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Binuclear rhodium(III) and iridium(III) monoselenocarboxylates: Synthesis, spectroscopy and structure of an ortho-metallated iridium complex featuring an IrCCC(μ -Se) chelate ring

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ABSTRACT

Monoselenocarboxylate-bridged binuclear complexes of Rh^{III} and Ir^{III}, $[(Cp^*MCl)_2(\mu-SeCOAr)_2]$ (1) (*M* = Rh or Ir; Cp* = pentamethylcyclopentadienyl; Ar = Ph, C₆H₄Me-4), have been isolated either by the reaction between $[Cp_2M_2(\mu-Cl)_2Cl_2]$ with KSeCOAr in acetonitrile or by treatment of $[Cp^*MCl(sol-vent)_2][PF_6]$ with KSeCOAr in acetone. The novel binuclear complexes, $[Cp^*IrCl(\mu-SeCOAr)(\kappa^2-SeCOC_6H_3R-)IrCp^*]$ (2) (*R* = H or Me-4) with ortho-metallation at one of the iridium centres have been isolated following the use of excess AgPF₆. The single crystal structure of $[Cp^*IrCl(\mu-SeCOC_6H_5)(\kappa^2-SeCOC_6H_4-)IrCp^*]$ (2a) exhibits two phenylcarboselenolate moieties situated in *syn* fashion with respect to the "Ir₂Se₂" plane, one of which leans towards the metal centre in order to undergo ortho-metallation after iridium–chlorine bond dissociation.

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The organometallic chemistry of group-8 metal complexes with chalcogen ligands has been progressing rapidly owing to their intriguing reactivities [1–4] and relevance in catalytic hydrodesul-furization reactions [5,6]. The chemistry of these complexes has been dominated by derivatives containing thiolato [7], hydrosulfido [1,8,9] or sulfido [10] ligands. These ligands invariably yield bi–, tri–, and tetra–nuclear complexes, whereas 1,1–dithiolates (RCS²₂, ROCS²₂, R₂NCS²₂, (RO)₂PS²₂) give mononuclear compounds [11–13].

Recently, we have investigated metal complexes containing selenocarboxylate ligands [14–16]. The facile cleavage of the C–Se bond has led us to develop a convenient synthetic route to selenide-bridged complexes, $[M_3(\mu-Se)_2(PP)_3]^{2+}$ (M = Pd or Pt) in high yields and metal selenide (MSe; M = Zn, Cd or Hg) nanoparticles. However, there is hardly any report dealing with classical or organometallic complexes of rhodium and iridium with chalcogeno-carboxylic acids [17]. In view of the above it was considered of interest to study selenocarboxylate complexes containing Cp*M^{III} unit (Cp* = pentamethylcyclopentadienyl).

Treatment of $[Cp_2M_2(\mu-Cl)_2Cl_2]$ with two equivalents of KSeC-OAr (prepared according to methods reported [18,19]) afforded selenocarboxylate-bridged binuclear complexes, $[(Cp^*MCl)_2 (\mu-SeCOAr)_2]$ (1) (M/Ar = Rh/Ph (1a), Rh/Tol (1b), Ir/Ph (1c) and Ir/Tol (1d), Tol = C_6H_4 Me-4). The iridium complexes were often contaminated with the starting material, the chloro-bridged dimer, $[Cp_{2}^{*}Ir_{2}(\mu-Cl)_{2}Cl_{2}]$ which could be separated by recrystallization. Reaction between $[Cp^{*}MCl(solvent)_{2}][PF_{6}]$ (prepared by treatment of $[Cp_{2}^{*}M_{2}(\mu-Cl)_{2}Cl_{2}]$ with AgPF₆ in 1:2 ratio in acetone) and KSeCOAr yielded **1** [20]. However, when the AgPF₆ amount was increased another binuclear complex was formed. Accordingly, the reaction between $[Cp_{2}^{*}Ir_{2}(\mu-Cl)_{2}Cl_{2}]$ with AgPF₆ in 1:3 ratio in acetone followed by treatment with KSeCOAr yielded $[Cp^{*}IrCl$ $(\mu-SeCOAr)(\kappa^{2}-SeCOC_{6}H_{3}R-)IrCp^{*}]$ (**2**) (R = H (**2a**), Me-4 (**2b**)) [21] (Scheme 1).

IR spectra of **1** and **2** displayed absorptions at \sim 1650 cm⁻¹, indicating the presence of uncoordinated carbonyl. The high energy bands of the electronic absorption spectra can be attributed to $\pi \rightarrow \pi^*$ transitions whereas the low energy bands (>400 nm for Rh^{III} complexes) may be assigned to metal-mediated LLCT transitions. The ¹H NMR spectra of **1** exhibited the expected resonances and peak multiplicities. The ¹H NMR spectra of **2** showed two closely spaced Cp* methyl signals due to two different Cp*Ir^{III} moieties. In the ${}^{13}C{}^{1}H$ NMR spectra of **1** the resonances due to the ring carbons of the Cp* are significantly downfield shifted with reference to the corresponding signals for the chloro-bridged derivatives, $[Cp_2^*M_2(\mu-Cl)_2Cl_2]$. The ⁷⁷Se{¹H} NMR spectra of **1a** and **1b** showed a triplet (Fig. 1), owing to the coupling with two ¹⁰³Rh nuclei which substantiates the presence of bridged selenium in the complex. The magnitude of ${}^{1}J({}^{103}Rh-{}^{77}Se)$ (~35 Hz) can be compared with rhodium(III) selenoether complexes (30-52 Hz) [22–24]. The ⁷⁷Se NMR resonances are considerably more shielded





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Fig. 1. 77 Se{¹H} NMR spectrum of [(Cp*RhCl)₂((μ -SeCOC₆H₅)₂] (1a) in CDCl₃, Inset showing triplet with 1 J(103 Rh- 77 Se) = 33 Hz.

than the signals observed for KSeCOAr and for $[M(SeCOAr)_2(tme-da)]$ (*M* = Zn, Cd) [16] where the selenolate ligand is monodentate.

An ORTEP drawing with atomic numbering scheme for the crystallographically analyzed [Cp*IrCl(μ -SeCOPh)(κ^2 -SeCOC₆H₄-) IrCp*] (**2a**) [25] is shown in Fig. 2. The molecule consists of two Cp*Ir^{III} fragments, held together by two bridging selenocarboxylate groups. One of the Cp*Ir fragment is coordinated to two Se atoms and a chloride ligand while the other Cp*Ir moiety is bonded to

the two bridging Se atoms and to the deprotonated *ortho*-carbon atom of a phenyl ring of one SeCOPh ligand. The Ar'CO ($Ar' = C_6H_4$ and Ph) groups on selenium are mutually *syn* and adopt an *exocyclic* configuration. Each iridium atom acquires a distorted octahedral configuration with the pentamethylcyclopentadienyl ring at one face. The Cp* rings are mutually *trans*.

The cyclometallation-formed five-membered chelate ring involving the Ir2Se1C28C29C34 atoms is planar and nearly per-



Fig. 2. ORTEP (50% probability thermal ellipsoids) diagram of [Cp*IrCl(μ-SeCOC₆H₅)(κ²-SeCOC₆H₄-)IrCp*] (2a). Selected bond lengths (Å) and bond angles(°): Ir1-Se1 and Ir2-Se2 2.512(2), Ir1-Se2 2.495(1), Ir2-Se1 2.445(2), Ir2-C34 2.076 (11), Ir1-Cl1 2.408(3), Se1-C28 1.951(14), Se2-C21 1.992(12), Ir1-C15 2.181(12), Ir2-C3 2.261(13), zlr2-Se2-lr1 98.16(6), lr2-Se1-lr1 90.50(6), Se1-lr2-Se2 81.30(6), Se1-lr1-Se2 80.33(6), lr1-Se2-C21 108.5(4), lr2-Se1-C28 97.6(5), lr1-Se1-C28 101.7(4), lr2-Se2-C21 103.1(4), Se1-Ir1-Cl1 85.19(11), Se2-Ir1-Cl1 80.27(9), Se1-Ir2-C34 84.3(4), Se2-Ir2-C34 91.2(3).

pendicular (86.37°) to the plane formed by the Ir2Se1Se2 atoms. The planarity is supported by the presence of three sp^2 carbon centres. The four-membered "Ir₂Se₂" ring is not quite planar (hinge angle 171.7°) with alternating long and short Ir–Se distances. The Ir-Se distances can be compared with the values reported in $[Cp^*Ir(\mu-Se_4)]_2$ (2.42–2.50 Å) [26] and $[Cp^*Ir(Se_4)(PMe_3)]$ (2.468(2)-2.472 (2)Å) [27]. The Ir-Ir separation of 3.784Å indicates the absence of any bonding interactions between them; Ir–Ir single bond distances vary between 2.65 and 3.1 Å. The η^5 – Cp*-to-Ir bond distances lie in the range between 2.160(12) and 2.261(13) Å with an average value of 2.19 Å. The Ir2-C34 distance involving the metallated carbon atom (a carbanion) is much smaller at 2.076(11) Å. The Ir-Cl bond length of 2.408(3) Å is well within the range reported for Ir^{III} complexes, e.g. $[Cp^*Ir(\mu-SH)Cl]_2$ (2.401(3) Å) [1,8].

The presence of one chloride and one carbanion binding moiety $Cp^*Ir(\mu-Se)_2$ in the same molecule allows us to point out the strong perturbation effect of the ortho-metallation. Due to the donor effect from the basic carbanion the average $Ir-C(Cp^*)$ bond distances are longer by about 0.04 Å for the cyclometallated iridium, Ir2 in comparison to Ir1 (Supplementary Table 1). Within the Ir-C(Cp*) group there also seems to be a higher degree of deviation from η^5 -symmetry for Ir2, in the direction of $(\eta^2 + \eta^3)$

Summarizing, the ortho-metallation observed here follows a general tendency of iridium(III) to engage in cyclometallation and of $[Cp^*Ir]^{2+}$ in particular to stabilize highly basic and π donating chelate configurations [28-32] such as 1,2-enediamido. To our knowledge, however, it is the first time that an [IrCCCSe] fivemembered chelate ring has been obtained, distinguished by three sp² carbon centres (including one aromatic carbanion C and one uncoordinated carbonyl function), and by one bridging selenolato-Se.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2010.01.012.

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- [20] Preparation of $[Cp_{2}^{*}Rh_{2}(\mu$ -SeCOPh)₂Cl₂] (**1a**): Method A, To an acetonitrile solution (10 cm^3) of $[Cp^*_2Rh_2(\mu-Cl)_2Cl_2]$ (104 mg, 0.17 mmol), a solution (10 cm³) of KSeCOPh (76 mg, 0.34 mmol) was added and stirred for 1 h under an argon atmosphere. The solvent was evaporated under vacuum and the residue was extracted with dichloromethane. Subsequent removal of the solvent in vacuo yielded a deep red solid which was recrystallized with chloroform-hexane mixture to give red crystals of the title complex (yield 89 mg, 58%). m.p. 125 °C (decomp.). IR (Nujol) v, cm⁻¹: 1673 (br) (C=O). UV-Vis (CH₂Cl₂), *λ*: 242, 296, 431 nm. Anal. Calc. for C₃₄H₄₀Cl₂O₂Rh₂Se₂.0.5CH₂Cl₂: C, 43.2; H, 4.3. Found: C, 42.9; H, 4.4%. ¹H NMR (CDCl₃): 1.62 (s, 30 H, Me (Cp⁺)); 7.60 (t), 7.76 (t), 8.30 (d) [Ph]. ¹³Cl¹H}NMR (CDCl₃): 9.7 (Me(Cp⁺)); 98.3 (Cp*); 129.1, 129.5, 135.0, 140.3 (-C₆H₅), 195.0 (CO). ⁷⁷Se{¹H} NMR (CDCl₃): 84 $^{1}J(^{103}Rh-^{77}Se) = 33$ Hz). Method B, In alternative to method A, reaction carried out in presence of AgPF₆, which essentially yielded the same complexes as mentioned above. A representative procedure has been described as follows. To an acetone solution of [Cp*2Rh2(µ-Cl)2Cl2] (110 mg, 0.17 mmol), solid AgPF₆ (90 mg, 0.36 mmol) was added and mixture was stirred for 1 h under argon in the dark room. The solution was filtered through Celite to get rid of AgCl. To the filtrate a methanolic solution of KSeCOPh (70 mg, 0.31) was added and reaction mixture was stirred for 2 h. Solvents were stripped off from reaction mixture and contents were extracted with dichloromethane. The filtrate was concentrated under reduced pressure and to this few drops of hexane were added to get an oily product which on drying gave the title complex. $[Cp_2^*Rh_2(\mu-SeCOC_6H_4Me-4)_2Cl_2]$ (1b): Anal. Calc. for C₃₆H₄₄Cl₂O₂Rh₂Se₂.0.5CH₂Cl₂: C, 44.5; H, 4.6. Found: C, 44.4; H, 4.5%. ¹H $\begin{array}{l} & (1,2,3) \\ & (1,3$ 1 1 102 102 107 1.61, 1.69 (Cp*); 7.48 (t, 7.5 Hz), 7.62 (t, 7.5 Hz) $[-C_6H_4-]$. ¹³C{¹H} NMR (CDCl₃): 9.2 (Me(Cp*)); 99.9 (Cp*); 128.5, 130.2, 133.7 [C₆H₅]. 171.3 (CO). $[Cp^*_{J17_{4}}]_{J2}$ ($pr^*_{J17_{4}}$) $(pr^*_{J17_{4}})_{J2}$ ($pr^*_{J17_{4}})_{J2}$) $(pr^*_{J17_{4}})_{J2}$ 6.6 Hz), 8.00 (t, 8.1 Hz) [$-C_6H_4-$], ¹³C[¹H] NMR (CDCl₃): 9.2 (Me(Cp^{*})); 21.8 (Me); 100.0 (Cp^{*}); 129.2, 130.2, 144.5 (C_6H_4); 171.5 (CO). [21] Preparation of [Cp^* IrCl(μ -SeCOC₆H₅)(κ ²-SeCOC₆H₄-)IrCp^{*}] (**2a**): Solid AgPF₆
- [21] Preparation of [Cp*IrCl(μ-SeCOC₆H₅)(κ²-SeCOC₆H₄-)IrCp*] (2a): Solid AgPF₆ (70 mg, 0.32 mmol) was added to an acetone solution of [Cp*₂Ir₂(μ-Cl)₂Cl₂] (90 mg, 0.11 mmol) and the reaction mixture was stirred for 1 h under argon in dark. Solution was filtered through Celite. A methanolic solution of KSeCOPh (60 mg, 0.27 mmol) was added to the above filtrate and reaction mixture was stirred for additional 2 h. The solvents were evaporated under vacuum and the residue was extracted with dichloromethane. The filtrate was concentrated

under reduced pressure and layered with hexane to afford orange-red crystals (yield 80 mg, 55%). m.p. 207 °C (decmp.). *Anal.* Calc. for $C_{34}H_{39}Cllr_2O_2Se_2$: C, 38.6; H, 3.7. Found: C, 38.8; H, 3.7%. IR (nujol) ν , cm⁻¹: 1673, 1658 (C=O). UV-Vis (CH₂Cl₂): 240, 379 nm. ¹H NMR (CDCl₃): 1.64, 1.65 (each s, Me(Cp^{*})); 6.91 (t), 7.23 (m), 7.36 (m), 7.52 (d), 7.58 (d), 7.79 (d) [Ph and $-C_6H_4-]$. [*Cp*trCl(µ-SecOC₆H₄-Me)(\kappa2-SecOC₆H₃Me-4-)<i>trCp**] (**2b**): *Anal.* Calc. for $C_{36}H_{43}Cllr_2O_2Se_2$: C, 39.8; H, 4.1. Found: C, 39.8; H, 4.2%. ¹H NMR (CDCl₃): 1.60, 1.64 (each s, Me(Cp*)); 2.09, 2.41 (each s, C₆H₄Me and C₆H₃Me); 7.17 (d), 7.62 (d) [-C₆H₄-]; 6.65 (s), 6.73 (d), 7.49 (d), [-C₆H₃(Me) –].

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