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Dinuclear Half-Sandwich Complexes Containing Bridging 1,2-Dicarba-*closo*-dodecaborane-1,2-dichalcogenolato Ligands. Molecular Structures of $Cp_2Fe_2(CO)_3[\mu\text{-}Se_2C_2(B_{10}H_{10})]$, $Cp_2Ru_2[\mu\text{-}S_2C_2(B_{10}H_{10})]_2$, and $Cp^*{}_2Ru_2(\mu\text{-}Se)[\mu\text{-}Se_2C_2(B_{10}H_{10})]$

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Summary: Three prototypes of dinuclear complexes were obtained from the reactions of dilithium 1,2-dicarba-closo-dodecaborane-1,2-dichalcogenolates, $(B_{10}H_{10})C_2(ELi)_2$ *(E = S, Se), with* $CpFe(CO)_2Cl$ *(**1**),* $CpRu(PPh_3)_2Cl$ *(**2**), or* $[Cp^*RuCl_2]_2$ *(**3**), respectively, and their structures have been determined by X-ray crystallography.*

Introduction

A number of *mono*nuclear 16e Cp and Cp* half-sandwich complexes of Co,[1] Rh,[2] Ir,[3,4,6d] and Re[5] have been described which contain a bidentate, chelating 1,2-dicarba-*closo*-dodecaborane-1,2-dichalcogenolato ligand, $[(B_{10}H_{10})C_2E_2]^{2-}$ (E = S, Se). They can be used as models to study the insertion of alkynes into one of the metal−chalcogen bonds;[1,4,6] this may lead to the formation of a metal-to-boron bond and/or substitution of the carborane cage in the positions B(3)/B(6).[6]

On the other hand, *di*nuclear Cp and Cp* half-sandwich compounds containing bridging $[(B_{10}H_{10})C_2E_2]^{2-}$ ligands are rare, the only defined example being $Cp_2Co_2\{\mu\text{-}S_2C_2(B_{10}H_{10})\}$.[1] We now report the synthesis and X-ray structural characterization of three additional examples with differing bridge systems.

Results and Discussion

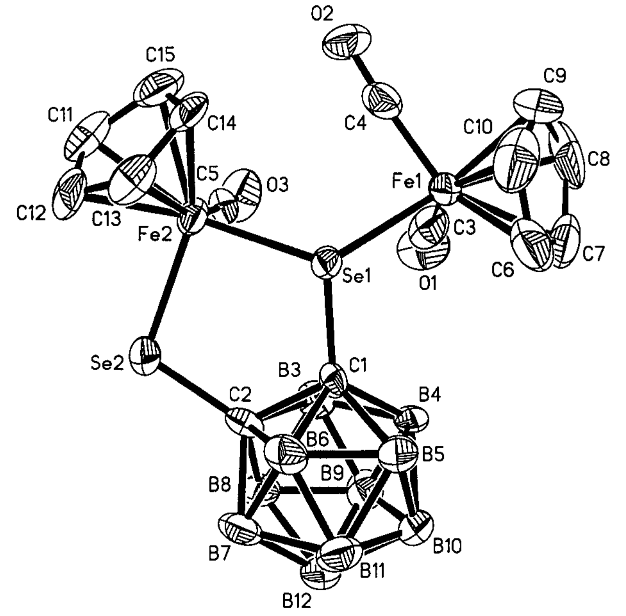

Figure 1. Molecular structure of **4**. Selected distances (Å) and angles (deg): Fe(1)−Se(1), 2.406(2); Fe(1)−C(3), 1.774(10); Fe(1)−C(4), 1.774(9); Fe(2)−Se(1), 2.3669(14); Fe(2)−Se(2), 2.384(2); Fe(2)−C(5), 1.737(9); Se(1)−C(1), 1.979(7); Se(2)−C(2), 1.932(7); C(1)−C(2), 1.639(9); Se(1)−Fe(1)−C(3), 96.7(3); Fe(1)−Se(1)−Fe(2), 116.87(6); C(1)−Se(1)−Fe(1), 107.9(2); C(1)−Se(1)−Fe(2), 104.7(2); Se(1)−Fe(2)−Se(2), 92.28(5); C(2)−Se(2)−Fe(2), 104.9(2); Se(1)−C(1)−C(2), 115.8(5); Se(2)−C(2)−C(1), 118.5(4).

Attempts to combine the $\{(B_{10}H_{10})C_2E_2\}$ (E = S, Se) building block with two 17e fragments such as $[CpFe(CO)_2]$ and $[CpRu(PPh_3)_2]$ were unsuccessful, although gold(I) complexes of the type $\{(B_{10}H_{10})C_2S_2\}(Au(PR_3))_2$ have been obtained,[7] and mercury(II)-bridged oligocarboranes are known.[8] Instead, $CpFe(CO)_2Cl$ (**1**) reacted with $(B_{10}H_{10})C_2(SeLi)_2$[2] in a molar ratio of 2:1 in Et_2O/THF to give black prismatic crystals of $Cp_2Fe_2(CO)_3\{\mu\text{-}Se_2C_2(B_{10}H_{10})\}$ (**4**) in 89% yield. The *o*-carborane-1,2-diselenolate bridge combines a [CpFe(CO)] and a $[CpFe(CO)_2]$ fragment (Figure 1); the iron atom Fe(2) carries only one carbonyl group in addition to a formal 3e chelate ligand, $[(B_{10}H_{10})C_2Se(Se\text{-}R)]^-$ (R = $CpFe(CO)_2$). The distances Fe−Se (236.69(14)−240.6(2) pm)

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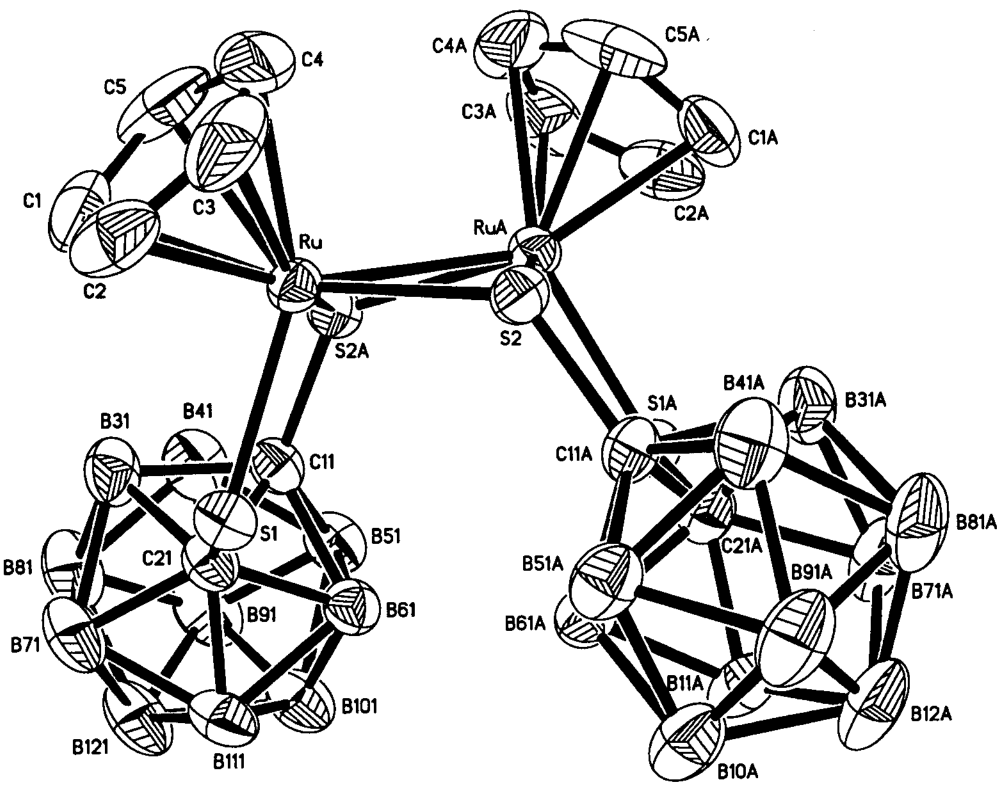

Figure 2. Molecular structure of **5**. Selected distances (Å) and angles (deg): Ru−S(1), 2.3766(11); Ru−S(2), 2.7784(10); Ru−S(2), 2.3124(12); Ru−S(2a), 2.2937(11); Ru−Ru(a), 2.7781(9); Ru(a)−S(2), 2.2937(11); S(1)−C(21), 1.789(4); S(2a)−C(11), 1.822(4); C(11)−C(21), 1.634(5); S(1)−Ru−S(2), 101.12(4); S(1)−Ru−S(2a), 89.28(3); S(1)−Ru−Ru(a), 112.81(3); S(2)−Ru−Ru(a), 52.60(3); S(2)−Ru−S(2a), 102.93(4); Ru−S(2)−Ru(a), 74.19(3); Ru−S(1)−C(21), 106.07(13); S(1)−C(21)−C(11), 117.6(3).

are similar to those in Fe(II) selenolate complexes.[9] The long Fe(1)···Fe(2) separation (406.7 pm) excludes any direct metal−metal interaction.

The comparable reaction of $CpRu(PPh_3)_2Cl$ (**2**) with the dilithium dithiolate reagent $(B_{10}H_{10})C_2(SLi)_2$[2] did not give a product analogous to **4** but the symmetrical dinuclear complex $Cp_2Ru_2[\mu\text{-}S_2C_2(B_{10}H_{10})]_2$ (**5**), with two *o*-carborane dithiolate bridges, in low yield (8%) (Figure 2). Each CpRu fragment is attached to one terminal and two bridging sulfur ligands. The Ru−Ru distance of 277.81(9) pm corresponds to a single bond.

With the chloro-bridged dimer $[Cp^*RuCl(\mu\text{-}Cl)]_2$ (**3**) as starting material, the reaction with dilithium diselenolate, $(B_{10}H_{10})C_2(SeLi)_2$,[2] in THF solution led to a black crystalline complex, $Cp^*_2Ru_2(\mu\text{-}Se)[\mu\text{-}Se_2C_2(B_{10}H_{10})]$ (**6**), in 40% yield. Again, each Ru center is connected to three selenium atoms which are all bridging (Figure 3). The Ru−Ru single-bond distance in **6** (278.77(9) pm) may therefore be compared with the corresponding distance in dinuclear complexes such as $[Cp^*_2Ru_2(\mu\text{-}SeC_6H_4\text{-}Me(4))_3]Cl$ (268.5(3) pm).[10] The remarkable formation of a monoselenide bridge can be ascribed to the steric congestion caused by the voluminous Cp* rings.

Experimental Section

General Considerations. All reactions and manipulations were carried out under a dry argon atmosphere by using standard Schlenk techniques. The use of dry solvents is necessary. The starting materials $CpFe(CO)_2Cl$ (**1**),[11] $CpRu(PPh_3)_2Cl$ (**2**),[12] $[Cp^*RuCl_2]_2$ (**3**)[13] and $(B_{10}H_{10})C_2(ELi)_2$ (E = S, Se)[2] were prepared according to the literature methods, while other chemicals were obtained commercially and used without further purification. The IR spectra were measured on a Bio-Rad FTS 135 (as the KBr pellet). NMR spectra were recorded on a Unity-400 spectrometer. Mass spectra were carried out on a Finnigan MAT 8500 (70 eV) instrument. Elemental analyses were carried out on a Perkin-Elmer 2400 Series II CHN analyzer.

Preparation of $Cp_2Fe_2(CO)_3[\mu\text{-}Se_2C_2(B_{10}H_{10})]$ (4). Complex **4** was obtained by adding a solution of $(B_{10}H_{10})C_2(SeLi)_2$[2] (0.44 mmol) in 40 mL of Et_2O to a solution of $CpFe(CO)_2Cl$ (**1**)[11] (0.187 g, 0.88 mmol) in 20 mL of THF. After 24 h of stirring at room temperature, the solvents were removed in vacuo and the residue was extracted with toluene. Recrystallization from toluene/hexane afforded 0.245 g (89%) of black prismatic crystals. Anal. Calcd for $C_{15}H_{20}B_{10}Fe_2O_3Se_2$: C, 28.78; H, 3.20. Found: C, 28.72; H, 3.16. IR (KBr): ν(B−H) 2582, ν(CO) 2041, 2006, and 1946 cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.25 (s, 5H, Cp), 4.50 ppm (s, 5H, Cp). ^{11}B NMR ($CDCl_3$): δ 0.42, −5.74, −9.62, −10.30, −11.10 ppm. LDI-MS: *m*/*e* 649 (M^+ + Na, 100%).

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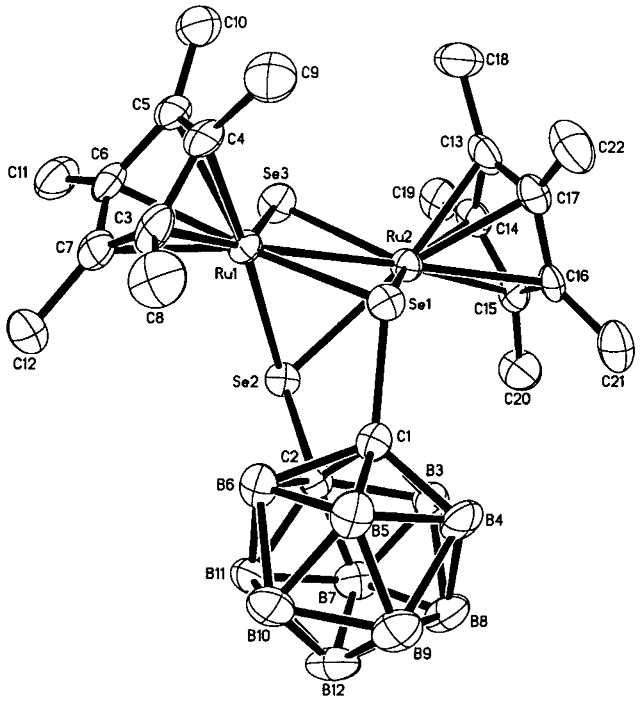

Figure 3. Molecular structure of **6**. Selected distances (Å) and angles (deg): Ru(1)−Se(1), 2.4237(9); Ru(1)−Se(2), 2.5399(9); Ru(1)−Se(3), 2.4430(10); Ru(1)−Ru(2), 2.7177(9); Ru(2)−Se(1), 2.4097(10); Ru(2)−Se(2), 2.5687(9); Ru(2)−Se(3), 2.4395(9); Se(1)−C(1), 1.981(7); Se(2)−C(2), 1.997(6); C(1)−C(2), 1.641(8); Se(1)−Ru(1)−Ru(2), 55.54(3); Se(1)−Ru(1)−Se(2), 79.40(3); Se(1)−Ru(1)−Se(3), 111.51(3); Se(2)−Ru(1)−Se(3), 69.71(3); Se(1)−Ru(2)−Se(2), 79.08; Se(1)−Ru(2)−Se(3), 112.12(3); Se(2)−Ru(2)−Se(3), 69.28(3); Ru(1)−Se(1)−Ru(2), 68.43(3); Ru(1)−Se(2)−Ru(2), 64.28(3); Ru(1)−Se(3)−Ru(2), 67.64(3); C(1)−Se(1)−Ru(1), 105.9(2); C(1)−Se(1)−Ru(2), 105.4(2); C(2)−Se(2)−Ru(1), 103.6(2); C(2)−Se(2)−Ru(2), 104.1(2); C(2)−C(1)−Se(1), 114.3(4).

Preparation of $Cp_2Ru_2[\mu\text{-}S_2C_2(B_{10}H_{10})]_2$ (5). A solution of $CpRu(PPh_3)_2Cl$ (**2**)[12] (0.58 g, 0.8 mmol) in 20 mL of THF was added to a solution of $(B_{10}H_{10})C_2(SLi)_2$[2] (0.8 mmol) in 40 mL of Et_2O. After the mixture was stirred for 24 h at 40 °C and worked up by extraction of the product with toluene (10 mL), recrystallization from THF/hexane gave 0.02 g (8%) of black prismatic crystals. IR (KBr): ν(B−H) 2552 cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.10 (Cp). ^{11}B NMR ($CDCl_3$): δ 0.77, −4.57, −6.32, −9.08 ppm. LDI-MS: *m/e* 746 (M^+, 100%); EI-MS (70 eV): *m/e* 746 (M^+, 8%), 540 ($(Cp_2Ru_2[S_2C_2(B_{10}H_{10})]^+$, 40%), 373 ($M^{2+}$, 18%), 142 ($(C_2(B_{10}H_{10})^+$, 80%).

Preparation of $Cp^*{}_2Ru_2(\mu\text{-}Se)[\mu\text{-}Se_2C_2(B_{10}H_{10})]$ (6). Complex **6** was synthesized by stirring a THF solution containing $[Cp^*RuCl_2]_2$ (**3**)[13] (0.073 g, 0.12 mmol) and $(B_{10}H_{10})C_2(SeLi)_2$[2] (0.24 mmol) at room temperature for 12 h. Purification by extraction of the product with toluene and crystallization from toluene/hexane at −20 °C gave 0.04 g (40%) of black prismatic crystals. Anal. Calcd for $C_{22}H_{40}B_{10}Ru_2Se_3$: C, 31.03; H, 4.70. Found: C, 30.34; H, 5.31. IR (KBr): ν(B−H) 2559, ν(Cp*) 1372 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.86 (Cp*). ^{11}B NMR ($CDCl_3$): δ −6.34, −7.53, −9.38, −11.44 ppm. ESI-MS: *m/e* 851 (M^+, 100%), 709 ($M^+ - C_2B_{10}H_{10}$, 60%), 630 ($M^+ - Se - C_2B_{10}H_{10}$, 100%).

X-ray Diffraction Studies. All three crystal structure determinations were carried out on a Siemens P4 diffractometer using Mo Kα radiation (λ = 0.710 73 Å) at 293(2) K and solved by direct methods using SHELXS-97.

Crystal data for **4**: $C_{15}H_{20}B_{10}Fe_2O_3Se_2$, dark brown prism, triclinic, space group $P\bar{1}$, a = 9.737(2) Å, b = 10.329(2) Å, c = 13.086(3) Å, α = 91.72(3)°, β = 104.85(3)°, γ = 113.69(3)°, V = 1152.8(4) $Å^3$, Z = 2, D_c = 0.902 g cm^{-3}, F(000) = 304, Siemens P4, Mo Kα radiation, 2θ range 3.26−48.06°; 4498 reflections collected, 3628 independent (R_{int} = 0.0356), 286 refined parameters, final R indices (observed data) R1 = 0.0436 and wR_2 = 0.0828, GOF 0.781, maximum/minimum residual electron density 0.780/−0.494 e $Å^{-3}$.

Crystal data for **5**·THF: $C_{14}H_{30}B_{20}Ru_2S_4{\cdot}C_4H_8O$, black needle, monoclinic, space group $C2/c$, a = 17.894(4) Å, b = 14.026(3) Å, c = 14.276(3) Å, β = 108.11(3)°, V = 3405.5(12) $Å^3$, Z = 4, D_c = 1.641 g cm^{-3}, F(000) = 1688, Siemens P4, Mo Kα radiation, 2θ range 5.80−56.02°, 4991 reflections collected, 4089 independent (R_{int} = 0.0260), 204 refined parameters, final R indices (observed data) R1 = 0.0412 and wR2 = 0.1175, GOF 0.882, maximum/minimum residual electron density 1.013/−0.828 e $Å^{-3}$.

Crystal data for **6**: $C_{22}H_{40}B_{10}Ru_2Se_3$, black prism, monoclinic, space group $P2_1/n$; a = 17.406(4) Å, b = 11.362(2) Å, c = 17.428(4) Å, β = 117.020(10)°, V = 3070.5(11) $Å^3$, Z = 4, D_c = 1.842 g cm^{-3}, F(000) = 1648, Siemens P4, Mo Kα radiation, 2θ range 4.44−50.10°; 6706 reflections collected, 5284 independent (R_{int} = 0.0287), 344 refined parameters, final R indices (observed data) R1 = 0.0359, wR2 = 0.0705, GOF 0.850, maximum/minimum residual electron density 0.674/−0.817 e $Å^{-3}$.

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Supporting Information Available: Listings of atomic coordinates, anisotropic thermal parameters, and bond lengths and angles for **4**−**6**; data are also available for these compounds in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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