Reactivity of Two MeCp-Cobalt Complexes Containing 1,2-Dicarba-closo-Dodecaborane-1,2-Dichalcogenolate \((S_2C_2B_{10}H_{10})^2^-\) Units toward Alkynes


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Abstract—Treatment of \(o\)-carborane, \(n\)-butyllithium, sulfur, and MeCpCo(CO)\(_2\) under argon leads to two MeCp-cobalt complexes MeCpCoS_2C_2B_{10}H_{10} (I) and (MeCp)_2CoS_2C_2B_{10}H_{10} (II). Complex I reacts with phenylacetylene or dimethyl acetylene dicarboxylate to afford \(B-H\) activated complex \((MeCpCoS_2C_2B_{10}H_{9})(Ph-C=CH_2)\) (III) and addition complex \((MeCpCoS_2C_2B_{10}H_{10})(MeO-C=C-C=O)_2Me\) (IV), respectively. Complex II reacts neither with phenylacetylene nor with dimethyl acetylene dicarboxylate. Complexes II–IV have been characterized by elemental analysis, mass, NMR spectroscopy, IR, and X-ray structural analyses (CIF files CCDC nos. 1045892 (II), 1045893 (III) and 1045894 (IV)).

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INTRODUCTION

Boron cluster compounds are a kind of distinctive covalent species with a unique molecular architecture, nonconventional cluster bonding, and unusual chemistry. They show rather specific properties not encountered in other types of compounds [1]. As this field of chemistry has been developed rapidly for almost half a century, major advances in theory and experiment on the boranes and carboranes have been established, and they have shown many practical applications [2, 3]. Siloxane-linked polymers containing \(m\)-carborane icosahedral units show extraordinary chemical and thermal stability. Derivatives of carboranes have been used in the areas of boron neutron capture therapy (BNCT) for tumors [4]. Besides, carboranes and their derivatives have also been used to synthesize catalysts [5], radiopharmaceuticals [6], polymers [7], and coordination compounds [8]. Among the known polyhedral carboranes, 1,2-dicarba-closo-dodecaborane (\(o\)-carborane) has been intensively studied due to its relatively easy preparation [9].

As the \(CH\) groups of \(o\)-carborane are weakly acidic and can be deprotonated by strong base such as \(n\)-butyllithium [10], it can be used to prepare a kind of mononuclear 16e half-sandwich complexes of Co, Rh, Ir, Ru, and Os containing a chelating 1,2-dicarba-closo-dodecaborane-1,2-dichalcogenolate ligand [8–13]. These sterically congested, coordinatively unsaturated compounds can be stored conveniently and used for the completion of various chemical transformations [11]. As the metal atoms of these half-sandwich complexes are coordinatively and electronically unsaturated, they can combine metal fragments to afford novel homometallic or heterometallic clusters containing metal-metal bonds [12]. They react with Lewis bases to give their corresponding 18-electron stable species [13]. Furthermore, the metal centers of these 16e compounds are electronically deficient and metal-chalcogen bonds are reactive, which render them interesting candidates for reactions with alkynes [14].

In the course of preparing the above mononuclear 16e compounds, some other binuclear [15–18], trinuclear [19], and multinuclear [20] carborane products have been successfully isolated. Furthermore, some species have shown further reactivity toward organic molecules [18, 21]. Recently, we have isolated a binuclear MeCp-cobalt carborane complex (II) in the course of preparing the mononuclear MeCp-cobalt carborane complex MeCpCoS_2C_2B_{10}H_{10} (I). To the best of our knowledge, the studies on the two carborane complexes are relatively less explored. Herein, we report the syntheses of the above carborane compounds I, II, their further reactivity toward organic molecules and preparation of complexes III and IV. Synthesis of complexes I–IV is given in Scheme.
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), phenylacetylene (Alfa Aesar), dimethyl acetylene dicarboxylate (Aldrich) and other chemicals were used as commercial products without further purification. MeCpCo(S2C2B10H10) (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 13C NMR spectra were reported in ppm with respect to CHCl3/CDCl3 (δ1H = 7.26, δ13C = 77.0) and 11B NMR spectra were reported in ppm with respect to external Et2O-BF3 (δ11B = 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 Micromass GC-TOF for EI-MS (70 eV).

Synthesis of complexes I and 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, sulfur (26.3 mg, 0.82 mmol) was added, followed by addition of MeCpCo(CO)I2 (163.7 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 complexes brown solid I (118.8 mg, 87% yield) and green solid II (3.8 mg, 2% yield). Crystals suitable for X-ray crystallography were obtained by slow diffusion of petroleum ether into a dichloromethane solution of the corresponding compound.

For C14H24B10Co2S2 (II)
anal. calcd., %: C, 34.85; H, 5.01.
Found, %: C, 34.49; H, 4.78.

EI-MS (m/z): calcd. for C14H24B10Co2S2, 482.45; found, 482.1 ([M]+, 100%). 1H NMR (δ, ppm): 4.98 (s., 2H, CH₃), 4.73 (s., 2H, CH₂), 1.90 (s., 3H, CH₃).
13C: 95.04 (MeCp–C); 87.33 (carborane–C); 78.75 (MeCp–CH); 75.53 (MeCp–CH); 13.94 (CH₃).
11B(1H) NMR (δ, ppm): −1.47, −5.23, −8.89 (2 : 3 : 5).
IR (ν, cm⁻¹): 2588 (B–H).

Synthesis of complex III. To a solution of I (103 mg, 0.3 mmol) in dry CH2Cl2 (20 mL) was added phenylacetylene (107 mg, 1.2 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–CH2Cl2 (1 : 2 v/v) gave pure compound III (64 mg, 48%) as black solid. Suitable single crystal of