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Syntheses of a dinuclear Ir complex containing bridging tetraselenide ligands [$(C_5Me_5)Ir(\mu\text{-}Se_4)_2Ir(C_5Me_5)$] and its conversion into $Ir_2Pd_2Se_3$ and $Ir_2Pd_3Se_5$ clusters

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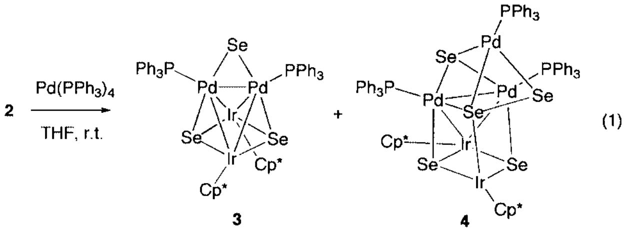
Treatment of $Cp^*IrCl(\mu\text{-}Cl)_2IrCp^*Cl$ ($Cp^* = \eta^5\text{-}C_5Me_5$) with Li_2Se_4 gave a tetraselenide-bridged diiridium complex $Cp^*Ir(\mu\text{-}Se_4)_2IrCp^*$, which reacted further with two equiv. of $Pd(PPh_3)_4$ to afford a mixture of bimetallic tetra- and penta-nuclear selenido clusters $(Cp^*Ir)_2\{Pd(PPh_3)\}_2(\mu_3\text{-}Se)_2(\mu_2\text{-}Se)$ and $(Cp^*Ir)_2\{Pd(PPh_3)\}_3(\mu_3\text{-}Se)_3(\mu_3\text{-}Se_2)$.

The chemistry of metal polysulfides has been progressing rapidly owing to their potential as synthetic reagents or catalysts as well as new materials. Stable polysulfide ligands are now known to be isolable with a variety of ring sizes and coordination modes,[1] which include a novel bridging nonasulfide chain in $Cp^*Ir(\mu\text{-}SPr^i)_2(\mu\text{-}S_9)IrCp^*$ ($Cp^* = \eta^5\text{-}C_5Me_5$) prepared in this laboratory.[2] Recently, the coordination chemistry of inorganic selenium and tellurium ligands has also been attracting considerable attention.[1b,3] Hence, our studies on dinuclear noble metal–sulfur complexes consisting of half-sandwich Cp*M units[4] have been extended to related noble metal–selenium compounds.[5] Now we have found that reaction of $Cp^*IrCl(\mu\text{-}Cl)_2IrCp^*Cl$ **1** with Li_2Se_4 gives a complex containing a unique diiridium core bridged by two Se_4 ligands, $Cp^*Ir(\mu\text{-}Se_4)_2IrCp^*$ **2**.†



3 **4**

The structure of **2** has been determined in detail by X-ray analysis (Fig. 1).‡ In **2**, each of the Ir atoms has a chelating Se_4 ligand and is further bonded to either an α- or β-Se atom in the other Se_4 ligand. The distance between the two 18-electron Ir(III) centres is 4.179(3) Å. The Ir–Se bond lengths, varying from 2.42 to 2.50 Å, are comparable to those in $Cp^*Ir(PMe_3)(Se_4)$ [2.468(2) and 2.472(2) Å][6] and slightly shorter than that in $[Ir(Me_2PCH_2CH_2PMe_2)_2(Se_4)]Cl$ [2.542(3) Å],[7] while the Se–Se bond distances (2.28–2.41 Å) are unexceptional when compared with those in chelating tri- to pentaselenide ligands previously reported.[3b,c] The two $IrSe_4$ planes are folded and have envelope geometries. Thus, in the ring consisting of Ir(1) and Se(1)–Se(4), the Ir(1), Se(1), Se(3) and Se(4) atoms are almost coplanar within 0.003(4) Å while the distance of Se(2) from this least-square plane is 1.31 Å. For the other ring, the Se(6) atom is displaced 1.36 Å from the least-square plane defined by the Ir(2), Se(5), Se(7) and Se(8) atoms which show deviations of $< 0.10(2)$ Å. The $M(\mu\text{-}Se_4)_2M$ core observed in **2** is unprecedented, although the sulfur analogue has been demonstrated *via* the Rh complex $Cp^*Rh(\mu_2\text{-}S_4)_2RhCp^*$ obtained from the reaction of $Cp^*{}_2Rh_2(CO)_2$ with S_8.[8] More recently, the Ir complex $Cp^*Ir(\mu_2\text{-}S_4)_2IrCp^*$, produced from the reaction of $Cp^*Ir(2,5\text{-}Me_2C_4H_2S)$ with S_8 has been shown unequivocally to have a similar $M(\mu\text{-}S_4)_2M$ core,[9] while the complex generated by photolysis or thermolysis of $Cp^*Ir(S_4)(CO)$ was also formulated as $Cp^*Ir(\mu_2\text{-}S_4)_2IrCp^*$ based on spectroscopic data.[10]§

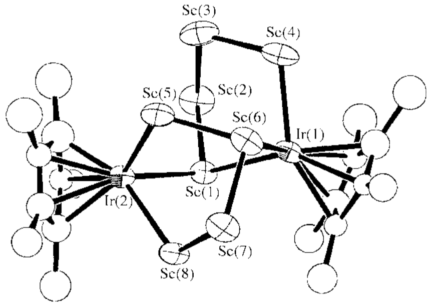


Fig. 1 Molecular structure of **2**. Hydrogen atoms are omitted for clarity. Selected bond distances (Å): Ir(1)–Se(1) 2.456(5), Ir(1)–Se(4) 2.468(5), Ir(1)–Se(6) 2.423(4), Ir(2)–Se(1) 2.454(5), Ir(2)–Se(5) 2.423(5), Ir(2)–Se(8) 2.496(5), Se(1)–Se(2) 2.405(7), Se(2)–Se(3) 2.285(7), Se(3)–Se(4) 2.309(8), Se(5)–Se(6) 2.312(7), Se(6)–Se(7) 2.391(7), Se(7)–Se(8) 2.325(7).

Although structures and reactivities of mixed-metal chalcogenido clusters are of particular interest, syntheses of mixed-metal selenido or tellurido clusters are still poorly explored in contrast to those of the corresponding sulfur compounds which have progressed rapidly. Employment of polychalcogenido complexes as precursors for synthesizing such clusters is essentially unexplored except for the reactions of certain dichalcogenido complexes with other low valent metal species giving chalcogenido clusters through E–E bond scission (E = S, Se or Te).[11] Transformation of **2** into mixed-metal clusters was therefore attempted, which led to the finding that when **2** was allowed to react with 2 equiv. of $Pd(PPh_3)_4$ in THF at room temperature, two readily characterizable Ir–Pd–Se clusters, $(Cp^*Ir)_2\{Pd(PPh_3)\}_2(\mu_3\text{-}Se)_2(\mu_2\text{-}Se)$ **3** and $(Cp^*Ir)_2\{Pd(PPh_3)\}_3(\mu_3\text{-}Se)_3(\mu_3\text{-}Se_2)$ **4**, were obtained in 11 and 12% yields, respectively.‡¶ In contrast, analogous treatment of **2** with $Pt(PPh_3)_4$ did not afford any tractable products.

Cluster **3** (Fig. 2) has a tetrahedral Ir_2Pd_2 framework having two capping selenido ligands on the Ir_2Pd faces and one bridging selenido ligand on the Pd–Pd bond. Among the six edges of the Ir_2Pd_2 tetrahedron, only the Ir–Ir separation of 3.4733(5) Å corresponds to a non-bonding interaction. The Ir–Se and Pd–Se bond lengths for the face-bridged Se(1) and Se(2) atoms, which are in the range 2.445(1)–2.455(1) Å, are slightly longer than the Pd(1)–Se and Pd(2)–Se distances for the edge-bridged Se(3) centre at 2.389(1) and 2.373(1) Å, respectively, and are not exceptional. In the ^1H and $^{31}P\{^1H\}$ NMR spectra, the protons of the two Cp* groups and the two P atoms appear

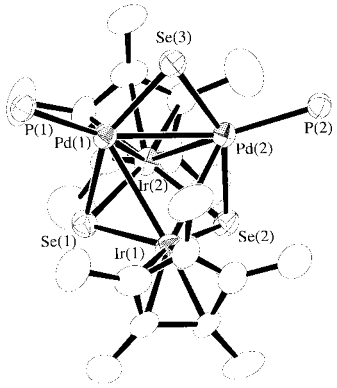


Fig. 2 Molecular structure of **3**. Hydrogen atoms are omitted for clarity. Selected interatomic distances (Å): Ir(1)–Pd(1) 2.9399(8), Ir(1)–Pd(2) 2.9530(8), Ir(2)–Pd(1) 2.9079(8), Ir(2)–Pd(2) 2.8584(8), Pd(1)–Pd(2) 2.773(1), Ir(1)–Ir(2) 3.4733(5).

as singlets, indicating a symmetrical structure with two mirror planes for **3** in solution.

Fig. 3 shows the structure of **4**,‡ whose core is composed of the $Ir_2Pd_2Se_3$ cluster framework of **3** as well as a triangular Pd(3)–Se(4)–Se(5) unit bound to it at the Pd(3) and Se(4) centres. The Se(4) atom is bound to Ir(2) and Pd(3) [2.472(1) and 2.526(1) Å], and weakly to Pd(2) [2.8510(9) Å], but not to Pd(1) [3.650(1) Å]. Owing to this unsymmetrical binding of the Se_2 ligand, no mirror plane exists for the cluster core and ^1H and ^{31}P NMR data are diagnostic of this structural feature. Metal–metal single-bonds are observed only for each of the three edges of the Ir(1)–Pd(1)–Pd(2) plane, although some bonding interaction may also be present between the Pd(1) and Pd(3) centres. Ignoring these metal–metal interactions, the geometries around Pd(1) and Pd(3) are distorted trigonal and square planar, respectively, while the Pd(2) atom has a trigonal pyramidal configuration with Se(4) at an apical position.

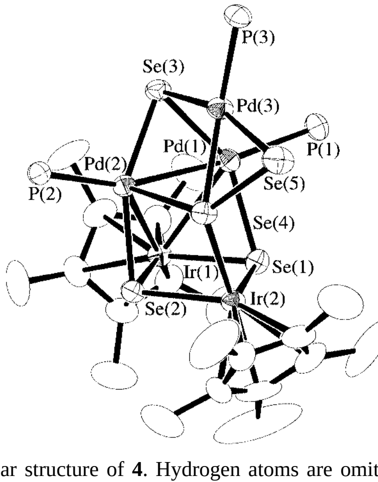


Fig. 3 Molecular structure of **4**. Hydrogen atoms are omitted for clarity. Selected interatomic distances (Å): Ir(1)–Pd(1) 2.8832(7), Ir(1)–Pd(2) 2.9175(8), Pd(1)–Pd(2) 2.7779(9), Ir(1)–Ir(2) 3.7640(4), Ir(2)–Pd(1) 3.9343(6), Ir(2)–Pd(2) 3.7644(7), Pd(1)–Pd(3) 3.079(9), Pd(2)–Pd(3) 3.2184(9).

In summary, a diiridium complex **2** containing two bridging Se_4 ligands has been prepared and characterized. A study on the reaction of **2** with $Pd(PPh_3)_4$ has verified that it serves as a versatile precursor for preparing mixed-metal Ir–Pd–Se clusters. It is of note that the sulfur analogue of **2**, $Cp^*Ir(\mu\text{-}S_4)_2IrCp^*$, did not give any characterizable products upon analogous treatment with $Pd(PPh_3)_4$. The reactivity of **2** towards other metal species as well as organic molecules is now under investigation.

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Notes and references

† Grey Se (1.74 g, 22.0 mmol) was suspended in THF (200 mL) and treated with 1.0 M $Li[BHEt_3]$ in THF (11 mL, 11 mmol) for 1 h at room temp. The resultant dark brown solution was warmed to 50 °C and **1** (1.99 g, 2.50 mmol) added. After stirring for 1 h at 50 °C, the mixture was dried *in vacuo* and the residue extracted with benzene. Addition of methanol to the concentrated extract afforded dark brown crystals of $\mathbf{2}\cdot C_6H_6$ (1.36 g, 40%). ^1H NMR ($CDCl_3$): δ 1.97, 1.71 (s, 15H, Cp*), 7.36 (s, 6H, C_6H_6). Anal. Calc. for $C_{26}H_{36}Se_8Ir_2$: C, 22.88; H, 2.66. Found: C, 22.71; H, 2.64%.

‡ *Crystal data*: $\mathbf{2}\cdot C_7H_8$ (obtained after recrystallization from toluene–MeOH): $C_{27}H_{38}Ir_2Se_8$, M = 1378.72, triclinic, space group $P\bar{1}$ (no. 2), a = 8.519(4), b = 14.081(3), c = 14.262(6) Å, α = 95.60(2), β = 94.51(5), γ = 91.88(3)°, U = 1695(1) Å^3, room temp., Z = 2, μ(Mo-Kα) = 164.64 cm^{-1}, R = 0.057 and R_w = 0.059 for 1658 reflections with $I > 3.00\sigma(I)$ and 178 variables.

3: $C_{56}H_{60}P_2Se_3Ir_2Pd_2$, M = 1629.16, monoclinic, space group $P2_1/c$ (no. 14), a = 18.844(4), b = 11.066(1), c = 26.778(2) Å, β = 104.843(8)°, U = 5409(1) Å^3, room temp., Z = 4, μ(Mo-Kα) = 76.87 cm^{-1}, R = 0.043 and R_w = 0.042 for 8181 reflections with $I > 3.00\sigma(I)$ and 587 variables.

$\mathbf{4}\cdot C_6H_6$: $C_{80}H_{81}P_3Se_5Ir_2Pd_3$, M = 2233.88, triclinic, space group $P\bar{1}$ (no. 2), a = 14.789(3), b = 16.151(3), c = 17.590(2) Å, α = 94.48(1), β = 99.85(1), γ = 108.86(1)°, U = 3877(1) Å^3, Z = 2, μ(Mo-Kα) = 65.63 cm^{-1}, R = 0.050 and R_w = 0.074 for 10195 reflections with $I > 3.00\sigma(I)$ and 587 variables. CCDC 182/1508. See http://www.rsc.org/suppdata/cc/a9/a909403b/ for crystallographic files in .cif format.

§ Reaction of **1** with Li_2S_4 gave fully characterizable $Cp^*Ir(\mu_2\text{-}S_4)_2IrCp^*$ in satisfactory yield, which will be reported in a subsequent paper.

¶ A THF solution (30 ml) of $\mathbf{2}\cdot C_6H_6$ (273 mg, 0.200 mmol) was treated with $Pd(PPh_3)_4$ (462 mg, 0.400 mmol) at room temperature for 1 day. The evaporated reaction mixture residue was extracted with benzene and subjected to column chromatography (Al_2O_3–benzene), affording first a dark brown band and then a green fraction. Recrystallization from benzene–hexane of the products from the latter and the former afforded green **3** (36 mg, 11% yield) and dark brown $\mathbf{4}\cdot C_6H_6$ (52 mg, 12% yield), respectively. **3**: ^1H NMR ($CDCl_3$): δ 1.38 (s, 30H, Cp*), 7.27–7.41 (m, 18H, Ph), 7.90–7.96 (m, 12H, Ph). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 24.2 (s). Anal. Calc. for $C_{56}H_{60}P_2Se_3Ir_2Pd_2$: C, 41.29; H, 3.71. Found: C, 41.46; H, 3.74%.

$\mathbf{4}\cdot C_6H_6$: ^1H NMR ($CDCl_3$): δ 1.45 and 1.54 (s, 15H, Cp*), 6.87–7.16 (m, 27H, Ph), 7.63–7.68 (m, 18H, Ph), 7.36 (s, 6H, C_6H_6). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 2.2 (dd, J 6 and 15 Hz, 1P), 10.0 (dd, J 15 and 179 Hz, 1P), 14.9 (dd, J 6 and 179 Hz, 1P). Anal. Calc. for $C_{80}H_{81}P_3Se_5Ir_2Pd_3$: C, 43.01; H, 3.65. Found: C, 42.93; H, 3.78%.

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