

Note

Synthesis of heteronuclear (MoRu₂) clusters from 16-electron half-sandwich complexes (*p*-Cymene)Ru[E₂C₂(B₁₀H₁₀)] (E = S, Se)

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Received 18 June 2005; received in revised form 21 September 2005; accepted 22 September 2005

Available online 25 October 2005

Abstract

The heterometallic cluster complexes {(*p*-Cymene)Ru[S₂C₂(B₁₀H₁₀)]}Mo(CO)₂{(CO)₃Ru[S₂C₂(B₁₀H₁₀)]} (**2**) and {(*p*-Cymene)Ru[Se₂C₂(B₁₀H₁₀)]}Mo(CO)₂ (**3**) (*p*-Cymene = η⁶-4-isopropyl-toluene) have been synthesized from the reactions of 16-electron half-sandwich ruthenium 1,2-dichalcogenolate carborane complexes (*p*-Cymene)Ru[E₂C₂(B₁₀H₁₀)] (E = S(**1a**), Se(**1b**)) with Mo(CO)₃(Py)₃ in the presence of BF₃ · Et₂O. The complexes of **2** and **3** were characterized by elemental analysis and IR, NMR spectra. The molecular structure of **2** has been characterized by single-crystal X-ray diffraction analysis. Complex **2** is unsymmetrical and the two Ru–Mo single bonds (2.7893(14), 2.8189(13) Å) are each supported by a symmetrically bridging *o*-carborane-1,2-dithiolato ligand.

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Keywords: Ruthenium; *p*-Cymene ligand; Dichalcogenolate ligand; Clusters; Molecular structure

1. Introduction

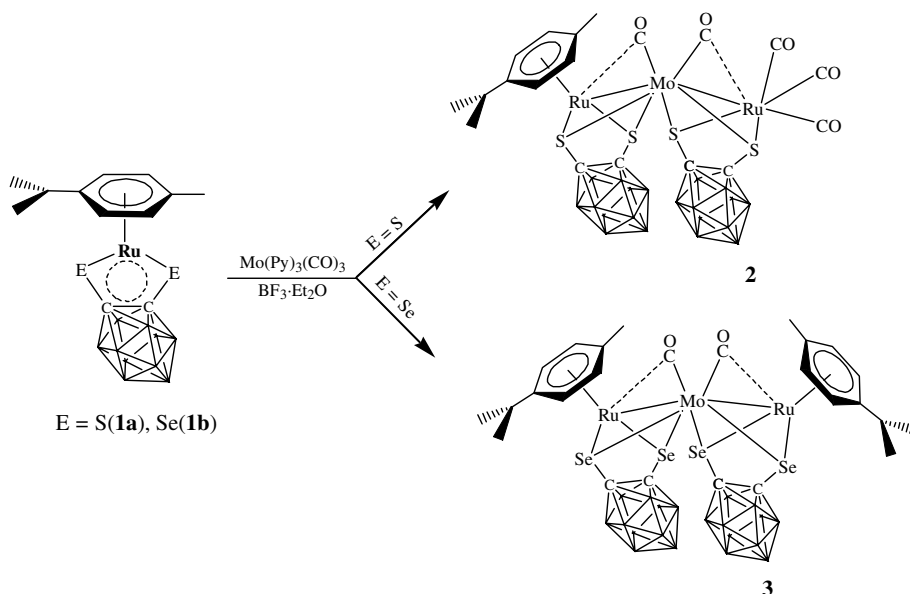
In the past few years, a fruitful investigation has been gained by introducing dichalcogenolate *o*-carboranyl ligands into the half-sandwich transition metal complexes [1]. A number of mononuclear 16 electron Cp and Cp* half-sandwich complexes of Co [2], Rh [3] and Ir [4] have been described which contain a bidentate, chelating 1,2-dicarba-*closo*-dodecaborane-1,2-dichalcogenolato ligand, [(B₁₀H₁₀)C₂E₂]²⁻ 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 and/or substitution of the carborane cage in the positions of B(3)/B(6) [6]. On the other hand, although 16-electron dichalcogenolene complexes have already been extended to the η⁶-arene system, complexes such as (*p*-Cymene)M[E₂C₂(B₁₀H₁₀)] (M = Ru, Os; E = S, Se) which have been synthesized and investigated [7], the coordination reactivity of 16-electron

ruthenium complex has not been explored so far, as to our knowledge. In this respect, we intended to investigate the reactions of (*p*-Cymene)Ru[E₂C₂(B₁₀H₁₀)] (E = S(**1a**), Se(**1b**)) whose *pseudo*-aromatic metallacycle can act as organometallic ligands. Herein, we report the reactivity of (*p*-Cymene)Ru[E₂C₂(B₁₀H₁₀)] (E = S(**1a**), Se(**1b**)) toward Mo(CO)₃(Py)₃ in the presence of BF₃ · Et₂O (Scheme 1).

2. Results and discussion

The 16-electron complexes (*p*-Cymene)Ru[E₂C₂(B₁₀H₁₀)] (E = S(**1a**), Se(**1b**)) can be synthesized from the reactions of [(*p*-Cymene)RuCl₂]₂ with dilithium dichalcogenolate carborane Li₂[E₂C₂(B₁₀H₁₀)] (E = S, Se) [7] in THF solution. The complex **1a** reacts with Mo(CO)₃(Py)₃ (Py = Pyridine, NC₅H₅) in the presence of more than three equivalents of BF₃ in diethyl ether to give the red, mixed-metal complexes {(*p*-Cymene)Ru[S₂C₂(B₁₀H₁₀)]}-Mo(CO)₂{(CO)₃Ru[S₂C₂(B₁₀H₁₀)]} (**2**) in moderate yield. The complex **2** is neutral, diamagnetic and air-sensitive in solution. In complex **2**, the Ru atoms have been reduced from Ru^{II} to Ru^I, apparently by the fragment [Mo(CO)₃], which is generated effectively from the combination of

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Scheme 1. Synthesis of complexes **2** and **3**.

[Mo(CO)₃(Py)₃] and BF₃ in diethyl ether solution [6,8]. Similar phenomenon was also found in the formation of carborane dichalcogenolate Rh complex {Cp'⁺Rh[E₂C₂(B₁₀H₁₀)]₂Mo(CO)₂(E = S, Se) [8]. Complex **2** shows excellent solubility in CH₂Cl₂ and toluene, slightly soluble in hexane.

The IR spectra of **2** in the solid state exhibits intense B–H stretching of carborane at about 2585(vs) cm⁻¹. Complex **2** reveals that, besides anticipated absorption of bridging CO at 1791 and 1872 cm⁻¹, there are two extraordinary

strong signals at 2037 and 2092 cm⁻¹, which is typical for terminal CO group. The ¹³C NMR spectrum shows three resonances for the CO groups, at 189.1, 187.4 and 186.1 ppm, respectively.

Fortunately, suitable single crystal of **2** was obtained by slowly diffusion of hexane into a dichloromethane solution. The molecular structure of **2** has been established by single-crystal X-ray structure analysis (Fig. 1). One of the ruthenium atoms of the Ru₂Mo backbone in **2** has retained its

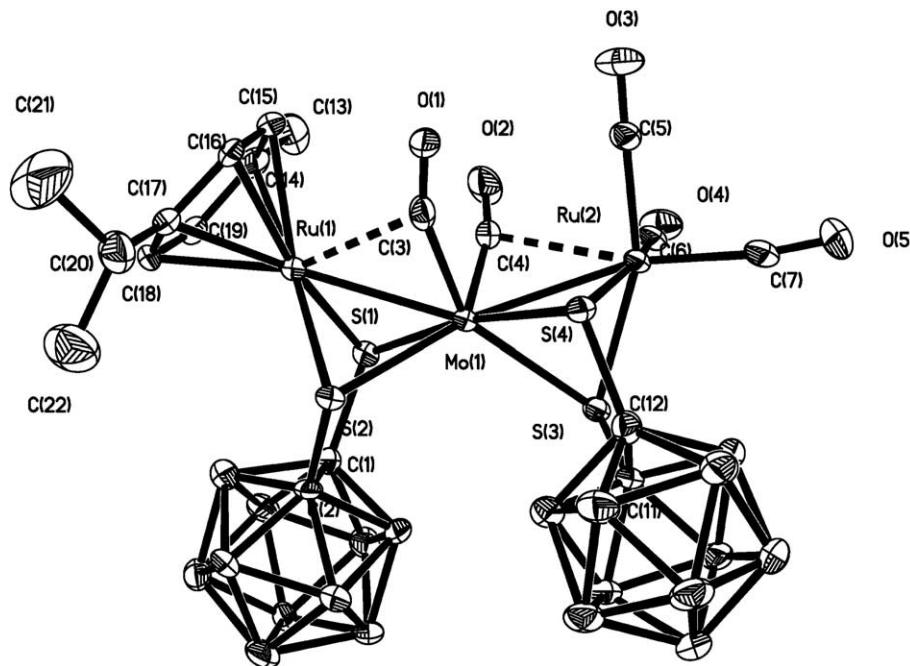
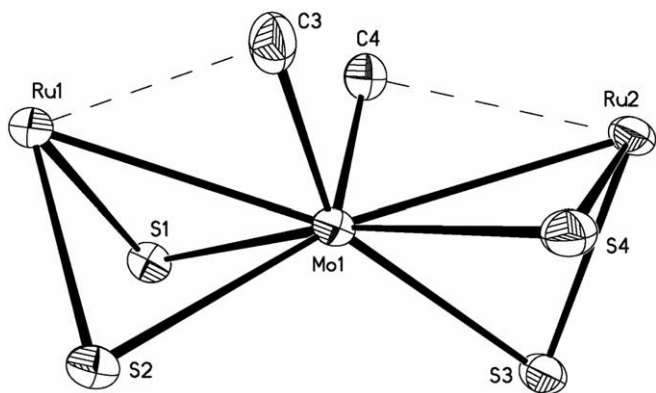


Fig. 1. Molecular structure of **2** (hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (°): Mo(1)–Ru(1) 2.7893(14), Mo(1)–Ru(2) 2.8189(13), Mo(1)–S(1) 2.505(3), Mo(1)–S(2) 2.569(3), Mo(1)–S(3) 2.588(3), Mo(1)–S(4) 2.564(3), Mo(1)–C(3) 1.967(12), Mo(1)–C(4) 1.954(13), Ru(2)–C(5) 1.933(11), Ru(2)–C(6) 1.899(13), Ru(2)–C(7) 1.927(13), Ru(1)–C(3) 2.458(11), Ru(2)–C(4) 2.644(11), Ru(1)–S(1) 2.367(3), Ru(1)–S(2) 2.393(3), Ru(2)–S(3) 2.426(3), Ru(2)–S(4) 2.405(3); Ru(1)–Mo(1)–Ru(2) 144.43(4), S(1)–Ru(1)–S(2) 78.56(9), S(4)–Ru(2)–S(3) 78.79(9), Mo(1)–C(3)–Ru(1) 77.3(4), Mo(1)–C(4)–Ru(2) 80.9(4), O(1)–C(3)–Mo(1) 158.3(9), O(2)–C(4)–Mo(1) 166.8(9), C(4)–Mo(1)–Ru(1) 86.8(3), C(3)–Mo(1)–Ru(1) 59.3(3).

Fig. 2. Molecular backbone of **2**.

p-Cymene ring and another Ru atom coordinates with three carbonyl ligands. The Mo center is eight-coordinate with a square-antiprismatic geometry. In complex **2**, the coordination environment of the Mo center connected to the non-metallic ligands (S and CO) is distorted trigonal-prismatic, the two S–Mo–S planes are twisted by 40.2° with respect to one another (Fig. 2). The two Ru–Mo single bonds (2.789 and 2.819 Å) are each supported by a symmetrically bridging *o*-carborane dithiolato ligand. The Ru(1)–Mo(1)–Ru(2) angle is 144.43(4)°. The planar *pseudo*-aromatic system of the two ruthenadithiolene heterocycles **1a** is no longer present in **2**, the dihedral angle at the S...S vector in the RuS₂C₂ ring is 134.9°. The dihedral angles of the S–Ru–Mo–S combination at the Ru–Mo vector are 83.6° and 91.3°, respectively.

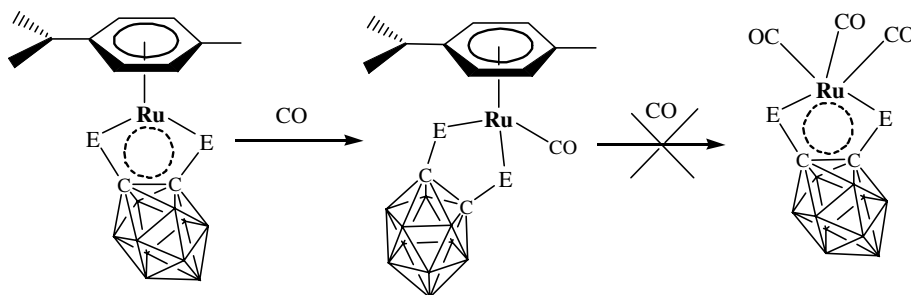
The analogous reaction has been extended to diselenolate carborane complex **1b**, the complex {(*p*-Cymene)Ru[Se₂C₂(B₁₀H₁₀)]₂Mo(CO)₂ (**3**) can be isolated as sole product in 54% yield by the reaction of **1b** with Mo(CO)₃(Py)₃ in the presence of more than three equivalents of BF₃ in diethyl ether solution. Complex **3** has similar solubility as complex **2**, but is much more sensitive. The IR spectra of **3** in the solid state also exhibits intense B–H stretching of carborane at 2581(vs) cm⁻¹. Complex **3** exhibits strong vibrations of carbon monoxide at about 1864 and 1783 cm⁻¹ in the region typical for bridging CO group, and no apparent evidence of the existence of the terminal CO as in complex **2**. The ¹³C NMR spectrum shows similar signals for the *p*-Cymene ring as **2**, but there is only one resonance at 186.7 ppm, which stands for the bridging CO

group according to relevant complexes. The chemical shifts of the *p*-Cymene in ¹H NMR are similar to those of the corresponding precursor **1a** [7] and the analogue compound **2** with a slight tendency to shift towards lower field. Therefore, we assume that in complex **3** both of the *p*-Cymene rings have been retained forming probably a symmetric structure. Additionally, the elemental analysis of **3** is also in agreement with this proposed component.

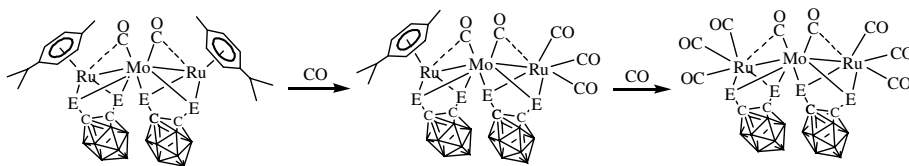
It has been already reported that when precursor **1a** is stirred in CH₂Cl₂ under carbon monoxide atmosphere, a 18-electron product of (*p*-Cymene)Ru[S₂C₂(B₁₀H₁₀)](CO) is formed (Scheme 2) [7], but there is no evidence of substitution of *p*-Cymene ring. And no similar substitution reaction is studied so far to our knowledge. In order to understand the mechanism of carbonyl substitution reaction on Ru atoms, we investigated the reactions of complexes **2** and **3** with excessive CO. Complex **2** was added in diethyl ether and the mixture was fed with carbon monoxide, the solution was stirred for prolonged hours before the solvent was removed under reduced pressure. Although there is no significant change of the residue's color, the IR spectra show that the absorption for alkyl vibration from the *p*-Cymene ring is significantly weaker than that of **2**. Complex **3** in THF solution was bubbled with CO gas and the terminal CO absorptions in 2098, 2064 and 2027 cm⁻¹ have been monitored by solution IR spectra. All of these indicate that the substitution of the *p*-Cymene ring is accomplished stepwise, partially due to the inducement from the central molybdenum atom. And this is the first example of the lose of the half-sandwich structure of transition metal due to the free carbonyl group either generated in situ or under a carbonyl monoxide atmosphere (see Scheme 3).

3. Experimental

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, (*p*-Cymene)Ru[E₂C₂(B₁₀H₁₀)] (**1a**, **1b**) [7] and Mo(CO)₃(Py)₃ [9], were prepared by slightly modified literature procedures. BF₃·Et₂O was purchased from Aldrich and was used without purification. Elemental analyses for C and H were carried



Scheme 2.



Scheme 3.

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 spectrometers in CDCl_3 solution. Infrared spectra were recorded on a Nicolet FT-IR 360 spectrometer.

3.1. Synthesis of $\{(p\text{-Cymene})\text{Ru}[\text{S}_2\text{C}_2(\text{B}_{10}\text{H}_{10})]\}\text{Mo}(\text{CO})_2\{(\text{CO})_3\text{Ru}[\text{S}_2\text{C}_2(\text{B}_{10}\text{H}_{10})]\}$ (**2**)

$\text{BF}_3 \cdot \text{Et}_2\text{O}$ (0.13 ml, 47%, 0.48 mmol) was added dropwise at room temperature to a mixture of **1a** (99.1 mg, 0.23 mmol) and $\text{Mo}(\text{CO})_3(\text{Py})_3$ (46.8 mg, 0.12 mmol) in diethyl ether (25 ml). The suspension was stirred for 10 h, and the color changed from dark blue to red-brown gradually. After evaporating the solvent under reduced pressure, the residue was re-dissolved in 3 ml of CH_2Cl_2 and chromatographed on silica gel. Complex **2** was isolated as sole band eluted with hexane and recrystallized from CH_2Cl_2 /hexane at -18°C to give 50.9 mg (45%) of **2** as red prismatic crystals. Elemental analysis Calc. for $\text{C}_{25}\text{H}_{48}\text{B}_{20}\text{MoO}_5\text{Ru}_2\text{S}_4$ (%): C, 27.93; H, 4.86. Found: C, 27.63; H, 4.71%. ^1H NMR (500 MHz, CDCl_3 , δ/ppm): 5.77 (m, 1H, C_6H_4), 5.58 (d, 1H, C_6H_4), 5.56 (d, 1H, C_6H_4), 5.11 (d, 1H, C_6H_4), 2.74 (m, 1H, CH), 2.16 (s, 3H, CH_3), 1.25 (d, 6H, CH_3). ^{13}C NMR (125 MHz, CDCl_3 , δ/ppm): 189.1 (CO), 187.4 (CO), 186.1 (CO), 113.5 (C_6H_4), 111.7 (C_6H_4), 100.1 (C_6H_4), 99.1 (C_6H_4), 96.8 (C_6H_4), 91.8 (C_6H_4), 91.1 (carborane), 90.8 (carborane), 32.2 (CH), 23.1 (CH_3), 19.1 (CH_3). ^{11}B NMR (160 MHz, CDCl_3 , δ/ppm): -4.1 , -7.4 , -10.1 , -10.9 . IR (KBr disk) $\nu = 2963$, 2924, 2869 cm^{-1} (C–H), $\nu = 2585$ cm^{-1} (B–H), $\nu = 2092$, 2037 cm^{-1} (CO), $\nu = 1872$, 1791 cm^{-1} (CO), $\nu = 1628$, 1442, 1384 cm^{-1} (C=C).

3.2. Synthesis of $[\{(p\text{-Cymene})\text{Ru}[\text{Se}_2\text{C}_2(\text{B}_{10}\text{H}_{10})]\}]_2\text{Mo}(\text{CO})_2$ (**3**)

Complex **3** was prepared from **1b** (136.1 mg, 0.25 mmol) and $\text{Mo}(\text{CO})_3(\text{Py})_3$ (53.0 mg, 0.13 mmol) in diethyl ether as described above. After $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (0.14 ml, 47%, 1 mmol) was added dropwise, the solution was stirred over night. The red-brown crystals (81.9 mg) of **3** were also obtained from recrystallization in hexane at -18°C along with a yield of 54%. Elemental analysis Calc. for $\text{C}_{26}\text{H}_{48}\text{B}_{20}\text{MoO}_2\text{Ru}_2\text{Se}_4$ (%): C, 25.45; H, 3.92. Found: C, 25.06; H, 3.93%. ^1H NMR (500 MHz, CDCl_3 , δ/ppm): 6.07–5.01 (m, 8 H, C_6H_4), 2.90 (m, 2H, CH), 2.22 (s, 6H, CH_3), 1.35 (d, 12H, CH_3). ^{13}C NMR (125 MHz, CDCl_3 , δ/ppm): 186.7 (CO), 112.0 (C_6H_4), 110.4 (C_6H_4), 98.8

Table 1
X-ray crystallographic data and processing parameters for **2**

Empirical formula	$\text{C}_{20}\text{H}_{36}\text{B}_{20}\text{Cl}_2\text{MoO}_5\text{Ru}_2\text{S}_4$
Formula weight	1069.91
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	
a (Å)	11.377(4)
b (Å)	25.615(8)
c (Å)	13.969(4)
α ($^\circ$)	90
β ($^\circ$)	100.611(5)
γ ($^\circ$)	90
Volume (Å ³)	4001(2)
Z	4
Calculated density (mg/m^3)	1.776
Absorption coefficient (mm^{-1})	1.431
$F(000)$	2096
Crystal size	$0.30 \times 0.10 \times 0.08$
θ Range for data collection ($^\circ$)	1.59–25.01
Limiting indices	$-13, 13; -29, 30; -16, 13$
Reflections collected/unique (R_{int})	16,777/7042 (0.0862)
Completeness to θ ($^\circ$)	25.01 (99.6%)
Maximum and minimum transmission	0.4926 and 0.3967
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	7042/0/507
Goodness-of-fit on F^2	1.024
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0680$, $wR_2 = 0.1425$
R indices (all data)	$R_1 = 0.1301$, $wR_2 = 0.1684$
Largest difference peak and hole ($\text{e}/\text{Å}^3$)	1.459 and -1.224

(C_6H_4), 97.7 (C_6H_4), 87.8 (carborane), 28.7 (CH), 22.0 (CH_3), 19.9 (CH_3). ^{11}B NMR (160 MHz, CDCl_3 , δ/ppm): -2.59 , -9.47 , -13.91 , -15.07 . IR (KBr disk) $\nu = 2962$, 2925, 2865 cm^{-1} (C–H), $\nu = 2581$ cm^{-1} (B–H), $\nu = 1864$, 1783 cm^{-1} (CO), $\nu = 1639$, 1442, 1379 cm^{-1} (C=C).

3.3. X-ray crystallography

Diffraction data of **2** were collected on a Bruker Smart APEX CCD diffractometer ($\text{MoK}\alpha$ radiation). The structures were solved by direct methods and subsequently refined on F^2 by using full-matrix least-squares techniques (SHELXL-97), all non-hydrogen atoms were refined anisotropically, and hydrogen atoms were located at calculated positions (see Table 1).

4. Supplementary materials

CCDC-275095 contains the supplementary crystallographic data for this paper, which can be obtained free of charge from the Cambridge Crystallographic Data Centre,

12 Union Road, Cambridge CB21EZ, UK; fax: +44 1223 336 033; or deposit@ccdc.cam.ac.uk.

Acknowledgments

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.

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