5); the dihedral angles: Se1–Rh1–Se2/Se1–C1–C2–Se2 28.2, Se3–Rh2–Se4/Se3–C53–C54–Se4 22.8.

(8.385 Å). The molecular structure is not symmetrical and the two cyclopentadienyl rings are criss-crossed with each other at a dihedral angle of 50.2°. The bond length of Rh(1)–C(5) is the longest among the bond lengths of rhodium and the five carbon atom in the cyclopentadienyl group. This indicates that there is a slight repulsion between the side-chain and the iodine atom. The bond length of Rh(1)–P(1) is 2.307 Å, which is a little shorter than the bond length of Rh(1)–I(1) 2.6730 Å and Rh–I(2) 2.6872 Å, due to the size difference between phosphorus and iodine.

The crystal structure of **10b** shows that the $O(CH_2CH_2C_5H_4)_2$ unit bridges a pair of $[Rh(Se_2C_2B_{10}H_{10})(PPh_3)]$ fragments to form a binuclear $O[CH_2CH_2(\eta^5\text{-}C_5H_4)Rh(PPh_3)(Se_2C_2B_{10}H_{10})]_2$ complex and the distance of Rh(1)–Rh(2) is 7.403 Å (Fig. 6). Both of the rhodium centers adopt a three-legged piano-stool conformation and have a six-coordinated geometry, taking the Cp ligand as a three-coordinated ligand. Angles between adjacent atoms around the rhodium atoms are nearly 90°. The five-membered metallacycle $RhSe_2C_2$ has a distorted envelop conformation similar to the $RhSe_2C_2$ ring found in $Cp^*Rh(PMe_3)(Se_2C_2B_{10}H_{10})$[4] and the RhS_2C_2 ring in $Cp^{tt}Rh(CNtBu)(S_2C_2B_{10}H_{10})$.[4] The bond angle Se(1)–Rh(1)–Se(2) in complex **10b** is 90.12°, which is typical for half-sandwich rhodium complexes. The disposition of the two Cp rings is similar to complex **3** with a relatively small dihedral angle. Interestingly we find the presence of a hydrogen bond between **10b** and solvent molecule CH_2Cl_2 in the crystal. One molecule of CH_2Cl_2 links two molecules of **10b** with two H ··· Se hydrogen bonds and channels are formed, seen from the stacking of the molecules along the *a*-axis.

Conclusions

In this article, four binuclear half-sandwich cobalt or rhodium halides with an ether chain-bridged bis(cyclopentadienyl) group were synthesized. The obtained complexes have been further converted to dinuclear half-sandwich *ortho*-carboranedichalocogenolato cobalt and rhodium complexes to examine the basic coordination properties of the ancillary bidentate dichalcogenolate-*ortho*-carboranyl ligand. Study of the crystal structures of complexes **3**, **5a**, **6a**, **6b**, **9** and **10b** indicates that the presence of the flexible ether chain-bridge makes it possible for the two Cp panels in each structure to have different dispositions, which are shown in the structures of complexes **3**, **5a** and **9**. On the other hand, because of the twisted flexible ether chain-bridge, channels were formed in the solid state and some solvent molecules could be trapped.

Experimental

General

All manipulations of the complexes were carried out using standard Schlenk techniques under nitrogen atmosphere. Solvents were dried by refluxing with appropriate drying agents and distilled under nitrogen prior to use. $[(THF)_3LiE_2C_2B_{10}H_{10}Li(THF)]_2$ (E = S (**a**), Se (**b**)),[16] $O(CH_2CH_2C_5H_5)_2$ (**1**),[9] $[Rh(COD)Cl]_2$[17] were synthesized according to the procedures described in the literature. Separation of product mixtures and purification of the components was accomplished by column chromatography over silica gel which had been activated at 200 °C overnight and kept under nitrogen before use. All other materials were obtained commercially and were used as received, except as noted. The elemental analyses were performed on a Rapid CHN-O 240C Analyzer. Infrared spectra were recorded on a Nicolet-FT-IR-50X spectrophotometer. ^{1}H, ^{13}C, ^{11}B and ^{31}P NMR spectra were obtained using Bruker DMX-500 and DMX-300 spectrophotometers in $CDCl_3$, respectively. Chemical shifts (downfield from TMS (^{1}H and ^{13}C), $BF_3{\cdot}OEt_2$ (^{11}B) and H_3PO_4 (^{31}P)) and coupling constants are reported in ppm and in Hz, respectively.

Preparation of $O[CH_2CH_2(\eta^5\text{-}C_5H_4)Co(CO)I_2]_2$ (3). A CH_2Cl_2 solution (40 ml) of **1** (536 mg, 2.65 mmol) and $Co_2(CO)_8$ (1.00 g, 2.92 mmol) was refluxed for 5 h and then solvent was removed *in vacuo.* The residue was chromatographed on silica gel column and eluted with diethyl ether–hexane (1 : 4). The orange band was collected. The solvent was evaporated under vacuum and afforded **2** (798 mg, 70%) as a red liquid. IR (film): ν = 2023, 1960 cm^{-1} (ν_{CO}), 1114 cm^{-1} (ν_{COC}), 1460, 1376, 1258, 800, 718 cm^{-1}. A solution containing iodine (508 mg, 2.0 mmol) in ether (20 ml) was added dropwise to a solution of **2** (430 mg, 1.0 mmol) in ether (20 ml) at 0 °C. The color of the solution changed from orange to dark purple and a black–purple precipitate was formed. The solution was allowed to warm to room temperature and then stirred for 2 h. After filtration, the black–purple solid was washed with ether (2 × 15 mL). Recrystallization of product from CH_2Cl_2–hexane afforded black–purple crystals of **3** (475 mg, 54%). Anal. Calc. for $C_{16}H_{16}Co_2I_4O_3$: C 21.79; H 1.83. Found: C 22.21; H 2.01%. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 5.65 (t, 4H, Cp), 5.42 (t, 4H, Cp), 3.92 (t, 4H, OCH_2, $J_{H\text{–}H}$ = 11.4 Hz), 3.12 (t, 4H, CH_2, $J_{H\text{–}H}$ = 11.4 Hz). IR (KBr disk): ν = 3091 cm^{-1} ($\nu_{C\text{–}H}$, Cp), 2062 cm^{-1} (ν_{CO}), 1107 cm^{-1} ($\nu_{C\text{–}O\text{–}C}$) 2891, 1624, 1473, 1410, 1347, 845 cm^{-1}.

Preparation of $O[CH_2CH_2(\eta^5\text{-}C_5H_4)Co(PPh_3)I_2]_2$ (4). To a solution of **3** (197 mg, 0.22 mmol) in CH_2Cl_2 (5 mL) was added a CH_2Cl_2 solution (5 mL) of PPh_3 (140 mg, 0.27 mmol) dropwise at room temperature. After it was stirred for 5 h, the solvent was removed under reduced pressure. The product was purified by column chromatography on silica. Recrystallization of the product from CH_2Cl_2–hexane afforded dark-green crystals of **4** (261 mg, 88%). Anal. Calc. for $C_{50}H_{46}Co_2I_4OP_2$: C 44.47; H 3.43. Found: C 44.20; H 3.40%. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.80–7.45 (m, 30H, Ph), 5.28 (t, 4H, Cp), 4.06 (t, 4H, Cp), 3.86 (t, 4H, OCH_2), 3.26 (t, 4H, CH_2). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 133.79, 133.73, 130.28, 127.71 (s, Ph), 104.18, 91.10, 79.58 (s, Cp), 69.79 (s, OCH_2), 29.44 (s, $CpCH_2$). ^{31}P NMR (202 MHz, $CDCl_3$, ppm): δ 33.02 (s). IR (KBr disk): ν = 1103 cm^{-1} ($\nu_{C\text{–}O\text{–}C}$, as), 3053, 2925, 1618, 1482, 1435, 738 cm^{-1}.

Preparation of $O[CH_2CH_2(\eta^5\text{-}C_5H_4)Co(PPh_3)(E_2C_2B_{10}H_{10})]_2$ (E = S (5a) and Se (5b)).

Method A. To a solution of **7a** (73 mg, 0.1 mmol) or **7b** (92 mg, 0.1 mmol) in CH_2Cl_2 (10 mL) was added a CH_2Cl_2 solution (5 mL) of PPh_3 (63 mg, 0.24 mmol) dropwise at 0 °C. After it was stirred for 5 h, the reaction mixture was concentrated. Hexane was added to the solution to cause separation of the crystals. The formed dark-green crystals **5a**$\cdot 3CH_2Cl_2$ (90.6 mg, 60%) or **5b** (93.8 mg, 65%) were collected by filtration and washed with hexane.

Method B. To a solution of **4** (135 mg, 0.10 mmol) in THF (10 mL) was added a diethyl ether solution (15 mL) of $Li_2E_2C_2B_{10}H_{10}$ (E = S or Se) (0.20 mmol) dropwise at 0 °C. After it was stirred for 10 h, the solvent was removed under reduced pressure. The main product was purified by column chromatography on silica. Recrystallization of the product from CH_2Cl_2–hexane afforded red crystals of **5a** (68 mg, 45%) or **5b** (68 mg, 47%).

5a. Anal. Calc. for $C_{54}H_{66}B_{20}Co_2OP_2S_4{\cdot}3CH_2Cl_2$: C 45.33; H 4.81; S 8.48. Found: C 45.20; H 4.79; S 8.45%. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.58–7.40 (m, 30H, Ph), 4.80 (t, 4H, Cp), 4.34 (t, 4H, Cp), 3.57 (t, 4H, OCH_2), 2.49 (t, 4H, CH_2). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 134.54, 132.37, 130.94, 128.35 (s, Ph), 117.22, 86.80, 85.83 (s, Cp), 68.63 (s, OCH_2), 28.63 (s, $CpCH_2$), 93.94 (s, C_2-carborane). ^{11}B NMR (160 MHz, $CDCl_3$, ppm): δ −0.3, −5.96. −9.61. ^{31}P NMR (202 MHz, $CDCl_3$, ppm): δ 34.33 (s). IR (KBr disk): ν = 1093 cm^{-1} ($\nu_{C\text{–}O\text{–}C}$, as), 2579 cm^{-1} ($\nu_{B\text{–}H}$), 3055, 2922, 2858, 1630, 1480, 1433, 1356, 855, 739, 695, 526 cm^{-1}.

5b. Anal. Calc. for $C_{54}H_{66}B_{20}Co_2OP_2Se_4$: C 44.95; H 4.61. Found: C 44.80; H 4.55. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.75–7.41 (m, 30H, Ph), 4.75 (t, 4H, Cp), 4.41 (t, 4H, Cp), 3.55 (t, 4H, OCH_2), 2.67 (t, 4H, CH_2). ^{11}B NMR (160 MHz, $CDCl_3$, ppm): δ −4.23, −7.89, −8.79, −13.4, −14.5. ^{31}P NMR (202 MHz, $CDCl_3$, ppm): δ 37.48 (s). IR (KBr disk): ν = 1096 cm^{-1} ($\nu_{C\text{–}O\text{–}C}$, as), 2576 cm^{-1} ($\nu_{B\text{–}H}$), 3054, 2922, 2857, 1629, 1478, 1433, 1383, 833, 693, 525 cm^{-1}.

Preparation of $O[CH_2CH_2(\eta^5\text{-}C_5H_4)]_2Co_2(S_2C_2B_{10}H_{10})$ (6a) and $O[CH_2CH_2(\eta^5\text{-}C_5H_4)\ Co(Se_2C_2B_{10}H_{10})]_2$ (7a). To a solution of $Li_2S_2C_2B_{10}H_{10}$ (0.360 mmol) in Et_2O (10 ml) was added a THF solution (20 ml) of **3** (156.0 mg, 0.177 mmol). The reaction mixture was stirred overnight at room temperature and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica. The component in the first band was eluted with CH_2Cl_2–hexane (1 : 1) and recrystallized from CH_2Cl_2–hexane at −18 °C to give green crystals of **6a** (5 mg, 5%). Anal. Calc. for $C_{16}H_{26}B_{10}Co_2OS_2$: C 36.64; H 5.00; S 12.20. Found: C 36.55; H 4.93; S 12.10%. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 5.33 (t, 4H, Cp), 4.70 (t, 4H, Cp), 3.66 (t, 4H, OCH_2, $J_{H\text{–}H}$ = 13.8 Hz), 2.26 (t, 4H, CH_2, $J_{H\text{–}H}$ = 11.5 Hz). ^{11}B NMR (160 MHz, $CDCl_3$, ppm): δ −3.72, −4.41, −5.31, −7.02, −8.23, −9.16, −11.61, −12.55. IR (KBr disk): ν = 1052 cm^{-1} ($\nu_{C\text{–}O\text{–}C}$, as), 2576 cm^{-1} ($\nu_{B\text{–}H}$), 3109, 2908, 1628, 1464, 1414, 1356, 857, 792, 725, 584 cm^{-1}. The second band was collected and recrystallized from CH_2Cl_2–hexane (3 : 1) to give yellow crystals of **7a** (80.1 mg, 62%). Anal. Calc. for $C_{18}H_{36}B_{20}Co_2OS_4$: C 29.58; H 4.97; S 17.51. Found: C 29.45; H 4.87; S 17.35%. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 5.42 (t, 4H, Cp), 5.26 (t, 4H, Cp), 3.84 (t, 4H, OCH_2), 2.22 (t, 4H, CH_2). ^{11}B NMR (160 MHz, $CDCl_3$, ppm): δ −6.76, −1.81, −8.67, −9.63, −10.77, −11.87, −12.87. IR (KBr disk): ν = 1103, 1061 cm^{-1} ($\nu_{C\text{–}O\text{–}C}$), 2579 cm^{-1} ($\nu_{B\text{–}H}$), 3110, 2961, 2860, 1628, 1474, 1410, 1357, 800, 722, 620 cm^{-1}.

Preparation of $O[CH_2CH_2(\eta^5\text{-}C_5H_4)]_2Co_2(Se_2C_2B_{10}H_{10})$ (6b) and $O[CH_2CH_2(\eta^5\text{-}C_5H_4)Co\ (Se_2C_2B_{10}H_{10})]_2$ (7b). Reaction of complex **3** (220 mg, 0.25 mmol) with $Li_2Se_2C_2B_{10}H_{10}$ (0.5 mmol) in THF solution (30 ml) by using a procedure similar to those used in the synthesis of **6a** and **7a**, led to **6b** as green crystals and **7b** as a red solid. **6b**: Anal. Calc. for $C_{16}H_{26}B_{10}Co_2OSe_2$: C 31.08; H 4.24.

Found: C 31.01; H 4.90%. ^{1}H NMR (500 MHz, CDCl$_3$, ppm): δ 5.17 (t, 4H, Cp), 4.65 (t, 4H, Cp), 3.66 (t, 4H, OCH$_2$, $J_{\text{H–H}}$ = 13.8 Hz), 2.42 (t, 4H, CH$_2$, $J_{\text{H–H}}$ = 11.5 Hz). ^{11}B NMR (160 MHz, CDCl$_3$, ppm): δ 3.72, −4.41, −5.31, −7.02, −8.23, −9.16, −11.61, −12.55. IR (KBr disk): ν = 1128, 1052 cm^{-1} ($\nu_{\text{C–O–C}}$), 2577 cm^{-1} ($\nu_{\text{B–H}}$), 3088, 2919, 2865, 1629, 1471, 1411, 1322, 809, 725, 626 cm^{-1}. **7b**: Anal. Calc. for $C_{18}H_{36}B_{20}Co_2OSe_4$: C 23.54; H 3.95. Found: C 23.49; H 3.90%. ^{1}H NMR (500 MHz, CDCl$_3$, ppm): δ 5.25 (t, 4H, Cp), 5.03 (t, 4H, Cp), 3.80 (t, 4H, OCH$_2$), 2.60 (t, 4H, CH$_2$). ^{11}B NMR (160 MHz, CDCl$_3$, ppm): δ −2.04, −3.00, −7.08, −7.89, −8.89, −9.91, −12.06, −13.37, −14.40, −15.58 IR (KBr disk): ν = 1125, 1050 cm^{-1} ($\nu_{\text{C–O–C}}$, as), 2577 cm^{-1} ($\nu_{\text{B–H}}$), 3090, 2920, 2860, 1630, 1474, 1410, 1322, 805, 725, 625 cm^{-1}.

Preparation of [O[CH$_2$CH$_2$(η^5-C$_5$H$_4$)RhI$_2$]$_2$]$_n$ (8). To a solution of **1** (1.54 g, 7.62 mmol) in 15 ml THF was added an excess of NaH at room temperature for about 5 h. The concentration of this solution was 0.2304 M by titration with standard hydrochloric acid. Then the THF solution (15 mL) of [O(CH$_2$CH$_2$C$_5$H$_4$Na)$_2$] (1.74 ml, 0.40 mmol) was added dropwise to a solution of [Rh(COD)Cl]$_2$ (400 mg, 0.81 mmol) in 15 ml THF at −78 °C. After stirring for 5 h at room temperature, the solvent was removed under vacuum. The residue was extracted in 20 ml diethyl ether to remove NaCl salt. To this obtained orange solution was added dropwise 15 ml diethyl ether containing I$_2$ (0.41 g, 1.6 mmol) at −78 °C. After 2 h stirring at room temperature, the upper clear solution was removed, and after washing with diethyl ether twice, afforded **8** (0.533 g, 72%) as a red insoluble solid. Anal. Calc. for $C_{14}H_{16}I_4ORh_2$: C 18.4; H 1.77. Found: C 18.8; H 1.85%. IR (KBr disk): ν = 3079, 2862, 1623, 1467, 1394, 1359, 1104, 846 cm^{-1}.

Preparation of O[CH$_2$CH$_2$(η^5-C$_5$H$_4$)Rh(PPh$_3$)I$_2$]$_2$ (9). To a solution of **8** (190.8 mg, 0.2 mmol) in CH$_2$Cl$_2$ (15 mL) was added a CH$_2$Cl$_2$ solution (10 mL) of PPh$_3$ (105 mg, 0.4 mmol) dropwise at 0 °C. After it was stirred for 3 h, the solvent was removed under reduced pressure. The product was purified by column chromatography on silica. Recrystallization of product from CH$_2$Cl$_2$–hexane afforded dark-red crystals of **9** (262 mg, 91%). Anal. Calc. for $C_{50}H_{46}I_4OP_2Rh_2$: C 41.75; H 3.22. Found: C 41.65; H 3.20%. ^{1}H NMR (500 MHz, CDCl$_3$, ppm): δ 7.65–7.39 (m, 30H, Ph), 5.48 (t, 4H, Cp), 4.82 (t, 4H, Cp), 3.69 (t, 4H, OCH$_2$, $J_{\text{H–H}}$ = 11.6 Hz), 3.02 (t, 4H, CH$_2$, $J_{\text{H–H}}$ = 14.9 Hz). ^{13}C NMR (125 MHz, CDCl$_3$, ppm): δ 134.45, 134.38, 130.84, 128.13 (s, Ph), 111.73, 91.97, 86.63 (s, Cp), 70.30 (s, OCH$_2$), 29.28 (s, CpCH$_2$). ^{31}P NMR (202 MHz, CDCl$_3$, ppm): δ 27.81 (d, $J_{\text{Rh–P}}$ = 142 Hz). IR (KBr disk): ν = 1092 cm^{-1} ($\nu_{\text{C–O–C}}$, as), 3049, 1618, 1479, 1433, 1391, 836, 745, 693, 524 cm^{-1}.

Preparation of O[CH$_2$CH$_2$(η^5-C$_5$H$_4$)Rh(PPh$_3$)(E$_2$C$_2$B$_{10}$H$_{10}$)]$_2$ (E = S (10a) and Se (10b)). To a solution of **9** (137 mg, 0.15 mmol) in THF (10 mL) was added a diethyl ether solution (15 mL) of Li$_2$E$_2$C$_2$B$_{10}$H$_{10}$ (E = S or Se) (0.30 mmol) dropwise at −78 °C. After it was stirred for 10 h, the solvent was removed under reduced pressure. The main product was purified by column chromatography on silica. Recrystallization of product from CH$_2$Cl$_2$–hexane afforded red crystals of **10a** or **10b**.

10a. (91.8 mg, 62%) Anal. Calc. for $C_{54}H_{66}B_{20}OP_2Rh_2S_4$: C 48.28; H 4.95; S 9.55. Found: C 47.98; H 4.85; S 9.32%. ^{1}H NMR (500 MHz, CDCl$_3$, ppm): δ 7.50–7.41 (m, 30H, Ph), 4.96 (t, 4H, Cp), 4.82 (t, 4H, Cp), 3.68 (t, 4H, OCH$_2$, $J_{\text{H–H}}$ = 11.9 Hz), 2.60 (t, 4H, CH$_2$, $J_{\text{H–H}}$ = 10.5 Hz). ^{13}C NMR (125 MHz, CDCl$_3$, ppm): δ 134.56, 131.93, 131.06, 128.26 (s, Ph), 121.45, 90.55, 89.95

Table 1 Crystallographic data for compounds **3**, **6a** and **6b**

	3	**6a**	**6b**
Empirical formula	$C_{16}H_{16}Co_2I_4O_3$	$C_{16}H_{26}B_{10}Co_2OS_2$	$C_{16}H_{26}B_{10}Co_2OSe_2$
M_r	881.75	524.45	618.25
Crystal system	Triclinic	Monoclinic	Orthorhombic
Space group	$P\bar{1}$	$P2_1/c$	$Pbca$
a/Å	6.775(2)	12.239(4)	13.145(4)
b/Å	12.876(4)	12.155(4)	15.462(5)
c/Å	13.096(4)	18.230(5)	23.036(7)
α/°	86.583(5)	90	90
β/°	85.367(4)	92.793(5)	90
γ/°	82.294(4)	90	90
V/Å^3	1127.1(6)	2708.8(14)	4682(2)
Z	2	4	8
F(000)	804	1064	1064
Crystal size/mm	0.10 × 0.08 × 0.05	0.15 × 0.10 × 0.08	0.20 × 0.10 × 0.02
θ Range/°	1.56–25.01	1.67–25.00	1.77–25.01
D_c/Mg m^{-3}	2.598	1.286	1.754
μ/mm^{-1}	6.961	1.386	4.535
No. reflns collected	4756	11212	18710
No. ind. reflns	3916	4775	4130
R_{int}	0.0337	0.0485	0.0446
No. of data/restraints/params	3916/0/226	4775/0/290	4130/0/290
Goodness-of-fit on F^2	0.813	0.919	0.891
R Indices ($I > 2\sigma I$)[a]	$R1 = 0.0428$	$R1 = 0.0544$	$R1 = 0.0372$
	$wR2 = 0.0881$	$wR2 = 0.1520$	$wR2 = 0.0827$
R Indices (all data)	$R1 = 0.0754$	$R1 = 0.0850$	$R1 = 0.0606$
	$wR2 = 0.0971$	$wR2 = 0.1626$	$wR2 = 0.0880$
$\Delta\rho_{\text{max, min}}$/e Å^{-3}	1.106, −0.824	0.956, −0.615	1.975, −0.265

[a] $R1 = \sum\|F_o| - |F_c\|/\sum|F_o|$; $R_w = [\sum w(|F_o{}^2| - |F_c{}^2|)^2/\sum w|F_o{}^2|^2]^{1/2}$.

Table 2 Crystallographic data for compounds **5a**, **9** and **10b**

	5a	**9**	**10b**
Empirical formula	$C_{54}H_{66}B_{20}Co_2OP_2S_4\cdot3CH_2Cl_2$	$C_{50}H_{46}I_4OP_2Rh_2$	$C_{54}H_{66}B_{20}OP_2Rh_2Se_4\cdot2CH_2Cl_2$
M_r	1510.09	1438.23	1700.72
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/n$	$P\bar{1}$	$P2_1/n$
a/Å	11.826(4)	8.080(3)	12.047(3)
b/Å	18.124(6)	17.147(6)	18.278(5)
c/Å	33.307(11)	17.467(6)	33.285(9)
α/°	90	90.537(5)	90
β/°	90.714(6)	94.058(5)	90.573(5)
γ/°	90	93.095(5)	90
V/Å^3	7138(4)	2410.3(15)	7329(3)
Z	4	2	4
F(000)	3088	1372	3352
Crystal size/mm	0.30 × 0.90 × 1.00	0.10 × 0.08 × 0.05	0.15 × 0.10 × 0.10
θ Range/°	1.28–27.15	1.17–25.01	1.27–25.01
D_c/Mg m^{-3}	1.405	1.982	1.541
μ/mm^{-1}	0.891	3.349	2.664
No. reflns collected	35152	10148	30475
No. ind. reflns	15557	8386	12901
R_{int}	0.1111	0.0453	0.0783
No. of data/restraints/params	15557/2/849	8386/0/532	12901/0/802
Goodness-of-fit on F^2	0.911	0.908	0.807
R Indices ($I > 2\sigma I$)^a	$R1 = 0.0813$ $wR2 = 0.2005$	$R1 = 0.0566$ $wR2 = 0.1217$	$R1 = 0.0562$ $wR2 = 0.1252$
R Indices (all data)	$R1 = 0.2023$ $wR2 = 0.2468$	$R1 = 0.1120$ $wR2 = 0.1521$	$R1 = 0.1553$ $wR2 = 0.1475$
$\Delta\rho_{\max,\min}$/e Å^{-3}	0.810, −0.986	1.195, −0.843	1.516, −0.574

^{a} $R1 = \sum\|F_o| - |F_c\|/\sum|F_o|$; $R_w = [\sum w(|F_o^2| - |F_c^2|)^2/\sum w|F_o^2|^2]^{1/2}$.

(s, Cp), 68.89 (s, OCH_2), 27.78 (s, $CpCH_2$), 92.15 (s, C_2-carborane). ^{11}B NMR (160 MHz, $CDCl_3$, ppm): δ −5.66, −9.94. ^{31}P NMR (202 MHz, $CDCl_3$, ppm): δ 38.46 (d, J_{Rh-P} = 148 Hz). IR (KBr disk): v = 1093 cm^{-1} (ν_{C-O-C}, as), 2575 cm^{-1} (ν_{B-H}), 3055, 2922, 2861, 1624, 1480, 1434, 1357, 840, 744, 695530 cm^{-1}.

10b. (140 mg, 55%) Anal. Calc. for $C_{54}H_{66}B_{20}OP_2Rh_2Se_4\cdot2CH_2Cl_2$: C 39.55; H 4.15. Found: C 38.89, H 4.09%. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.46–7.39 (m, 30H, Ph), 4.98 (t, 4H, Cp), 4.94 (t, 4H, Cp), 3.68 (t, 4H, OCH_2, J_{H-H} = 11.9 Hz), 2.76 (t, 4H, CH_2, J_{H-H} = 10.5 Hz). ^{11}B NMR (160 MHz, $CDCl_3$, ppm): δ −5.09, −8.58, −11.12. ^{31}P NMR (202 MHz, $CDCl_3$, ppm): δ 38.40 (d, J_{Rh-P} = 148 Hz). IR (KBr disk): v = 1093 cm^{-1} (ν_{C-O-C}, as), 2575 cm^{-1} (ν_{B-H}), 3053, 2922, 2857, 1577, 1478, 1433, 1384, 827, 743, 694, 529 cm^{-1}.

Crystal structure determinations

Crystals of **3**, **5a**, **6a**, **6b**, **9** and **10b** suitable for X-ray crystallography were grown by slow diffusion of hexane into CH_2Cl_2 or THF solution. The single crystals of **3**, **5a**, **6a**, **6b**, **9** and **10b** were sealed in glass capillaries and were sequentially mounted on a CCD-Bruker Smart diffractometer. All the determinations of unit cell and intensity data were performed with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). All the data were collected at room temperature using the ω scan technique. These structures were solved by direct methods, expanded using Fourier techniques and refined on F^2 by a full-matrix least-squares method. The non-hydrogen atoms were refined anisotropically and hydrogen atoms were included but not refined. All the calculations were carried out with Siemens SHELXTL PLUS program.[18] Details of crystal data for complexes **3**, **5a**, **6a**, **6b**, **9** and **10b** are summarized in Tables 1 and 2.

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For crystallographic data in CIF or other electronic format see DOI: 10.1039/b611266h

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