



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

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ARTICLE INFO

Article history:

Received 11 May 2008

Received in revised form 21 June 2008

Accepted 24 June 2008

Available online 28 June 2008

Keywords:

Carborane

Iridium

Rhodium

Binuclear complexes

Molecular structures

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.

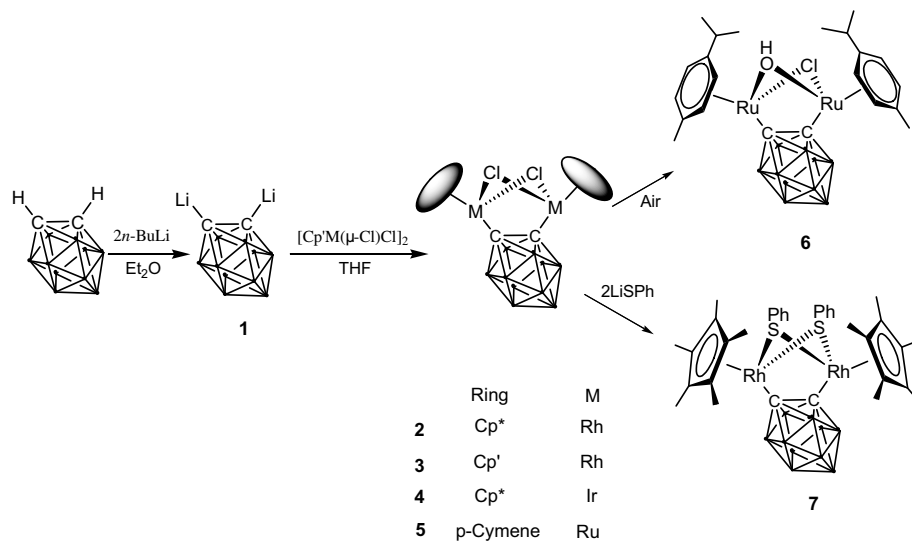
2. Results and discussion

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 carborane $1,2\text{-C}_2\text{B}_{10}\text{H}_{12}$ 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

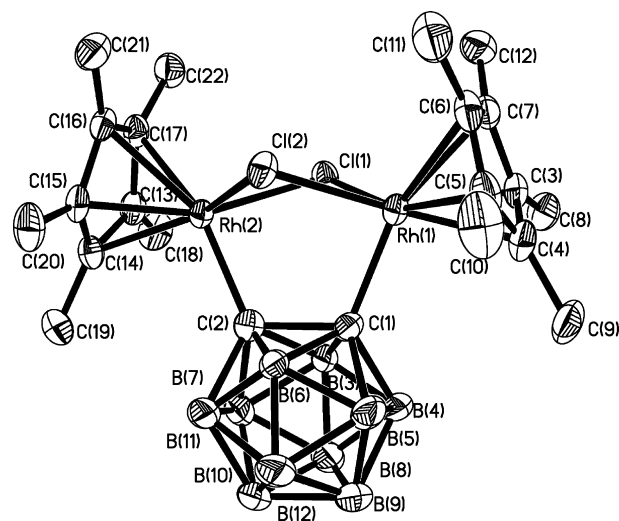


Fig. 1. Crystal structure of complex 2 showing 30% probability ellipsoids. The hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Rh(1)–Cl(1), 2.4371(14); Rh(1)–Cl(2), 2.4574(15); Rh(1)–C(1), 2.114(6); Rh(2)–C(2), 2.097(6); Rh(2)–Cl(1), 2.4338(14); Rh(2)–Cl(2), 2.4380(15);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

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