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Heteronuclear Molybdenum and Nickel Derivatives of the 16-Electron Half-Sandwich Complex $Cp'Rh[E_2C_2(B_{10}H_{10})]$ (E = S, Se)[†]

Shuyi Cai, Jian-Qiang Wang, and Guo-Xin Jin*

Laboratory of Molecular Catalysis and Innovative Material, Department of Chemistry, Fudan University, Shanghai, 200433, People's Republic of China

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Two prototypes of hetero-trinuclear complexes containing metal−metal bondings $\{Cp'Rh[\mu\text{-}E_2C_2(B_{10}H_{10})]\}_2Mo(\mu\text{-}CO)_2$ ($Cp' = \eta^5\text{-}1,3\text{-}{}^tBu_2C_5H_3$, E = S(**2a**), Se(**2b**)), $\{Cp'Rh[\mu\text{-}E_2C_2(B_{10}H_{10})]\}_2Ni$ (E = S (**4a**), Se (**4b**)) were obtained from the reactions of 16-electron complexes $Cp'Rh[E_2C_2(B_{10}H_{10})]$ (E = S (**1a**), Se (**1b**)) with low-valence transition metal complexes, such as $[Mo(CO)_3(NC_5H_5)_3]$ and $Ni(COD)_2$, respectively. The molecular structures of $Cp'Rh[Se_2C_2(B_{10}H_{10})]$ (**1b**), $(Cp'Rh)_2[S_2C_2(B_{10}H_{10})]$ (**3a**), $\{Cp'Rh[\mu\text{-}E_2C_2(B_{10}H_{10})]\}_2Mo(\mu\text{-}CO)_2]$ (E = S (**2a**), Se (**2b**)), and $\{Cp'Rh[\mu\text{-}E_2C_2(B_{10}H_{10})]\}_2Ni$ (E = S (**4a**), Se (**4b**)) have been determined by X-ray crystallography. All these complexes were characterized by elemental analysis and IR and NMR spectra.

Introduction

During the past decade, considerable attention has been devoted to metal complexes containing chelating 1,2-dicarba-*closo*-dodecaborane-1,2-dichalcogenolate ligands, to take advantage of their unique molecular structure.[1] A number of mononuclear 16-electron Cp and Cp* half-sandwich complexes of Co,[2] Rh,[3] and Ir[4] have been described that contain a bidentate, chelating 1,2-dicarba-*closo*-dodecaborane-1,2-dichalcogenolato ligand, $[(B_{10}H_{10})C_2E_2]^{2-}$ (E = S, Se), and a "pseudo-aromatic" metalladichalcogenolene five-membered ring. These compounds have been used as models to study the insertion of alkynes into one of the metal−sulfur bonds;[5] this may lead to the formation of a metal-to-boron bond or substitution of the carborane cage in the positions of B(3)/B(6).[6,8a]

In the course of our study on the syntheses and reactivities of multinuclear metals bridged with 1,2-dicarba-*closo*-dodecaborane-1,2-dichalcogenolate ligands, we realized that the 16e half-sandwich complexes $Cp^*M[E_2C_2(B_{10}H_{10})]$ [M = Co, Rh, Ir; E = S, Se] could serve as promising precursors for the synthesis of mixed-metal clusters.[7] We have developed this methodology to build up clusters with oligonuclear framework, and some heterometallic clusters have been synthesized in such a manner that the products contain metal−metal bonds;[8] however, rhodium−molybdenum and rhodium−nickel mixed-metal clusters formed through a rhodachalcogenolato heterocycle supported by 1,2-dicarba-*closo*-dodecaborane-1,2-dichalcogenolates have not been reported before, to the best of our knowledge. Aiming at the development of versatile and rational methods for the synthesis of heterometallic cluster complexes in which carborane 1,2-dichalcogenolates act as bridging chelate ligands, we now report the trinuclear complexes obtained from a half-sandwich rhodium carborane dichalcogenolate complex, $Cp'Rh[E_2C_2(B_{10}H_{10})]$ (E = S (**1a**), Se (**1b**), $Cp' = \eta^5\text{-}1,3\text{-}{}^tBu_2C_5H_3$), by reactions with $Mo(CO)_3(NC_5H_5)_3$ and $Ni(C_8H_{12})_2$ to give $\{Cp'Rh[E_2C_2(B_{10}H_{10})]\}_2Mo(CO)_2$ (E = S (**2a**), Se (**2b**)) together with $(Cp'Rh)_2[E_2C_2(B_{10}H_{10})]$ (E = S (**3a**), Se (**3b**)) and $\{Cp'Rh[E_2C_2(B_{10}H_{10})]\}_2Ni$ (E = S (**4a**), Se (**4b**)), respectively.

Results and Discussion

Synthesis and Characterization. The voluminous di-*tert*-butyl-substituted Cp half-sandwich rhodium com-

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[†] $Cp'Rh[E_2C_2(B_{10}H_{10})] = \eta^5$-(1,3-di(*tert*-butyl)cyclopentadienyl-[1,2-dicarba-*closo*-dodecaborane(12)-dichalcogenolate]rhodium.

* Corresponding author. Tel: +86-21-65643776. Fax: + 86-21-65641740. E-mail: gxjin@fudan.edu.cn.

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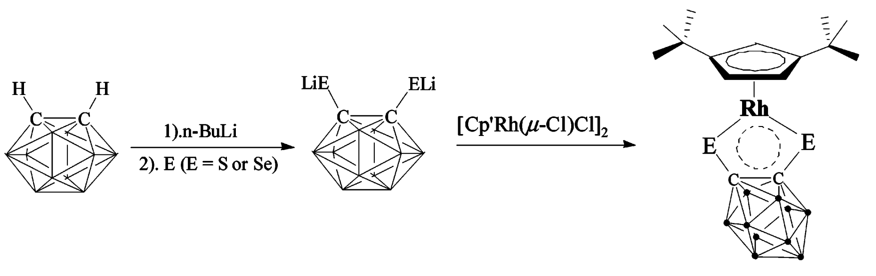
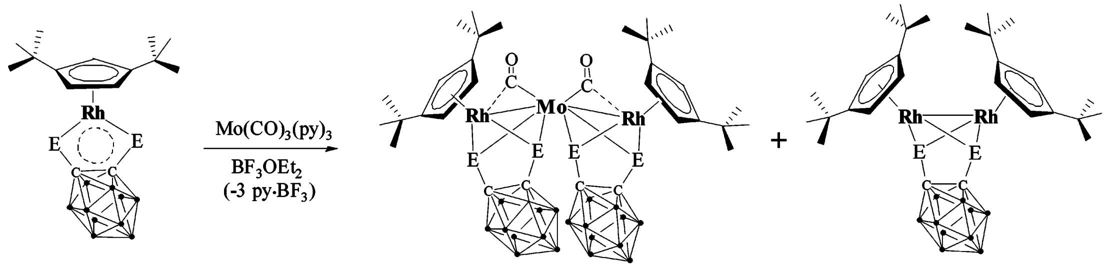
Scheme 1. Synthesis of 1a and 1b



E = S(**1a**), Se(**1b**)

Scheme 2. Synthesis of 2a,b and 3a,b



1a, 1b

2a, 2b

3a, 3b

plex [Cp′Rh(μ-Cl)Cl]$_2$ reacts with dilithium dichalcogenolate carborane $Li_2E_2C_2B_{10}H_{10}$ (E = S, Se) to afford the green 16-electron dithiolene and diselenolene complexes Cp′Rh[$E_2C_2(B_{10}H_{10})$] (E = S (**1a**), Se (**1b**)) (Scheme 1). We have previously reported the corresponding pentamethyl cyclopentadienyl half-sandwich complexes Cp*Rh[$E_2C_2(B_{10}H_{10})$] (E = S, Se) and investigated the addition reactions at the rhodium atom.[3]

The molecular structure of **1b** and selected distances and angles are presented in Figure 1. Complex **1b** crystallizes in the form of dark green prisms in the orthorhombic space group *Pnma* with four molecules in the unit cell. The molecule of **1b** corresponds to point group symmetry C_{2v} with two perpendicular mirror planes. In **1b**, the rhodadiselenene ring is coplanar with centers of both the Cp′ ring and the *ortho*-dicarbadodecarborane. The Rh−Se distances (Rh−Se(1) = 2.3510(11) Å, Rh−Se(2) = 2.3596(11) Å) are significantly shorter than the Rh−Se distances in the 18-electron complex Cp*Rh(PMe_3)[$Se_2C_2(B_{10}H_{10})$] (2.470(1)−2.458(1) Å). Complex **1b** is similar to other 16-electron half-sandwich Rh and Ir complexes Cp*M[$E_2C_2(B_{10}H_{10})$] (M = Rh, Ir; E = S, Se) and has the pseudo-aromatic $RhSe_2C_2$ system.[3]

Complexes **1a** and **1b** can react with $Mo(CO)_3(py)_3$ (py = pyridine, NC_5H_5) in the presence of more than 3 equiv of BF_3 in diethyl ether to give the purple mixed-metal complexes **2a**,**b** together with the red dirhodium complexes **3a**,**b** as byproduct, respectively (Scheme 2). The complexes **2a**,**2b** and **3a**,**3b** are neutral, diamagnetic, and air-sensitive in solution. In complexes **2a**,**2b**, the Rh atoms have been reduced from Rh^{III} to Rh^{II}, appar-

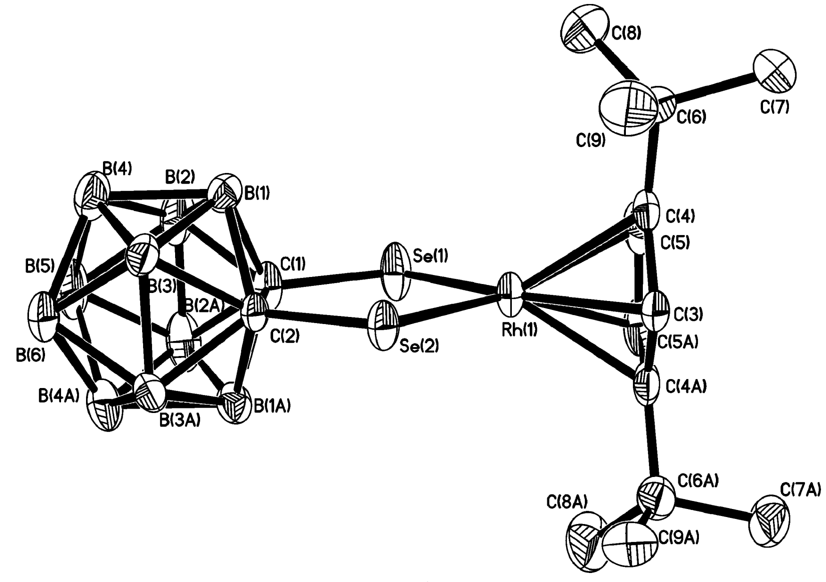


Figure 1. Molecular structure of **1b**. Selected bond lengths (Å) and angles (deg): Rh−Se(1), 2.3510(11); Rh−Se(2), 2.3596(11); C(1)−C(2), 1.644(9); Se(1)−C(1), 1.948(7); Se(2)−C(2), 1.938(5); Se(1)−Rh−Se(2), 94.10(4); Rh−Se(1)−C(1), 105.4(2); Rh−Se(2)−C(2), 105.1(2); Se(1)−C(1)−C(2), 117.2(4); Se(2)−C(2)−C(1), 118.1(4).

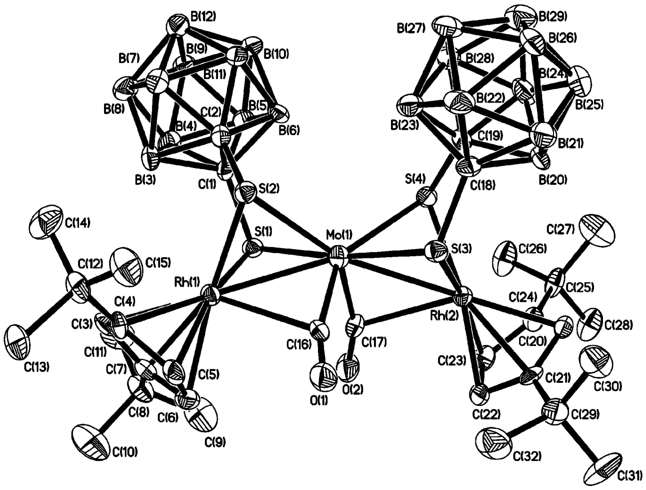


Figure 2. Molecular structure of **2a**. Selected distances (Å) and angles (deg): Mo(1)−Rh(1), 2.7742(13); Mo(1)−Rh(2), 2.7705(13); Mo(1)−S(1), 2.510(3); Mo(1)−S(2), 2.552(3); Mo(1)−C(16), 1.978(12); Mo(1)−C(17), 1.945(13); Rh(1)−S(1), 2.352(3); Rh(1)−S(2), 2.363(3); Rh(1)−C(16), 2.537(11); Rh(2)−C(17), 2.477(12); Rh(1)−Mo(1)−Rh(2), 146.05(4); S(1)−Mo(1)−S(2), 73.36(9); S(1)−Mo(1)−S(3), 172.82(10); S(1)−Mo(1)−Rh(1), 52.58(7); S(1)−Mo(1)−C(16), 109.7(3); S(1)−Rh(1)−S(2), 79.78(10); S(1)−Rh(1)−Mo(1), 57.92(7); Mo(1)−C(16)−O(1), 164.6(10); Mo(1)−C(16)−Rh(1), 74.7(4); Rh(1)−C(16)−O(1), 120.6(9).

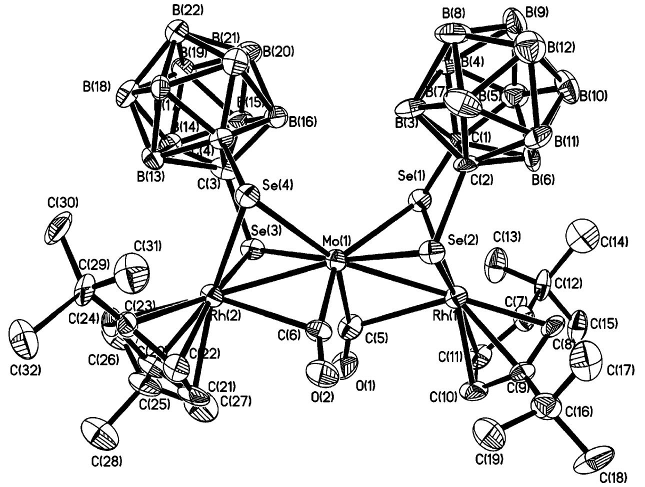


Figure 3. Molecular structure of **2b**. Selected distances (Å) and angles (deg): Mo(1)−Rh(1), 2.798(3); Mo(1)−Rh(2), 2.803(3); Mo(1)−Se(1), 2.656(3); Mo(1)−Se(2), 2.618(3); Mo(1)−C(5), 1.974(19); Mo(1)−C(6), 1.995(19); Rh(1)−Se(1), 2.454(2); Rh(1)−Se(2), 2.456(2); Rh(1)−C(5), 2.55(2); Rh(2)−C(6), 2.59(2); Rh(1)−Mo(1)−Rh(2), 147.18(7); Se(1)−Mo(1)−Se(2), 75.11(8); Se(1)−Mo(1)−Se(3), 98.60(8); Se(1)−Mo(1)−Rh(1), 53.40(6); Se(1)−Mo(1)−C(5), 89.0(6); Se(1)−Rh(1)−Se(2), 81.82(8); Se(1)−Rh(1)−Mo(1), 53.40(6); Mo(1)−C(5)−O(1), 164(2); Mo(1)−C(5)−Rh(1), 75.11(7); Rh(1)−C(5)−O(1), 120.7(17).

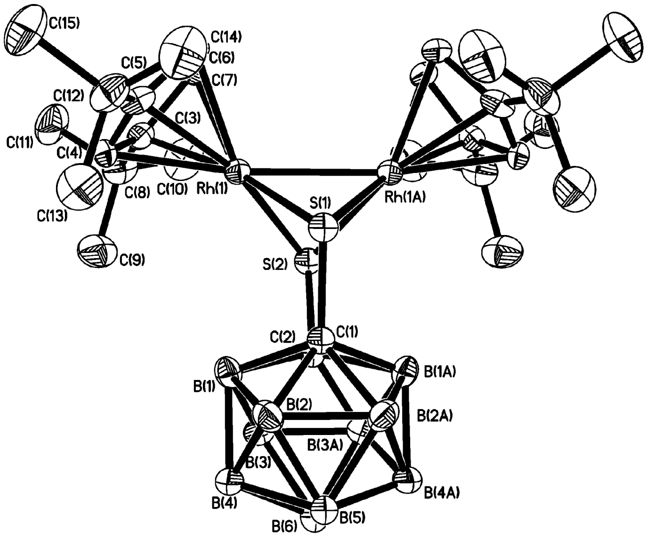


Figure 4. Molecular structure of **3a**. Selected distances (Å) and angles (deg): Rh(1)−Rh(1A), 2.5654(13); S(1)−C(1), 1.854(13); Rh(1)−S(1), 2.339(3); C(1)−C(2), 1.597(17); Rh(1)−S(2), 2.348(3); Cp′$_{\text{(center)}}$−Rh(1), 1.830(5); S(1)−Rh(1)−S(2), 80.05(10); S(1)−Rh(1)−Rh(1A), 56.75(4); Rh(1)−S(1)−Rh(1A), 66.50(9); Rh(1)−S(2)−Rh(1A), 66.23(9); C(1)−S(1)−Rh(1), 104.3(3); C(2)−S(2)−Rh(1), 104.5(4); C(2)−C(1)−S(1), 112.8(8).

ently by the fragment [Mo(CO)$_3$], which is generated effectively from the combination of [Mo(CO)$_3$(py)$_3$] and BF$_3$.[12a] A similar phenomenon was also found in the formation of phenyl dithiolato cobalt complex [(η^5-C$_5$H$_5$)Co(S$_2$C$_6$H$_4$)]$_2$Mo(CO)$_2$.[12b,c]

The IR spectra of the products **2a**−**3b** in the solid state exhibit intense B−H stretching of carborane at about 2610(vs) and 2590(vs) cm^{-1}. Complexes **2a**,**2b** exhibited strong vibrations of carbon monoxide at about 1890(vs) and 1850(vs) cm^{-1} in the region typical for a CO bridge, which is in agreement with the data of the structures.

The molecular structures of **2a**, **2b**, and **3a** have been established by single-crystal X-ray structure analysis (Figures 2, 3, and 4). The rhodium atoms of the Rh$_2$Mo backbone in **2a**,**2b** have retained their Cp′ rings, and the Mo center is eight-coordinate with a square-antiprismatic geometry. In complex **2a**, the coordination environment of the Mo center connected to the nonmetallic ligands (S and CO) is distorted trigonal-prismatic, and the two S−Mo−S planes are twisted by 44.6° with respect to one another. The two Rh−Mo single bonds (2.7705(13) and 2.7742(13) Å) are each supported by a symmetrically bridging *o*-carborane dithiolato ligand. The Rh(1)−Mo(1)−Rh(2) angle is 146.05(4)°. The planar pseudoaromatic system of the two rhodadithiolene heterocycle **1a** is no longer present in **2a**, and the dihedral angle at the S···S vector in the RhS$_2$C$_2$ ring is 134°. The selenolate complex **2b** is isomorphous to the complex **2a**. Complex **2b** also contains two carborane diselenolato chelate ligands, which are arranged so that both Se atoms bridge rhodium and molybdenum to form the intramolecular Rh−Mo single bonds (2.803(3) and 2.798(3) Å). Similarly, the pseudoaromatic RhSe$_2$C$_2$ system in **1b** has also been destroyed. This is particularly evident from

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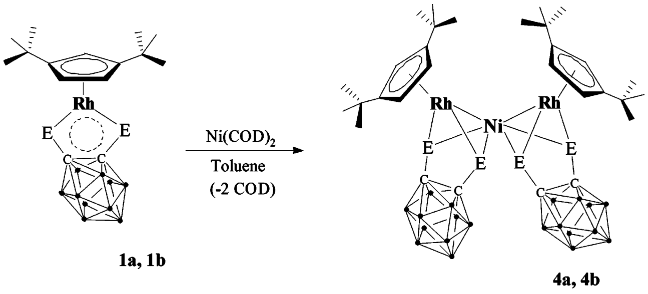
Scheme 3. Synthesis of 4a,b



the fact that on going from **1b** to **2b**, the Rh−Se bond length grows significantly from 2.3553 Å (av) to 2.4560 Å (av), while the Se−Rh−Se angle decreases from 94.10(4)° to 81.91(8)°.

The dinuclear Rh^{II} complex **3a** contains one carborane dithiolato chelate ligand, which is arranged so that both S atoms bridge two rhodium atoms (Figure 4). The molecule contains a mirror plane. The Rh−Rh distance of 2.5654(13) Å corresponds to a metal−metal single bond;[13] thus **3a** is formally an 18-electron complex. **3a** is similar to the corresponding cobalt complex (CpCo)$_2$[S$_2$C$_2$(B$_{10}$H$_{10}$)], which was reported by Ko et al.[2]

The related reaction between **1a**,**1b** and Ni(COD)$_2$ (COD = cyclo-*octa*-1,5-diene, C$_8$H$_{12}$) in toluene leads to the air-sensitive, violet hetero-trinuclear complexes **4a** and **4b** in about 50% yields (Scheme 3). The characterization of the products **4a**,**4b** is based on elemental analyses and X-ray diffraction studies. The structures of **4a**,**4b** have been determined by X-ray analyses using single crystals grown from toluene/hexane. The molecular structures of **4a** and **4b** are depicted in Figures 5 and 6. Both the molecules contain a C_2 axis. In complex **4a**, the four sulfur atoms of the *o*-carborane dithiolate **1a** surround the central nickel atom in a distorted tetrahedral arrangement; the two S−Ni−S planes are twisted by 79.1° with respect to one another. As in **2a** the rhodadithiolene heterocycles are nonplanar in **4a** as a result of the coordination of the S atoms to Ni. The Rh−Ni distances in **4a** (2.458(6) Å) may therefore be compared with the corresponding distances in clusters such as [NiRh$_{14}$(CO)$_{28}$]$^{4-}$ (2.481(1)−2.532(1) Å) and [Ni$_6$Rh$_3$(CO)$_{17}$]$^{3-}$ (2.531(1)−2.758(1) Å).[14] The Rh−S distances (2.325(6) and 2.357(6) Å) in **4a** are longer than that of a "pseudoaromatic" five-membered rhodadithiolene ring in Cp′Rh[S$_2$C$_2$(B$_{10}$H$_{10}$)][3] (2.247(2) and 2.251(2) Å). In complex **4b**, the Rh and Ni atoms are both bridged by diselenolate ligands, and the Rh−Ni distances (2.4921(15) Å) and the capping angles (Ni(1)−Se(1)−Rh(1) (62.67(4)°) indicate the strong direct interaction between Rh and Ni atoms. The Rh−Se distance (2.4430 Å (av)) in **4b** is slightly longer than that of a five-membered rhodadithiolene ring in 16-electron complex **1b** (2.3553 Å (av)).

In summary, the formation of a hetero metal−metal bond in complexes **2a**,**2b** and **4a**,**4b** by the reactions of the 16-electron complexes **1a**,**1b** involve redox processes during which Rh is partially reduced by low-valence transition metal complexes, such as the fragment [Mo(CO)$_3$] or Ni(COD)$_2$.

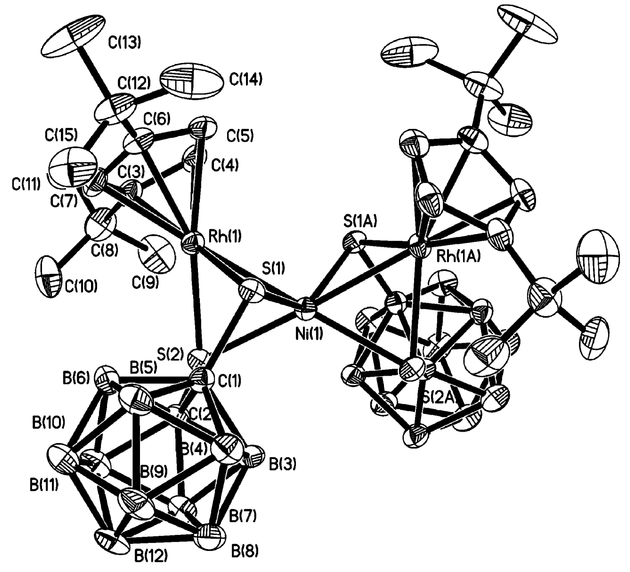


Figure 5. Molecular structure of **4a**. Selected distances (Å) and angles (deg): Rh(1)−Ni(1), 2.458(6); Rh(1)−S(1), 2.325(6); Rh(1)−S(2), 2.357(6); Ni(1)−S(1), 2.277(7); Ni(1)−S(2), 2.304(6); S(1)−C(1), 1.818(8); C(1)−C(2), 1.628(11); S(1)−Rh(1)−S(2), 81.79(8); S(2)−Rh(1)−Ni(1), 57.12(5); S(1)−Ni(1)−S(2), 84.01(7); Ni(1)−S(1)−Rh(1), 63.64(6); S(2)−Ni(1)−S(2A), 122.84(14); S(2)−Ni(1)−Rh(1), 59.24(6); Rh(1)−Ni(1)−Rh(1A), 118.95(6).

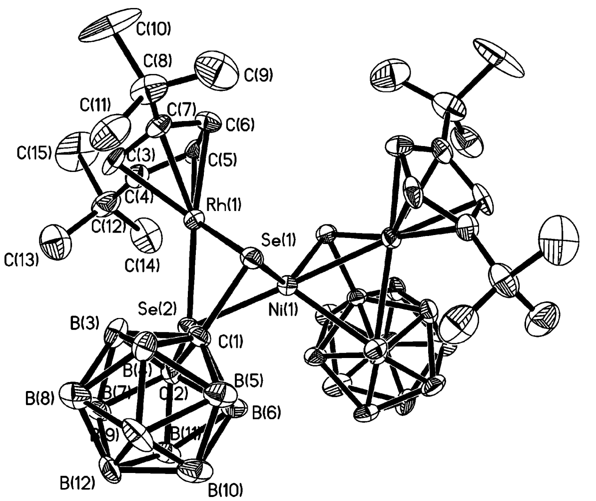


Figure 6. Molecular structure of **4b**. Selected distances (Å) and angles (deg): Rh(1)−Ni(1), 2.4921(15); Rh(1)−Se(1), 2.4280(15); Rh(1)−Se(2), 2.4580(17); Ni(1)−Se(1), 2.3628(15); Ni(1)−Se(2), 2.3804(16); Se(1)−C(1), 1.977(10); C(1)−C(2), 1.629(15); Se(1)−Rh(1)−Se(2), 83.49(5); Se(2)−Rh(1)−Ni(1), 57.38(3); Se(1)−Ni(1)−Se(2), 86.61(4); Ni(1)−Se(1)−Rh(1), 62.67(4); Se(2)−Ni(1)−Se(2A), 120.12(12); Se(2)−Ni(1)−Rh(1), 60.54(4); Rh(1)−Ni(1)−Rh(1A), 119.14(11).

Experimental Section

General Procedures. All manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques, and all solvents were dried and deoxygenated before use. The solvents diethyl ether, toluene, and *n*-hexane were refluxed and distilled over sodium/benzophenone ketyl under

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Table 1. Crystal and Data Collection Parameters of Complexes 1b, 2a, 2b, 3a, 4a, and 4b

	1b	**2a**	**2b**	**3a**	**4a**	**4b**
formula	$C_{15}H_{31}B_{10}RhSe_2$	$C_{32}H_{62}B_{20}MoO_2Rh_2S_4$	$C_{32}H_{62}B_{20}MoO_2Rh_2Se_4$	$C_{34}H_{64}B_{10}Rh_2S_2$	$C_{30}H_{62}B_{20}NiRh_2S_4$	$C_{30}H_{62}B_{20}NiRh_2Se_4$
fw	580.33	1125.02	1312.62	850.89	1031.77	1219.37
cryst color	green	purple	purple	red	violet	violet
cryst syst	orthorhombic	monoclinic	monoclinic	monoclinic	rhombohedral	hexahongal
space group	*Pnma*	*P*2(1)/*n*	*P*2(1)/*n*	*P*2(1)/*m*	*R*32	*R*32
a, Å	22.400(7)	9.8867(13)	9.991(3)	11.221(2)	20.67(5)	20.882(2)
b, Å	15.332(5)	22.777(3)	23.134(6)	18.010(4)	20.67(5)	20.882(2)
c, Å	6.956(2)	24.723(3)	24.827(6)	11.883(3)	29.81(11)	30.075(5)
α, deg	90	90	90	90	90	90
β, deg	90	92.101(2)	92.530(5)	107.027(3)	90	90
γ, deg	90	90	90	90	120	120
V, Å^3	2388.9(14)	5563.6(13)	5733(3)	2296.2(8)	11035(57)	11357(2)
Z	4	4	4	2	9	9
D_{calcd}, Mg/m^3	1.614	1.343	1.521	1.196	1.397	1.605
abs coeff, mm^{-1}	3.762	0.986	3.351	0.829	1.239	3.923
F(000)	1136	2264	2552	844	4716	5364
cryst size, mm	0.08 × 0.05 × 0.05	0.20 × 0.10 × 0.08	0.20 × 0.10 × 0.08	0.35 × 0.30 × 0.30	0.25 × 0.20 × 0.20	0.10 × 0.10 × 0.05
θ range, deg	1.82 to 25.01	1.22 to 25.01	1.20 to 25.01	1.79 to 25.01	1.33 to 26.00	1.31 to 25.01
no. of indep reflns	9418	23 168	24 012	9630	16 844	16 000
no. of reflns obsd	2192 [R(int) = 0.0501]	9770 [R(int) = 0.0908]	10 103 [R(int) = 0.1478]	4166 [R(int) = 0.0768]	4835 [R(int) = 0.0696]	4469 [R(int) = 0.0990]
no. refinement method	1544 ($>2\sigma$)	4487 ($>2\sigma$)	3649 ($>2\sigma$)	3466 ($>2\sigma$)	3893 ($>2\sigma$)	2709 ($>2\sigma$)
no. of data/restraints/params	2192/0/148	9770/0/563	10 103/0/582	4166/23/253	4835/0/274	4469/0/265
goodness-of-fit[a] on F^2	0.964	0.906	0.949	1.225	1.127	0.945
final R indices [$I > 2\sigma(I)$][b]	R1 = 0.0391 wR2 = 0.0744	R1 = 0.0600 wR2 = 0.1614	R1 = 0.0741 wR2 = 0.1942	R1 = 0.0905 wR2 = 0.2197	R1 = 0.0515 wR2 = 0.1286	R1 = 0.0483 wR2 = 0.1010
R indices (all data)	R1 = 0.0676 wR2 = 0.0829	R1 = 0.1405 wR2 = 0.1854	R1 = 0.2103 wR2 = 0.2367	R1 = 0.1064 wR2 = 0.2288	R1 = 0.0745 wR2 = 0.1401	R1 = 0.1003 wR2 = 0.1173
larg diff peak and hole, e Å^{-3}	1.668 and −0.402	1.503 and −0.481	1.441 and −0.798	1.892 and −1.477	1.321 and −0.405	0.932 and −0.427

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

nitrogen prior to use. The starting materials, $[Cp'Rh(\mu\text{-}Cl)Cl]_2$,[9] and $Li_2E_2C_2B_{10}H_{10}$ (E = S, Se)[7] were prepared by slightly modified literature procedures. $Ni(COD)_2$ was purchased from Aldrich and was used without purification. Elemental analyses for C and H were carried out on an Elementar III Vario EI analyzer. ^1H (500 MHz), ^{11}B (160 MHz), and ^{13}C (125 MHz) NMR measurements were obtained on a Bruker AC500 spectrometer in $CDCl_3$ solution. Infrared spectra were recorded on a Nicolet FT-IR 360 spectrometer with samples prepared as Nujol mulls.

Synthesis of $Cp'Rh[E_2C_2(B_{10}H_{10})]$ (E = S (1a), Se (1b)). $[Cp'Rh(\mu\text{-}Cl)Cl]_2$ (0.35 g, 0.50 mmol) in THF (50 mL) was added to a solution of $Li_2E_2C_2B_{10}H_{10}$ (E = S, Se)[7] in ether (100 mL) and kept at room temperature to stir for 6 h. After removal of the solvent, the residue was chromatographed on silica gel. Elution with CH_2Cl_2 gave a dark green zone. Evaporation and crystallization from CH_2Cl_2/hexane afforded **1a** (0.34 g, 70.0%) or **1b** (0.40 g, 69%) as prismatic crystals. Complex **1a**: Anal. Calcd (%) for $C_{15}H_{31}B_{10}RhS_2$: C, 36.96; H, 6.46. Found: C, 37.04; H, 6.42. ^1H NMR (500 MHz, $CDCl_3$, δ/ppm): 1.21(s, 18H, *tBu*), 5.04(t, 1H, *Cp′*), 5.25(d, 2H, *Cp′*). ^{11}B NMR (160 MHz, $CDCl_3$, δ/ppm): −6.34, −7.53, −9.38, −11.4. IR (KBr disk): ν 2623, 2603, 2568 cm^{-1} (B−H). Complex **1b**: Anal. Calcd (%) for $C_{15}H_{31}B_{10}RhSe_2$: C, 31.09; H, 5.42. Found: C, 31.05; H, 5.38. ^1H NMR (500 MHz, $CDCl_3$, δ/ppm): 1.18(s, 18H, *tBu*), 5.13(t, 1H, *Cp′*), 5.32(d, 2H, *Cp′*). ^{11}B NMR (160 MHz, $CDCl_3$, δ/ppm): −5.36, −7.51, −9.68, −11.37. IR (KBr disk): ν 2608, 2598, 2562 cm^{-1} (B−H).

Synthesis of $\{Cp'Rh[E_2C_2(B_{10}H_{10})]\}_2Mo(CO)_2$ (E = S (2a), Se (2b)) and $(Cp'Rh)_2[E_2C_2(B_{10}H_{10})]$ (E = S (3a), Se (3b)). $BF_3\cdot OEt_2$ (0.15 mL, 47%, 0.5 mmol) was added to a 100 mL Schlenk tube containing $[Mo(CO)_3(py)_3]$ (0.042 g, 0.10 mmol) and **1a** (0.097 g, 0.20 mmol) or **1b** (0.116 g, 0.20 mmol) in diethyl ether (40 mL). The color of the solution changed gradually from green to dark purple. After stirring for 5 h at room temperature, the solvent was evaporated to dryness under vacuum. The residue was redissolved in 2 mL of CH_2Cl_2 and chromatographed on silica gel. Elution with CH_2Cl_2/hexane (1:6) gave two color zones, which contain **2a** (64 mg, 57%) and **3a** (8 mg, 9%) or **2b** (68 mg, 52%) and **3b** (6 mg, 6%). The compound in the first zone was recrystallized from cyclohexane to give red crystals of **3a** or **3b**. Complex **3a**: Anal. Calcd (%) for $C_{28}H_{52}B_{10}Rh_2S_2$: C, 43.86; H, 6.84. Found: C, 43.62; H, 6.90. ^1H NMR (500 MHz, $CDCl_3$, δ/ppm): 1.29(s, 36H, *tBu*), 4.98(t, 2H, *Cp′*), 5.30(d, 4H, *Cp′*). ^{11}B NMR (160 MHz, $CDCl_3$, δ/ppm): −2.2, −4.6, −10.5. IR (KBr disk): ν 2605.5, 2576.2 cm^{-1} (B−H). Complex **3b**: Anal. Calcd (%) for $C_{28}H_{52}B_{10}Rh_2Se_2$: C, 39.08; H, 6.09. Found: C, 39.44; H, 6.20. ^1H NMR (500 MHz, $CDCl_3$, δ/ppm): 1.27(s, 36H, ^{t}Bu), 4.96(t, 2H, *Cp′*), 5.27(d, 4H, *Cp′*). ^{11}B NMR (160 MHz, $CDCl_3$, δ/ppm): −2.1, −4.3, −10.8. IR (KBr disk): ν 2602, 2570 cm^{-1} (B−H). The compound in the second zone was recrystallized from CH_2Cl_2/hexane (1:4) to give purple crystals of **2a** or **2b**. Complex **2a**: Anal. Calcd (%) for $C_{32}H_{62}B_{20}MoO_2Rh_2S_4$: C, 34.16; H, 5.62. Found: C, 34.69; H, 5.67. ^1H NMR (500 MHz, $CDCl_3$, δ/ppm): 1.25(s, 36H, ^{t}Bu), 5.05(t, 2H, *Cp′*), 5.26(d, 4H, *Cp′*). ^{13}C NMR (125 MHz, $CDCl_3$, δ/ppm): 29.8 (s, $(\mathit{Me}_3C)_2C_5H_3$), 30.4(s, $(Me_3\mathit{C})_2C_5H_3$), 94.9(s, $\mathit{C}_2B_{10}H_{10}$), 79.5(d, *Cp′*, $^1J_{(Rh,C1)}$ = 4.6 Hz), 81.3(d, *Cp′*, $^1J_{(Rh,C2)}$ = 6.3 Hz), 120.5(d, *Cp′*, $^1J_{(Rh,C3)}$ = 8.25 Hz). ^{11}B NMR (160 MHz, $CDCl_3$, δ/ppm): −2.9, −4.2, −9.3, −13.0, 14.1. IR (KBr disk): ν 2594, 2566 cm^{-1} (B−H); 1883, 1838 cm^{-1}(C═O). Complex **2b**: Anal. Calcd (%) for $C_{32}H_{62}B_{20}MoO_2Rh_2Se_4$: C, 29.28; H, 4.76. Found: C, 29.44; H, 4.81. ^1H NMR (500 MHz, $CDCl_3$, δ/ppm): 1.21 (s, 36H, ^{t}Bu), 5.09(t, 2H, *Cp′*), 5.27(d, 2H, *Cp′*). ^{13}C NMR (125 MHz, $CDCl_3$, δ/ppm): 29.7(s, $(\mathit{Me}_3C)_2C_5H_3$), 31.1(s, $(Me_3\mathit{C})_2C_5H_3$), 75.9(s, $\mathit{C}_2B_{10}H_{10}$), 79.1(d, *Cp′*, $^1J_{(Rh,C1)}$ = 4.5 Hz), 79.9(d, *Cp′*, $^1J_{(Rh,C2)}$ = 6.3 Hz), 118.3(d, *Cp′*, $^1J_{(Rh,C3)}$ = 8.13 Hz). ^{11}B NMR (160 MHz, $CDCl_3$, δ/ppm): −2.6, −7.0, −9.0, −14.0, −15.1. IR (KBr disk): ν 2593, 2563 cm^{-1} (B−H); 1903, 1865 cm^{-1} (C═O).

Synthesis of $\{Cp'Rh[E_2C_2(B_{10}H_{10})]\}_2Ni$ (E = S (4a), Se (4b)). $Ni(COD)_2$ (0.028 g, 0.10 mmol) was added to a solution of **1a** (0.097 g, 0.20 mmol) or **1b** (0.0116 g, 0.20 mmol) in 30 mL of toluene at room temperature. The suspension was kept stirring at 50 °C for 48 h. The solvent was then evaporated to dryness under vacuum, and the residue was purified by column chromatography on silica with toluene/hexane (1:2) as eluent to give **4a** (52 mg, 50.4%) or **4b** (67 mg, 54.9%). The complexes were recrystallized from hexane at −20 °C to afford violet crystals of **4a** and **4b**. Complex **4a**: Anal. Calcd (%) for $C_{30}H_{62}B_{20}NiRh_2S_4$: C, 34.89; H, 6.06. Found: C, 34.74; H, 6.07. ^1H NMR (500 MHz, $CDCl_3$, δ/ppm): 1.31(s, 36H, ^{t}Bu), 5.25(t, 2H, *Cp′*), 5.61(d, 4H, *Cp′*). ^{11}B NMR (160 MHz, $CDCl_3$, δ/ppm): −5.8, −7.8, −8.9, −10.8. IR (KBr disk): ν 2570 cm^{-1} (B−H). Complex **4a**: Anal. Calcd (%) for $C_{30}H_{62}B_{20}NiRh_2Se_4$: C, 31.52; H, 5.12. Found: C, 31.42; H, 5.15. ^1H NMR (500 MHz, $CDCl_3$, δ/ppm): 1.35(s, 36H, ^{t}Bu), 5.25(t, 2H, *Cp′*), 5.61(d, 4H, *Cp′*). ^{11}B NMR (160 MHz, $CDCl_3$, δ/ppm): −7.4, −9.3, −12.9, −14.3. IR (KBr disk): ν 2595.4, 2568.9 cm^{-1} (B−H).

X-ray Data Collection, Structure Determination, and Refinement. Suitable single crystals of complexes **1b**−**4b** were sealed under nitrogen in Lindemann glass capillaries for X-ray strucrtural analysis. Diffraction data were collected on a Bruker SMART Apex CCD diffractometer using graphite-monochromated Mo Kα (λ = 0.71073 Å) 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.[10] The structures were solved by direct methods using the SHELXL-97 program.[11] 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 is given in Table 1.

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Supporting Information Available: Crystallographic data for **1b**, **2a**, **2b**, **3a**, **4a**, and **4b** are available free of charge via the Internet at http//www.pubs.acs.org.

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