Novel Group 9 Metal Complexes Containing an *S,S′*-Chelating *o*-Carboranyl Ligand System: Synthesis, Crystal Structures, and Electrochemical Properties of Dinuclear [{(cod)M}$_2$(*S,S′*-$S_2C_2B_{10}H_{10}$)] (cod = 1,5-cyclooctadiene; M = Rh or Ir)] and Mononuclear Cp*CoI[*S,S′*-S(S=PMe_2)$C_2B_{10}H_{10}$] Metal Complexes

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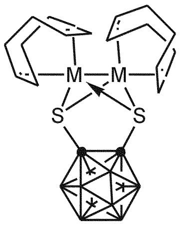
The synthesis of novel group 9 metal complexes containing the *S,S′*-chelate ligands, $Li_2S_2C_2B_{10}H_{10}$ (**2a**) and LiS(S=PMe_2)$C_2B_{10}H_{10}$ (**2b**), is described. Two new dinuclear complexes of the type [{(cod)M}$_2$(*S,S′*-$S_2C_2B_{10}H_{10}$)] (cod = 1,5-cyclooctadiene; M = Rh (**3a**), or Ir (**3b**)) were synthesized by the reaction of chloride-bridged dimers [M(μ-Cl)(cod)]$_2$ with one molar equivalent of the corresponding dilithium dithiolato ligand $Li_2S_2C_2B_{10}H_{10}$ (**2a**). X-ray crystal structure analysis of **3a** revealed a dinuclear structure in which each (cod)Rh unit is attached to a distinct sulfur atom of a 1,2-dithio-*o*-carboranyl ligand (**2a**). Additionally, the electrochemical properties of **3a** and **3b** were investigated by cyclic voltammetry. In an analogous manner, reaction of the lithium dithiolato ligand LiS(S=PMe_2)$C_2B_{10}H_{10}$ (**2b**) with Cp*CoI_2(CO) produced a mononuclear dithiolato complex, [Cp*CoI{(*S,S′*-S(S=PMe_2)$C_2B_{10}H_{10}$)}] (**4**), which was characterized by single-crystal X-ray analysis.

Key Words : Group 9 metal complexes, *S,S′*-Chelate ligands, Dinuclear metal complexes, *o*-Carboranyl ligands

Introduction

Interest in dinuclear metal complexes has increased in recent years 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. Among the dinuclear metal complexes synthesized to date, those in which the two metal atoms are held in close proximity by sulfur-containing bridging ligands (*e.g.*, thiolate,[1] aminothiolate,[2] and phosphinothiolate[3]) have received particular attention.[4] Recent reports of unusually stable *P,S*-,[5] *C,N*-,[6] *C,P*-,[7] *N,P*-,[8] *N,S*-,[9] and *S,S′*-chelating[10] *o*-carboranyl metal complexes suggest that the chelation characteristics, rigid conformation, and *o*-carboranyl backbone of dithiolates may make these ligands particularly well suited to the stabilization of dinuclear metal intermediates in organometallic reactions.[11]

Our research is currently focused on dinuclear complexes of the type [{(cod)M}$_2$(*S,S′*-$S_2C_2B_{10}H_{10}$)] (cod = 1,5-cyclooctadiene; M = Rh (**3a**) or Ir (**3b**)) with an *S,S′*-chelating dithiolato ligand such as *S,S′*-$S_2C_2B_{10}H_{10}$ (**2a**), as shown in Chart 1. The ligand **2** was chosen on account of its coordinating sulfur functions that can be readily utilized as bridging ligands by incoming metal fragments to form dinuclear metal complexes.



[{(cod)M}$_2$(*S,S′*-$S_2C_2B_{10}H_{10}$)] (M = Rh (**3a**); Ir (**3b**))

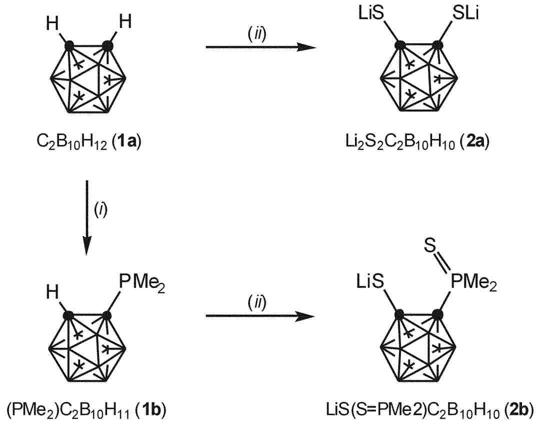
Chart 1

To widen our knowledge of dinuclear metal complexes containing sulfur-containing bridging ligands, in the present study we extended the study of these complexes through a systematic investigation of the complexes formed by rhodium(I) and iridium(I) with the previously unexplored *S,S′*-chelate ligands **2**. The structures of the dinuclear rhodium and iridium complexes of general formula [{(cod)M}$_2$(*S,S′*-$S_2C_2B_{10}H_{10}$)] (cod = 1,5-cyclooctadiene; M = Rh (**3a**), or Ir (**3b**)) were determined by X-ray crystallography and cyclic voltammetry.

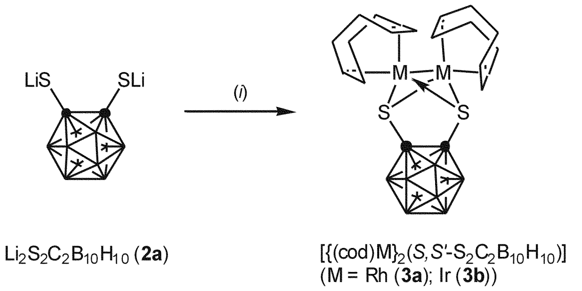
Results and Discussion

Ligand Synthesis. Reaction of the known *o*-carborane reagents *o*-carborane $C_2B_{10}H_{12}$ (**1a**) and (dimethylphosphino)-*o*-carborane (PMe_2)$C_2B_{10}H_{11}$ (**1b**) with 2 and 1 equiv of Bu^{n}Li, followed by the addition of sulfur in THF at low temperature (Scheme 1), results in virtually quantitative formation of the corresponding dilithium dithiolato ligand $Li_2S_2C_2B_{10}H_{10}$ (**2a**) and monolithium dithiolato ligand LiS(S=PMe_2)$C_2B_{10}H_{10}$ (**2b**), respectively.

The dithiolato ligands **2** are readily soluble in Et_2O and THF and are somewhat less soluble in benzene and toluene. The pure THF-free lithium dithiolates **2** are yellowish, off-



Scheme 1. Synthesis of the *S,S'*-chelating ligand **2**. [a]Legend: (i) (a) $LiBu^n$, THF, -78 °C; (b) PMe_2Cl, THF, 25 °C; (ii) (a) $LiBu^n$, THF, -78 °C; (b) S_8, THF, 25 °C.



Scheme 2. Synthesis of the *S,S'*-chelathing dinuclear metal(cod) complexes. [a]Legend: (i) $[M(\mu\text{-}Cl)(cod)]_2$(M = Rh, Ir), THF, 25°C.

white powders which, although slightly hygroscopic, can be handled safely in air for several minutes. Solutions of **2** slowly decompose upon exposure to air.

Reaction of $Li_2S_2C_2B_{10}H_{10}$(2a) with $[M(\mu\text{-}Cl)(cod)]_2$ (M = Rh, Ir; cod = cycloocta-1,5-diene). *S,S'*-chelated dithiolato dinuclear metal complexes, $[\{(cod)M\}_2(S,S'\text{-}S_2C_2B_{10}H_{10})]$ (**3**), were prepared by reacting the dimeric metal complexes with one molar equivalent of the corresponding dilithium dithiolate **2a** (Scheme 2).

Column chromatography was used to isolate the pure products, which ranged in color from yellow to orange. Typically, the yields of **3** were on the order of 79%-86%. Elemental analysis showed that the air-stable complexes **3** have compositions corresponding to a 2 : 1 metal complex of the M(cod) fragment and dithiolato ligand **2a**. Complexes **3** were further characterized by IR and NMR (^{1}H and ^{13}C) spectroscopy. The ^{1}H NMR spectra of **3** showed signals corresponding to the methylene protons (δ 2.2-3.0) and olefinic protons (δ 5.0-5.3) of the ligand cyclooctadiene. The IR spectra of **3** exhibited one ν (C=C) stretching band at about 1437-1439 cm^{-1} and an intense B-H stretch at about 2560-2606 cm^{-1}. The above spectral data suggest that the *S,S'*-chelates **3** have the structure shown in Scheme 2.

Formation of Dinuclear Group 9 Metal Complexes $[\{(cod)M\}_2(S,S'\text{-}S_2C_2B_{10}H_{10})]$ (3). X-ray crystallographic (vide infra) and elemental analyses indicate that the product is an unprecedented bimetallic species, [{(cod)Rh}$_2$(*S,S'*-

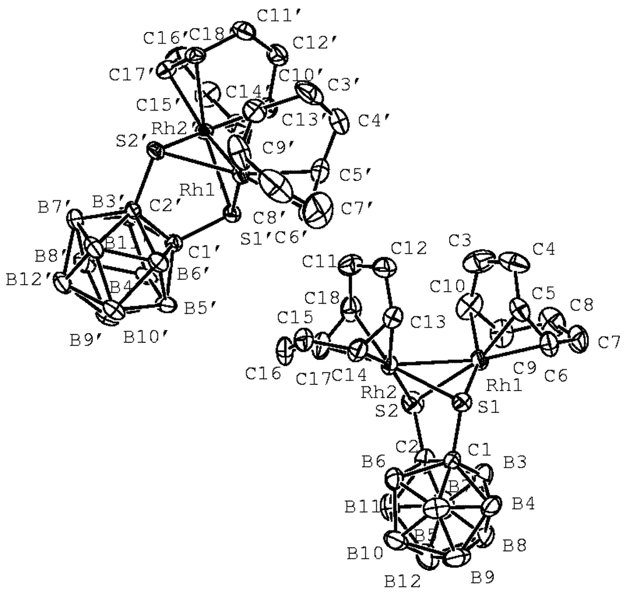


Figure 1. Molecular structure of **3a** with atom labeling; ellipsoids show 30% probability levels, the unlabeled atoms are carbon atoms, and hydrogen atoms have been omitted for clarity. The asymmetric unit contains two independent molecules with almost identical structures.

Table 1. X-ray Crystallographic Data and Processing Parameters for Compounds **3a** and **4**

	3a	**4**
Formula	$C_{36}H_{68}B_{20}S_4Rh_4$	$C_{14}H_{31}B_{10}PS_2ICo$
Fw	1256.98	588.41
Cryst class	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
Z	2	4
Cell constants		
a, Å	11.793(1)	11.9948(9)
b, Å	13.8105(7)	14.4331(9)
c, Å	17.8692(9)	14.8906(8)
α, deg	95.873(4)	
β, deg	102.462(6)	101. 729(5)
γ, deg	113.662(8)	
V, Å^3	2544.1(3)	2524.1(3)
μ, mm^{-1}	1.468	2.133
Cryst size, mm	0.55 × 0.54 × 0.40	0.37 × 0.32 × 0.12
d_{calcd}, g/cm^3	1.641	1.548
F(000)	1256	1168
Radiation	Mo Kα (λ = 0.7107)	Mo Kα (λ = 0.7107)
θ range, deg	1.19 to 25.97	1.73 to 25.97
h, k, l *collected*	$-4 \le h \le 14$, $7 \le k \le 15$, $22 \le l \le 21$	$0 \le h \le 14$, $0 \le k \le 17$, $18 \le l \le 4$
No. of rflns measd	10539	3710
No. of unique rflns	9986	3653
No. of rflns used in refinement (I > 2σ(I))	7848	2172
No. of params	597	279
$R_1{}^a$ (I > 2σ(I))	0.0608	0.0726
$wR_2{}^a$ (all data)	0.1595	0.1865
GOF	1.045	1.093

[a]$R_1 = \Sigma ||F_o|-|F_c||$(based on reflections with $F_o^2 > 2\sigma F^2$); [b]$wR_2 = [\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$; $w = 1/[\sigma^2(F_o^2)+(0.095P)^2]$; $P = [\max(F_o^2, 0)+2F_c^2]/3$(also with $F_o^2 > 2\sigma F^2$)

Table 2. Selected Interatomic Distances (Å) for Compounds **3a** and **4**

Compound **3a** (i)									
Rh(1)-C(5)	2.110(9)	Rh(1)-C(10)	2.116(1)	Rh(1)-S(2)	2.409(3)	Rh(1)-Rh(2)	2.8988(9)	Rh(2)-C(14)	2.267(6)
Rh(1)-C(6)	2.110(9)	Rh(1)-C(9)	2.145(1)	Rh(1)-S(1)	2.410(3)	Rh(2)-C(13)	2.094(9)	Rh(2)-C(18)	1.863(6)
Rh(2)-C(17)	2.137(9)	Rh(2)-S(2)	2.373(3)	Rh(2)-S(1)	2.419(2)				
Compound **3a** (ii)									
Rh(1')-C(9')	2.110(1)	Rh(1')-C(10')	2.129(9)	Si(1)-C(1)	1.91(2)	Rh(2')-C(13')	2.117(8)	Rh(2')-C(14')	2.133(8)
Rh(1')-C(5')	2.119(9)	Rh(1')-S(1')	2.390(2)	Ir(1)-C(13)	2.289(6)	Rh(2')-C(18')	2.125(7)	Rh(2')-S(2')	2.4012(2)
Rh(1')-C(6')	2.127(9)	Rh(1')-S(2')	2.4131(2)	Rh(1')-Rh(2')	2.892(9)	Rh(2')-C(17')	2.125(8)	Rh(2')-S(1')	2.411(2)
Compound **4**									
I-Co(1)	2.6141(2)	Co(1)-C(8)	2.067(1)	Co(1)-C(6)	2.088(1)	Co(1)-C(9)	2.099(1)	Co(1)-C(7)	2.113(1)
Co(1)-C(5)	2.118(2)	Co(1)-S(2)	2.280(4)	Co(1)-S(1)	2.289(3)	S(1)-P(1)	1.970(5)	S(2)-C(2)	1.792(1)
P(1)-C(3)	1.767(1)	P(1)-C(4)	1.815(1)	P(1)-C(1)	1.846(2)				

Table 3. Selected Interatomic Angles (deg) Compounds **3a** and **4**

Compound **3a** (i)							
C(5)-Rh(1)-C(6)	38.3(4)	C(5)-Rh(1)-C(9)	90.5(4)	C(5)-Rh(1)-S(2)	158.1(3)	C(9)-Rh(1)-S(2)	102.0(3)
C(5)-Rh(1)-C(10)	83.0(5)	C(6)-Rh(1)-C(9)	80.8(4)	C(6)-Rh(1)-S(2)	161.0(3)	C(5)-Rh(1)-S(1)	91.7(3)
C(6)-Rh(1)-C(10)	97.1(5)	C(10)-Rh(1)-C(9)	37.0(4)	C(10)-Rh(1)-S(2)	96.2(4)	C(6)-Rh(1)-S(1)	95.2(3)
C(10)-Rh(1)-S(1)	152.5(3)	C(9)-Rh(1)-S(1)	170.5(3)	S(2)-Rh(1)-S(1)	78.91(9)	C(5)-Rh(1)-Rh(2)	106.5(3)
C(6)-Rh(1)-Rh(2)	136.8(3)	C(10)-Rh(1)-Rh(2)	102.4(3)	C(9)-Rh(1)-Rh(2)	134.5(3)	S(2)-Rh(1)-Rh(2)	52.11(7)
S(1)-Rh(1)-Rh(2)	53.26(6)	C(13)-Rh(2)-C(14)	37.7(4)	C(13)-Rh(2)-C(18)	82.1(4)	C(14)-Rh(2)-C(18)	89.7(4)
C(13)-Rh(2)-C(17)	97.1(4)	C(14)-Rh(2)-C(17)	80.9(4)	C(18)-Rh(2)-C(17)	37.8(4)	C(13)-Rh(2)-S(2)	158.3(3)
C(14)-Rh(2)-S(2)	162.1(3)	C(18)-Rh(2)-S(2)	99.9(3)	C(17)-Rh(2)-S(2)	97.5(3)	C(13)-Rh(2)-S(1)	89.1(2)
C(14)-Rh(2)-S(1)	98.7(3)	C(18)-Rh(2)-S(1)	153.2(3)	C(17)-Rh(2)-S(1)	168.8(3)	S(2)-Rh(2)-S(1)	79.45(9)
C(13)-Rh(2)-Rh(1)	105.2(2)	C(14)-Rh(2)-Rh(1)	138.5(3)	C(18)-Rh(2)-Rh(1)	105.0(3)	C(17)-Rh(2)-Rh(1)	133.1(3)
S(2)-Rh(2)-Rh(1)	53.26(7)	S(1)-Rh(2)-Rh(1)	52.98(6)	C(1)-S(1)-Rh(1)	101.3(3)	C(1)-S(1)-Rh(2)	99.6(3)
Rh(1)-S(1)-Rh(2)	73.77(8)	C(2)-S(2)-Rh(2)	99.8(3)	C(2)-S(2)-Rh(1)	102.3(3)	Rh(2)-S(2)-Rh(1)	74.63(8)
Compound **3a** (ii)							
C(9')-Rh(1')-C(5')	95.8(4)	C(9')-Rh(1')-C(6')	81.5(5)	C(5')-Rh(1')-C(6')	37.7(4)	C(9')-Rh(1')-C(10')	37.6(4)
C(5')-Rh(1')-C(10')	81.9(4)	C(6')-Rh(1')-C(10')	91.5(4)	C(9')-Rh(1')-S(1')	166.4(3)	C(5')-Rh(1')-S(1')	92.2(3)
C(6')-Rh(1')-S(1')	98.5(4)	C(10')-Rh(1')-S(1')	155.4(3)	C(9')-Rh(1')-S(2')	95.8(3)	C(5')-Rh(1')-S(2')	155.5(3)
C(6')-Rh(1')-S(2')	166.5(3)	C(10')-Rh(1')-S(2')	94.4(3)	S(1')-Rh(1')-S(2')	81.03(7)	C(9')-Rh(1')-Rh(2')	134.1(4)
C(5')-Rh(1')-Rh(2')	104.5(3)	C(6')-Rh(1')-Rh(2')	136.7(4)	C(10')-Rh(1')-Rh(2')	104.9(3)	S(1')-Rh(1')-Rh(2')	53.28(5)
S(2')-Rh(1')-Rh(2')	52.89(5)	C(13')-Rh(2')-C(18')	82.5(3)	C(13')-Rh(2')-C(17')	91.2(3)	C(18')-Rh(2')-C(17')	38.3(3)
C(13')-Rh(2')-C(14')	38.0(3)	C(18')-Rh(2')-C(14')	97.0(3)	C(17')-Rh(2')-C(14')	81.3(3)	C(13')-Rh(2')-S(2')	151.7(2)
C(18')-Rh(2')-S(2')	90.0(2)	C(17')-Rh(2')-S(2')	99.7(2)	C(14')-Rh(2')-S(2')	169.5(2)	C(13')-Rh(2')-S(1')	95.7(2)
C(18')-Rh(2')-S(1')	157.2(2)	C(17')-Rh(2')-S(1')	163.9(2)	C(14')-Rh(2')-S(1')	95.3(2)	S(2')-Rh(2')-S(1')	80.85(7)
C(13')-Rh(2')-Rh(1')	102.6(2)	C(18')-Rh(2')-Rh(1')	105.4(2)	C(17')-Rh(2')-Rh(1')	139.5(2)	C(14')-Rh(2')-Rh(1')	131.2(2)
S(2')-Rh(2')-Rh(1')	53.26(5)	S(1')-Rh(2')-Rh(1')	52.62(6)	C(1')-S(1')-Rh(1')	99.2(2)	C(1')-S(1')-Rh(2')	99.2(2)
Rh(1')-S(1')-Rh(2')	74.09(6)	C(2')-S(2')-Rh(2')	99.2(2)	C(2')-S(2')-Rh(1')	98.8(2)	98.8(2)	73.85(5)
Compound **4**							
C(8)-Co(1)-C(6)	66.0(5)	C(8)-Co(1)-C(9)	37.8(6)	C(6)-Co(1)-C(7)	38.7(6)	C(9)-Co(1)-C(7)	65.4(6)
C(2)-Si(2)-Ir(1)	105.1(6)	C(8)-Co(1)-C(7)	40.6(5)	C(8)-Co(1)-C(5)	66.1(6)	C(6)-Co(1)-C(5)	40.4(6)
C(9)-Co(1)-C(5)	39.1(6)	C(7)-Co(1)-C(5)	66.9(6)	C(8)-Co(1)-S(2)	99.9(5)	C(6)-Co(1)-S(2)	124.1(5)
C(9)-Co(1)-S(2)	133.7(5)	C(7)-Co(1)-S(2)	94.7(5)	C(5)-Co(1)-S(2)	161.5(5)	C(8)-Co(1)-S(1)	155.5(4)
C(6)-Co(1)-S(1)	90.5(3)	C(9)-Co(1)-S(1)	126.9(6)	C(7)-Co(1)-S(1)	122.5(4)	C(5)-Co(1)-S(1)	91.7(4)
S(2)-Co(1)-S(1)	99.27(1)	C(8)-Co(1)-I	101.9(4)	C(6)-Co(1)-I	147.6(5)	C(9)-Co(1)-I	86.6(4)
C(7)-Co(1)-I	142.1(4)	C(5)-Co(1)-I	107.4(5)	S(2)-Co(1)-I	86.67(1)	S(1)-Co(1)-I	94.34(1)
P(1)-S(1)-Co(1)	110.61(2)	C(2)-S(2)-Co(1)	116.8(5)				

$S_2C_2B_{10}H_{10}$)] (**3a**), in which the two rhodium centers are connected by a dithiolato ligand. The molecular structure of **3a** is shown in Figure 1, and a listing of selected bond lengths and angles for **3a** is given in Tables 2 and 3. The asymmetric unit contains two independent molecules with almost identical structures, one of which is shown in Figure 2.

Each Rh atom is four-coordinate and displays a square-

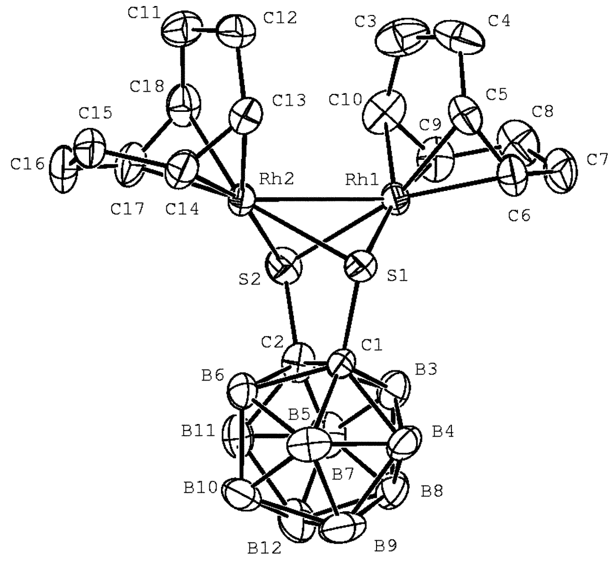
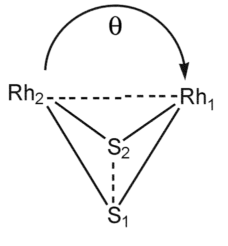


Figure 2. One representative structure of **3a** in the asymmetric unit.

planar geometry. The carborane cage is coordinated bidentately through two S atoms to the Rh(I) ion, while cod is η^4-coordinated to the metal. A number of structures containing the Rh_2S_2 motif have been reported previously,[12] but to the best of our knowledge, this is the first report of a dinuclear Rh(I) structure possessing an *o*-carboranyl dithiolato ligand. Structural data for **3a** indicate that a dithiolate ligand acts as a bridge between the metal atoms, giving a hinged central Rh_2S_2 ring, as shown in Chart 2. When both bridging groups are connected to the bulky *o*-carboranyl unit, as in complex **3a**, there is a significant distortion away from planarity with a value of $\theta = 76.98(9)^\circ$. Therefore, the folding along the S-S axis imposes shorter M-M distances (*e.g.*, Rh-Rh = 2.8988(9) Å in **3a**), giving enhanced metal-metal interactions in these species. This distance is shorter than in previously prepared dinuclear Rh(I) analogs (2.9-3.4 Å).[2a,3,12d,12g-i]

Both of the Rh-S bond lengths [2.410(3) and 2.409(3) Å] are typical.[13] The cyclooctadienyl ring exhibits a boat conformation with Rh-C and C-C bond distances within the normal range for Rh(I)-cod complexes.[14] The bond lengths and angles associated with the cod and coordinated dithiolato ligand in **2a** are unexceptional when compared to other *o*-carborane substituted compounds.



	Dihedral Angle θ (°)	Rh-Rh Distance (A)
3a	76.98(9)	2.8988(9)

Chart 2

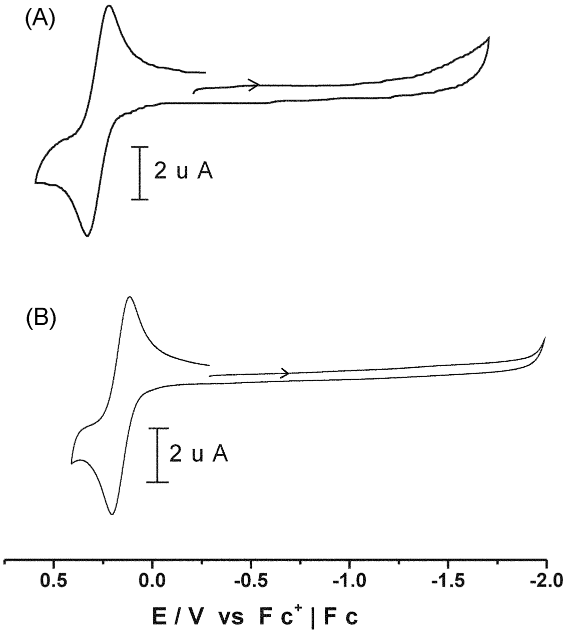
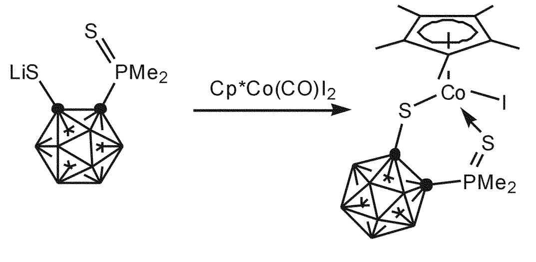


Figure 3. Cyclic voltammograms of 1 mM **3a** (A) and **3b** (B) in CH_2Cl_2 containing 0.1 M TBAB at a platinum disk electrode with negative initial scan direction and scan rate of 0.1 Vs^{-1}.

Cyclic voltammograms (CVs) of complexes **3a** and **3b** (Figure 3) were measured in CH_2Cl_2. Interestingly, the CVs for **3a** and **3b** show reversible oxidation waves at $E_{1/2}$ values of 0.28 and 0.17 V *vs*. $Fc^+ | Fc$, respectively. In a recent study of $[\{(Cp)Co\}_2(S,S'\text{-}S_2C_2B_{10}H_{10})]$,[15a] we observed a reversible oxidation wave at an $E_{1/2}$ of 0.19 V, which we assigned to the redox wave of the bimetallic Co-Co bond by removal/addition of an electron. An analogous electron transfer series including a bimetallic species with Ru^{3+}-Ru^{3+} metal centers has been observed for the oxidation of $Cp^*Ru(\mu\text{-}SPh)_3RuCp^*$.[15b] In contrast, no reversible redox waves were observed in the CVs of the mononuclear complexes $[L_1M(S,S'\text{-}S_2C_2B_{10}H_{10})]$ or $[L_1M(S,S'\text{-}S_2C_2B_{10}H_{10})(L_2)]$ [L_1 = Cp, Cp* or arene; M = Co, Rh, Ir, Ru; L_2 = Lewis bases such as PEt_3, Bu^tNC, and CO] between -0.5 and +0.5 V *vs*. $Fc^+|Fc$.[15a,c] Thus, the reversible oxidation wave of **3a** and **3b** can be assigned to the oxidation-reduction of the dinuclear Rh-Rh and Ir-Ir bonds, respectively. The reversibility of the M-M redox wave seems to stem from the low angular distortion of both the M-*S*-C-C'-*S'* five-membered ring and flexible M-*S*-*S'* bicyclic triangles, which maintains the intimacy of the two nuclei, enabling the M-M bond to reform after oxidation. We suspect that such a reversible redox wave could be used for the electrochemical recognition of the M-M bond in dinuclear complexes of the type $[(LM)_2(S,S'\text{-}S_2C_2B_{10}H_{10})]$ [L = cod or Cp].

Synthesis and Characterization of Mononuclear Metal Complexes $Cp^*CoI[S,S'\text{-}S(S{=}PMe_2)C_2B_{10}H_{10}]$ (4). To further elucidate the chemistry of *o*-carboranyl dithiolate and assess its ability to form reactive transition metal complexes, we examined its reactions with a selection of cyclopentadienyl transition-metal complexes. This work was also undertaken as part of our ongoing interest in obtaining coordinatively unsaturated low-valent metal complexes, capable of binding biologically interesting substrates such as acetylene, CO, diazenes, or dinitrogen. We were therefore keen to investigate the possibility of synthesizing such coordinatively unsaturated low-valent metal complexes bearing both bulky *o*-carborane and cyclopentadienyl units that might potentially stabilize the metal center, as shown in Equation 1. The reaction of $Cp^*Co(CO)I_2$ (1.0 mmol) with the monolithium salt $LiS(S{=}PMe_2)C_2B_{10}H_{10}$ (**2b**) (1.0 equiv) in THF afforded **4** as an air-stable red solid in 83% yield (Eq. 1).



(1)

$LiS(S{=}PMe2)C_2B_{10}H_{10}$ (**2b**) $Cp^*CoI[$*S*,*S'*$\text{-}S(S{=}PMe_2)C_2B_{10}H_{10}]$(**4**)

The $^{31}P\{^1H\}$ NMR spectrum of **4** exhibited a singlet signal at δ 37.19. ^1H NMR data for **4** were consistent with the structure determined by X-ray diffraction. The structure of **4** is closely related to the phosphine adducts of the cobalt thiolato complex $[(\eta^5\text{-}Cp^*)Co($*S*,*S'*$\text{-}S_2C_2B_{10}H_{10})(PEt_3)]$.[15a] The ORTEP diagram in Figure 4 shows that the cobalt assumes a three-legged piano-stool configuration with a six-membered dithiametallacyclic ring. This configuration arises due to the insertion of the coordinated dithiolato ligand at the cobalt(III) metal center. The Co-S bond lengths in **4** are similar [Co(1)-S(1) = 2.289(3) Å and Co(1)-S(2) = 2.280(3) Å], and are in good agreement with the literature values for a wide variety of Co-S σ bonds. In addition, The Co-S distance (2.2845 (av.) Å) of complex **4** at the formally 18-electron cobalt center is significantly longer than that (2.113(2) (av.) Å) of the 16-electron complex $[(\eta^5\text{-}Cp)Co($*S*,*S'*$\text{-}S_2C_2B_{10}H_{10})]$.[16] The Co-S bond lengths (2.2845 (av.) Å) and S(1)-Co(1)-S(2) bond angle (99.3(1)) in **4** are both somewhat greater than the corresponding parameters in $[(Cp)Co(S_2C_2(COOMe)_2(COOMe)_2)(P(OMe)_3)]$ (2.231(1) (av.) Å and 90.26(5)°).[17] The six-membered Co-S-C-C-P-S ring is nonplanar, with dihedral angles between the planes defined by [Co(1), S(1), P(1), S(2)] and [P(1), C(1), C(2), S(2)] of 48.1(3)°.

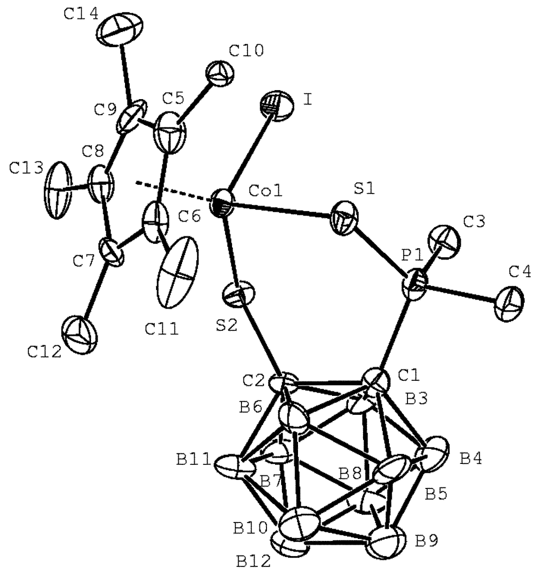


Figure 4. Molecular structure of **4** with atom labeling; ellipsoids show 30% probability levels, the unlabeled atoms are carbon atoms, and hydrogen atoms have been omitted for clarity.

Conclusion

The dithiolato ligands **2** are representative of a series of easily synthesized chelating ligands in which the two sulfur atoms can be independently introduced in consecutive synthetic steps. This characteristic of these ligands affords great flexibility, and should allow fine tuning of their steric and electronic properties so as to form thiolato bridged dinuclear species. The results presented here for complexes **3** are the first detailed structural data ever to be reported for an *S,S'*-chelating *o*-carboranyl dithiolate with intramolecular coordination, and they nicely demonstrate the variety of dinuclear coordinations possible with *S,S'*-chelating dithiolato ligands. In addition, our findings for complex **4** demonstrate that the steric bulk of the pentamethylcyclopentadienyl group plays an important role in determining the type of reaction. Specifically, the bulkiness of the pentamethylcyclopentadienyl ligand in **4** hampers the formation of a bimetallic complex similar to **3**; instead it favors the formation of a mononuclear complex. During the course of this work we also determined the electrochemical characteristics of dinuclear complexes of the type $[\{(cod)M\}_2($*S*,*S'*$\text{-}S_2C_2B_{10}H_{10})]$, which may, when used in conjunction with X-ray analysis, prove useful for the recognition of the M-M bond.

Experimental Section

General Procedures. All manipulations were performed under a dry, oxygen-free, nitrogen or argon atmosphere using standard Schlenk techniques or in a Vacuum Atmosphere HE-493 dry box. THF was freshly distilled over potassium benzophenone. Toluene was dried and distilled from sodium benzophenone. Dichloromethane and hexane were dried and distilled over CaH_2. ^{13}C, ^1H, and ^{31}P NMR spectra were recorded on a Varian Gemini 2000 spectrometer operating at 50.3, 200.1, and 80.0 MHz, respectively. All proton and carbon chemical shifts were measured relative to internal residual benzene from the lock solvent (99.5% $CDCl_3$) and then referenced to Me_4Si (0.00 ppm). The ^{31}P NMR spectra were recorded with 85% H_3PO_4 as an external standard. IR spectra were recorded on a Biorad FTS-165 spectrophotometer. Elemental analyses were performed with a Carlo Erba Instruments CHNS-O EA1108 analyzer. All melting points were uncorrected.

All the electrochemical measurements were carried out in CH_2Cl_2 solutions containing 1.0 mM metal complex and 0.1 M tetrabutylammonium fluoroborate (TBAB) at room temperature using a BAS 100B electrochemical analyzer. A platinum disk (dia. 1.6 mm) and platinum wire were used as a working and counter electrodes. The reference electrode used was Ag | $AgNO_3$, and all the potential values shown were calibrated *vs*. the Fc^+ | Fc redox couple, unless otherwise specified. The $E_{1/2}$ value indicated is the average of E_{pa} and E_{pc} for the reversible redox waves.

o-Carborane was purchased from the Katechem and used without purification. The following starting materials were prepared according to literature procedures: $Li_2S_2C_2B_{10}H_{10}$ (**2a**),[18] Cp*Co(CO)I_2,[19] (PMe_2)$C_2B_{10}H_{11}$ (**1b**),[20] [Rh(μ-Cl)(cod)]$_2$,[21] and [Ir(μ-Cl)(cod)]$_2$.[22]

[{(cod)Rh}$_2$(*S,S'*-$S_2C_2B_{10}H_{10}$)] (3a). To $C_2B_{10}H_{12}$ (**1a**) (0.43 g, 3.0 mmol) dissolved in hexane (20 mL) at -10 °C was added a solution of Bu^{n}Li in hexane (6.0 mmol). The resulting mixture was stirred for 12 h at room temperature. The white precipitate formed was separated from the solution by decantation. The solid $Li_2C_2B_{10}H_{10}$ was washed twice with 30 mL of pentane and dried in vacuo; yield 0.45 g (2.9 mmol, 96%). $Li_2C_2B_{10}H_{10}$ (0.16 g, 1.0 mmol) dissolved in THF (30 mL) was slowly added to a suspension of sublimed sulfur (0.07 g, 2.2 mmol) in THF (20 mL) at -78 °C. The solution was warmed to room temperature, and [Rh(μ-Cl)(cod)]$_2$ (0.49 g, 1.0 mmol) was added. The reaction mixture was then allowed to react at 0 °C for 1 h, and the solution was stirred for another 2 h at room temperature. The solution gradually turned dark brown, suggesting the formation of a dithiolato metal complex. The solution was reduced in vacuo to about half its original volume, and some insoluble material was removed by filtration. The solvent was removed under vacuum, and the resulting residue was taken up in a minimum of methylene chloride and then transferred to a column of silica gel. The crude residue was purified by column chromatography affording > 95% pure complex as orange crystals. Yield: 0.54 g (0.86 mmol, 86%). Data for **3a**. Anal. Calcd for $C_{18}H_{34}B_{10}S_2Rh_2$: C, 34.40; H, 5.45%. Found: C, 34.43; H, 5.40%. IR (KBr, cm^{-1}): ν (B-H) 2606, 2572, 2560; ν (C=C), 1437. ^{1}H NMR (200.13 MHz, ppm, $CDCl_3$): 5.25 (br, 4H, =C*H* cod), 2.94 (br, 4H, C*H*$_{exo}$ cod), 2.32 (br, 4H, C*H*$_{endo}$ cod). ^{13}C{^{1}H}NMR (50.3 MHz, ppm, $CDCl_3$): 100.49 (s, =*C*H cod), 77.80 (s, *C*$_2$B$_{10}$), 30.49, 27.55 (s, *C*H cod).

[{(cod)Ir}$_2$(*S,S'*-$S_2C_2B_{10}H_{10}$)] (3b). A solution of freshly prepared $Li_2S_2C_2B_{10}H_{10}$ (**2a**) (0.22 g, 1.0 mmol) in THF (30 mL) was added over 1 h to a suspension of [Ir(μ-Cl)(cod)]$_2$ (0.67 g, 1.0 mmol) in toluene (20 mL) at -78 °C. The reaction mixture was stirred for 12 h at room temperature, after which the suspended solid was collected by filtration. The solution was further reduced in vacuo to about half its original volume, and some insoluble material was removed by filtration. The solvent was removed under vacuum, and the resulting residue was taken up in a minimum of methylene chloride and then transferred to a column of silica gel. The crude residue was purified by column chromatography affording > 95% pure complex as yellow crystals. Yield: 0.64 g (0.79 mmol, 79%). Data for **3b**. Anal. Calcd for $C_{18}H_{34}B_{10}S_2Ir_2$: C, 26.79; H, 4.25%. Found: C, 26.83; H, 4.33%. IR (KBr, cm^{-1}): ν (B-H) 2604, 2573, 2561; ν (C=C), 1439. ^{1}H NMR (200.13 MHz, ppm, $CDCl_3$): 4.98 (br, 4H, =C*H* cod), 2.36 (br, 4H, C*H*$_{exo}$ cod), 2.18 (br, 4H, C*H*$_{endo}$ cod). ^{13}C{^{1}H}NMR (50.3 MHz, ppm, $CDCl_3$): 106.01 (s, =*C*H cod), 83.46 (s, *C*$_2$B$_{10}$), 36.28, 30.23 (s, *C*H cod).

Preparation of Cp*CoI[*S,S'*-S(S=PMe_2)$C_2B_{10}H_{10}$](4). To (PMe_2)$C_2B_{10}H_{11}$ (**1b**) (0.61 g, 3.0 mmol) dissolved in hexane (20 mL) at -10 °C was added a solution of Bu^{n}Li in hexane (3.1 mmol). The resulting mixture was stirred for 12 h at room temperature. The white precipitate formed was separated from the solution by decantation. The solid Li(PMe_2)$C_2B_{10}H_{11}$ was washed twice with 30 mL of pentane and dried in vacuo; yield 0.61 g (2.9 mmol, 97%). Li(PMe_2)$C_2B_{10}H_{11}$ (0.21 g, 1.0 mmol) dissolved in THF (30 mL) was slowly added to a suspension of sublimed sulfur (0.035 g, 1.1 mmol) in THF (20 mL) at -78 °C. The solution was warmed to room temperature, and Cp*Co(CO)I_2 (0.48 g, 1.0 mmol) was added. The reaction mixture was then allowed to react at 0 °C for 1 h, and the solution was stirred for another 2 h at room temperature. The solution gradually turned dark red, suggesting the formation of an *o*-carboranyl dithiolato metal complex. The solution was reduced in vacuo to about half its orginal volume, and some insoluble material was removed by filtration. The solvent was removed under vacuum, and the resulting residue was taken up in a minimum of methylene chloride and then transferred to a column of silica gel. The crude residue was purified by column chromatography affording > 98% pure complex as red crystals. Yield: 0.49 g (0.83 mmol, 83%). Data for **4**. Anal. Calcd for $C_{14}H_{31}B_{10}S_2PCoI$: C, 28.58; H, 5.31%. Found: C, 28.61; H, 5.33%. IR (KBr, cm^{-1}): ν (B-H) 2602, 2576. ^{1}H NMR (200.13 MHz, ppm, $CDCl_3$): 1.97 (d, $^2J_{P\text{-}H}$ = 5.3 Hz, 6H, P*Me*$_2$), 1.65 (s, 15H, C$_5$*Me*$_5$). ^{13}C{^{1}H}NMR (50.3 MHz, ppm, $CDCl_3$): 92.60 (s, *C*$_5$Me$_5$), 11.26 (d, $^1J_{P\text{-}C}$ = 42.0 Hz, P*Me*$_2$), 9.11 (s, C$_5$*Me*$_5$). ^{31}P{^{1}H} NMR (80.0 MHz, ppm, $CDCl_3$): 37.19 (d, $^2J_{P\text{-}H}$ = 5.3 Hz, *P*Me$_2$).

X-ray Crystallography. Suitable crystals of **3a** and **4** were obtained by slow diffusion of hexane into a methylene chloride solution of the complexes at room temperature and were mounted on a glass fiber. Crystal data and experimental details are given in Table 1. The data sets for **3a** and **4** were collected on an Enraf CAD4 automated diffractometer. Mo-Kα radiation (λ = 0.7107 Å) was used for all structures. Each structure was solved by the application of direct methods using the SHELXS-96 program[23a] and least-squares refinement using SHELXL-97.[23b] All non-hydrogen atoms in compounds **3a** and **4** were refined anisotropically. All other hydrogen atoms were included in calculated positions.

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Supporting Information Available: Crystallographic data (excluding structure factors) for the structures (**3a** and **4**) are reported in this paper. This material is available free of charge via the internet at *http://pubs.acs.org*. These data have also been deposited with the Cambridge Crystallographic Data Centre as supplementary publication Nos. CCDC-2370003 (**3a**) and -2370004 (**4**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, (+44) 1223-336-033; e-mail, deposit@ccdc.cam.ac.uk).

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