

Rational synthesis of trinuclear (WIr_2) cluster from the 16-electron half-sandwich complex $Cp^*Ir[Se_2C_2(B_{10}H_{10})]$ [☆]

Jian-Qiang Wang, Linhong Weng, Guo-Xin Jin ^{*}

Laboratory of Molecular Catalysis and Innovative Material, Department of Chemistry, Fudan University, Handan Road 220, Shanghai 200433, China

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Dedicated to Professor Hemult G. Alt on the occasion of his 60th birthday

Abstract

A trinuclear cluster $\{Cp^*Ir[Se_2C_2(B_{10}H_{10})]\}_2W(CO)_2$ (**3**) containing Ir–W bonding was obtained from the reaction of 16-electron complex $Cp^*Ir[Se_2C_2(B_{10}H_{10})]$ with $[W(CO)_3(py)_3]$ in the presence of $BF_3 \cdot OEt_2$, and its structure has been determined by X-ray crystallography.

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1. Introduction

During the last decade considerable attention has been devoted to the metal complexes with dichalcogenolate *o*-carboranyl ligands, to take the advantage of their unique molecular structure [1,2]. A number of mononuclear 16 electron Cp and Cp^* half-sandwich complexes of Co [3], Rh [4] and Ir [5] have been described which contain a bidentate 1,2-dichalcogenolate carborane ligands, $[(B_{10}H_{10})C_2E_2]^{2-}$ and a “pseudo-aromatic” metalladichalcogenolene five-membered ring. These complexes have been used as models to study the insertion of alkynes into one of the metal–sulfur bonds [6]; 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) [7]. On the other hand, no reports on heteronuclear metal–metal

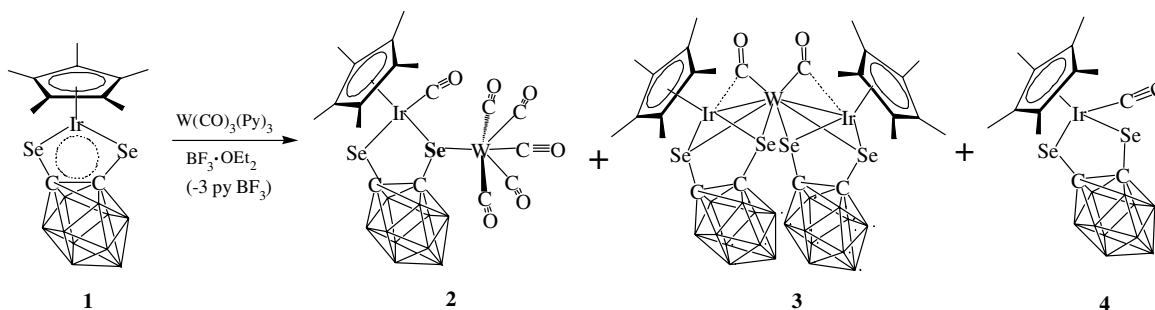
bond formation by the “pseudo-aromatic” metallacycle complexes are available to our knowledge. We now report a trinuclear complex obtained from a half-sandwich iridium carborane diselenolato complex, $Cp^*Ir[Se_2C_2(B_{10}H_{10})][5]$ (**1**, $Cp^* = \eta^5-C_5Me_5$), by reaction with $W(CO)_3(NC_5H_5)_3$ in the presence of $BF_3 \cdot OEt_2$ to give $\{Cp^*Ir[Se_2C_2(B_{10}H_{10})]\}_2W(CO)_2$ (**3**) together with binuclear complex $Cp^*Ir(CO)[Se_2C_2(B_{10}H_{10})]W(CO)_5$ (**2**) and mononuclear complex $Cp^*Ir(CO)[Se_2C_2(B_{10}H_{10})]$ (**4**).

The 16-electron complex **1**, which was synthesized from half-sandwich iridium dichloride complex $[Cp^*IrCl_2]_2$ with dilithium carborane diselenolato [5], reacts with $W(CO)_3(py)_3$ ($py = \text{Pyridine}, NC_5H_5$) in the presence of more than three equivalents of BF_3 in diethyl ether to give the dark red, hetero-trinuclear complex **3** together with the orange binuclear complex **2** and yellow 18-electron mononuclear carbonyl complex **4** (Scheme 1). Complexes **2**, **3** and **4** are diamagnetic. In complex **3**, the Ir atoms have been reduced from Ir^{III} to Ir^{II} , apparently by the fragment $[W(CO)_3]$ which is generated effectively from the combination of $[W(CO)_3(py)_3]$ and BF_3 [8]. Similar phenomenon was

[☆] $Cp^*Ir[Se_2C_2(B_{10}H_{10})] = \eta^5$ -pentamethylcyclopentadienyl-[1,2-dicarba-*closo*-dodecaborane(12)-diselenolato] iridium.

^{*} Corresponding author. Tel.: +86 21 65643776; fax: +86 21 65641740.

E-mail address: gxjin@fudan.edu.cn (G.-X. Jin).



Scheme 1. Synthesis of complexes 2–4.

also found in the formation of phenyl dithiolato cobalt complex $[\{\eta^5-C_5H_5\}Co(S_2C_6H_4)_2Mo(CO)_2]$ [9]. The mononuclear carbonyl complex 4 can be easily prepared by the addition reaction of 16-electron complex 1 with CO gas in CH_2Cl_2 solution.

X-ray structure analyses were carried out for complexes 2, 3 and 4 (Figs. 1–3, respectively). The *o*-carborane-1,2-diselenolato bridges combines a $[Cp^*Ir(CO)]$ and a $[W(CO)_5]$ fragments in 2 (Fig. 1). The Ir 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 Ir–Se bond distances (2.4770(15)–2.4903(16) Å) are similar to those in selenolato complexes, such as $Cp^*Ir(PMe_3)(Se_2C_2B_{10}H_{10})$ [5] and $Cp^*Ir(CO)(SePh)_2-Mo(CO)_4$ [10]. The long Ir(1)···W(2) separation (4.362 Å) and the obtuse angle (Ir(1)–Se(1)–W(2): 114.85(5)°) indicate that direct bonding interaction between two metals is absent.

The iridium atoms of the Ir_2W backbone in 3 have retained their Cp* rings. The W center is eight-coordinate with a dodecahedral geometry, the two Se–W–Se planes are twisted by 31.7° with respect to one another. The coordination environment of the W center with respect to the $IrSe_2$ ligand units is distorted trigonal-prismatic. The two Ir–W single bonds (2.7704(9) and 2.8081(8) Å) which are each supported by a symmetrically bridging *o*-carborane diselenolato ligand may therefore be compared with the corresponding distance in sulfido bridged Ir–W complexes such as $[Ir(PPh_3)_2(\mu_3-S)(\mu_2-S)_3\{W(S_2CNEt_2)_2(\mu_2-Cl)\}]$ (2.859(2), 2.878(2) Å) [11] and $[(Me_2Tp)W(\mu-S)_3IrCp^*][PF_6]$ (2.6415(6) Å) [12]. The Ir–Se bond distances (2.4386(11)–2.4828(11) Å) are longer than corresponding 16-electron complex 1 (2.3656(9)–2.3753(9) Å) [5]. The Ir(1)–W(1)–Ir(2) angle is in 146.776(19)°. The planar pseudoaromatic system of the two heterocycles 1 is no longer present in 3, the dihedral angle at the Se···Se vector in the $IrSe_2C_2$ ring is 133.5°.

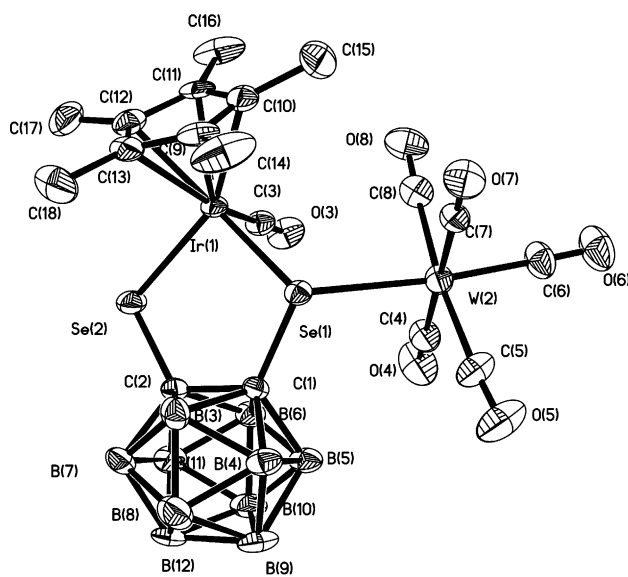


Fig. 1. Molecular structure of 2. Selected bond distances (Å) and angles (°): Ir(1)–Se(1) 2.4903(16), Ir(1)–Se(2) 2.4770(15), Ir(1)–C(3) 1.827(11), W(2)–Se(1) 2.6846(18), Se(1)–C(1) 1.959(10), Se(2)–C(2) 1.933(10), C(1)–C(2) 1.667(15) and Se(1)–Ir(1)–Se(2) 92.06(6), Se(1)–Ir(1)–C(3) 91.1(3), Ir(1)–Se(1)–W(2) 114.84(5), Ir(1)–Se(1)–C(1) 104.1(3), Ir(1)–Se(2)–C(2) 104.7(3).

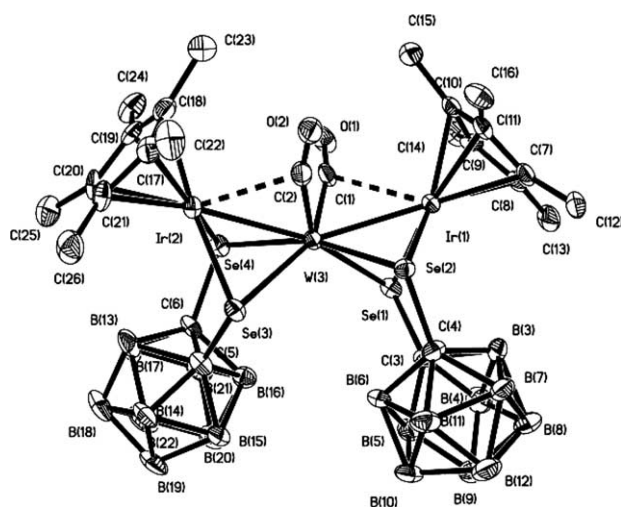


Fig. 2. Molecular structure of 3. Selected bond distances (Å) and angles (°): W(3)–Ir(1) 2.7704(9), W(3)–Ir(2) 2.8081(8), W(3)–Se(1) 2.6449(13), W(3)–Se(2) 2.6014(10), W(3)–C(1) 1.980(10), W(3)–C(2) 1.955(12), Ir(1)–Se(1) 2.4828(11), Ir(1)–Se(2) 2.4386(11), Ir(1)–C(1) 2.620(9), Ir(2)–C(2) 2.547(10) and Ir(1)–W(3)–Ir(2) 146.776(19), Se(1)–W(3)–Se(2) 76.00(3), Se(1)–W(3)–Se(3) 120.33(3), Se(1)–W(3)–Ir(1) 54.52(2), Se(1)–W(3)–C(1) 80.1(3), Se(1)–Ir(1)–Se(2) 82.04(3), Se(1)–Ir(1)–W(3) 60.16(3), W(3)–C(1)–O(1) 166.6(8), W(3)–C(1)–Ir(1) 72.6(3), Ir(1)–C(1)–O(1) 120.9(7).

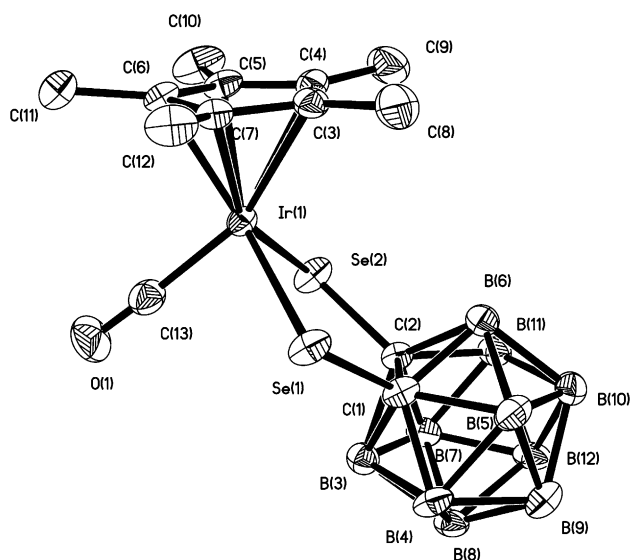


Fig. 3. Molecular structure of **4**. Selected bond distances (Å) and angles (°): Ir(1)–Se(1) 2.4707(10), Ir(1)–Se(2) 2.4731(10), Ir(1)–C(13) 1.878(8), Se(1)–C(1) 1.937(6), C(1)–C(2) 1.644(8) and Se(1)–Ir(1)–Se(2) 91.84(2), Se(1)–Ir(1)–C(13) 88.2(2), C(13)–Ir(1)–Se(2) 87.8(2).

The molecule of **4** (Fig. 3) contains a mirror plane and is isomorphous to that of the analogous sulfido complex, Cp*Ir(CO)[S₂C₂(B₁₀H₁₀)] [**5b**], and similar to Cp*Rh(PMe₃)[Se₂C₂(B₁₀H₁₀)] [**4b**] and Cp*Rh(CN^tBu)[Se₂C₂(B₁₀H₁₀)] [**4b**]. The dihedral angle along the Se··Se vector is 164.5°, whereas it is 180° in 16-electron complex **1** [5].

The formation of hetero metal–metal bond in complex **3** by the reaction of the 16-electron half-sandwich iridium complex **1** involves redox processes during which Ir is partially reduced by low-valence transition metal complex, such as the fragment [W(CO)₃].

2. Experimental

All reactions were carried out under a nitrogen atmosphere, using standard Schlenk techniques.

Synthesis of **2**, **3** and **4**: To a solution of **1** [5] (125 mg, 0.20 mmol) and [W(CO)₃(py)₃] [8] (51 mg, 0.10 mmol) in diethyl ether (50 ml), BF₃·OEt₂ (0.26 ml, 47%, 1.0 mmol) was added dropwise at room temperature. The deep blue suspension was stirred for 3 days and gradually changed to deep brown color. The solvent was then evaporated to dryness under vacuum, and the components of the residue were separated by column chromatography on silica. The component in the first band was eluted with toluene/hexane (1:4) and recrystallized from toluene/hexane at –18 °C to give orange crystals of **2** (68 mg, 35%); and the component in second band was recrystallized from toluene/hexane to afford deep red crystals of **3** (23 mg, 15%). **2**, Elemental analysis Calc. for C₁₈H₂₅B₁₀IrO₆Se₂W (%): C, 22.07; H, 2.57. Found: C, 22.36; H, 2.62%. ¹H NMR (500 MHz, CDCl₃):

δ = 1.91(s, C₅Me₅, 30 H); ¹¹B NMR(160 MHz, CDCl₃): δ = –2.6, –5.1(sh), –6.2(sh), –8.1, –8.9, –13.9, –15.1. IR (KBr pellet): ν = 2569 cm^{–1}(νB–H), 2073, 2042, 1987, 1927, 1913 cm^{–1}(νCO). **3**, Elemental analysis Calc. for C₂₆H₅₀B₂₀Ir₂O₂Se₄W (%): C, 20.89; H, 3.37. Found: C, 21.08; H, 3.51%. ¹H NMR (500 MHz, CDCl₃): δ = 1.90(s, C₅Me₅, 30H); ¹¹B NMR(160 MHz, CDCl₃): δ = –3.2, –5.1, –6.1, –8.1, –11.6. IR (KBr pellet): ν = 2579, 2553 cm^{–1}(νB–H), 1862, 1814 cm^{–1}(νCO). The complex **4** was eluted with CH₂Cl₂/hexane (1:3). Recrystallization from toluene/hexane at –18 °C gave yellow-green crystals of **4** (35 mg, 26%). Elemental analysis Calc. for C₁₃H₁₀B₁₀IrOSe₂ (%): C, 23.82; H, 3.84. Found: C, 24.03; H, 3.85%. ¹H NMR (500 MHz, CDCl₃, 25 °C): δ = 1.89(s, C₅Me₅, 15H); ¹¹B NMR(160 MHz, CDCl₃): δ = –4.3, –6.0, –8.3, –10.1, –12.5. IR (KBr pellet): ν = 2961 cm^{–1}(νC–H), 2563 cm^{–1}(νB–H), 2041 cm^{–1}(νCO).

Crystal data for **2**: C₁₈H₂₅B₁₀WO₆IrSe₂ (Mr = 979.45), Triclinic, space group *P* $\bar{1}$, *a* = 9.807(6), *b* = 11.185(7), *c* = 15.206(10) Å, α = 103.850(8)°, β = 95.351(9)°, γ = 110.167(8)°, *V* = 1491.5(17) Å³, *D*_c = 2.181 mg/m³, *Z* = 2, μ = 10.781 mm^{–1}, 6273 measured, 5175 unique, 358 variables, GOF = 1.016, *R*₁ = 0.0449 [*I* > 2σ(*I*)], *wR*₂ = 0.1156 (all unique reflections). For **3**: C₂₆H₅₀B₂₀WO₂Ir₂Se₄ (Mr = 1494.95), monoclinic, space group *P*2(1)/*c*, *a* = 14.218(4), *b* = 21.491(7), *c* = 15.457(5) Å, β = 109.605(4)°, *V* = 4449(2) Å³, *D*_c = 2.232 mg/m³, *Z* = 4, μ = 11.846 mm^{–1}, 20232 measured, 8656 unique, 527 variables, GOF = 0.951, *R*₁ = 0.0442 [*I* > 2σ(*I*)], *wR*₂ = 0.0950 (all unique reflections). For **4**: C₁₃H₂₅B₁₀OIrSe₂ (Mr = 655.55), Orthorhombic, space group *P*2(1)2(1)2(1), *a* = 9.423(3), *b* = 13.543(4), *c* = 17.282(5) Å, *V* = 2205.4(12) Å³, *D*_c = 1.974 mg/m³, *Z* = 4, μ = 9.356 mm^{–1}, 9277 measured, 3903 unique, 249 variables, GOF = 1.059, *R*₁ = 0.0241 [*I* > 2σ(*I*)], *wR*₂ = 0.0529 (all unique reflections). Diffraction data of **2**, **3** and **4** were collected at 293 K on a Bruker Smart APEX CCD diffractometer (Mo Kα radiation). The structures were solved by direct methods and subsequently refined on *F*² by full-matrix least-squares techniques (SHELXL-97). All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were located at calculated positions. CCDC-237895 (**2**), CCDC-237896 (**3**) and CCDC-237897 (**4**) contain the supplementary crystallographic data for this paper. These data 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.

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