



Half-sandwich binuclear carbaborane compounds: *Closo*-carbaboranes as good σ -donor ligands

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ABSTRACT

The synthesis of half-sandwich binuclear transition-metal complexes containing the $\text{Cab}^{\text{C,C}}$ chelate ligands ($\text{Cab}^{\text{C,C}} = \text{C}_2\text{B}_{10}\text{H}_{10}$ (**1**)) is described. **1Li**₂ was reacted with chloride-bridged dimers $[\text{Cp}^* \text{RhCl}(\mu\text{-Cl})]_2$ ($\text{Cp}^* = \eta^5\text{-C}_5(\text{CH}_3)_5$), $[\text{Cp}' \text{RhCl}(\mu\text{-Cl})]_2$ ($\text{Cp}' = \eta^5\text{-1,3-}^i\text{Bu}_2\text{C}_5\text{H}_3$), $[\text{Cp}^* \text{IrCl}(\mu\text{-Cl})]_2$ and $[(p\text{-cymene})\text{RuCl}(\mu\text{-Cl})]_2$ to give half-sandwich binuclear complexes $[\text{Cp}^* \text{Rh}(\mu\text{-Cl})]_2(\text{Cab}^{\text{C,C}})$ (**2**), $[\text{Cp}' \text{Rh}(\mu\text{-Cl})]_2(\text{Cab}^{\text{C,C}})$ (**3**), $[\text{Cp}^* \text{Ir}(\mu\text{-Cl})]_2(\text{Cab}^{\text{C,C}})$ (**4**) and $[(p\text{-cymene})\text{Ru}(\mu\text{-Cl})]_2(\text{Cab}^{\text{C,C}})$ (**5**), respectively. Addition reactions of the ruthenium complex **5** with air gave $[(p\text{-cymene})_2\text{Ru}_2(\mu\text{-OH})(\mu\text{-Cl})](\text{Cab}^{\text{C,C}})$ (**6**), rhodium complex **2** with LiSPh gave $[\text{Cp}^* \text{Rh}(\mu\text{-SPh})]_2(\text{Cab}^{\text{C,C}})$ (**7**). The complexes were characterized by IR, NMR spectroscopy and elemental analysis. In addition, X-ray structure analysis were performed on complexes **2–7** where the potential C,C-chelate ligand was found to coordinate in a bidentate mode as a bridge.

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1. Introduction

In the past few years, interest in binuclear metal complexes has increased, due to the fact that the reactivity and properties of a metal may be strongly modified by the presence of another metallic center in close proximity. In fact, binuclear metal complexes are known to be active catalysts for a variety of transformations, in particular hydroformylation catalyzed by Rh_2 [**1**] and Ru_2 [**2**] complexes; alkene [**3**] and alkyne [**4**] hydrogenation catalyzed by Ir_2 complexes. One of the main reasons is the interest in the cooperative influence [**5**] of neighboring metal centers on catalytic reactions.

Recent reports of unusually stable functionalized *o*-carboranyl ligands C,N- [**6**], C,P- [**7**], N,S- [**8**], N,P- [**9**], S,S'- [**10**] and cyclopentadiene-substituted [**11**] as chelating ligands for metal complexes seem to imply that the chelation rigid conformation, and the *o*-carboranyl ligand backbone might be ideal for the stabilization of possible metal intermediates for organometallic reactions. In addition, a few examples of neutral σ -bonded transition-metal carbaborane complexes involving single carbon-transition metal bonds have been described [**12–16**]. However, to the best of our knowledge, there is no report on using non-functionalized $\text{Cab}^{\text{C,C}}$ ligand as chelating bridge for the late transition-metal complexes. In order to understand the chemistry of transition-metal complexes containing potential chelating $\text{Cab}^{\text{C,C}}$ ligand, herein we report the

synthesis of a series of binuclear transition-metal complexes containing $\text{Cab}^{\text{C,C}}$ as bridge.

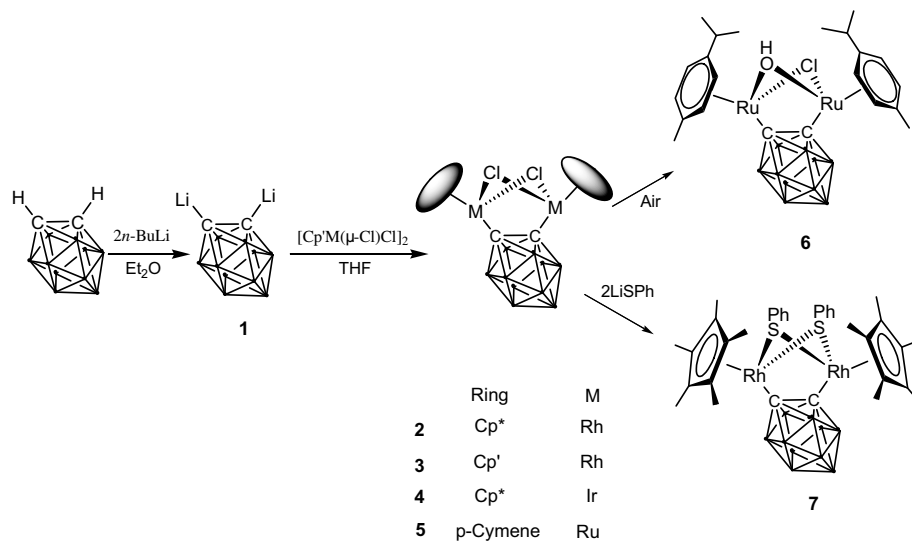
2. Results and discussion

2.1. Synthesis and characterization

Many of these transition-metal carbametallaboranes compounds are relatively unstable via cleavage of the metal–carbon bond. We attempt to use the voluminous Cp^* , Cp' or *p*-cymene ligands to shield one hemisphere of co-ordination shell of transition-metal to form half-sandwich structure in the protected space below the cyclopentadienyl ligands, benefiting building a bond between the metal and carbon atom via an electron donating moiety carbaborane.

The icosahedral carbaborane $1,2\text{-C}_2\text{B}_{10}\text{H}_{12}$ contains relatively positive C atoms and can be easily lithiated by *n*-BuLi at the carbon positions to give dilithialdicarbaborane. The reaction of the dimeric metal complexes and 1 equiv of the corresponding lithium compound $\text{Li}_2\text{Cab}^{\text{C,C}}$ (Scheme 1) results in the formation of the half-sandwich C,C-chelated metal complexes $[\text{Cp}^* \text{Rh}(\mu\text{-Cl})]_2(\text{Cab}^{\text{C,C}})$ (**2**), $[\text{Cp}' \text{Rh}(\mu\text{-Cl})]_2(\text{Cab}^{\text{C,C}})$ (**3**), $[\text{Cp}^* \text{Ir}(\mu\text{-Cl})]_2(\text{Cab}^{\text{C,C}})$ (**4**) and $[(p\text{-cymene})\text{Ru}(\mu\text{-Cl})]_2(\text{Cab}^{\text{C,C}})$ (**5**) as shown in Scheme 1. The complexes **2–5** have been isolated as related stable at room temperature, orange, transparent crystals. A detailed analysis of the spectroscopic data (¹H NMR, ¹¹B NMR and IR spectra) showed that the *ortho*-carborane ligand **1** is coordinated to the two metals through the carbon atoms. The half-sandwich complexes **2–5** are soluble in THF and CH_2Cl_2 , sparingly soluble in hexane. In addition,

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Scheme 1. Synthesis of complexes 2–7.

hydroxyl could easily replace one chloride in complex 5 to give complex 6 in excellent yields, and SPh took the place of two chloride atoms in complex 2 to give complex 7. Attempts to synthesis binuclear Ruthenium complex with two bridging OH groups was also carried out. However, when exposed to larger volume of air, complex 5 and 6 will decompose, instead of further hydroxyl replacement. Compounds 6 and 7 were fully characterized by NMR spectroscopy and elemental analysis.

The complexes are neutral diamagnetic and air sensitive in solution. The spectroscopic and analytical data of these complexes are in agreement with the formation of transition-metal complexes containing with both carborane ligands and Cp*/Cp'/p-cymene ligands. The IR spectra of the products in the solid state exhibit intense B–H stretching of carborane at about 2570 (vs) cm^{-1} . In the ^1H NMR spectra of complex 6, the OH resonance is not observed, according to the literature [17], presumably owing to an H/D exchange with the deuterated solvent.

Crystals suitable for X-ray crystallography of 2–5 were obtained by slow diffusion of hexane into dichloromethane solution of the corresponding complexes. The ORTEP are presented in Figs. 1–4, respectively. Crystallographic data and processing parameters are given in Table 1. The ORTEP diagrams of 2–5 (Figs. 1–4) show that the four complexes have similar structures. The dinuclear complexes bridged by one carborane chelate ligand and two chloride atoms. A coordinated Cp*, Cp' or the benzene ring completes the pseudo-octahedral coordination of the metal atoms. The five-membered M(1)–C–C–M(2)–Cl ring is folded with dihedral angle between the planes by [M(1), C(2), C(1), M(2)] and [M(1), Cl, M(2)] being 66.8, 71.8° (2); 65.6, 63.3° (3); 69.3, 67.8° (4), 68.1, 68.5° (5), respectively. The M–C distances of carboranes are 2.114, 2.097 Å for compound 2; 2.095, 2.097 Å for compound 3; 2.117, 2.100 Å for compound 4 and 2.085, 2.135 Å for compound 5, typical σ -bonds [18]. The long M–M distances ($d_{\text{Rh–Rh}} = 3.477$ (2), 3.486 Å (3), $d_{\text{Ir–Ir}} = 3.512$ Å (4), $d_{\text{Ru–Ru}} = 3.548$ Å (5)) confirmed the absence of bonding interactions between the two metals. Of particular interest is the long C–C distance in the *o*-carboranyl cage. This distance is longer (1.76 Å (2), 1.70 Å (3), 1.82 Å (4), 1.78 Å (5)) compared with 1.64–1.67 Å found in other ordered crystal structures of *o*-carborane derivatives [19]. The steric requirements of the bridging *o*-carboranyl ligand hold the two Cp*, Cp' or benzene rings so that they are not parallel but exhibit a dihedral angle of 151.7° (2), 166.6° (3), 143.2° (4), 157.8° (5). The bridging M–Cl bonds distances, average 2.343 Å (2), 2.437 Å

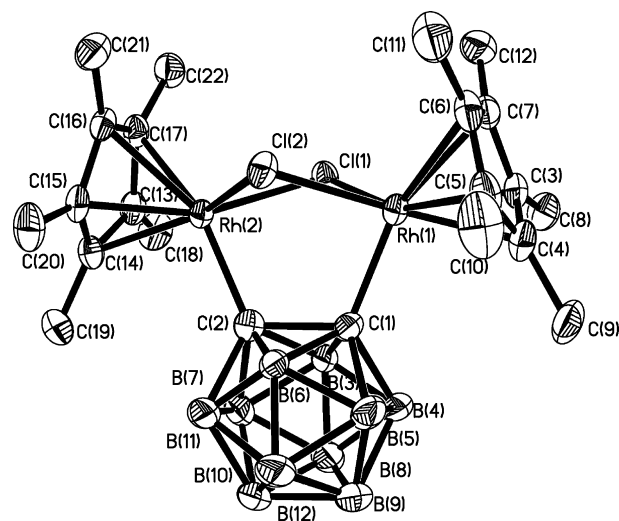


Fig. 1. Crystal structure of complex 2 showing 30% probability ellipsoids. The hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Rh(1)–Cl(1), 2.4371(14); Rh(1)–Cl(2), 2.4574(15); Rh(1)–C(1), 2.114(6); Rh(2)–C(2), 2.097(6); Rh(2)–Cl(1), 2.4338(14); Rh(2)–Cl(2), 2.4380(15); C(1)–C(2), 1.758(8); C(1)–Rh(1)–Cl(2), 87.63(15); C(2)–Rh(2)–Cl(1), 87.39(17); Cl(1)–Rh(2)–Cl(2), 82.15(5); Rh(2)–Cl(1)–Rh(1), 90.46(5); Rh(2)–Cl(2)–Rh(1), 89.89(5).

(3), 2.424 Å (4), 2.441 Å (5), fall in the range of M–Cl distances found in related M–chloride related compounds [20].

The crystallographic data for complex 6 and 7 are given in Table 1. The ORTEP diagrams of 6 and 7 (Figs. 5 and 6) showed that the two compounds have similar structures with compound 4 and 2, respectively, except that one chloride was replaced by hydroxyl group in compound 6 and both chloride were taken by SPh in compound 7. The M–M distance is $d_{\text{Ru–Ru}} = 3.415$ Å (6) and $d_{\text{Rh–Rh}} = 3.515$ Å (7), respectively, demonstrates that no metal–metal bond exists. In compound 6, the dihedral angles of [M(1), C(2), C(1), M(2)] with [M(1), Cl(1), M(2)] is 67.8°, and [M(1), C(2), C(1), M(2)] with [M(1), O(1), M(2)] is 65.6°, which are smaller than its precursor compound 4, probably as a result of the maximal space requirement for the hydroxyl. In compound 7, the dihedral angles between [M(1), C(1), C(2), M(2)] and [M(1), S, M(2)] are 61.6 and 71.1°, also smaller than the corresponding rhodium complex 2, which due to the steric hindrance of SPh group. The M–C distances

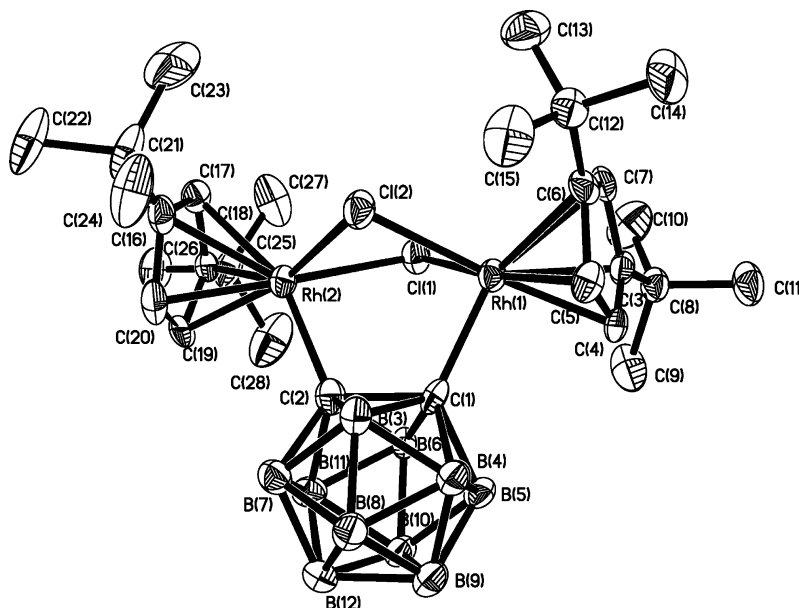


Fig. 2. Crystal structure of complex **3** showing 30% probability ellipsoids. The hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Rh(1)–Cl(2) 2.4153(18), Rh(1)–Cl(1) 2.4536(18), Rh(1)–C(1) 2.095(7), Rh(2)–C(2) 2.097(7), Rh(2)–Cl(2) 2.4071(18), Rh(2)–Cl(1) 2.4733(17), C(1)–C(2) 1.702(8), C(1)–Rh(1)–Cl(1) 87.87(18), C(1)–Rh(1)–Cl(2) 89.04(16), Cl(2)–Rh(1)–Cl(1) 78.30(6), C(2)–Rh(2)–Cl(2) 87.90(17), C(2)–Rh(2)–Cl(1) 87.88(17), Rh(1)–Cl(1)–Rh(2) 90.06(6), Rh(2)–Cl(2)–Rh(1) 92.57(6).

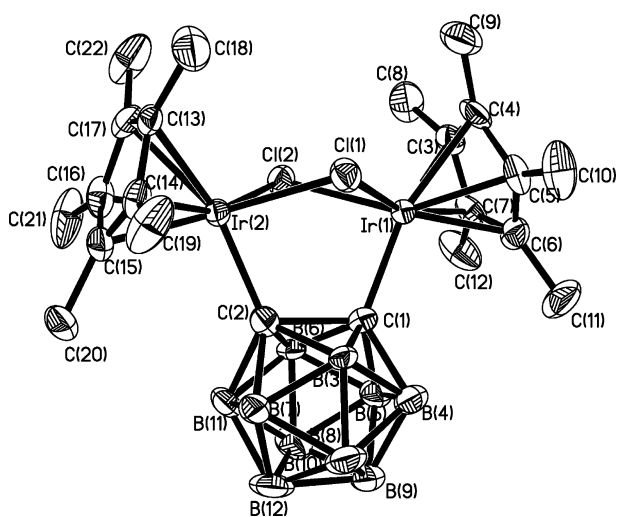


Fig. 3. Crystal structure of complex **4** showing 30% probability ellipsoids. The hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ir(1)–C(1) 2.117(8), Ir(1)–Cl(1) 2.417(2), Ir(1)–Cl(2) 2.435(2), Ir(2)–C(2) 2.100(8), Ir(2)–Cl(2) 2.418(2), Ir(2)–Cl(1) 2.429(2), C(1)–C(2) 1.823(11), C(1)–Ir(1)–Cl(1) 85.8(2), C(1)–Ir(1)–Cl(2) 87.9(2), Cl(1)–Ir(1)–Cl(2) 79.85(7), C(2)–Ir(2)–Cl(2) 86.2(2), C(2)–Ir(2)–Cl(1) 86.5(2), Ir(1)–Cl(1)–Ir(2) 92.87(8), Ir(2)–Cl(2)–Ir(1) 92.73(7).

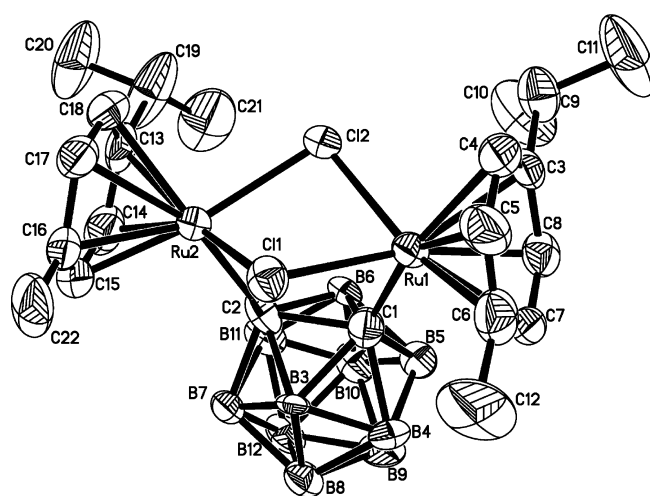


Fig. 4. Crystal structure of complex **5** showing 30% probability ellipsoids. The hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ru(1)–C(1) 2.085(11), Ru(1)–Cl(1) 2.434(3), Ru(1)–Cl(2) 2.443(3), Ru(2)–C(2) 2.135(10), Ru(2)–Cl(2) 2.430(3), Ru(2)–Cl(1) 2.457(3), C(1)–C(2) 1.782(13), C(1)–Ru(1)–Cl(1) 85.4(3), C(1)–Ru(1)–Cl(2) 86.2(3), Cl(1)–Ru(1)–Cl(2) 79.42(9), C(2)–Ru(2)–Cl(2) 85.1(3), C(2)–Ru(2)–Cl(1) 86.4(3), Cl(2)–Ru(2)–Cl(1) 79.23(9), Ru(1)–Cl(1)–Ru(2) 92.99(9), Ru(2)–Cl(2)–Ru(1) 93.45(8).

are 2.124, 2.130 Å for compound **6**; 2.107, 2.116 Å for compound **7**, also typical σ -bonds. C–C distance of *o*-carboranyl is 1.692 and 1.746 Å, respectively, which are shorter than their corresponding compounds.

In summary, we have synthesized a series of binuclear half-sandwich iridium, rhodium and ruthenium complexes containing Cab^C as bidentate bridging ligand. A combination of X-ray crystallographic and spectroscopic studies confirms the nature of these half-sandwich complexes. For the first time, non-functionalized *o*-carborane can be used as a bridge to join the two metals together to give half-sandwich complexes.

3. Experimental section

3.1. General procedure

All manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques; all solvents were dried and deoxygenated before use, except the synthesis of compound **6**. The solvents diethyl ether, toluene, and *n*-hexane were refluxed and distilled over sodium/benzophenone ketyl under nitrogen prior to use. The starting materials, [Cp^{*}RhCl₂]₂ [20], [Cp^{*}RhCl₂]₂ [20], [Cp^{*}RhCl₂]₂ [21] and [(*p*-cymene)RuCl₂]₂ [22] were prepared by slightly modified literature procedures. ¹H and ¹¹B NMR spectra

Table 1
Summary of crystallographic data for **2**, **3**, **4**, **5**, **6**, **7**

	2	3	4	5	6	7
Chemical formula	C ₂₂ H ₄₀ B ₁₀ Cl ₂ Rh ₂	C ₂₈ H ₅₂ B ₁₀ Cl ₂ Rh ₂	C ₂₂ H ₄₀ B ₁₀ Cl ₂ Ir ₂	C ₂₂ H ₃₈ B ₁₀ Cl ₂ Ru ₂	C ₂₃ H ₄₁ B ₁₀ Cl ₃ ORu ₂	C _{24.50} H ₅₁ B ₁₀ Cl ₁ Rh ₂ S ₂
Formula weight	689.36	773.52	867.94	683.66	750.15	759.14
Temperature (K)	293(2)	293(2)	293(2)	298(2)	298(2) K	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system, space group	Monoclinic, <i>P2(1)/n</i>	Triclinic, <i>P</i> – 1	Monoclinic, <i>P2(1)/n</i>	Monoclinic, <i>P2(1)/n</i>	Monoclinic, <i>P2(1)/c</i>	Triclinic, <i>P</i> – 1
<i>a</i> (Å)	11.002(2)	10.427(3)	11.367(3)	9.857(2)	11.795(3)	11.742(4)
<i>b</i> (Å)	14.369(3)	12.294(4)	14.300(4)	18.439(5)	14.060(4)	11.996(4)
<i>c</i> (Å)	18.844(4)	15.606(4)	18.440(6)	16.677(4)	20.253(5)	16.800(5)
α (°)	90	107.974(5)	90	90	90	86.408(4)
β (°)	100.426(4)	92.548(5)	94.433(4)	103.038(5)	106.833(3)	71.221(4)
γ (°)	90	107.442(5)	90	90	90	63.243(4)
Volume (Å ³)	2929.8(11)	1794.6(9)	2988.4(16)	2953.0(13)	3214.8(14)	1991.0(10)
<i>Z</i>	4	2	4	4	4	2
<i>D</i> _{calc} (mg/m ³)	1.563	1.431	1.929	1.538	1.550	1.490
Absorption coefficient (mm ⁻¹)	1.322	1.087	9.089	1.216	1.207	1.266
<i>F</i> (000)	1384	788	1640	1368	1504	774
Crystal size	0.10 × 0.05 × 0.05	0.10 × 0.08 × 0.05	0.10 × 0.10 × 0.08	0.05 × 0.05 × 0.02	0.15 × 0.15 × 0.05	0.15 × 0.15 × 0.10
Theta range for data collection (°)	1.79–26.01	1.39–25.01	1.80–26.00	1.67–26.01	1.79–25.01	1.29–26.01
Reflections collected	13207	7645	13517	13446	13230	9026
Independent reflections [<i>R</i> _{int}]	5760 [0.1089]	6255 [0.0385]	5871 [0.0481]	5803 [0.1148]	5665 [0.0178]	7590 [0.0176]
Completeness to theta (°)	26.01 (99.7%)	25.01 (98.8%)	26.00 (99.9%)	26.01 (99.8%)	25.01 (99.9%)	26.01 (96.9%)
Max. and min. transmission	0.9369 and 0.8792	0.9476 and 0.8990	0.5301 and 0.4634	0.9761 and 0.9417	0.9421 and 0.8397	0.9053 and 0.8627
Data/restraints/parameters	5760/0/345	6255/0/389	5871/0/335	5803/1/341	5665/7/372	7590/0/480
Goodness-of-fit on <i>F</i> ²	0.948	0.750	0.980	0.762	1.032	1.001
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0639, <i>wR</i> ₂ = 0.1116	<i>R</i> ₁ = 0.0492, <i>wR</i> ₂ = 0.0740	<i>R</i> ₁ = 0.0382, <i>wR</i> ₂ = 0.0827	<i>R</i> ₁ = 0.0612, <i>wR</i> ₂ = 0.1130	<i>R</i> ₁ = 0.0309, <i>wR</i> ₂ = 0.0831	<i>R</i> ₁ = 0.0320, <i>wR</i> ₂ = 0.0723
Largest difference peak and hole (e/Å ³)	0.960 and –0.548	0.672 and –0.578	1.386 and –2.176	0.915 and –0.406	0.899 and –0.495	0.649 and –0.480

$$R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|, \quad wR_2 = [\sum (|F_o|^2 - |F_c|^2)^2 / \sum (F_o^2)]^{1/2}.$$

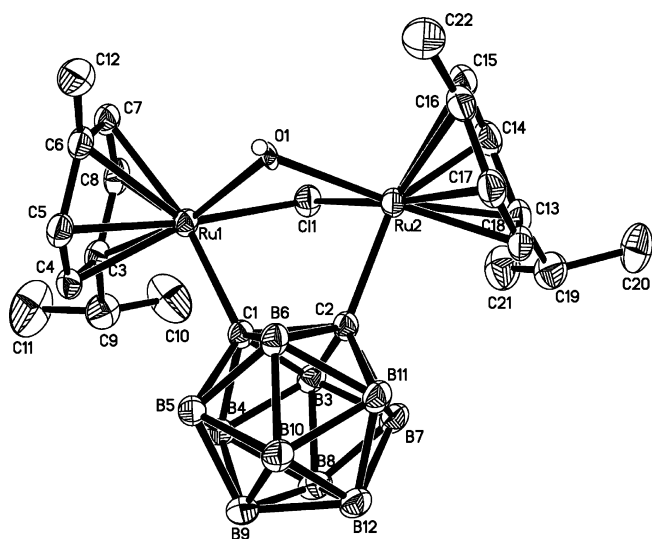


Fig. 5. Crystal structure of complex **6** showing 30% probability ellipsoids. The hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ru(1)–C(1) 2.124(3), Ru(1)–O(1) 2.202(2), Ru(1)–Cl(1) 2.4455(10), Ru(1)–Ru(2) 3.4153(7), Ru(2)–C(2) 2.130(3), Ru(2)–O(1) 2.203(2), Ru(2)–Cl(1) 2.4442(11), O(1)–H(1) 0.795(10), C(1)–C(2) 1.692(4), C(1)–Ru(1)–O(1) 85.48(10), C(1)–Ru(1)–Cl(1) 88.08(9), O(1)–Ru(1)–Cl(1) 76.63(7), C(1)–Ru(1)–Ru(2) 66.05(9), O(1)–Ru(1)–Ru(2) 39.18(6), Cl(1)–Ru(1)–Ru(2) 45.68(2), O(1)–Ru(2)–Cl(1) 76.63(7), C(2)–Ru(2)–Ru(1) 66.14(9), O(1)–Ru(2)–Ru(1) 39.14(6), Cl(1)–Ru(2)–Ru(1) 45.71(2), Ru(2)–Cl(1)–Ru(1) 88.61(3), Ru(1)–O(1)–Ru(2) 101.68(11), Ru(1)–O(1)–H(1) 124(3), Ru(2)–O(1)–H(1) 120(3).

were recorded on a VAVCE-DMX 500 Spectrometer in CDCl₃. Elemental analysis was performed on an Elementar vario EL III Analyzer. IR (KBr) spectra were recorded on the Nicolet FT-IR spectrophotometer.

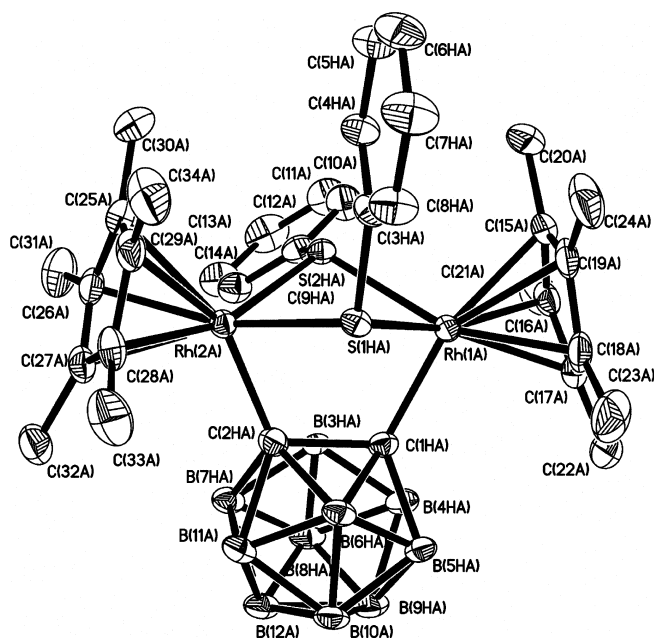


Fig. 6. Crystal structure of complex **7** showing 30% probability ellipsoids. The hydrogen atoms and solvent CH₂Cl₂ are omitted for clarity. Selected bond lengths (Å) and angles (°): Rh(1)–C(1) 2.107(3), Rh(1)–S(1) 2.3866(11), Rh(1)–S(2) 2.4527(11), Rh(2)–C(2) 2.116(4), Rh(2)–S(1) 2.3856(11), Rh(2)–S(2) 2.3934(10), C(1)–C(2) 1.746(5), C(1)–Rh(1)–S(1) 83.78(10), C(1)–Rh(1)–S(2) 90.02(9), S(1)–Rh(1)–S(2) 76.82(3), C(2)–Rh(2)–S(1) 83.59(10), C(2)–Rh(2)–S(2) 89.22(10), S(1)–Rh(2)–S(2) 77.98(3), Rh(2)–S(1)–Rh(1) 94.88(3), Rh(2)–S(2)–Rh(1) 92.99(3).

3.2. Synthesis of [Cp**Rh*(μ-Cl)]₂[C₂(B₁₀H₁₀)] (2)

To a stirred solution of *ortho*-carborane (75 mg, 0.5 mmol) in 20 mL Et₂O, which was cooled to –78 °C, was added 1.6 M *n*-BuLi

(0.63 mL, 1 mmol) via a syringe. The resulting white suspension was stirred at room temperature for 1 h and then transferred through a cannula to a suspension of $[\text{Cp}^*\text{RhCl}_2]_2$ (0.31 g, 0.50 mmol) in THF (20 mL). After being stirred for 6 h, the solvent was removed under vacuum, and components of the residue were separated by column chromatography on silica. The component was eluted with $\text{CH}_2\text{Cl}_2/\text{hexane}$ (1:6) and recrystallized from $\text{CH}_2\text{Cl}_2/\text{hexane}$ to give 234 mg (68%) orange crystals. IR (KBr disk): $\nu = 2955, 2921, 2852 \text{ cm}^{-1}$ (C–H); $\nu = 2566 \text{ cm}^{-1}$ (B–H). ^1H NMR (500 MHz, CDCl_3 , δ/ppm): 1.55 (s, 30H, CH_3); ^{11}B NMR (160 MHz, CDCl_3 , δ/ppm): –2.45, –3.83, –4.25, –8.69, –13.01, –14.88. Elemental Anal. Calc. for $\text{C}_{22}\text{H}_{40}\text{B}_{10}\text{Cl}_2\text{Rh}_2$: C, 38.33; H, 5.85. Found: C, 38.57; H, 5.89%.

3.3. Synthesis of $[(\eta^5\text{-}1,3\text{-}^t\text{Bu}_2\text{C}_5\text{H}_3)\text{Rh}(\mu\text{-Cl})_2][\text{C}_2(\text{B}_{10}\text{H}_{10})]$ (3)

To a stirred solution of *ortho*-carborane (75 mg, 0.5 mmol) in 20 mL Et_2O , which was cooled to -78°C , was added 1.6 M *n*-BuLi (0.63 mL, 1 mmol) via a syringe. The resulting white suspension was stirred at room temperature for 1 h and then transferred through a cannula to a suspension of $[(\eta^5\text{-}1,3\text{-}^t\text{Bu}_2\text{C}_5\text{H}_3)\text{RhCl}_2]$ (0.35 g, 0.50 mmol) in THF (20 mL). After being stirred for 6 h, the solvent was then evaporated to dryness under vacuum, and components of the residue were separated by column chromatography on silica. The component in the first band was eluted with $\text{CH}_2\text{Cl}_2/\text{hexane}$ (1:3) and recrystallized from hexane to afford 271 mg (70%) yellow crystals of 3. IR (KBr disk): $\nu = 2962, 2908, 2872 \text{ cm}^{-1}$ (C–H), $\nu = 2561 \text{ cm}^{-1}$ (B–H). ^1H NMR (500 MHz, CDCl_3 , δ/ppm): 1.17 (s, 18H, *t*-Bu), 1.25 (s, 18H, *t*-Bu), 4.52 (s, 1H, Cp'), 4.80 (s, 1H, Cp'), 5.06 (s, 2H, Cp'), 5.21 (s, 2H, Cp'); ^{11}B NMR (160 MHz, CDCl_3 , δ/ppm): –2.19, –3.12, –4.52, –9.98, –13.42, –15.61. Elemental Anal. Calc. for $\text{C}_{28}\text{H}_{52}\text{B}_{10}\text{Cl}_2\text{Rh}_2$: C, 43.48; H, 6.78. Found: C, 43.30; H, 6.70%.

3.4. Synthesis of $[\text{Cp}^*\text{Ir}(\mu\text{-Cl})_2][\text{C}_2(\text{B}_{10}\text{H}_{10})]$ (4)

To a stirred solution of *ortho*-carborane (75 mg, 0.5 mmol) in 20 mL Et_2O , which was cooled to -78°C , was added 1.6 M *n*-BuLi (0.63 mL, 1 mmol) via a syringe. The resulting white suspension was stirred at room temperature for 1 h and then transferred through a cannula to a suspension of $[\text{Cp}^*\text{IrCl}_2]_2$ (400 mg, 0.5 mmol) in THF (20 mL). After being stirred for 6 h, the solvent was removed under vacuum, and components of the residue were separated by column chromatography on silica. The component was eluted with $\text{CH}_2\text{Cl}_2/\text{hexane}$ (1:6) and recrystallized from $\text{CH}_2\text{Cl}_2/\text{hexane}$ to give 269 mg (62%). ^1H NMR (500 MHz, CDCl_3 , δ/ppm): 1.68 (s, 30H, CH_3); ^{11}B NMR (160 MHz, CDCl_3 , δ/ppm): –7.72, –8.54, –9.41, –10.07, –11.03, –14.11. IR (KBr disk): $\nu = 2963, 2915 \text{ cm}^{-1}$ (C–H), $\nu = 2564 \text{ cm}^{-1}$ (B–H). Elemental Anal. Calc. for $\text{C}_{22}\text{H}_{40}\text{B}_{10}\text{Cl}_2\text{Ir}_2$: C, 30.44; H, 4.64. Found: C, 30.54; H, 4.66%.

3.5. Synthesis of $\{(p\text{-cymene})\text{Ru}\}_2(\mu\text{-Cl})_2[\text{C}_2(\text{B}_{10}\text{H}_{10})]$ (5)

To a stirred solution of *ortho*-carborane (28 mg, 0.2 mmol) in 20 mL Et_2O , which was cooled to -78°C , was added 1.6 M *n*-BuLi (0.25 mL, 0.4 mmol) via a syringe. The resulting white suspension was stirred at room temperature for 1 h and then transferred through a cannula to a suspension of $[(p\text{-cymene})\text{RuCl}_2]_2$ (122 mg, 0.2 mmol) in THF (20 mL). After being stirred for 16 h, the solvent was removed under vacuum, and components of the residue were separated by column chromatography on silica. The component was eluted with CH_2Cl_2 and recrystallized from $\text{CH}_2\text{Cl}_2/\text{hexane}$ to give 103 mg (75%). IR (KBr disk): $\nu = 3069 \text{ cm}^{-1}$ (C–H, C_6H_4); $\nu = 2962, 2924, 2871 \text{ cm}^{-1}$ (C–H, CH_3); $\nu = 2559 \text{ cm}^{-1}$ (B–H); $\nu = 1629, 1535, 1466, 1383 \text{ cm}^{-1}$ (C=C). ^1H

NMR (500 MHz, CDCl_3 , δ/ppm): 5.66, 5.56, 5.32, 4.87 (m, 8H, C_6H_4); 2.99 (m, 2H, CH); 2.30 (s, 6H, CH_3); 1.43 (d, 12H, CH_3). ^{11}B NMR (160 MHz, CDCl_3 , δ/ppm): –2.12, –3.06, –5.88, –8.81, –12.13, –14.38. Elemental Anal. Calc. for $\text{C}_{22}\text{H}_{38}\text{B}_{10}\text{Cl}_2\text{Ru}_2$: C, 38.65; H, 5.60. Found: C, 38.71; H, 5.67%.

3.6. Synthesis of $\{(p\text{-cymene})\text{Ru}\}_2(\mu\text{-Cl})(\mu\text{-OH})[\text{C}_2(\text{B}_{10}\text{H}_{10})]$ (6)

In the CH_2Cl_2 (5 mL) solution of **5** (34 mg, 0.05 mmol) was injected some air, then kept stirring over night, removed the solvent, and recrystallization through $\text{CH}_2\text{Cl}_2/\text{hexane}$ (3:1), complex **6** (30 mg, 90%) was obtained as red crystals. IR (KBr disk): $\nu = 3057 \text{ cm}^{-1}$ (C–H, C_6H_4); $\nu = 2963, 2868, 2801 \text{ cm}^{-1}$ (C–H, CH_3); $\nu = 2568 \text{ cm}^{-1}$ (B–H); $\nu = 1633, 1560, 1466, 1382 \text{ cm}^{-1}$ (C=C). ^1H NMR (500 MHz, CDCl_3 , δ/ppm): 5.33, 5.29, 5.14, 4.97 (m, 8H, C_6H_4); 2.51 (m, 2H, CH); 2.05 (s, 6H, CH_3); 1.38 (d, 12H, CH_3). ^{13}C NMR (125 MHz, CDCl_3 , δ/ppm): 101.5 (C-carborane); 82.7, 87.0 (C_6H_4); 29.7 (CH), 22.2 (CH_3), 18.7 (CH_3). ^{11}B NMR (160 MHz, CDCl_3 , δ/ppm): –6.73, –7.85, –8.81, –10.64. Elemental Anal. Calc. for $\text{C}_{22}\text{H}_{39}\text{B}_{10}\text{ClORu}_2$: C, 39.72; H, 5.91. Found: C, 39.89; H, 6.00%.

3.7. Synthesis of $[\text{Cp}^*\text{Rh}(\mu\text{-SPh})_2][\text{C}_2(\text{B}_{10}\text{H}_{10})]$ (7)

A 1.60 M solution of *n*-BuLi in *n*-hexane (0.32 mL, 0.50 mmol) was added dropwise to a solution of HSPH (92 mg, 0.50 mmol) in ether (20 mL) with stirring at 0°C . The mixture was allowed to warm to room temperature and stirred for 30 min. A solution of **2** (172 mg, 0.25 mmol) in THF (10 mL) was slowly added with stirring. The reaction mixture kept at room temperature to stir for 4 h. The solvent was then evaporated to dryness under vacuum, and components of the residue were separated by column chromatography on silica. The component was eluted with $\text{CH}_2\text{Cl}_2/\text{hexane}$ (1:1) and recrystallized from $\text{CH}_2\text{Cl}_2/\text{hexane}$ at -18°C gave orange crystals of **7** (140 mg, 78%). Elemental Anal. Calc. for $\text{C}_{24.5}\text{H}_{51}\text{B}_{10}\text{Rh}_2\text{ClS}_2$: C, 38.76; H, 6.77. Found: C, 38.98; H, 6.84%. ^1H NMR (500 MHz, CDCl_3 , δ/ppm): 1.42 (s, 15H, CH_3), 5.30 (s, 1H, CH_2Cl_2), 7.14 (m, 4H, SPh), 7.24 (m, 4H, SPh), 7.31 (m, 2H, SPh); ^{11}B NMR (160 MHz, CDCl_3 , δ/ppm): –3.52, –7.63, –11.54; IR (KBr disk): $\nu = 3060, 2960, 2923, 2855 \text{ cm}^{-1}$ (C–H), $\nu = 2543 \text{ cm}^{-1}$ (B–H), $\nu = 1668, 1642, 1580 \text{ cm}^{-1}$ (C=C/Ph).

X-ray Data Collection Structure Determination, and Refinement. Suitable single crystals of complex **2–7** were sealed under nitrogen in Lindemann glass capillaries for X-ray structural analysis. Diffraction data were collected on a Bruker SMART Apex CCD diffractometer using graphite-monochromated Mo $\text{K}\alpha$ ($\lambda = 0.71073 \text{ \AA}$) radiation. During the intensity data collection, no significant decay was observed. The intensities were corrected for Lorentz-polarization effects and empirical absorption with the SADABS program [23]. The structures were solved by direct methods using the SHELXL-97 program [24]. All non-hydrogen atoms were found from the difference Fourier syntheses. The H atoms were included in calculated positions with isotropic thermal parameters related to those of the supporting carbon atoms but were not included in the refinement. All calculations were performed using the Bruker Smart program. A summary of the crystallographic data and selected experimental information are given in Table 1.

4. Supplementary material

CCDC 629757, 629758, 629759, 629760, 629761 and 629762 contains the supplementary crystallographic data for **2**, **3**, **4**, **5**, **6** and **7**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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