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Reactivity of Two 16e Half-Sandwich Cobalt Complexes Containing 1,2-Dicarba-*closo*-Dodecaborane-1,2-Dichalcogenolate $(E_2C_2B_{10}H_{10})^{2-}$ (E = S, Se) Units toward Triphenylphosphine[1]

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Abstract—Treatment of *o*-carborane, *n*-butyllithium, sulfur (or selenium) and $MeCpCo(CO)I_2$ (or $Cp^*Co(CO)I_2$) (Cp* = pentamethylcyclopentadienyl) under argon leads to half-sandwich carborane complex $MeCpCo(S_2C_2B_{10}H_{10})$ (**I**) (or $Cp^*Co(Se_2C_2B_{10}H_{10})$ (**II**)). Complex **I** reacts with triphenylphosphine to afford addition product $MeCpCo(S_2C_2B_{10}H_{10})(PPh_3)$ (**III**). However, **II** does not react with triphenylphosphine. Complexes **II** and **III** have been characterized by elemental analysis, mass, NMR spectroscopy, IR and X-ray structural analyses (CIF files CCDC nos. 1571705 (**II**) and 1571706 (**III**)).

Keywords: o-carborane, half-sandwich, reactivity, synthesis

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INTRODUCTION

Carboranes are a group of polyhedral clusters derived from boranes and borane anions by introduction of one or more C–H or C–R vertices [1]. Carboranes have been extensively studied since the early work on them was reported in the 1960s [2]. Because of their unique molecular architectures, physical and chemical properties, carboranes and their derivatives have been used in a number of diverse fields such as boron neutron capture therapy (BNCT), boron carbide-type ceramics, complexing agents for extraction of metal ions, nonlinear optics, conducting polymers [3], catalysis [4, 5], coordination compounds [6]. Of all the small carborane clusters, the most intensively studied carboranes are based on the 12-vertex icosahedron with two carbon and ten boron vertices, which have three isomeric geometries: *o*-carborane, *m*-carborane, *p*-carborane. Experiments shows that the carborane cages are rather stable under many reaction conditions and exhibits phenomenal thermal stability in temperatures up to 400°C. However, *o*-carborane rearranges to *m*-carborane when heated to 400–500°C under inert atmosphere, and the *m*-carborane isomerizes to *p*-carborane between 600 and 700°C [7]. Of the above three isomeric geometries, *o*-carborane has been most studied for its easy synthesis [8]. Because of the strong electron-withdrawing character of the *o*-carborane unit, the carborane cage C–H vertices are weakly acidic [9]. As a result, the acidity of carborane C–H groups can be used to prepare many C-substituted carboarne derivatives [10].

Recently, many kinds of 16e half-sandwich carborane compounds containing metal ions have been synthesized [11–13]. Due to the electron deficiency at the metal ions centers, these sterically congested, mononuclear coordination compounds can be used for further transformations in a controlled way under various conditions [14]. These 16e half-sandwich carborane compounds can react with metal fragments to give multinuclear complexes containing M–M bonds [15]. They undergo addition reactions with bidentate, tridentate and tetradentate ligands to lead to multinuclear complexes [16]. Furthermore, these 16e half-sandwich carborane compounds containing coordinatively unsaturated metal centers could serve as interesting candidates for reactions with unsaturated substrates such as alkynes [17]. The reactions range from addition reaction and catalytic cyclotrimerization of alkynes to metal-induced B–H activation [18, 19]. Previous studies have shown that the types and structures of the products are dependant on the influencing factors such as metal center, chalcogen element, substrate, ancillary ligand, reaction temperature, solvent and the ratio of the reactants [19]. For instance, the reaction of $CpCo(S_2C_2B_{10}H_{10})$ with phenylacetylene leads to two 18e products: the alkyne double-inserted product at the Co–S bond and the product with the alkyne reduced to an alkane [20]. However,

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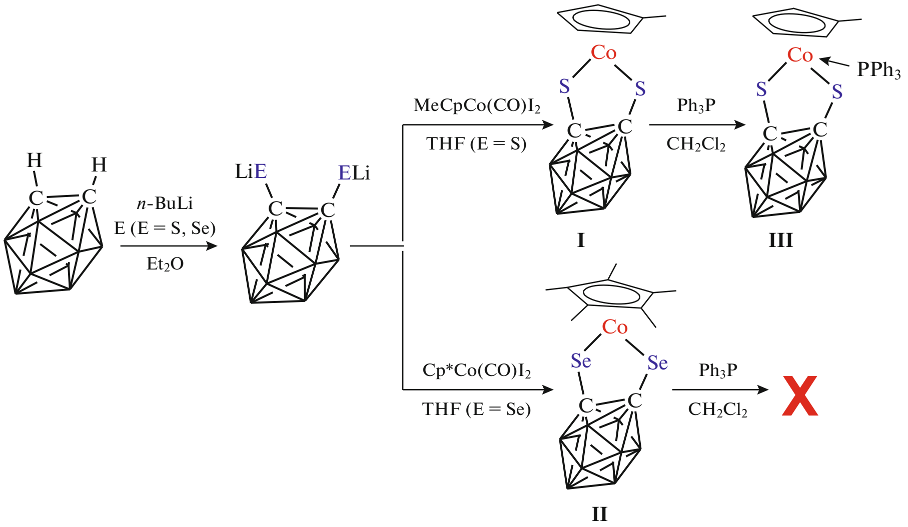
$CpCo(Se_2C_2B_{10}H_{10})$ does not react with phenylacetylene at ambient temperature [21]. Recently, we have studied the reactions of triphenylphosphine with 16e half-sandwich carborane compounds. We find that triphenylphosphine can react with $MeCpCo(S_2C_2B_{10}H_{10})$ but does not react with some other 16e carborane complexes. Herein, we report the reactions of triphenylphosphine with $MeCpCo(S_2C_2B_{10}H_{10})$ and $Cp^*Co(Se_2C_2B_{10}H_{10})$ (Cp^* = pentamethylcyclopentadienyl).



EXPERIMENTAL

Materials and methods. All experiments were carried out under an argon atmosphere using standard Schlenk techniques. Solvents were dried by refluxing over sodium (petroleum ether, ether, and THF) or calcium hydride (dichloromethane) under nitrogen and then distilled prior to use. *n*-Butyllithium (2.0 M in cyclohexane, Aldrich), *o*-carborane (Acros), triphenylphosphine (Aladdin) and other chemicals were used as commercial products without further purification. $MeCpCo(S_2C_2B_{10}H_{10})$ (**I**) was prepared according to literature [22]. Elemental analysis was performed in an elementar vario EL III elemental analyzer. NMR data were recorded on a Bruker DRX-500 spectrometer. ^1H NMR and ^{13}C NMR spectra were reported in ppm with respect to $CHCl_3/CDCl_3$ ($\delta\ ^1H = 7.26$, $\delta\ ^{13}C = 77.0$) and ^{11}B NMR spectra were reported in ppm with respect to external $Et_2O\text{-}BF_3$ ($\delta\ ^{11}B = 0$). The IR spectra were recorded on a Bruker Vector 22 spectrophotometer with KBr pellets in the 4000–400 cm^{-1} region. The mass spectra were recorded on Thermo Fisher Scientific for ESI-MS.

Synthesis of complex II. To a solution of *o*-carborane (57.7 mg, 0.4 mmol) in dry diethylether (20 mL) was added a 2.0 M solution of *n*-butyllithium (0.4 mL, 0.8 mmol). After 30 min, selenium (64.7 mg, 0.82 mmol) was added, followed by addition of $Cp^*Co(CO)I_2$ (185.6 mg, 0.39 mmol) in dry THF (25 mL) at 0°C. The resulting mixture was stirred for 0.5 h, and then the temperature gradually rose to ambient temperature. The solvents were evaporated under reduced pressure. The components of the residue were separated by column chromatography on silica gel. Elution with dichloromethane–petroleum ether (1 : 1, v/v) gave pure brown solid complexes **II** (177.9 mg, 90% yield). Crystals suitable for X-ray crystallography were obtained by slow diffusion of petroleum ether into a dichloromethane solution of the corresponding compound.

For $C_{12}H_{25}B_{10}Se_2Co_2$		
Anal. calcd., %	C, 29.16	H, 5.10
Found, %	C, 29.24	H, 4.99

ESI-MS (negitive mode, CH_3OH): *m*/*z* = 493.17 $[C_{12}H_{25}B_{10}CoSe_2\text{-}H]^-$. ^1H NMR (δ, ppm): 1.62 (s, 15H, $Cp^*\text{–}CH_3$). ^{13}C: 90.89 ($Cp^*\text{–}C_{ring}$); 75.04 (carborane–*C*); 10.75 ($Cp^*\text{–}CH_3$). $^{11}B\{^1H\}$ NMR (δ, ppm): –1.27, –2.74, –5.64, –8.62 (2 : 2 : 3 : 3). IR (ν, cm^{-1}): 2585 (B–H).

Synthesis of complex III. To a solution of **I** (103.3 mg, 0.3 mmol) in dry CH_2Cl_2 (20 mL) was added triphenylphosphine (78.7 mg, 0.3 mmol). The resulting mixture was stirred for 10 h at ambient temperature. After removal of the solvent, the residue was chromatographed on silica gel. Elution with petroleum ether–CH_2Cl_2 (1 : 2, v/v) gave pure compound **III** (167.4 mg, 92% yield) as black solid. Suitable single crystal of **III** was obtained by slow diffusion of petroleum ether into its CH_2Cl_2 solution.

For $C_{26}H_{32}B_{10}S_2PCo$ (**III**)

Anal. calcd., %	C, 51.47	H, 5.32
Found, %	C, 51.51	H, 5.27

ESI-MS (negitive mode, CH_3OH): $m/z = 715.08$ $[C_{26}H_{32}B_{10}CoS_2P + DMSO + CH_3O]^-$. ^1H NMR (δ, ppm): 7.63–7.40 (m., 15H, Ph), 4.79 (s., 2H, MeCp–C*H*), 4.37 (s., 2H, MeCp–C*H*), 1.87 (s., 3H, CH_3). ^{13}C NMR (δ, ppm): 134.58 (Ph–*C*H); 134.50 (Ph–*C*H); 132.52 (Ph–*C*); 132.05 (Ph–*C*); 130.87 (Ph–*C*H); 130.85 (Ph–*C*H); 128.31 (Ph–*C*H); 128.21 (Ph–*C*H); 116.94 (MeCp–*C*); 99.96 (carborane–*C*); 93.91 (MeCp–*C*H); 87.23 (MeCp–*C*H); 85.59 (MeCp–*C*H); 77.20 (MeCp–*C*H); 67.57 (carborane–*C*); 13.61 (CH_3). $^{11}B\{^1H\}$ NMR (δ, ppm): –1.57, –4.73, –7.69 (3 : 3 : 4). IR (ν, cm^{-1}): 2578 (B–H).

X-ray crystallographic studies. Suitable single crystals of **II** and **III** were selected and mounted in air onto thin glass fibers. X-ray diffraction data were collected on a Bruker SMART APEX II CCD diffractometer at 291(2) K using MoK_α radiation ($\lambda = 0.71073$ Å) by multi-scan mode. The SAINT program was used for integration of the diffraction profiles. The structures were solved by direct methods using the SHELXS-97 [23] program package and refined against F^2 by full-matrix least-squares with SHELXL-97 [24]. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms on carbon were set in calculated positions and refined as riding. The crystallographic data are summarized in Table 1 and selected bond lengths and angles are listed in Table 2 containing the supplementary crystallographic data for this article. Copies of the data can be obtained free of charge from the Cambridge Crystallographic Data Centre (nos. 1571705 (**II**) and 1571706 (**III**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

The reactivity of 16e half-sandwich carborane compounds with Lewis bases has been investigated [25]. Triphenylphosphine is also a Lewis base. In order to study the ancillary ligands and chalcogen element of 16e half-sandwich carborane compounds on their reactivity toward triphenylphosphine, we set out to prepare **I** as well as **II** and investigate the reactions of **I** and **II** with triphenylphosphine. First of all we conducted the reaction of **I** with triphenylphosphine. As expected, we have successfully isolated and characterized interesting stable 1 : 1 adduct compound **III** in 92% yield. The solid-state structure of **III** (Fig. 1b) shows that it is an addition structure. There are one lone pair electrons in triphenylphosphine. Triphenylphosphine reacts with **I** by coordinate-covalent bond to form **III**. Consequently, the cobalt ion in **III** is coordinatively saturated. The P–Co distance is 2.2199(5) Å and falls in the normal coordinative bond P → Co bond range. Three phenyl rings are nearly planar. However, the five-membered ring S(1)C(1)C(2)S(2)Co(1) is no longer planar because of the insertion of triphenylphosphine. The dihedral angle between the planes S(1)Co(1)S(2) and S(1)C(1)C(2)S(2) at the S(1)···S(2) vector is 154.5°. The spectroscopic and analytical data of **III** are consistent with its solid-state structure. In the ^1H NMR data, two signals at 4.79 and 4.37 ppm are assigned to four CH groups in MeCp ring, while the singlet at 1.87 ppm is the resonance of the CH_3 group in the MeCp ring.

In order to study the reactivity of triphenylphosphine with other 16e half-sandwich carborane compounds, we prepared **II** as well as $Cp^*Co(S_2C_2B_{10}H_{10})$ and $Me_4CpCo(S_2C_2B_{10}H_{10})$. The synthesis and structures of $Cp^*Co(S_2C_2B_{10}H_{10})$ [25] and $Me_4CpCo(S_2C_2B_{10}H_{10})$ [26] have been reported previously. To the best of our knowledge, there is no document about the synthesis of **II**. We prepared $Cp^*Co(Se_2C_2B_{10}H_{10})$ according to the synthesis of $Me_4CpCo(S_2C_2B_{10}H_{10})$. Recrystallizaiton from CH_2Cl_2–petrol ether (2 : 1) afforded the crystals suitable for X-ray crystallography. The molecular structure of **II** is shown in Fig. 1a. Five atoms Co(1)Se(1)C(1)C(2)Se(2) forms a five-membered ring and the five-membered ring is nearly planar with a dihedral angle (178.1°) at the Se(1)···Se(2) vector. Besides, **II** has been also characterized by elemental analysis, IR, MS, ^1H NMR, ^{11}B NMR and ^{13}C NMR. All characterization results demonstrate the consistence of the structure both in solution and solid states. For example, the chemical environment of 15 hydrogen atoms in the ancillary ligands Cp* is identical. As a consequence, in the ^1H NMR data, there is only one singlet at 1.62 ppm assigned to CH_3 in the Cp* ring. While in the ^{13}C NMR spectra, two signals at 90.89 and 10.75 ppm are assigned to two kind of carbon atoms in the Cp* unit.

As like **I**, **II** is also a 16e half-sandwich carborane compound and should react with triphenylphosphine. But unfortunately, **II** does not react with triphenylphosphine. The main reason is that the large Cp* blocks the generation of the P–Co bond. In order to verify our deduction, we set about conducting another two experiments: the reactions of triphenylphosphine with both $Cp^*Co(S_2C_2B_{10}H_{10})$ and $Me_4CpCo(S_2C_2B_{10}H_{10})$. The reaction results show that triphenylphosphine reacts neither with $Cp^*Co(S_2C_2B_{10}H_{10})$ nor with $Me_4CpCo(S_2C_2B_{10}H_{10})$.

Table 1. Crystallographic data and structural refinement details of complexes **II** and **III**

Parameter	Value	
	II	**III**
Crystal size, mm	0.20 × 0.18 × 0.15	0.30 × 0.15 × 0.10
Formula weight	494.27	606.63
Temperature, K	296(2)	123(2)
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/c$	$Pbca$
a, Å	8.8845(19)	15.4399(11)
b, Å	15.034(3)	17.4038(12)
c, Å	16.338(4)	21.5148(16)
α, deg	90.00	90.00
β, deg	101.235(4)	90.00
γ, deg	90.00	90.00
V, Å^3	2140.4(8)	5781.3(7)
Z	4	8
ρ_{calcd}, g cm^{-3}	1.5341	1.394
μ, mm^{-1}	4.195	0.812
F(000)	968	2496
θ Range, deg	2.23–25.62	2.31–27.49
Reflections collected	11636	49559
Independent reflections (R_{int})	3759 (0.0528)	6632 (0.0529)
Reflections observed ($I > 2\sigma(I)$)	2549	5628
Data/restraints/parameters	3759/0/231	6632/0/362
GOOF	1.042	1.087
R_1, wR_2 ($I > 2\sigma(I)$)	0.0702, 0.1802	0.0318, 0.0800
R_1, wR_2 (all data)	0.1028, 0.2034	0.0422, 0.0844
Largest difference peak/hole, e Å^{-3}	2.629/–0.794	0.384/–0.364

Table 2. Selected bond lengths (Å) and bond angles (deg) for **II** and **III**

Bond	d, Å	Angle	ω, deg
		II	
C(1)–C(2)	1.631(11)	Se(1)Co(1)Se(2)	98.01(5)
C(1)–Se(1)	1.943(7)	C(1)C(2)Se(2)	116.6(5)
C(2)–Se(2)	1.929(8)	C(2)C(1)Se(1)	117.6(5)
Se(1)–Co(1)	2.2540(14)	C(1)Se(1)Co(1)	103.3(2)
Se(2)–Co(1)	2.2456(14)	C(2)Se(2)Co(1)	104.4(2)
		III	
C(1)–C(2)	1.663(2)	S(1)Co(1)S(2)	92.702(18)
C(1)–S(1)	1.7848(17)	C(1)C(2)S(2)	117.07(11)
C(2)–S(2)	1.7842(18)	C(2)C(1)S(1)	116.11(11)
S(1)–Co(1)	2.2620(5)	C(1)S(1)Co(1)	103.52(6)
S(2)–Co(1)	2.2437(5)	C(2)S(2)Co(1)	103.45(6)
Co(1)–P(1)	2.2199(5)	S(1)Co(1)P(1)	90.588(18)
P(1)–C(9)	1.8277(17)	S(2)Co(1)P(1)	92.041(19)
P(1)–C(15)	1.8320(17)	Co(1)P(1)C(9)	108.86(6)
P(1)–C(21)	1.8296(17)	Co(1)P(1)C(15)	115.76(6)
		Co(1)P(1)C(21)	119.75(6)

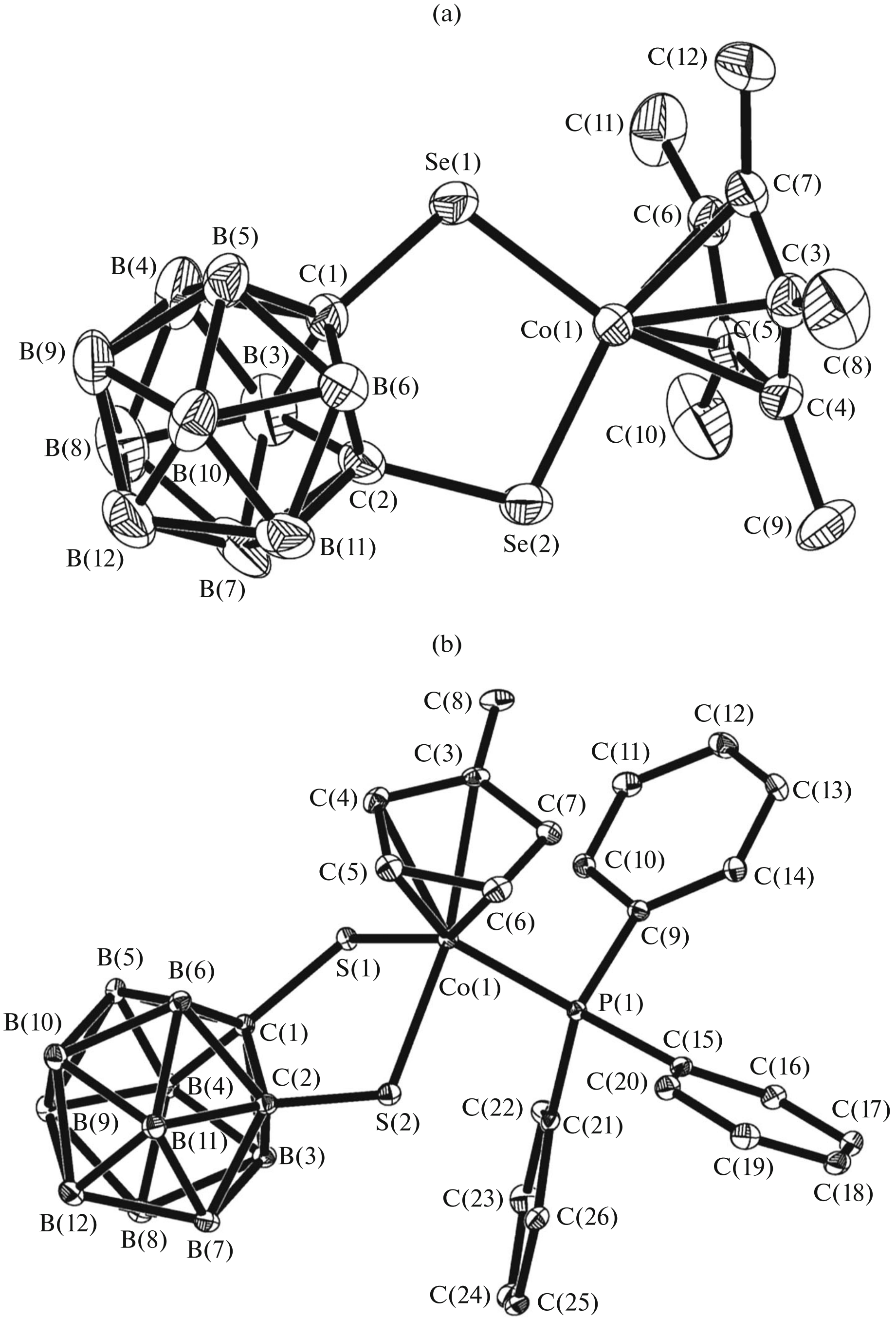


Fig. 1. Molecular structures of **II** (a) and **III** (b).

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