5280 *Organometallics* **2005,** *24,* 5280−5286

Heteronuclear Tungsten and Cobalt Derivatives of the 16-Electron Half-Sandwich Complex $Cp^*Rh[E_2C_2(B_{10}H_{10})]$ (E = S, Se)

Shuyi Cai and Guo-Xin Jin*

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

Received July 17, 2005

The 16-electron half-sandwich rhodium complex $[Cp^*Rh\{E_2C_2(B_{10}H_{10})\}]$ [E = S (**1a**), Se (**1b**)] ($Cp^* = \eta^5\text{-}C_5Me_5$) reacted with $W(CO)_3(py)_3$ in the presence of $BF_3{\cdot}Et_2O$ in THF solution to afford $\{Cp^*Rh[E_2C_2(B_{10}H_{10})]\}_2W(CO)_2$ (E = S (**2a**); Se (**2b**)), $(Cp^*Rh)_2[S_2C_2(B_{10}H_{10})]$ (**3**), $Cp^*Rh[S_2C_2(B_{10}H_{10})]W(CO)_2[S_2C_2(B_{10}H_{10})]$ (**4**), and $Cp^*Rh(CO)[Se_2C_2(B_{10}H_{10})]W(CO)_5$ (**5**). The trinuclear clusters $\{Cp^*Rh[E_2C_2(B_{10}H_{10})]\}[Co_2(CO)_5]$ [E = S (**6a**), Se (**6b**)] were obtained from the reactions of **1a** and **1b** with $Co_2(CO)_8$ in the presence of Me_3NO. The complexes have been fully characterized by IR and NMR spectroscopy as well as by element analyses. The X-ray crystal structures of complexes **2**−**6** are reported.

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 "pseudoaromatic" 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]

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 an oligonuclear framework, and some heterometallic clusters have been synthesized in such a manner that the products contain metal−metal bonds.[6a,8] Recently we reported metalladichalcogenolate cluster complexes $\{Cp'Rh[E_2C_2(B_{10}H_{10})]\}_2Ni$ and $\{Cp'Rh[E_2C_2(B_{10}H_{10})]\}_2Mo(CO)_2$ ($Cp' = \eta^5\text{-}1,3\text{-}{}^tBu_2C_5H_3$; E = S; Se);[9] however, related rhodium−tungsten and rhodium−cobalt 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 and dinuclear complexes obtained from a half-sandwich rhodium carborane dichalcogenolate complex, $Cp^*Rh[E_2C_2(B_{10}H_{10})]$ (E = S (**1a**), Se (**1b**)) ($[Cp^*Rh\{E_2C_2(B_{10}H_{10})\}]$ = [η^5-pentamethylcyclopentadienyl-[1,2-dicarba-*closo*-dodecaborane(12)-dichalcogenolato]rhodium]), by reactions with $W(CO)_3(NC_5H_5)_3$ in the presence of $BF_3{\cdot}Et_2O$ and $Co_2(CO)_8$ in the presence of Me_3NO, respectively, to give $\{Cp^*Rh[E_2C_2(B_{10}H_{10})]\}_2W(CO)_2$ (E = S (**2a**); Se (**2b**)), $(Cp^*Rh)_2[S_2C_2(B_{10}H_{10})]$ (**3**), $\{Cp^*Rh[S_2C_2(B_{10}H_{10})]\}\{W(CO)_2[S_2C_2(B_{10}H_{10})]\}$ (**4**), $Cp^*Rh(CO)[Se_2C_2(B_{10}H_{10})]W(CO)_5$ (**5**), and $\{Cp^*Rh[E_2C_2(B_{10}H_{10})]\}[Co_2(CO)_5]$ [E = S (**6a**), Se (**6b**)], respectively.

---

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

(1) (a) Hawthorne, M. F.; Zheng, Z.-P. *Acc. Chem. Res.* **1997**, *30*, 267. (b) Xie, Z. *Acc. Chem. Res.* **2003**, *36*, 1. (c) Jin, G.-X. *Coord. Chem. Rev.* **2004**, *248*, 587.

(2) (a) Kim, D. H.; Ko, J.; Park, K.; Kang, S. O. *Organometallics* **1999**, *18*, 2738. (b) Won, J. H.; Kim, D. H.; Kim, B. Y.; Kim, S. J.; Lee, C.; Cho, S.; Ko, J.; Kang, O. *Organometallics* **2002**, *21*, 1443. (c) Hou, X.-F.; Wang, X.; Wang, J.-Q.; Jin, G.-X. *J. Organomet. Chem.* **2004**, *689*, 2228.

(3) (a) Herberhold, M.; Jin, G.-X.; Yan, H.; Milius, W.; Wrackmeyer, B. *J. Organomet. Chem.* **1999**, *587*, 252. (b) Kong, Q.; Jin, G.-X.; Cai, S.-Y.; Weng, L.-H. *Chin. Sci. Bull.* **2003**, *48*, 1733. (c) Lee, J.-D.; Kim, B.-Y.; Lee, C.; Lee, Y.-J.; Ko, J.; Kang, S. O. *Bull. Korean Chem. Soc.* **2004**, *25*, 1012.

(4) (a) Herberhold, M.; Jin, G.-X.; Yan, H.; Milius, W.; Wrackmeyer, B. *Eur. J. Inorg. Chem.* **1999**, 873. (b) Bae, J. Y.; Park, Y. I.; Ko, J.; Park, K. I.; Cho, S. I.; Kang, S. O. *Inorg. Chim. Acta* **1999**, *289*, 141.

(5) (a) Herberhold, M.; Yan, H.; Milius, W.; Wrackmeyer, B. *Chem. Eur. J.* **2002**, *8*, 388. (b) Herberhold, M.; Yan, H.; Milius, W.; Wrackmeyer, B. *Chem. Eur. J.* **2000**, *6*, 3026.

(6) (a) Herberhold, M.; Yan, H.; Milius, W.; Wrackmeyer, B. *Angew. Chem., Int. Ed.* **1999**, *38*, 3689. (b) Jin, G.-X.; Wang, J.-Q.; Zhang, Z.; Weng, L.-H.; Herberhold, M. *Angew. Chem., Int. Ed.* **2005**, *44*, 259.

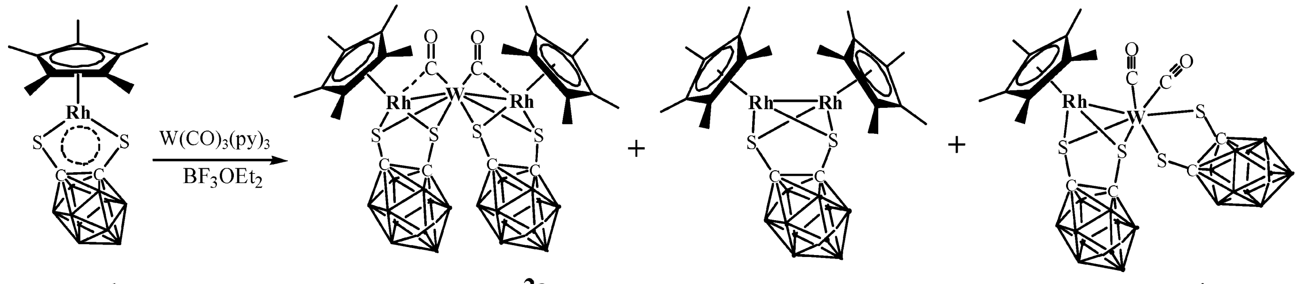
(7) (a) Lu, S.-X.; Jin, G.-X.; Eibl, S.; Herberhold, M.; Xin, Y. *Orgnometallics* **2002**, *21*, 2533. (b) Yu, X.-Y.; Jin, G.-X.; Hu, N.-H.; Weng, L.-H. *Organometallics* **2002**, *21*, 5540. (c) Yu, X.-Y.; Lu, S.-X.; Jin, G.-X.; Weng, L.-H. *Inorg. Chim. Acta* **2004**, *357*, 361.

(8) (a) Wang, J.-Q.; Hou, X. F.; Weng, L.-H.; Jin, G.-X. *Organometallics* **2005**, *24*, 826. (b) Wang, J.-Q.; Hou, X. F.; Weng, L.-H.; Jin, G.-X. *J. Organomet. Chem.* **2005**, *690*, 249 (c) Cai, S. Y.; Hou, X. F.; Weng, L.-H.; Jin, G.-X. *J. Organomet. Chem.* **2005**, *690*, 910. (d) Wang, J.-Q.; Weng, L.-H.; Jin, G.-X. *Rev. Inorg. Chem.* **2005**, *25*, 55. (e) Li, W.; Weng, L.-H.; Jin, G.-X. *Inorg. Chem. Commun.* **2004**, *7*, 1174.

(9) Cai, S. Y.; Wang, J. Q.; Jin, G.-X. *Organometallics* **2005**, *24*, 4226.

10.1021/om050598p CCC: $30.25

Scheme 1. Synthesis of 2a, 3, and 4



1a **2a** **3** **4**

Results and Discussion

Synthesis and Characterization. We have reported previously that treatment of $[Cp^*Rh(\mu\text{-}Cl)Cl]_2$ with dilithium dichalcogenolato carboranes gives the 16-electron dithiolene and diselenolene complexes **1a**,**b** and investigated the addition reactions at the rhodium atom.[3a] The complex **1a** can react with $W(CO)_3(py)_3$ (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** and **4** together with the red dirhodium complex **3** as byproduct, respectively (Scheme 1). Complex **4** can be obtained in higher yield when longer reaction times are applied.

The complexes **2a**, **3**, and **4** are neutral, diamagnetic, and air-sensitive in solution. In complex **2a**, the Rh atoms have been reduced from Rh^{III} to Rh^{II}, apparently by the fragment $[W(CO)_3]$, which is generated effectively from the combination of $[W(CO)_3(py)_3]$ and BF_3.[10] A similar phenomenon was also found in the formation of phenyl dithiolato cobalt complex $[(\eta^5\text{-}C_5H_5)Co(S_2C_6H_4)]_2\text{-}Mo(CO)_2$[11] and carborane dichalcogenolato molybdenum complexes $\{Cp'Rh[E_2C_2(B_{10}H_{10})]\}_2Mo(CO)_2$ ($Cp' = \eta^5\text{-}1,3\text{-}{}^tBu_2C_5H_3$, E = S, Se). As the main product, dinuclear dithiolato carborane complex $\{Cp^*Rh[S_2C_2(B_{10}H_{10})]\}\{W(CO)_2[S_2C_2(B_{10}H_{10})]\}$ (**4**) satisfies the 18-electron rule. The corresponding cobalt complex $\{Cp'Co[S_2C_2(B_{10}H_{10})]\}\{W(CO)_2[S_2C_2(B_{10}H_{10})]\}$ has been recently reported.[8e]

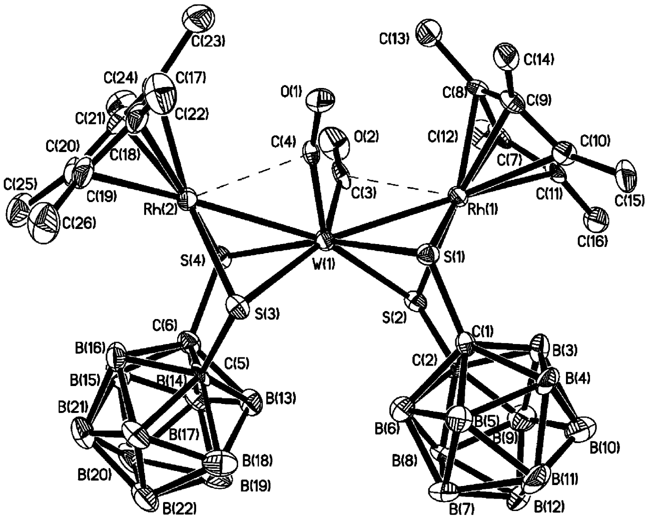


Figure 1. Molecular structure of **2a**. Selected bond lengths (Å) and angles (deg): W(1)−Rh(1) 2.7461(16), W(1)−Rh(2) 2.7891(14), W(1)−S(1) 2.496(3), W(1)−S(2) 2.528(3), W(1)−C(3) 2.002(13), W(1)−C(4) 1.973(14), Rh(1)−S(1) 2.337(3), Rh(1)−S(2) 2.407(3), Rh(1)−C(3) 2.574(12), Rh(2)−C(4) 2.550(12); Rh(1)−W(1)−Rh(2) 145.23(3), S(1)−W(1)−S(2) 74.40(10), S(1)−W(1)−S(3) 92.73(11), S(1)−W(1)−Rh(1) 52.69(8), S(1)−W(1)−C(3) 114.6(3), S(1)−Rh(1)−S(2) 79.62(11), S(1)−Rh(1)−W(1) 58.16(8), W(1)−C(3)−O(2) 162.3(10), W(1)−C(3)−Rh(1) 72.5(4), Rh(1)−C(3)−O(2) 125.1(9).

The IR spectra of the products **2a**, **3**, and **4** in the solid state exhibit intense B−H stretching of carborane at about 2580(vs) cm^{-1}. Complex **2a** exhibited strong vibrations of carbon monoxide at about 1885(vs) and 1828(vs) cm^{-1} in the region typical for a CO bridge, and the IR spectra of **4** showed strong stretching frequencies for the carbonyl groups at 1988(vs) and 1925(vs) cm^{-1} in the region typical for terminal CO, which is in agreement with the data of the structures.

The molecular structures of **2a**, **3**, and **4** have been established by single-crystal X-ray structure analysis (Figures 1, 2, and 3). The rhodium atoms of the Rh_2W backbone in **2a** have retained their Cp* rings, and the W center is eight-coordinate with a square-antiprismatic geometry. In complex **2a**, the coordination environment of the W center connected to the nonmetallic ligands (S and CO) is distorted trigonal-prismatic, and the two S−W−S planes are twisted by 33.9° with respect to one another. The coordination environment of the W center with respect to RhS_2 ligand units is distorted trigonal-prismatic. The two Rh−W single bonds (2.7461(16) and 2.7891(14) Å) are each supported by a symmetrically bridging *o*-carborane dithiolato ligand and may therefore be compared with the corresponding distance in sulfide-bridged Rh−W complexes such as trinuclear sulfide cluster $[Cp^*RhCl(\mu\text{-}S)_2W]_2$ (2.908(2) Å),[12] $[Rh(COD)]_2\text{-}WS_4$ (2.87, 2.84 Å),[13] and $[(Me_2Tp)W({=}S)(\mu\text{-}S)_2Rh(cod)]$ (2.852(1) Å).[14] The Rh(1)−W(1)−Rh(2) angle is 145.23(3)°. The planar pseudoaromatic system of the two rhodadithiolene heterocycles in **1a** is no longer present in **2a**, and the dihedral angle at the S···S vector in the RhS_2C_2 ring is 131°.

The new dinuclear Rh^{II} complex **3** contains one carborane dithiolato chelate ligand, which is arranged so that both S atoms bridge two rhodium atoms (Figure 2). The molecule contains a mirror plane. The Rh−Rh distance of 2.6245(9) Å corresponds to a metal−metal

---

[10] Nesmeyanov, A. N.; Krivykh, V. V.; Kaganovich, V. S.; Rybinskaya, M. I. *J. Organomet. Chem.* **1975**, *102*, 185.

[11] (a) Nihei, M.; Nankawa, T.; Kurihara, M.; Nishihara, H. *Angew. Chem., Int. Ed.* **1999**, *38*, 1098. (b) Muratsugu, S.; Nakagawa, N.; Habe, S.; Namiki, K.; Murata, M.; Nishihara, H. In *5th Japan-China Joint Symposium on Metal Cluster Compounds*; Japan, 2004; p 59.

[12] Howard, K. E.; Rauchfuss, Th. B.; Wilson, S. R. *Inorg. Chem.***1988**, *27*, 3561.

[13] Howard, K. E.; Rauchfuss, Th. B. *J. Am. Chem. Soc.* **1986**, *108*, 297.

[14] Seino, H.; Iwata, N.; Wawarai, N. Hidai, M.; Mizobe, Y. *Inorg. Chem.* **2003**, *42*, 7387.

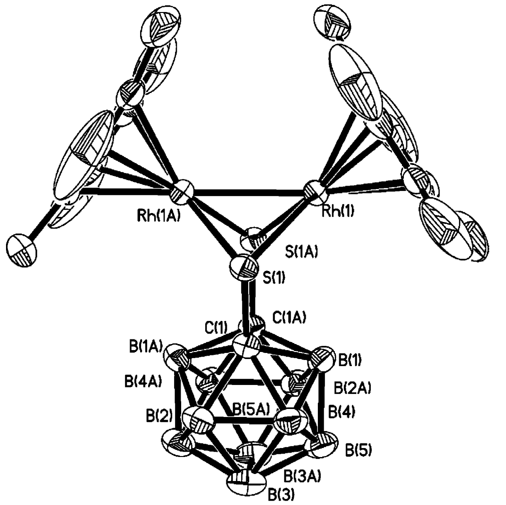


Figure 2. Molecular structure of **3**. Selected bond lengths (Å) and angles (deg): Rh(1)−Rh(1A) 2.6245(9), Rh(1)−S(1) 2.3429(14), Rh(1)−S(1A) 2.3360(13), S(1)−C(1) 1.830(5), C(1)−C(1A) 1.624(9); S(1)−Rh(1)−S(1A) 80.76(6), S(1)−Rh(1)−Rh(1A) 55.75(4), Rh(1)−S(1)−Rh(1A) 68.24(4), C(1)−S(1)−Rh(1) 103.05(16), C(1A)−C(1)−S(1) 112.61(15).

single bond;[9,15] thus **3** is formally an 18-electron complex. **3** is similar to the analogous Cp′ complex $(Cp'Rh)_2[S_2C_2(B_{10}H_{10})]$ (Cp′ = η^5-1,3-^{t}Bu$_2$C$_5$H$_3$)[9] and corresponding cobalt complex $(CpCo)_2[S_2C_2(B_{10}H_{10})]$, which was reported by Ko et al.[2]

The heteronuclear complex **4** contains two *o*-carborane thiolato ligands, one $[S_2C_2(B_{10}H_{10})]^{2-}$ is attached to the Cp*Rh fragment, and μ-S$_2$ is bridging to W(CO)$_2$[S$_2$C$_2$(B$_{10}$H$_{10}$)]. The W center has seven-coordination geometry, having two terminal carbonyl ligands (the W−C−O bond angles of 171.5(10)° and 176.6(11)° are nearly linear), two sulfur atoms of dithiolate-carborane, and another two μ-S$_2$ bridges to the Rh atom. The planar pseudoaromatic system of the rhodadithiolene heterocycle **1a** is also no longer present in **4**, and the dihedral angle at the S···S vector in the RhS$_2$C$_2$ ring is 136°. The five-membered metallacycle W(1)S(3)S(4)C(4)C(5) is almost planar, the dihedral angle along the S···S vector being 179.65°. The W−Rh distance (2.7407(14) Å in **4**, cf. 2.885(1) Å in Cp*Rh(PMe$_3$)[WS$_4$][16]) is comparatively short, only slightly longer than the sum of the atomic radii (1.345 (Rh) and 1.37 (W) Å, respectively). This can be taken to indicate that direct interaction between the two different transition metals exists, in addition to the *o*-carborane dithiolato ligand connection.[17] Direct metal−metal bonding is supported by the fact that the Rh−S−W angles (68.62(8)° and 68.52(8)° in **4**, cf. 77.5(1)° and 77.2(1)° in Cp*Rh(PMe$_3$)[WS$_4$]) are acute.

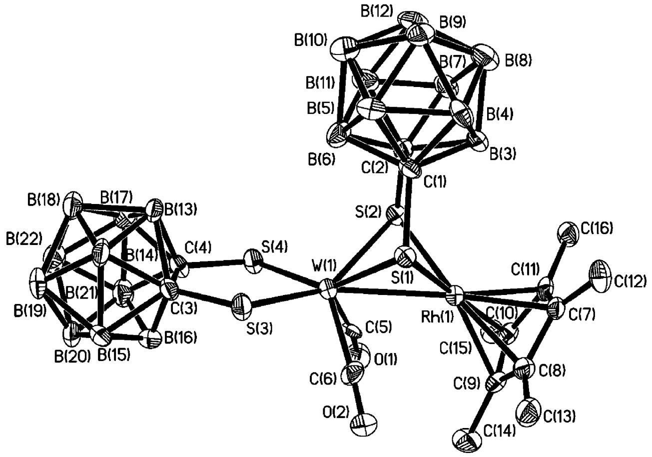
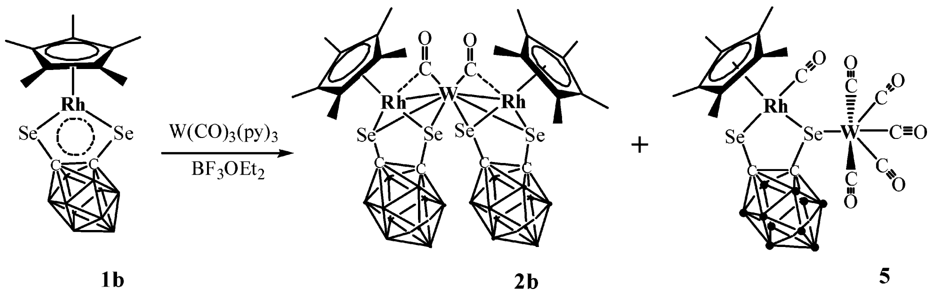


Figure 3. Molecular structure of **4**. Selected bond lengths (Å) and angles (deg): W(1)−Rh(1) 2.7407(14), W(1)−S(1) 2.491(3), W(1)−S(3) 2.368(3), W(1)−C(5) 1.934(17), W(1)−C(6) 2.007(13), Rh(1)−S(1) 2.368(3), Rh(1)−S(2) 2.374(3); S(1)−W(1)−S(2) 75.68(10), S(3)−W(1)−S(4) 86.14(11), S(1)−W(1)−S(4) 148.52(11), S(1)−W(1)−Rh(1) 53.58(7), S(1)−W(1)−C(6) 76.6(3), S(1)−Rh(1)−S(2) 80.25(11), S(1)−Rh(1)−W(1) 57.80(7), W(1)−C(5)−O(1) 171.5(10), W(1)−C(6)−O(2), 176.6(11), Rh(1)−S(2)−W(1) 68.52(8), Rh(1)−S(1)−W(1) 68.62(8).

The analogous reaction of **1b** with W(CO)$_3$(py)$_3$ (py = pyridine, NC$_5$H$_5$) in the presence of more than 3 equiv of BF$_3$ in diethyl ether affords the purple, trinuclear complex **2b** in 23% yield together with the orange binuclear complex **5** in 52% yield (Scheme 2). Complexes **2b** and **5** are diamagnetic. The ^{13}C NMR spectrum of **5** in CDCl$_3$ solution shows a singlet at 197.67 ppm due to a carbonyl carbon atom connected with Rh and another one at 210.21 ppm due to carbon connected to W, according to the peak indensity. The IR spectra of the products **2b** and **5** in the solid state exhibit intense B−H stretching of carborane at about 2575(vs) cm^{-1}. Complex **2b** exhibited strong vibrations of carbon monoxide at about 1876(vs) and 1817(vs) cm^{-1} in the region typical for a CO bridge, and the IR spectra of **5** showed strong stretching frequencies for the multicarbonyl groups at 2028(vs), 1960(vs), 1917(vs), and 1888(vs) cm^{-1} in the region typical for terminal CO, which is in agreement with the data of the structure.

An X-ray crystallographic structure analysis was carried out for $\{Cp^*Rh[Se_2C_2(B_{10}H_{10})]\}_2W(CO)_2$ (**2b**) (Figure 4). The unit cell of **2b** contains two crystallographically independent, but chemically similar molecules, which are related by a noncrystallographical pseudoinversion center. Figure 4 shows a view of only one of the molecules. The diselenolate complex **2b** is isomorphous to the complex **2a**. The complex **2b** also

Scheme 2. Synthesis of 2b and 5



1b **2b** **5**

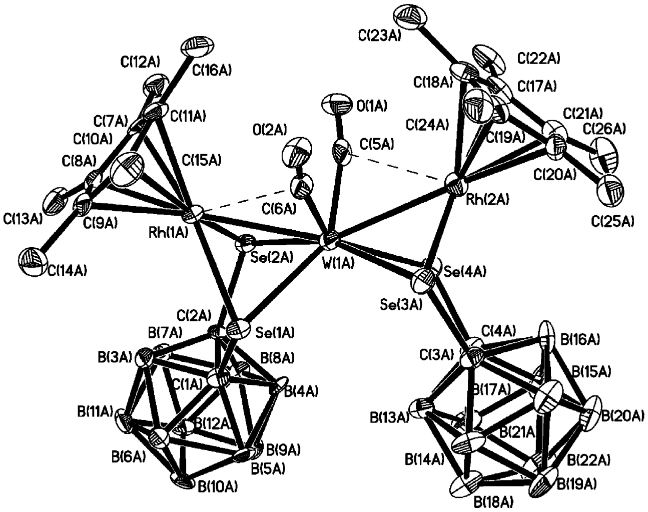


Figure 4. Molecular structure of **2b**. Selected bond lengths (Å) and angles (deg): W(1A)−Rh(1A) 2.7607(12), W(1A)−Rh(2A) 2.7517(12), W(1A)−Se(1A) 2.6119(12), W(1A)−Se(2A) 2.6310(12), W(1A)−C(5A) 2.001(11), W(1A)−C(6A) 1.992(11), Rh(1A)−Se(1A) 2.5054(13), Rh(1A)−Se(2A) 2.4497(13); Rh(1A)−W(1A)−Rh(2A) 143.16(3), Se(1A)−W(1A)−Se(2A) 76.52(4), Se(1A)−W(1A)−Se(3A) 125.23(4), Se(1A)−W(1A)−Rh(1A) 55.51(3), Se(1A)−W(1A)−C(5A) 144.9(3), Se(1A)−Rh(1A)−Se(2A) 81.86(4), Se(1A)−Rh(1A)−W(1A) 59.23(3), W(1A)−C(5A)−O(1A) 167.3(9).

contains two carborane diselenolato chelate ligands, which are arranged so that both Se atoms bridge rhodium and tungsten to form intramolecular Rh−W single bonds (2.7607(12) and 2.7517(12) Å). The coordination environment of the W center with respect to $RhSe_2$ ligand units is distorted trigonal-prismatic; two Se−W−Se planes are twisted by 42.0° with respect to one another.

The dinuclear complex **5** can be recrystallized from hexane to give well-formed orange single crystals in the triclinic space group $P\bar{1}$ with two molecules in the unit cell. The *o*-carborane-1,2-diselenolate bridges combine a [Cp*Rh(CO)] and a [$W(CO)_5$] fragment in **5** (Figure 5). The Rh atom carries one carbonyl group in addition to a formal 4e chelate ligand $[(B_{10}H_{10})C_2Se(Se{-}R)]^{2-}$ (R = $W(CO)_5$). The Rh−Se bond distances (2.458(2)−2.4799(18) Å) are similar to those in selenolate complexes, such as Cp*Rh(PMe_3)[$Se_2C_2(B_{10}H_{10})$] and Cp*Rh(PMe_3)$(SePh)_2$.[3a] The long Rh(1)···W(1) separation (4.37 Å) and the obtuse angle (Rh(1A)−Se(2A)−W(1A) 115.93(6)°) indicate that a direct bonding interaction between the two metals is absent.

The related reaction between **1a**, **1b**, and $Co_2(CO)_8$ in the presence of Me_3NO in toluene at room temperature leads to dark red products {Cp*Rh[$E_2C_2(B_{10}H_{10})$]}[$Co_2(CO)_5$] [E = S (**6a**), Se (**6b**)] in about 80% yields, respectively (Scheme 3). Both compounds are neutral, diamagnetic, and air-sensitive in solution. The characterizations of the products **6a**,**b** are based on elemental analyses and X-ray diffraction studies. The IR spectra of **6a**,**b** show strong stretching frequencies for the carbonyl groups at 2055, 2033, 2017, 1989, 1812 cm^{-1} for **6a** and 2051, 2029, 2013, 1985, 1809 cm^{-1} for **6b**, the band (around 1810 cm^{-1}) in the region typical for CO bridges. Apparently, there are two kind of ν(CO) frequencies for the $Co_2(CO)_5$ moieties. The ^{13}C NMR spectrum of **6a**,**b** in $CDCl_3$ solution shows only one resonance at $\delta = 186$ ppm for the CO group.

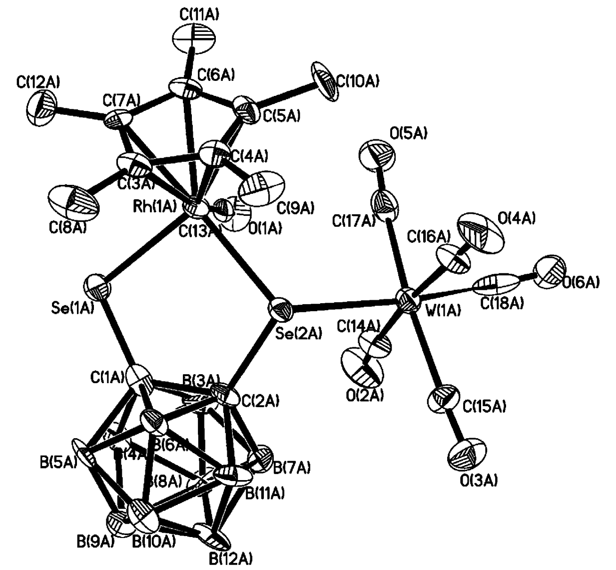
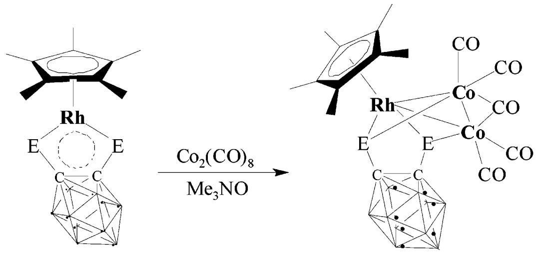


Figure 5. Molecular structure of **5**. Selected bond lengths (Å) and angles (deg): Rh(1A)−Se(1A) 2.4641(18), Rh(1A)−Se(2A) 2.478(2), Rh(1A)−C(13A) 1.893(16), W(1A)−Se(2A) 2.6775(18), W(1A)−C(14A) 2.050(16), W(1A)−C(18A) 1.87(2); Se(1A)−Rh(1A)−Se(2A) 92.91(6), Se(1A)−Rh(1A)−C(13A) 86.2(4), Se(2A)−Rh(1A)−C(13A) 91.3(5), Se(2A)−W(1A)−C(14A) 97.6(5), C(14A)−W(1A)−C(18A) 90.0(7), C(14A)−W(1A)−C(15A) 89.3(7), Rh(1A)−Se(2A)−W(1A) 115.93(6), Rh(1A)−C(13A)−O(1A) 176.4(13), W(1A)−C(14A)−O(2A) 175.1(18), W(1A)−C(18A)−O(6A) 177.1(15).

Scheme 3. Synthesis of 6a,b



1a, **1b**

E = S(**6a**), Se(**6b**)

The structures of **6a**,**b** have been determined by X-ray analyses using single crystals grown from toluene/hexane, after chromatography on silica. Both of them are in the form of dark red prisms in the orthorhombic space group *Pbca* with eight molecules in the unit cell. The molecular structures and selected bond distances and angles of **6a** and **6b** are depicted in Figures 6 and 7.

Compound **6a** has a closed $RhCo_2$ triangular core, in which the two Rh−Co edges are bridged by μ_3-S ligands, and the Co−Co edge is bridged by a μ_2-CO ligand. The Rh−Co distances (Rh(1)−Co(1) 2.6057(9) Å, Rh(1)−Co(2) 2.6399(9) Å) are very short and clearly indicative of bonding interactions, compared with the Rh−Co bond

---

(15) (a) Connelly, N. G.; Johnson, G. A.; Kelly, B. A.; Woodward, P. *J. Chem. Soc., Chem. Commun.* **1977**, 436. (b) Herberhold, M.; Jin, G.-X.; Rheingold, A. L. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 656. (c) Nishioka, T.; Nakamura, S.; Kaneko, Y.; Suzuki, T.; Kinoshita, I.; Kiyooka, S.; Isobe, K. *Chem. Lett.* **1996**, 911.

(16) Herberhold, M.; Jin, G.-X.; Rheingold, A. L. *Z. Anorg. Allg. Chem.* **2005**, *631*, 135.

(17) Greaney, M. A.; Coyle, C.; Harmer, L. M.; Jordan, A. A.; Stiefel, E. I. *Inorg. Chem.* **1989**, *28*, 912.

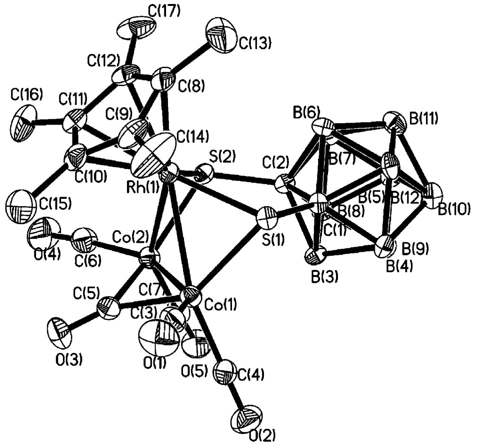


Figure 6. Molecular structure of **6a**. Selected bond lengths (Å) and angles (deg): Co(1)−Co(2) 2.4465(11), Rh(1)−Co(1) 2.6057(9), Rh(1)−Co(2) 2.6399(9), Rh(1)−S(1) 2.3110(15), Rh(1)−S(2) 2.3245(14), Co(1)−S(1) 2.2724(16), Co(2)−S(2) 2.2399(16), Co(1)−C(5) 1.907(6), Co(2)−C(5) 1.905(6), Co(1)−C(3) 1.798(6), Co(1)−C(4) 1.789(7), Co(2)−C(6) 1.813(7), Co(2)−C(7) 1.777(6); Co(1)−Rh(1)−Co(2) 55.60(2), Co(1)−Rh(1)−S(1) 54.66(4), Co(2)−Rh(1)−S(2) 53.18(4), S(1)−Rh(1)−S(2) 90.66(5), Rh(1)−Co(1)−Co(2) 62.91(3), Rh(1)−Co(2)−Co(1) 61.49(3), Co(2)−Co(1)−C(5) 50.03(18), Co(1)−Co(2)−C(5) 50.11(18), Co(1)−C(5)−Co(2) 79.9(2), Rh(1)−S(1)−Co(1) 69.29(4), Rh(1)−S(2)−Co(2) 70.64(4), C(3)−Co(1)−C(4) 95.5(3), C(6)−Co(2)−C(7) 96.4(3).

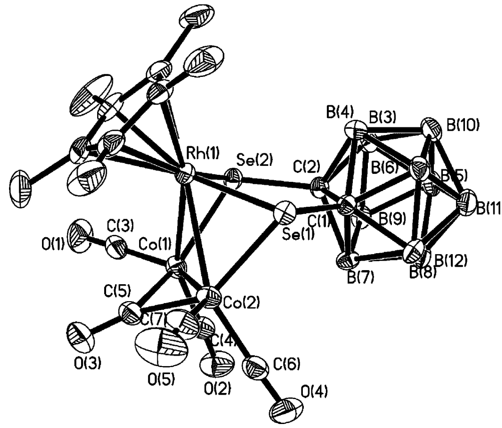


Figure 7. Molecular structure of **6b**. Selected bond lengths (Å) and angles (deg): Co(1)−Co(2) 2.4478(11), Rh(1)−Co(2) 2.6583(9), Rh(1)−Co(1) 2.6197(9), Rh(1)−Se(1) 2.4271(8), Rh(1)−Se(2) 2.4159(8), Co(2)−Se(1) 2.3452(10), Co(1)−Se(2) 2.3754(10), Co(1)−C(5) 1.904(5), Co(2)−C(5) 1.903(6), Co(2)−C(7) 1.814(6), Co(2)−C(6) 1.784(6), Co(1)−C(3) 1.796(6), Co(1)−C(4) 1.777(6); Co(1)−Rh(1)−Co(2) 55.26(2), Co(2)−Rh(1)−Se(1) 54.70(3), Co(1)−Rh(1)−Se(2) 56.12(2), Se(1)−Rh(1)−Se(2) 92.13(2), Rh(1)−Co(2)−Co(1) 61.57(3), Rh(1)−Co(1)−Co(2) 63.17(3), Co(1)−Co(2)−C(5) 49.99(16), Co(2)−Co(1)−C(5) 49.98(17), Co(1)−C(5)−Co(2) 80.0(2), Rh(1)−Se(1)−Co(2) 67.68(2), Rh(1)−Se(2)−Co(1) 66.28(2), C(6)−Co(2)−C(7) 96.5(3), C(3)−Co(1)−C(4) 96.3(3).

of [CoRh(CO)$_4$(μ-H)(μ-P^{t}Bu$_2$)(^{t}Bu$_2$PH)] (2.7470(6) Å).[18] The Co(1)−Co(2) distance is 2.4465(11) Å, typical of a Co−Co single bond.[15b,19] Due to the coordination of the S atoms to Co, the pseudoaromatic rhodadithiolato heterocyclic system is destroyed and bent with a dihedral angle of 161.5° along the S···S vector. Each Co atom bears two terminal CO ligands; the remaining CO group bridges the Co(1)−Co(2) metal−metal bond. The Co(1)−C(5) and Co(2)−C(5) bonds are 1.907(6) and 1.905(6) Å, similar to the bridging Co−C distances of $Co_2(CO)_8$ (mean value 1.92 Å)[20] and longer than Co−C (C of terminal CO group) (range 1.78−1.81 Å). The molecular structure of the diselenolate complex **6b** is isomorphous to that of **6a**. Compound **6b** also contains three metal atoms, with a triangular core similar to that of **6a**. In complex **6b**, three metal−metal bonds (Co(1)−Co(2) 2.4478(11), Rh(1)−Co(2) 2.6583(9), Rh(1)−Co(1) 2.6197(9) Å) indicate the strong direct interactions. The dihedral angle (165.4°) along the Se···Se vector is almost identical with that in **6a**, whereas it is 180° in the analogous parent diselenolene complex Cp*Ir[Se_2C_2($B_{10}H_{10}$)].[4a]

In summary, the formation of a hetero metal−metal bond in complexes **2a**,**b**, **4**, and **6a**,**b** by the reactions of the 16-electron complexes **1a**,**b** involves redox processes during which Rh is partially reduced by low-valence transition metal complexes, such as the fragment [W(CO)$_3$] or $Co_2(CO)_8$.

Experimental Section

General Procedures. All manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques. All solvents were dried and deoxygenated before use. The solvents diethyl ether, toluene, THF, and *n*-hexane were refluxed and distilled over sodium/benzophenone ketyl under nitrogen prior to use. The starting materials Cp*Rh[E_2C_2($B_{10}H_{10}$)] (E = S (**1a**), Se (**2b**))[3a] and W(CO)$_3$(py)$_3$[21] were prepared by slightly modified literature procedures. BF_3·Et_2O, Me_3NO, and $Co_2(CO)_8$ were purchased from Aldrich and used without purification. Elemental analyses for C and H were carried out on an Elementar III Vario EI analyzer. ^{1}H(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[S_2C_2($B_{10}H_{10}$)]}$_2$W(CO)$_2$ (2a), (Cp*Rh)$_2$[S_2C_2($B_{10}H_{10}$)] (3), and {Cp*Rh[S_2C_2($B_{10}H_{10}$)]}{W(CO)$_2$[S_2C_2($B_{10}H_{10}$)]} (4). BF_3·OEt_2 (0.15 mL, 47%, 0.5 mmol) was added to a 100 mL Schlenk tube containing **1a** (89 mg, 0.20 mmol) and W(CO)$_3$(py)$_3$ (76 mg, 0.15 mmol) in diethyl ether (40 mL). The deep green suspension was stirred for 2 days and gradually changed to red. 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 CH_2Cl_2/hexane (1:6) and recrystallized from hexane to afford 24 mg (21%) of red crystals of **2a**. Anal. Calcd for $C_{26}H_{50}B_{20}O_2Rh_2S_4W$: C, 27.64; H, 4.43. Found: C, 27.99; H, 4.57. ^{1}H NMR (500 MHz, $CDCl_3$, δ/ppm): 1.87(s, 30H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$, δ/ppm): 9.44(s, CH$_3$), 84.78(s, CS), 100.90(d, C_5(CH$_3$)$_5$, $^1J_{C-Rh}$ = 6.67 Hz). ^{11}B NMR (160 MHz, $CDCl_3$, δ/ppm): −4.23(2B), −7.64(2B), −8.89(2B), −11.42(4B). IR (KBr disk): ν = 2961, 2923, 2855 cm^{-1} (C−H); ν = 2576 cm^{-1} (B−H); ν = 1885, 1828 cm^{-1} (CO). The component in the second band was recrystallized from CH_2Cl_2/hexane (1:4) to give 11 mg (16%) of brown crystals of **3**. Anal. Calcd for $C_{22}H_{40}B_{10}Rh_2S_2$: C, 38.68; H, 5.91. Found: C, 38.97; H, 5.95. ^{1}H NMR

---

(18) Bottcher, H. C.; Craf, M.; Merzweiler, K.; Wagner, C. *Z. Anorg. Allg. Chem.* **2001**, *627*, 903.

(19) (a) Sly, W. G. *J. Am. Chem. Soc.* **1959**, *81*, 18. (b) Brown, D. A. *J. Chem. Phys.* **1960**, *33*, 1037.

(20) Summer, G. G.; Klug, H. P.; Alexander, L. E. *Acta Crystallogr.* **1964**, *17*, 732.

(21) (a) Hieber, W.; Muhlbauer, F. *Z. Anorg. Allg. Chem.* **1935**, *221*, 337. (b) Westland, A. D.; Muriithi, N. *Inorg. Chem.* **1973**, *12*, 2356. (c) Nesmeyanov, A. N.; Krivykh, V. V.; Kaganovich, V. S.; Rybinskaya, M. I. *J. Organomet. Chem.* **1975**, *102*, 185.

(500 MHz, $CDCl_3$, δ/ppm): 1.86(s, 30H, C*H*$_3$). IR (KBr disk): ν = 2957, 2910 cm^{-1} (C−H); ν = 2581 cm^{-1} (B−H). The component in the third band was eluted with CH_2Cl_2/hexane (1:2). Recrystallization from CH_2Cl_2/hexane at −18 °C gave violet crystals of **4** (96 mg, 49%). Anal. Calcd for $C_{17}H_{37}B_{20}Cl_2O_2RhS_4W$: C, 20.91; H, 3.82. Found: C, 21.40; H, 3.84. ^1H NMR (500 MHz, $CDCl_3$, δ/ppm): 1.99(s, 15H, C*H*$_3$). ^{13}C NMR (125 MHz, $CDCl_3$, δ/ppm): 8.33(s, *C*H$_3$), 79.40(s, *C*S), 91.26(s, *C*S), 100.48(d, $C_5(CH_3)_5$, $^1J_{C-Rh}$ = 6.00 Hz), 218.75(s, *C*O). ^{11}B NMR (160 MHz, $CDCl_3$, δ/ppm): −4.15(2B), −7.65(2B), −8.91(2B), −11.51(4B). IR (KBr disk): ν = 2962, 2922 cm^{-1} (C−H), ν = 2593 cm^{-1} (B−H); ν =1988, 1925 cm^{-1} (CO).

Synthesis of $Cp^*Rh(CO)[Se_2C_2(B_{10}H_{10})]W(CO)_5$ (5) and $\{Cp^*Rh[Se_2C_2(B_{10}H_{10})]\}_2W(CO)_2$ (2b). $BF_3\cdot OEt_2$ (0.15 mL, 47%, 0.5 mmol) was added to a 100 mL Schlenk tube containing **1b** (0.109 g, 0.20 mmol) and $W(CO)_3(py)_3$ (76 mg, 0.15 mmol) in diethyl ether (40 mL). The deep green suspension was stirred for 3 days at room temperature and gradually changed to red. The solvent was then evaporated to dryness under vacuum, and components of the residue were separated by column chromatography on silica with CH_2Cl_2/hexane (1:3) as eluent. The compound in the first zone was recrystallized from hexane to give 93 mg (52%) of orange crystals of **5**. Anal. Calcd for $C_{18}H_{25}B_{10}O_6RhSe_2W$: C, 24.27; H, 2.81. Found: C, 23.92; H, 2.77. ^1H NMR (500 MHz, $CDCl_3$, δ/ppm): 1.94(s, 15H, C*H*$_3$). ^{13}C NMR (125 MHz, $CDCl_3$, δ/ppm): 9.86(s, *C*H$_3$), 68.53(s, *C*Se), 101.79(d, $C_5(CH_3)_5$, $^1J_{C-Rh}$ = 5.50 Hz), 197.67(s, Rh-*C*O), 210.21(s, W-*C*O). ^{11}B NMR (160 MHz, $CDCl_3$, δ/ppm): −4.38(2B), −7.84(2B), −8.90(2B), −11.18(4B). IR (KBr disk): ν = 2923, 2853 cm^{-1} (C−H); ν = 2579 cm^{-1} (B−H); ν = 2028, 1960, 1916.8, 1887.7 cm^{-1} (CO). The compound in the second zone was recrystallized from CH_2Cl_2 to give 30 mg (23%) of red crystals of **2b**. Anal. Calcd for $C_{26}H_{50}B_{20}O_2Rh_2Se_4W$: C, 23.70; H, 3.80. Found: C, 23.54; H, 3.92. ^1H NMR (500 MHz, $CDCl_3$, δ/ppm): 1.85(s, 30H, C*H*$_3$). ^{13}C NMR (125 MHz, $CDCl_3$, δ/ppm): 9.60(s, *C*H$_3$), 71.64(s, *C*Se), 101.72(d, $C_5(CH_3)_5$, $^1J_{C-Rh}$ = 6.67 Hz). ^{11}B NMR (160 MHz, $CDCl_3$, δ/ppm): −4.46(2B), −7.57(2B), −8.86(2B), −10.65(4B). IR (KBr disk): ν = 2959, 2908 cm^{-1} (C−H); ν = 2573 cm^{-1} (B−H); ν = 1879, 1817 cm^{-1} (CO).

Synthesis of $\{Cp^*Rh[E_2C_2(B_{10}H_{10})]\}[Co_2(CO)_5]$ [E = S (6a), Se (6b)]. To a solution of either **1a** (89 mg, 0.2 mmol) or **1b** (109 mg, 0.2 mmol) in toluene (30 mL) were added $Co_2(CO)_8$ (0.2 mmol, 68 mg) and Me_3NO (0.6 mmol, 45 mg). The color of the solution changed immediately from green to dark red. After stirring for 3 h, the solvent was evaporated under reduced pressure. The residue was redissolved in 5 mL of toluene and chromatographed on silica gel. Elution with toluene/hexane (1:5) gave a dark red zone, which contained **6a** (111 mg, 79%) or **6b** (131 mg, 82%), respectively. Crystals of **6a**,**b** were obtained from toluene/hexane (1:1). Complex **6a**: Anal. Calcd for $C_{17}H_{25}B_{10}Co_2O_5RhS_2$: C, 29.07; H, 3.59. Found: C, 29.16; H, 3.56. ^1H NMR (500 MHz, $CDCl_3$, δ/ppm): 1.87(s, 30H, C*H*$_3$). ^{13}C NMR (125 MHz, $CDCl_3$, δ/ppm): 10.33(s, *C*H$_3$), 98.52(s, *C*S), 106.56(s, $C_5(CH_3)_5$), 186.36(s, *C*O). ^{11}B NMR (160 MHz, $CDCl_3$, δ/ppm): −2.25, −3.17, −5.71, −7.53, −8.87, −12.67, −14.96. IR (KBr disk): ν = 2958, 2914 cm^{-1} (C−H); ν = 2590 cm^{-1} (B−H); ν = 2055, 2033, 2017, 1989, 1812 cm^{-1} (CO). Complex **6b**: Anal. Calcd for $C_{17}H_{25}B_{10}Co_2O_5RhSe_2$: C, 25.65; H, 3.16. Found: C, 25.68; H, 3.12. ^1H NMR (500 MHz, $CDCl_3$, δ/ppm): 1.92(s, 30H, C*H*$_3$). ^{13}C NMR (125 MHz, $CDCl_3$, δ/ppm): 9.97(s, *C*H$_3$), 67.85(s, *C*Se), 105.72(s, $C_5(CH_3)_5$), 186.04(s, *C*O). ^{11}B NMR (160 MHz, $CDCl_3$, δ/ppm): −2.65, −3.47, −5.88, −7.82, −8.87, −13.96, −15.13. IR (KBr disk): ν = 2960, 2910, 2831 cm^{-1} (C−H); ν = 2585 cm^{-1} (B−H); ν = 2585 cm^{-1} (B−H); ν = 2051, 2029, 2013, 1985, 1809 cm^{-1} (CO).

X-ray Data Collection, Structure Determination, and Refinement. Suitable single crystals of complexes **2a**−**6b** 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-

Table 1. Crystallographic Data and Structure Refinement Parameters for 2a, 2b, 3, 4, 5, 6a, and 6b

	2a	2b	3	4	5	6a	6b
chemical formula	$C_{26}H_{50}B_{20}O_2Rh_2S_4W$	$C_{52}H_{100}B_{40}O_4Rh_4Se_8W_2$	$C_{22}H_{40}B_{10}Rh_2S_2$	$C_{17}H_{37}B_{20}Cl_2O_2RhS_4W$	$C_{36}H_{50}B_{20}O_{12}Rh_2Se_4W_2$	$C_{17}H_{25}B_{10}Co_2O_5RhS_2$	$C_{17}H_{25}B_{10}Co_2O_5RhSe_2$
fw	1128.77	2632.74	682.58	975.57	1780.32	702.36	796.16
temp, K	293(2)	293(2)	293(2)	298(2)	298(2)	293(2)	293(2)
λ, Å	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
cryst size, mm^3	0.12 × 0.08 × 0.06	0.20 × 0.08 × 0.05	0.10 × 0.08 × 0.06	0.20 × 0.10 × 0.02	0.10 × 0.05 × 0.04	0.10 × 0.10 × 0.05	0.10 × 0.08 × 0.05
cryst syst	monoclinic	monoclinic	monoclinic	triclinic	triclinic	orthorhombic	orthorhombic
space group	*P*2(1)/*c*	*P*2(1)/*n*	*C*2/*c*	$P\bar{1}$	$P\bar{1}$	*Pbca*	*Pbca*
a, Å	14.086(7)	27.721(9)	18.071(3)	12.287(6)	11.273(3)	10.123(2)	10.129(2)
b, Å	21.333(10)	13.841(5)	12.410(2)	13.278(6)	14.837(4)	15.764(4)	16.048(4)
c, Å	15.408(8)	25.617(9)	15.353(3)	13.865(6)	19.172(6)	34.566(8)	34.604(8)
α, deg	90	90	90	73.666(7)	68.450(5)	90	90
β, deg	109.958(7)	114.495(4)	114.356(3)	65.349(7)	80.684(5)	90	90
γ, deg	90	90	90	73.831(7)	89.393(5)	90	90
V, $Å^3$	4352(4)	8944(5)	3136.7(10)	1939.0(15)	2939.2(15)	5516(2)	5625(2)
ρ, g cm^{-3}	1.723	1.955	1.445	1.671	2.012	1.691	1.880
Z	4	4	4	2	2	8	8
μ, mm^{-1}	3.606	6.578	1.197	3.764	6.981	1.960	4.362
final *R* indices [$I > 2\sigma(I)$][a]	R1 = 0.0565 wR2 = 0.1227	R1 = 0.0382 wR2 = 0.0564	R1 = 0.0433 wR2 = 0.0979	R1 = 0.0630 wR2 = 0.1480	R1 = 0.0535 wR2 = 0.0945	R1 = 0.0535 wR2 = 0.1034	R1 = 0.0429 wR2 = 0.0802
R indices (for all data)	R1 = 0.1182 wR2 = 0.1428	R1 = 0.0993 wR2 = 0.0664	R1 = 0.0659 wR2 = 0.1074	R1 = 0.1015 wR2 = 0.1614	R1 = 0.1312 wR2 = 0.1107	R1 = 0.0756 wR2 = 0.1204	R1 = 0.0672 wR2 = 0.0882

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

monochromated Mo Kα ($\lambda = 0.71073$ 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.[22] The structures were solved by direct methods using the SHELXL-97 program.[23] 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.

Acknowledgment. Financial support by the National Science Foundation of China for Distinguished Young Scholars (29925101, 20421303) and by the Doctoral Fund of the Education Ministry of China (No.20020246011) is gratefully acknowledged.

Supporting Information Available: The crystallographic data for **2a**, **2b**, **3**, **4**, **5**, and **6a**,**b** are available free of charge via the Internet at http//pubs.acs.org.

OM050598P

---

(22) Sheldrick, G. M. *SADABS*, *A Program for Empirical Absorption Correction*; University of Göttingen: Göttingen, Germany, 1998.

(23) Sheldrick, G. M. *SHELXL-97*, *Program for the Refinement of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1997.