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New Diiridium(I) and Diiridium(I,III) Complexes containing Thiolate Ligands. Crystal Structures of [(cod)Cl(SC_6F_5)Ir(μ-SC_6F_5)$_2$Ir(cod)] and [{Ir(μ-SC_6F_5)$(CO)_2$}$_2$] (cod = cycloocta-1,5-diene)

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The complex [{Ir(μ-Cl)(cod)}$_2$] **1** (cod = cycloocta-1,5-diene) was treated with HSR (R = C_6F_5)–NEt_3 to give the dinuclear iridium(I) complex [{Ir(μ-SR)(cod)}$_2$] **2** and with HSR only to give a mixture of **2** and the unusual mixed-valence complex [(cod)Cl(SR)Ir(μ-SR)$_2$Ir(cod)] **3**; complex **2** was treated with CO to yield [{Ir(μ-SR)$(CO)_2$}$_2$] **4**, the structure of which, together with that of **2**, has been characterised by single-crystal X-ray diffraction.

During recent years the synthesis and characterisation of thiolate-containing compounds have received much attention. Thiolate ligands form very stable bonds with transition metals (soft–soft matching) and stabilise di- and poly-nuclear complexes.[1] These exhibit a great variety of reactions[2] and it is possible to stabilise unsaturated species by ligand–metal interactions.[3]

In this group of compounds, special attention has been paid to the rhodium and iridium bimetallic complexes [{M(μ-X)-L_2}$_2$] [M = Rh or Ir; L = CO, cycloocta-1,5-diene (cod), phosphine, *etc.*; X = thiolate, halide, amido, imidazolyl, pyrazolate, *etc.*] due to their application as very active hydrogenation and hydroformylation catalysts and as models for studying the hydrodesulfurization reaction mechanism. Both metals can be involved in a co-operative manner and such an effect has been proposed[4] and the nature of the bridging ligands has proved to be very important.[5]

Oxidative addition reactions to Vaska's iridium(I) complexes, [IrX(CO)$(PR_3)_2$], X = halide, R = alkyl or aryl, have been widely studied and the mechanism is well established, although recently there has been renewed interest in the study of factors influencing the thermodynamics and kinetics of such reactions by computational methods. The results are very often in disagreement with previous interpretations. Nevertheless, these reactions of dimeric complexes are not as well studied and they can lead to $M^{II}M^{II}$, $M^{III}M^{III}$ or $M^{I}M^{III}$ species. The two former types are well known while mixed-valence complexes (M = Rh or Ir) have been proposed on spectroscopic evidence.[6] Recently an X-ray crystal structure for [Ir_2(Me)I(μ-NHC$_6$H$_4$Me-*p*)$_2$-$(CO)_4$] has been reported.[7]

In the context of our programme of preparation and reactivity of thiolate transition-metal complexes, we report here the preparation of some dimeric iridium complexes containing SR (R = C_6F_5). Typical substitution reactions of Cl by SR in **1** with Pb$(SC_6F_5)_2$ or Tl(SC_6F_5), as employed for rhodium complexes[8] did not lead to the desired product.

Reaction of [{Ir(μ-Cl)(cod)}$_2$] **1** with stoichiometric amounts of HSR–NEt_3 in acetone at room temperature yielded the bis(dithiolate) complex [{Ir(μ-SR)(cod)}$_2$] **2**.† In the absence of NEt_3 the reaction with HSR gave **2** as the main product, but the 16–18 electron complex [(cod)Cl(SR)Ir(μ-SR)$_2$Ir(cod)] **3** was isolated unexpectedly as a by-product in the form of red crystals. The reactivity of **2** and **3** with CO is different; **2** gives [{Ir-(μ-SR)$(CO)_2$}$_2$] **4**, whilst for **3**, cod is partially substituted probably at the d^8 centre. The reaction however is more complex than expected and the carbonylated product has not been fully characterised. Further studies on the reactivity of these systems are in progress.

The reactions can be rationalised according to Scheme 1 although it was not possible to isolate the intermediates. Steps (*i*) and (*ii*) can be interpreted as two consecutive two-electron, two-centre[5] additions of HSR with reductive elimination of HCl. This has been previously reported[9] as a secondary reaction in the addition of PhSSPh to **1** probably due to the presence of HSPh as an impurity leading to [{Ir(μ-SPh)(cod)}$_2$] as a by-product. Step (*iii*) is an oxidative two-electron, two-

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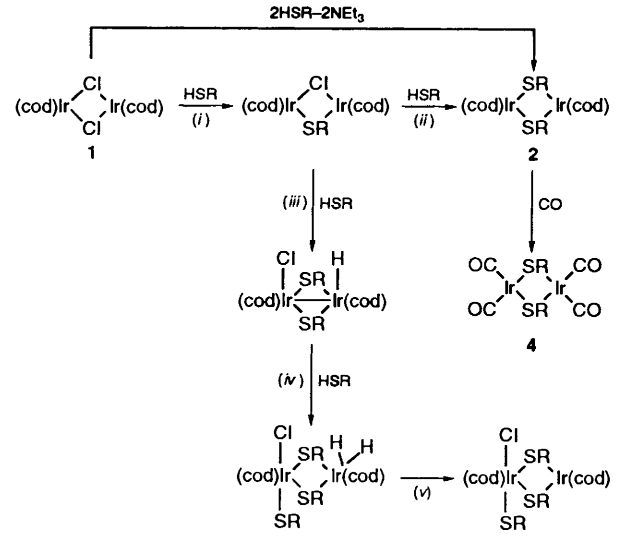
† Preparation of complexes. To a solution of **1** (0.144 g, 0.215 mmol) in acetone (15 cm^3) were added HSR (0.06 cm^3, 0.43 mmol) and NEt_3 (0.06 cm^3, 0.43 mmol). The solution was stirred at room temperature for 30 min. Complex **2** was obtained in 70% yield as a yellow microcrystalline product. It was filtered off, washed with water and methanol, and vacuum dried (Found: C, 33.00; H, 2.30. $C_{28}H_{24}F_{10}Ir_2S_2$ requires C, 33.65; H, 2.40%). A second batch of product was obtained by reducing the volume and cooling the filtrate. By working under the same reaction conditions described above, but adding only HSR to the acetone solution of **1**, complex **2** was obtained as a precipitate. After filtering off the yellow precipitate, the solution was reduced in volume and cooled to 0 °C, **3** appeared as a red crystalline product in 10% yield (Found: C, 33.20; H, 2.00. $C_{34}H_{24}ClF_{15}Ir_2S_3$ requires C, 33.10; H, 1.95%); *m/z* 1233 (M^+), 1034 (M^+ – SR) and 999 (M^+ – SR –Cl). Complex **4** was obtained by bubbling CO through a hexane suspension of the precursor **2**. The orange precipitate could be conveniently recrystallised from acetone–hexane by cooling to –20 °C (Found: C, 21.60. $C_{16}F_{10}Ir_2O_4S_2$ requires C, 21.50%); ν_{CO}(KBr)/cm^{-1} 2093, 2066 and 2016.

Complexes **2**–**4** show typical bands for the SC_6F_5 groups at 1513, 1478, 1089, 980 and 847 cm^{-1}. The tetracarbonyl complex **4** shows three ν_{CO} vibrations characteristic of C_{2v} symmetry.



Scheme 1 R = C_6F_5

centre addition of HSR with concomitant migration of SR to the more favourable bridged position giving the iridium(II) complex. Further two-electron, two-centre oxidation would produce the iridium(III) complex in step (*iv*). Reductive elimination of H_2 in step (*v*) would yield the final 16–18 electron complex **3**. Both reaction paths (*ii*) and (*iii*)–(*v*) can be envisaged as in possible competition. Factors governing the extent of each can be thermodynamic or kinetic in nature. We have found * that the effect of the solvent has proved to be very important in related iridium thiolate chemistry. Polar solvents such as acetone or non-polar solvents such as toluene or cyclohexane can give products of different nuclearity or different isomers under the same reaction conditions.

There have been attempts to correlate the Ir ··· Ir distance in the starting material with whether one- or two-centre addition occurs. Intuitively the former should be favoured by long distances and the latter by short ones. Experimentally, however, no such correlation is observed.

Figs. 1 and 2 show perspective views of the complexes [{Ir(μ-SR)(CO)$_2$}$_2$] and [(cod)Cl(SR)Ir(μ-SR)$_2$Ir(cod)] respectively.† In both molecules the two Ir atoms are bridged by two S atoms. In complex **4** each Ir is linked to two carbonyl groups. Both metal centres show square-planar geometry. The dihedral angle between the two IrS_2 planes is 114.05°, the complex adopting a butterfly-like configuration. The Ir ··· Ir distance is 3.066(1) Å and intermetallic and Ir–S distances are similar to those found in analogous compounds for which a metal–metal interaction has been suggested.[16] The Ir–C(carbonyl) distances (in the range 1.85–1.88 Å) are in agreement with previously reported Ir–CO bond distances.[17]

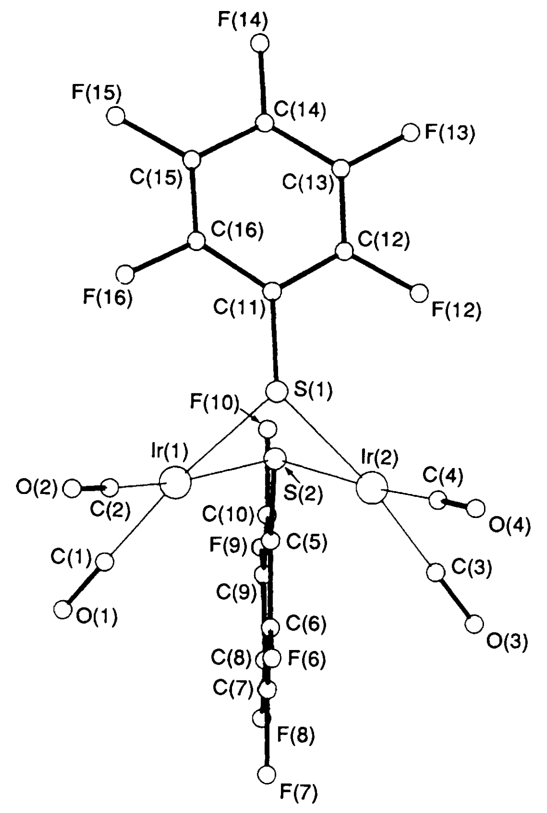


Fig. 1 PLUTO[10] view of [{Ir(μ-SR)(CO)$_2$}$_2$] showing the atomic numbering; Ir(1) ··· Ir(2) 3.066(1), Ir(1)–S(1) 2.402(3), Ir(1)–S(2) 2.375(2), Ir(2)–S(1) 2.399(2), Ir(2)–S(2) 2.384(2) Å, Ir(1)S(1)S(2)–Ir(2)S(1)S(2) 114.05°

The two metal atoms in complex **3** have very different co-ordination geometries; while Ir(1) is attached to two bridging S atoms and one cod ligand in a square-planar configuration, Ir(2) has two additional co-ordinated ligands, SC_6F_5 and Cl leading to octahedral geometry. The Ir ··· Ir distance is 3.660(1) Å and the dihedral angle is 151.99°. The Ir ··· Ir and Ir(2)–S distances are longer than those found in complex **4**. Within the co-ordination sphere of Ir(2) deviations from perfect octahedral co-ordination are found which are probably due to the unsymmetrical nature of the co-ordinating ligands. Atoms C(34) and C(27) are in the plane of S(11), S(12) and S(21) while C(30), C(31) and Cl are in apical positions. The conformation of the cod ligands is similar to that found in analogous complexes.[18] The Ir(1) ··· F(12) distance is 3.053(7) Å and could be considered as an agostic interaction, being possibly responsible for the lack of reactivity on that centre. Unfortunately crystals of **2** could not be grown to enable a direct comparison with complexes **3** and **4**.

Acknowledgements

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† Crystal data. $C_{16}F_{10}Ir_2O_4S_2$ **4**, $M = 894.7$, triclinic, $P\bar{1}$, $a = 10.697(1)$, $b = 10.775(4)$, $c = 11.088(1)$ Å, $\alpha = 78.46(1)$, $\beta = 65.88(1)$, $\gamma = 61.22(1)°$, $U = 1023.3(4)$ Å^3, $Z = 2$, $D_c = 2.9065$ g cm^{-3}, $F(000) = 808$, λ(Mo-Kα) = 0.7107 Å, $T = 293$ K, specimen 0.24 × 0.37 × 0.35 mm, 4806 reflections for $2 < \theta < 28°$, 3510 reflections with $I > 2\sigma(I)$, weighting scheme, empirical as to give no trends in $\langle w\Delta^2F\rangle$ when analysed versus $\langle F_o\rangle$ or $\langle \sin\theta/\lambda\rangle$; $R = 0.027$, $R' = 0.028$. $C_{34}H_{24}ClF_{15}Ir_2S_3$ **3**, $M = 1233.6$, monoclinic, $P2_1/n$, $a = 11.745(1)$, $b = 28.382(5)$, $c = 13.003(1)$ Å, $\beta = 112.242(1)°$, $U = 4012(1)$ Å^3, $Z = 4$, $D_c = 2.0023$ g cm^{-3}, $F(000) = 2264.0$, λ(Mo-Kα) = 0.7107 Å, specimen 0.24 × 0.27 × 0.38 mm, 9595 reflections for $2 < \theta < 28°$, 5062 reflections $I > 2\sigma(I)$, weighting scheme, empirical as to give no trends in $\langle w\Delta^2F\rangle$ when analysed versus $\langle F_o\rangle$ or $\langle \sin\theta/\lambda\rangle$; $R = 0.050$, $R' = 0.054$. Enraf-Nonius CAD-4 four-circle diffractometer. Computer and programs: VAX 11/750, DIRDIF,[11] DIFABS,[12] XRAY 80,[13] PESOS[14] and PARST.[15] Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

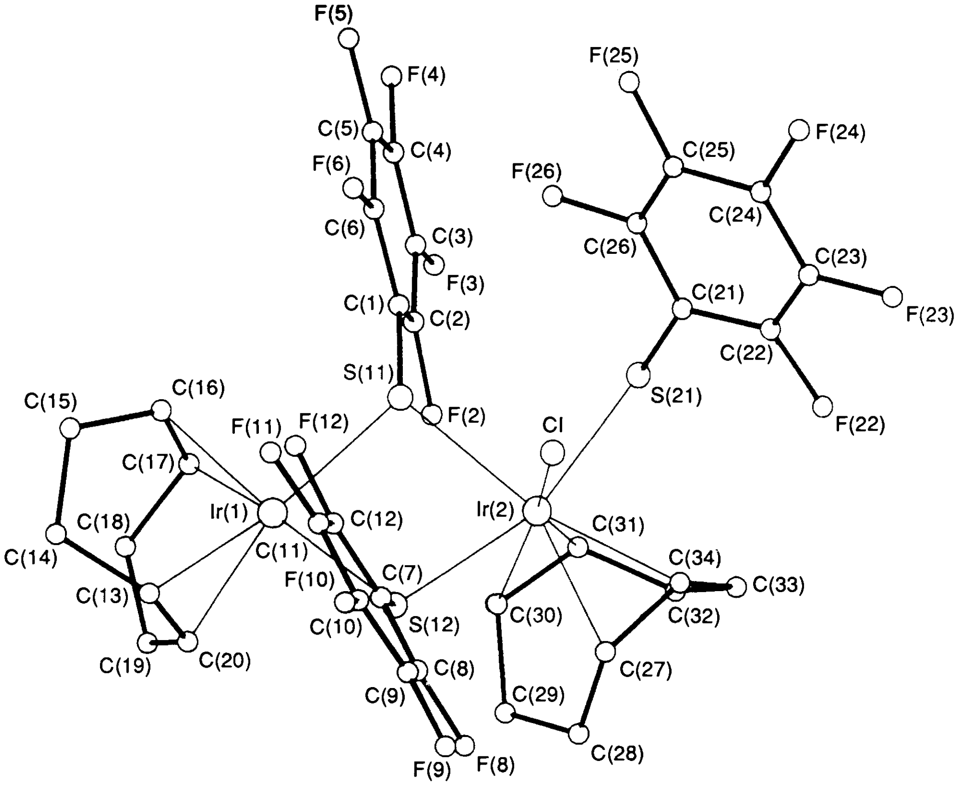

Fig. 2 PLUTO[10] view of [(cod)Cl(SR)Ir(μ-SR)$_2$Ir(cod)] showing the atomic numbering; Ir(1) ··· Ir(2) 3.660(1), Ir(1)–S(11) 2.338(2), Ir(1)–S(12) 2.367(3), Ir(2)–S(11) 2.455(3), Ir(2)–S(12) 2.486(3), Ir(2)–S(21) 2.427(3), Ir(1) ··· F(12) 3.053(7) Å, Ir(1)S(11)S(12)–Ir(2)S(11)S(12) 151.99°

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