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Pentafluorobenzenethiolato derivatives of the platinum group metals

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Contents

Abbreviations: bipy, $C_{10}H_8N_2$; Bu, C_4H_9; COD, 1,5-C_8H_{12}; Cp, C_5H_5; Cp*, C_5Me_5; Cp′, C_5Me_4Et; Cy, cyclohexyl; dppe, $(C_6H_5)_2PC_2H_4P(C_6H_5)_2$; dppm, $(C_6H_5)_2PCH_2P(C_6H_5)_2$; DCP, dicyclopentadiene; Et, C_2H_5; IQ, isoquinoline; L1, $CH_3SCH_2CH(Me)_5CH_3$; L2, $CH_3SCH(Me)CH(Me)SCH_3$; L3, CH_3SCH_2-$CH(CF_3)SCH_3$; L4, $CH_3SCH(CF_3)CH(CF_3)SCH_3$; L5, $C_6F_5SC_2H_4SC_6F_5$; L6, $C_6HF_4SC_2H_4SC_6HF_4$; L7, $C_6H_4FSC_2H_4SC_6H_4F$; L8, $C_6H_4(CF_3)SC_2H_4SC_6H_4(CF_3)$; Me, CH_3; NBD, 2,5-norbornadiene; NM, *N*-methylimidazole; ^{i}Pr, $CH(CH_3)_2$; Ph, C_6H_5; py, C_5H_5N; Q, quinoline; SX, SC_6F_5; X, C_6F_5.

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Abstract

Coordination chemistry involving fluorinated thiolates is an area of great current interest. This review is focused on the pentafluorobenzenethiolate ion [$(SC_6F_5)^-$] derivatives of the platinum group metals. For each pair of metallic centres—Ru, Os; Rh, Ir; Pd, Pt—a literature survey brings together the known compounds and their relevant data, whereas recent selected results, particularly those from our group, are discussed. The chemical richness of this area is exemplified through some specific compounds of special interest such as $[Ru(SC_6F_5)_2(PMe_2Ph)_2]$, as a stable example of a 14-electron compound bearing two C–H–Ru agostic bonds; $[Os(SC_6F_5)_2(PMe_2Ph)_3]$, with a rare trigonal-bipyramidal geometry in the solid state; $[Cp^*Rh(\mu\text{-}SC_6F_5)_3RhCp^*][Cp^*Rh(SC_6F_5)_3]$ which undergo an unusual rearrangement in solution; $[Ir_3(\mu\text{-}SC_6F_5)_3(\mu\text{-}CO)(CO)_3(PPh)_3]$, a trimetallic compound bearing an $Ir_3(\mu\text{-}SC_6F_5)_3$ skeleton; $[Pd_2(\mu\text{-}SC_6F_5)_2(\eta^3\text{-}C_3H_5)_2]$, with an interesting fluxional behaviour involving rotating allyl moieties and inversion at the sulfur atoms and $[(SC_6F_5)_2Pt(\mu\text{-}SC_6F_5)_2Pt(SC_6F_5)_2]$, which is a fully fluorinated, homoleptic platinum complex.

Keywords: Pentafluorobenzenethiolato derivatives; Platinum group metals; Fluorinated thiolates

1. Introduction

Coordination chemistry developed from fluorinated thiolates is an area of great current interest because of its relevance to catalytic processes involving metals in sulfur-containing environments [1–9]. Fluorinated thiolates have proved to be active intermediates in desulfurisation processes [10] and are interesting also due to the ability of these ligands to stabilise unusual geometries, oxidation states and intra- or inter-molecular interactions [11–14].

With thiolate ligands, manipulation of steric and electronic properties of these pseudohalide groups is possible by varying the basicity—fluorine content for example—and/or bulkiness of the R substituents [15]. It has been shown that, depending on the basicity of R, thiolates stabilise monomers, dimers as well as polymeric compounds. Dimeric homo- and hetero-metallic species are formed either by bridging sulfur atoms or using assisted thiolate ligands with another donor group [16].

Fluorinated thiolates also allow the formation of unsaturated metal centres through intramolecular ligand–metal interactions, which give rise to carbon–fluorine metal bonds, and a wide range of dynamic behaviours [17,18].

This review is focused on the pentafluorobenzenethiolate ion $(SC_6F_5)^-$-derivatives of the platinum-group metals. For each pair of metallic centres—Ru, Os; Rh, Ir; Pd, Pt—a literature survey (up to February 1998) has been summarised in tables that bring together the known compounds, whereas recent selected results from our group are briefly discussed. For simplicity, the pentafluorobenzenethiolate ion is denoted by $SX = (SC_6F_5)^-$ throughout this paper. Other abbreviations are listed on the previous page.

Table 1
Ruthenium and osmium compounds with $(SC_6F_5)^-$

Ruthenium compounds	Ref.[a]
Monometallic	
$[Ru(SX)(CO)_2(Cp^*)]$	[19]
$[Ru(SX)(Cp^*)(PMe_3)_2]$	[19]
$[Ru(SX)(CO)_2(Cp)]$	[20]
$[Ru(SX)H(CO)(P^iPr_3)_2]$	[21]
$[Ru(SX)_2(PPh_3)_2]$	[22,**26**]
$[Ru(SX)_2(bipy)_2]$	[**24**]
$[Ru(SX)_2(CO)_2(PPh_3)_2]$	[23,25]
$[Ru(SX)_2(CO)_2(PMe_2Ph)_2]$	[25]
$[Ru(SX)_2(CO)_2(PMePh_2)_2]$	[25]
$[Ru(SX)_2(CO)_2(PEt_2Ph)_2]$	[25]
$[Ru(SX)_2(CO)_2(PEtPh_2)_2]$	[25]
$[Ru(SX)_3(PPh_3)_2]$	[**23**,**26**]
$[Ru(SX)_3(PMe_2Ph)_2]$	[**23**,**26**]
$[Ru(SX)_3(PEt_2Ph)_2]$	[26]
Bimetallic	
$[\{Ru(\mu\text{-}SX)(CO)_3\}_2]$	[**27**]
$[\{Ru(\mu\text{-}SX)(bipy)(PPh_3)_2\}_2]^{2+}$	[28]
$[\{Ru(\mu\text{-}SX)(Cp)\}_2(dppm)]$	[19]
$[\{Ru(\mu\text{-}SX)(CO)(Cp)\}_2]$	[20]
$[Ru_2(\mu\text{-}SX)_2(CO)_5(PPh_3)]$	[**27**]
$[Ru_2(\mu\text{-}SX)_2(\mu\text{-}S)(X)(Cp^*)_2]$	[**19**]
$[Ru_2(\mu\text{-}SX)(\mu\text{-}S)(X)(Cp')_2]$	[19]
$[Ru_2(\mu\text{-}SX)(\mu\text{-}S)(X)(CO)(Cp^*)_2]$	[19]
$[Ru_2(\mu\text{-}SX)(\mu\text{-}S)(X)(CO)(Cp')_2]$	[19]
$[Ru_2(\mu\text{-}SX)_2(CO)(Cp_2)]$	[19]
Trimetallic	
$[Ru_3(\mu\text{-}SX)(CO)_9]$	[27]
$[Ru_3(\mu\text{-}SX)_3(CO)_3(Cp)_3]$	[20]

Osmium compounds	Ref.[a]
Monometallic	
$[Os(SX)H(CO)(P^iPr_3)_2]$	[21]
$[Os(SX)Cl(N_2)(PMe_2Ph)_3]$	[**29**,**30**]
$[Os(SX)Br(N_2)(PMe_2Ph)_3]$	[30]
$[Os(SX)_2(CO)_2(PMe_2Ph)_2]$	[31]
$[Os(SX)_2(CO)_2(PMePh_2)_2]$	[31]
$[Os(SX)_2(CO)_2(PEt_2Ph)_2]$	[**31**]
$[Os(SX)_2(CO)_2(PEtPh_2)_2]$	[31]
$[Os(SX)_2(OSCMe)(PMe_2Ph)_2]$	[**32**]
$[Os(SX)_2(OSCPh)(PMe_2Ph)_2]$	[32]
$[Os(SX)_2(O_2CC_6F_5)(PMe_2Ph)_2]$	[32]
$[Os(SX)_2(O_2CC_6H_4(CF_3)\text{-}2)(PMe_2Ph)_2]$	[33]
$[Os(SX)_2(O_2CC_6H_4(CF_3)\text{-}3)(PMe_2Ph)_2]$	[33]
$[Os(SX)_2(O_2CC_6H_4(CF_3)\text{-}4)(PMe_2Ph)_2]$	[33]
$[Os(SX)_2(O_2CC_6H_4F\text{-}2)(PMe_2Ph)_2]$	[33]

Table 1 (*Continued*)

Ruthenium compounds	Ref.[a]
$[Os(SX)_2(O_2CC_6H_4F\text{-}3)(PMe_2Ph)_2]$	[33]
$[Os(SX)_2(O_2CC_6H_4F\text{-}4)(PMe_2Ph)_2]$	[33]
$[Os(SX)_2(O_2CCH_3)(PMe_2Ph)_2]$	[33]
$[Os(SX)_2(O_2CCF_3)(PMe_2Ph)_2]$	[33]
$[Os(SX)_2(O_2CPh)(PMe_2Ph)_2]$	[**34**]
$[Os(SX)_2Cl(SC_6H_4F\text{-}3)(PMe_2Ph)]$	[35]
$[Os(SX)_2Cl(SC_6H_4(CF_3)\text{-}3)(PMe_2Ph)]$	[**35**]
$[Os(SX)_2(S_2C_6F_4)(PMe_2Ph)]$	[**36**]
$[Os(SX)_2(o\text{-}OSC_6F_4)(PMe_2Ph)]$	[36]
$[Os(SX)_3Cl(PMe_2Ph)]$	[**34**]
$[Os(SX)_3(PMe_2Ph)_2]$	[31,33,**36**]
$[Os(SX)_3(PMePh_2)_2]$	[31]
$[Os(SX)_3(PEt_2Ph)_2]$	[31]
$[Os(SX)_3(PEtPh_2)_2]$	[31]
$[Os(SX)_3Br(PMe_2Ph)]$	[33]
$[Os(SX)_4(PPh_3)]$	[35]
$[Os(SX)_4(PMe_2Ph)]$	[35]

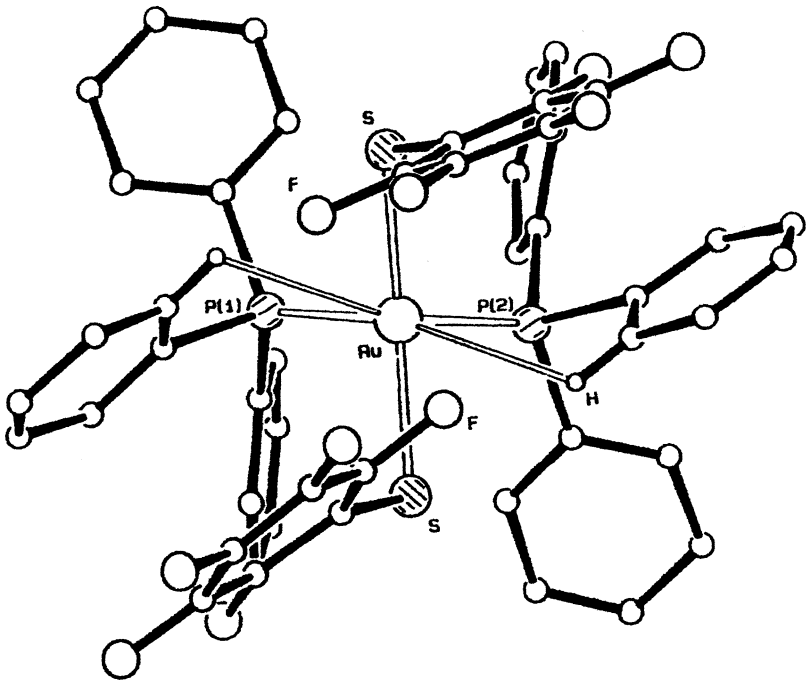


Fig. 1. X-ray diffraction structure of $[Ru(SX)_2(PPh_3)_2]$. Reprinted from Ref. [26] with permission from Elsevier Science.

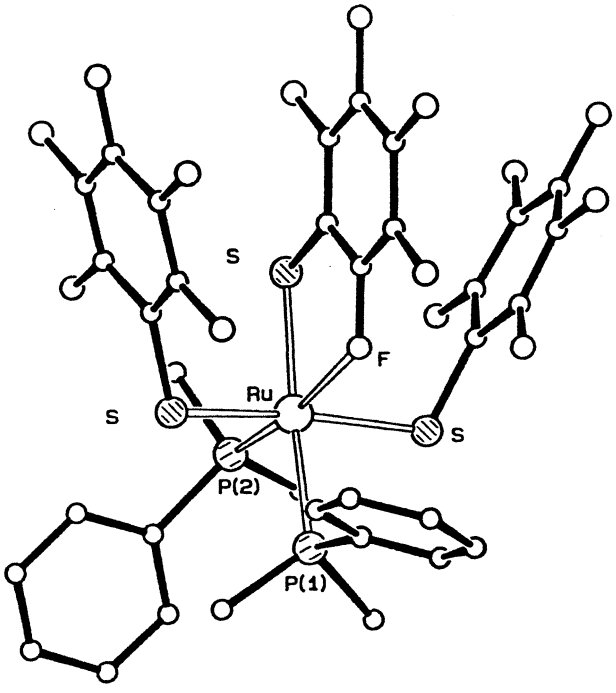


Fig. 2. X-ray diffraction structure of $[Ru(SX)_3(PMe_2Ph)_2]$. Reprinted from Ref. [26] with permission from Elsevier Science.

2. Ru and Os compounds

Table 1 collects the published ruthenium and osmium derivatives of $(SC_6F_5)^-$ = SX.

2.1. Ruthenium

Monometallic ruthenium derivatives of $SC_6F_5^-$ are known for both Ru(II) and Ru(III) species. Penta coordinate compounds display either square-pyramid or trigonal-bipyramid structures.

$[Ru(SX)_2(PPh_3)_2]$ is particularly interesting since it is a remarkably stable 14-electron compound. Treatment of $[RuCl_2(PPh_3)_2]$ with $Pb(SC_6F_5)_2$ in acetone gave the diamagnetic complex $[Ru(SX)_2(PPh_3)_2]$. Its solid state structure (Fig. 1), it shows a pseudo 2-fold symmetry about the ruthenium, and can be considered to be greatly distorted octahedral, consisting of two *trans* thiolate groups and two *cis* phosphines, with the remaining two coordination sites occupied by hydrogens from the *ortho*-carbon of a phenyl group of each of the phosphine ligands, forming two Ru–H–C agostic interactions [37].

The Ru–P–C angles in the chelating rings are, at about 103°, much smaller than the other Ru–P–C angles (116.9 and 122.6°), and reflect the strains involving in artachieving the agostic bonding; these must be overcome by the attractive Ru–H–C

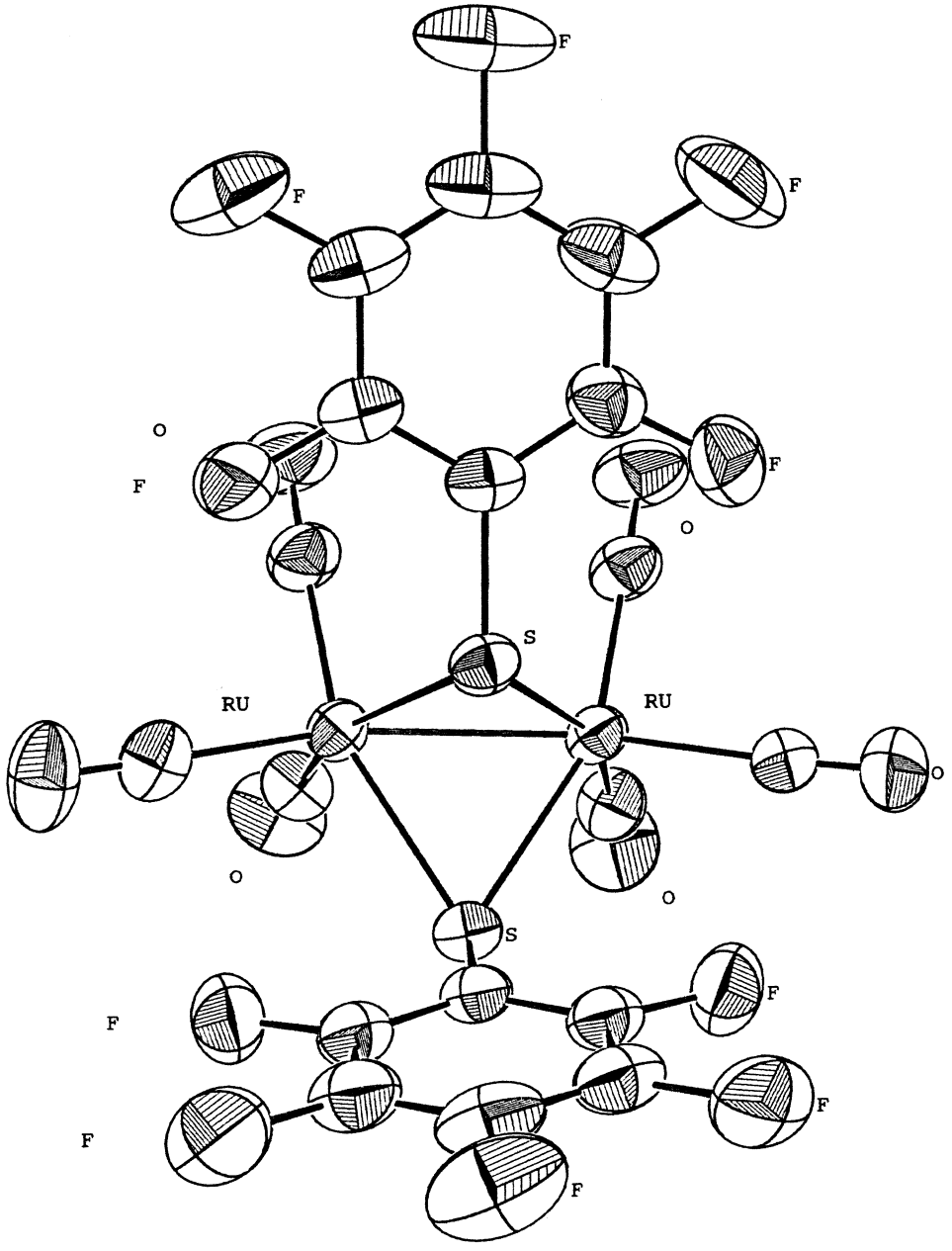


Fig. 3. X-ray diffraction structure of [{Ru(μ-SX)(CO)$_3$}$_2$] [27].

interaction. Filling the vacant octahedral sites of the metal must also be energetically favourable.

As expected, $[Ru(SX)_2(PPh_3)_2]$ reacts with carbon monoxide to afford $[Ru(SX)_2(CO)_2(PPh_3)_2]$ [23], but similar reactions with other substrates such as olefins or alkynes fail to produce the simple addition products predicted.

$[Ru(SX)_3(PMe_2Ph)_2]$ is also an interesting complex with an unsaturated ruthenium centre. Here the fluorinated moiety is involved in a Ru–F–C interaction giving rise to what can be described as a chelating sulfur–fluorine ligand, as shown in Fig. 2.

Metal–fluorocarbon interactions, although weak, may prove to be more widespread that might have been supposed and it is perhaps significant that the Ru–F–C interaction occurs in a complex of ruthenium(III), but only Ru–H–C interactions occur in the complex of ruthenium(II); it appears that the more electrophilic ruthenium(III) metal centre is required to promote the fluorocarbon interaction.

Carbonylation of $[Ru(SX)_3(PR_3)_2]$ in the presence of amalgamated Zn, afford the compounds $[Ru(SX)_2(CO)_2L_2]$, $L = PMe_2Ph$, $PMePh_2$, PEt_2Ph and $PEtPh_2$ for which different isomers have been spectroscopically established [25].

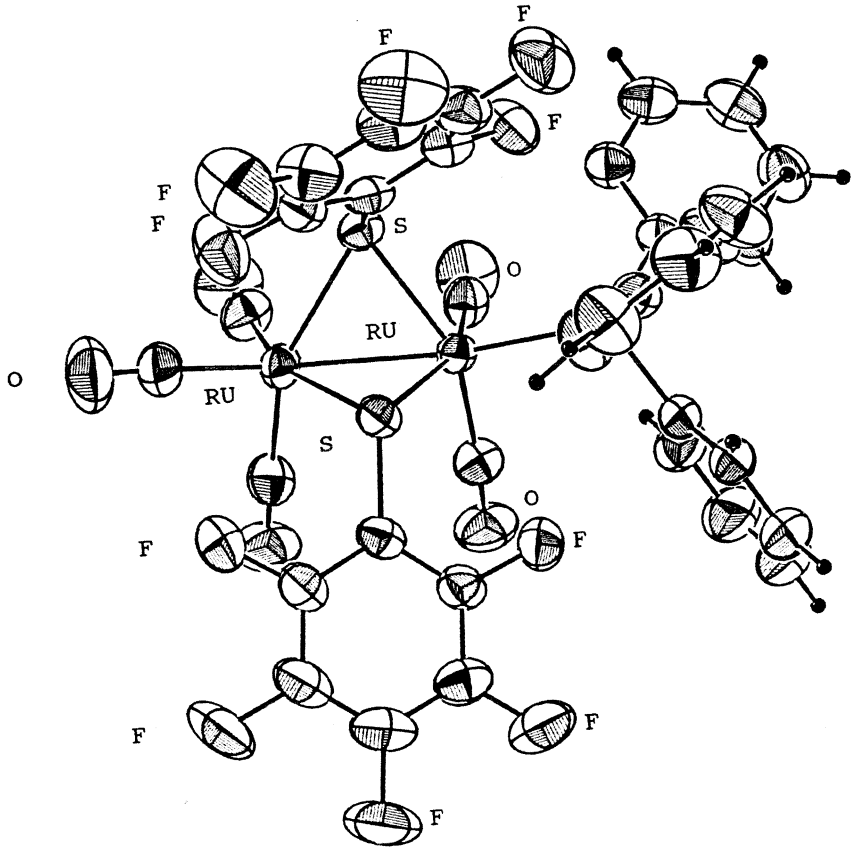


Fig. 4. X-ray diffraction structure of $[Ru_2(\mu\text{-}SX)_2(CO)_5(PPh_3)]$ [27].

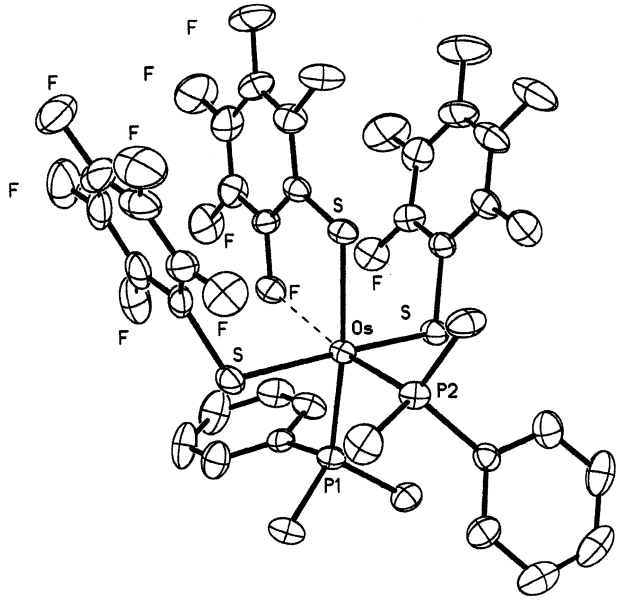


Fig. 5. X-ray diffraction structure of $[Os(SX)_3(PMe_2Ph_2)_2]$. Reprinted from Ref. [36] with permission from Elsevier Science.

Relatively few examples of SC_6F_5 derivatives with more than one ruthenium centre are known. The anion $[Ru_3Cl(CO)_{11}]^-$ reacts with $Pb(SC_6F_5)_2$ to give a mixture of the fully characterised dimer $[\{Ru(\mu\text{-}SX)(CO)_3\}_2]$ and a minor product

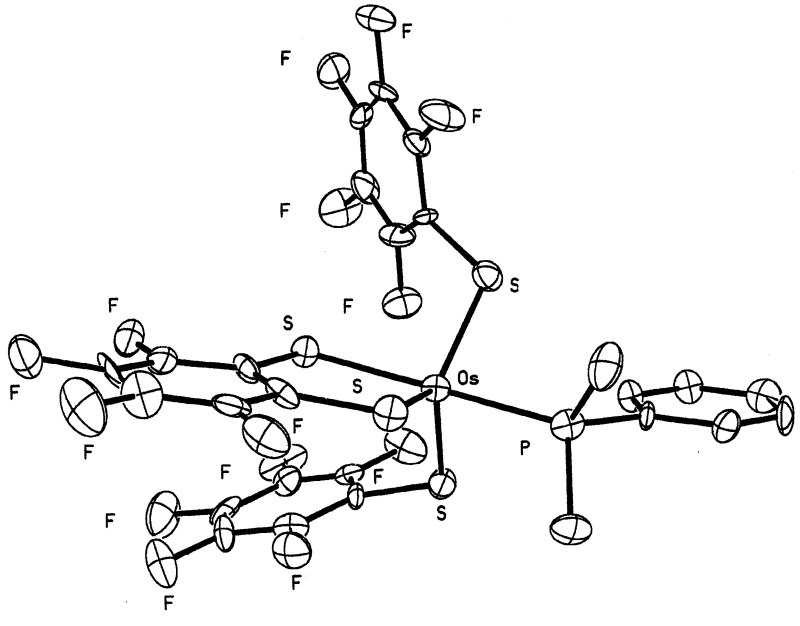


Fig. 6. X-ray diffraction structure of $[Os(SX)_2(o\text{-}S_2C_6F_4)(PMe_2Ph_2)]$. Reprinted from Ref. [36] with permission from Elsevier Science.

Table 2
Rhodium and iridium compounds with $(SC_6F_5)^-$

Rhodium compounds	Ref.[a]
Monometallic	
$[Rh(SX)(CO)(PPh_3)_2]$	[38]
$[Rh(SX)(CO)_2(PPh_3)]$	[39]
$[Rh(SX)(COD)(PPh_3)]$	[39]
$[Rh(SX)(SEt_2)(COD)]$	[39]
$[Rh(SX)(SMe_2)(COD)]$	[39]
[Rh(SX)(py)(COD)]	[39]
$[Rh(SX)(P(C_6H_4Me\text{-}4)_3)(COD)]$	[39]
$[Rh(SX)(P(C_6H_4Me\text{-}3)_3)(COD)]$	[39]
$[Rh(SX)(CNBu)_2(dppm)]^+$	[40]
$[Rh(SX)H_2(PPh_3)_3]$	[41]
$[Rh(SX)(SO_2)(CO)(PPh_3)_3]$	[42]
$[Rh(SX)(PPh_3)_2(py)]$	[43]
$[Rh(SX)(PPh_3)_2(3\text{-Mepy})]$	[43]
$[Rh(SX)(PPh_3)_2(2\text{-Mepy})]$	[43]
$[Rh(SX)(PPh_3)_2(2,6\text{-}Me_2py)]$	[43]
$[Rh(SX)(PPh_3)_2(Q)]$	[43]
$[Rh(SX)(PPh_3)_2(IQ)]$	[43]
$[Rh(SX)(PPh_3)_2(NM)]$	[43]
$[Rh(SX)H(C_2Ph)(PPh_3)_2(py)]$	[43]
$[Rh(SX)H(C_2Ph)(PPh_3)_2(2\text{-Mepy})]$	[43]
$[Rh(SX)H(C_2Ph)(PPh_3)_2(3\text{-Mepy})]$	[43]
$[Rh(SX)H(C_2Ph)(PPh_3)_2(2,6\text{-}Me_2py)]$	[43]
$[Rh(SX)H(C_2Ph)(PPh_3)_2(Q)]$	[43]
$[Rh(SX)H(C_2Ph)(PPh_3)_2(IQ)]$	[43]
$[Rh(SX)H(C_2Ph)(PPh_3)_2(NM)]$	[43]
$[Rh(SX)_2(Cp^*)]$	[44]
$[Rh(SX)_2(Cp^*)(PPh_3)]$	[44]
$[Rh(SX)_2(CO)(Cp^*)]$	[44]
$[Rh(SX)_2H(PPh_3)(py)_2]$	[43]
$[Rh(SX)_2H(PPh_3)(3\text{-Mepy})_2]$	[43]
$[Rh(SX)_2H(PPh_3)(IQ)_2]$	[43]
$[Rh(SX)_2H(PPh_3)(NM)_2]$	[43]
$[Rh(SX)_2H(PPh_3)(py)(2\text{-Mepy})]$	[43]
$[Rh(SX)_2H(PPh_3)(py)(2,6\text{-}Me_2py)]$	[43]
$[Rh(SX)_2H(PPh_3)(py)(Q)]$	[43]
$[Rh(SX)_2H(PPh_3)(3\text{-Mepy})(2\text{-Mepy})]$	[43]
$[Rh(SX)_2H(PPh_3)(3\text{-Mepy})(2,6\text{-}Me_2py)]$	[43]
$[Rh(SX)_2H(PPh_3)(3\text{-Mepy})(Q)]$	[43]
$[Rh(SX)_2H(PPh_3)(IQ)(2\text{-Mepy})]$	[43]
$[Rh(SX)_2H(PPh_3)(IQ)(2,6\text{-}Me_2py)]$	[43]
$[Rh(SX)_2H(PPh_3)(IQ)(Q)]$	[43]
$[Rh(SX)_2H(PPh_3)(NM)(2\text{-Mepy})]$	[43]
$[Rh(SX)_2H(PPh_3)(NM)(2,6\text{-}Me_2py)]$	[43]
$[Rh(SX)_2H(PPh_3)(NM)(Q)]$	[43]
$[Rh(SX)_2(CNBu)_4]^+$	[40]
$[Rh(SX)_3]$	[45]
$[Rh(SX)_3(SEt_2)_3]$	[46]
$[Rh(SX)_3(Cp^*)]^-$	[**47**]

Table 2 (*Continued*)

Rhodium compounds	Ref.[a]
Bimetallic	
$[\{Rh(\mu\text{-}SX)(CO)_2\}_2]$	[38,48,49]
$[\{Rh(\mu\text{-}SX)(COD)\}_2]$	[**28**,**39**,50]
$[\{Rh(\mu\text{-}SX)(C_2H_4)_2\}_2]$	[38]
$[\{Rh(\mu\text{-}SX)(DCP)\}_2]$	[28]
$[\{Rh(\mu\text{-}SX)(CO)(PPh_3)\}_2]$	[38,49]
$[\{Rh(\mu\text{-}SX)(CO)(P(C_6H_5(SO_3H)\text{-}3)_3\}_2]$	[6]
$[Rh_2(\mu\text{-}SX)_2(\mu\text{-}Pz)(Cp^*)_2]^+$	[51]
$[Rh_2(\mu\text{-}SX)_3(Cp^*)_2]^+$	[**47**]
Hetero-bimetallic	
$[Rh(COD)(\mu\text{-}SX)_2Ni(dppe)]^+$	[52]
Tetrametallic	
$[Rh(\mu\text{-}SX)(NBD)]_4$	[28]
Hetero-tetrametallic	
$[Rh_2Ni_2(\mu\text{-}SX)_4(dppe)]$	[52]

Iridium compounds	Ref.[a]
Monometallic	
$[Ir(SX)(CO)(PPh_3)_2]$	[42]
$[Ir(SX)H_2(CO)(PPh_3)_2]$	[42]
$[Ir(SX)HCl(CO)(PPh_3)_2]$	[42]
$[Ir(SX)HBr(CO)(PPh_3)_2]$	[42]
$[Ir(SX)HI(CO)(PPh_3)_2]$	[42]
$[Ir(SX)Cl_2(CO)(PPh_3)_2]$	[42]
$[Ir(SX)(O_2)(CO)(PPh_3)_2]$	[42]
$[Ir(SX)I(CH_3)(CO)(PPh_3)_2]$	[42]
$[Ir(SX)H(CO)(PPh_3)_2]$	[42]
$[Ir(SX)(SO_2)(CO)(PPh_3)_2]$	[42]
$[Ir(SX)(SO_2)(CO)(PPh_3)_2]$	[42]
$[Ir(SX)_2Cl(CO)(PPh_3)_2]$	[42]
$[Ir(SX)_2(Cp^*)]$	[**47**]
$[Ir(SX)_2(Cp^*)(PPh_3)]$	[44]
$[Ir(SX)_2(CO)(Cp^*)]$	[44]
Bimetallic	
$[\{Ir(\mu\text{-}SX)(CO)_2\}_2]$	[**53**]
$[\{Ir(\mu\text{-}SX)(COD)\}_2]$	[53]
$[Ir(COD)(\mu\text{-}SX)_2Ir(SX)Cl(COD)]$	[**53**]
Trimetallic	
$[Ir_3(\mu\text{-}SX)_3(CO)_5(PPh_3)_2]$	[**53**]
Hetero-trimetallic	
$[\{Ir(\mu\text{-}SX)_2Cl(Cp^*)\}_2Pt]$	[**54**]

[a] Bold references indicate that the X-ray diffraction structure is known.

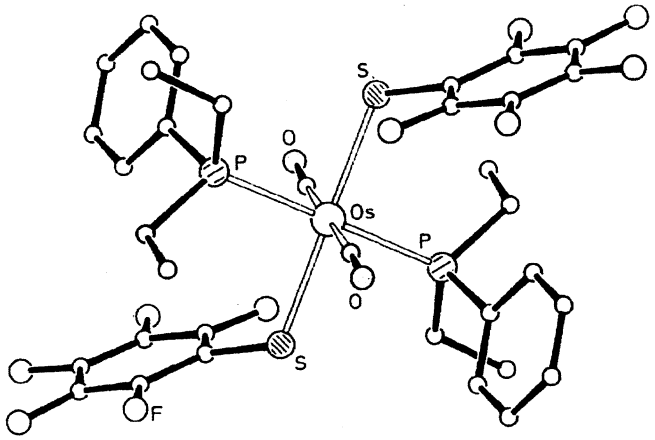


Fig. 7. X-ray diffraction structure of *trans-trans-trans*-[$Os(SX)_2(CO)_2(PEt_2Ph)_2$]. Reprinted from Ref. [31] with permission from RSC.

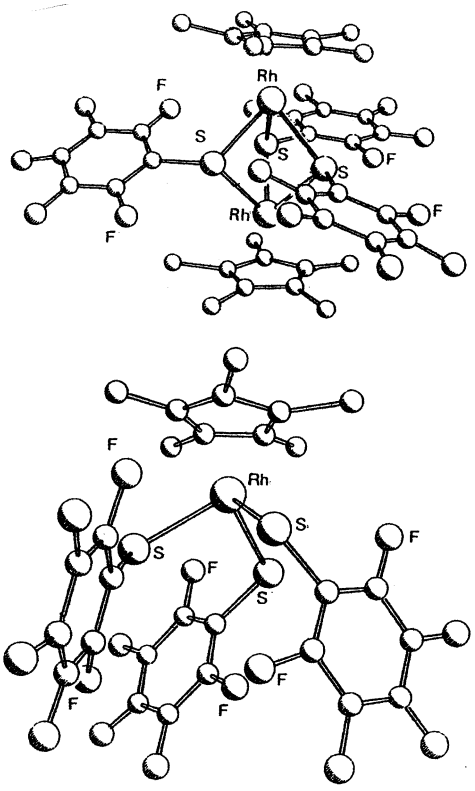


Fig. 8. X-ray diffraction structure of [(Cp*)Rh(μ-$SX)_3$Rh(Cp*)][(Cp*)Rh$(SX)_3$]. Reprinted from Ref. [47] with permission from RSC.

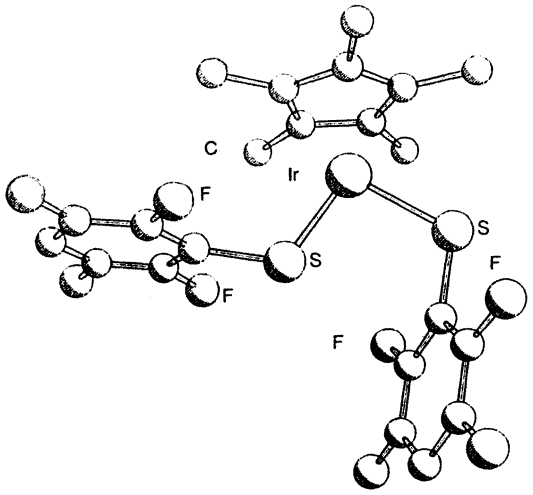


Fig. 9. X-ray diffraction structure of $[Ir(SX)_2(Cp^*)]$. Reprinted from Ref. [47] with permission from RSC.

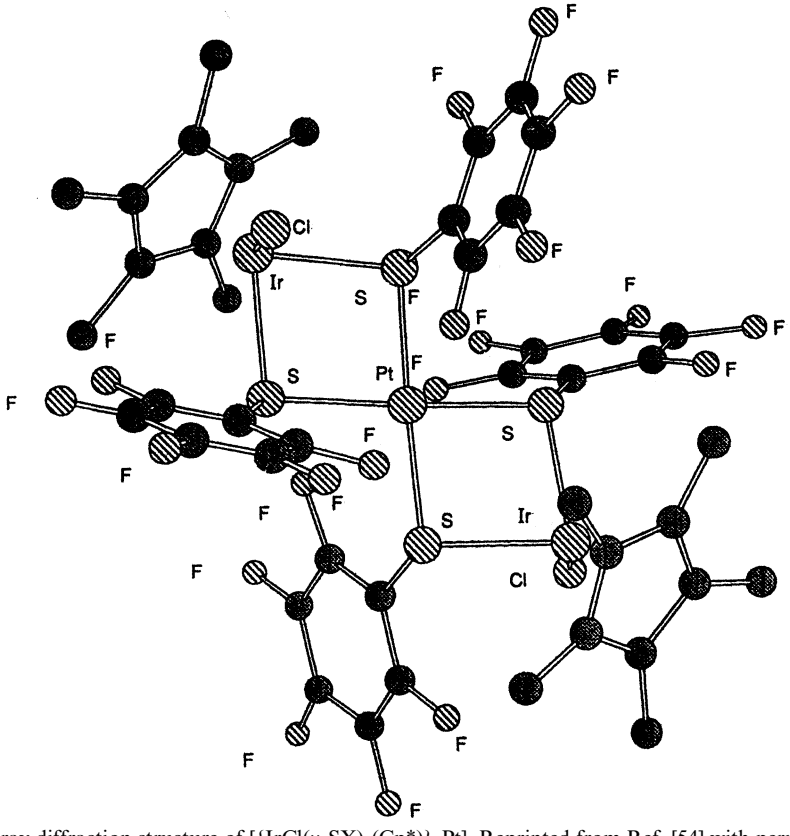


Fig. 10. X-ray diffraction structure of $[\{IrCl(\mu\text{-}SX)_2(Cp^*)\}_2Pt]$. Reprinted from Ref. [54] with permission from RSC.

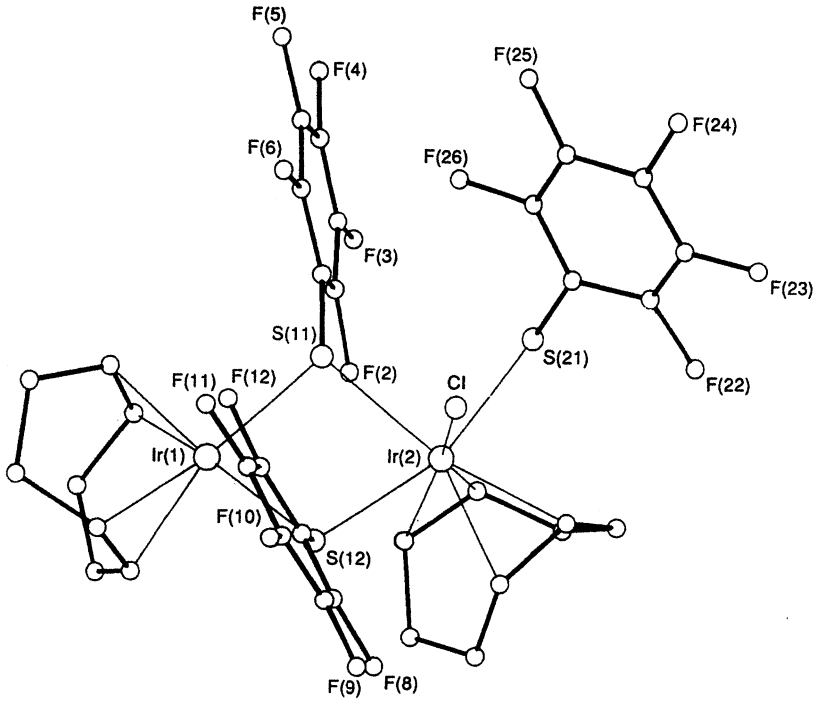


Fig. 11. X-ray diffraction structure of [(COD)Ir(μ-SX)$_2$Ir(SX)(Cl)(COD)]. Reprinted from Ref. [53] with permission from RSC.

which, based on spectroscopic evidence, has been postulated as [Ru$_3$(μ-SX)(CO)$_9$] [27]. The X-ray diffraction structure of the dimer, shown in Fig. 3, has been determined.

The binuclear carbonyl [{Ru(μ-SX)(CO)$_3$}$_2$] reacts with triphenyl phosphine to give the unusual compound [Ru$_2$(μ-SX)$_2$(CO)$_5$(PPh$_3$)]. The X-ray diffraction structure of this asymmetrical complex (see Fig. 4) shows that only one, out of two equivalent CO ligands, have been replaced by the phosphine. A Ru–Ru bond (2.668(6) Å) has been assumed in this compound

2.2. Osmium

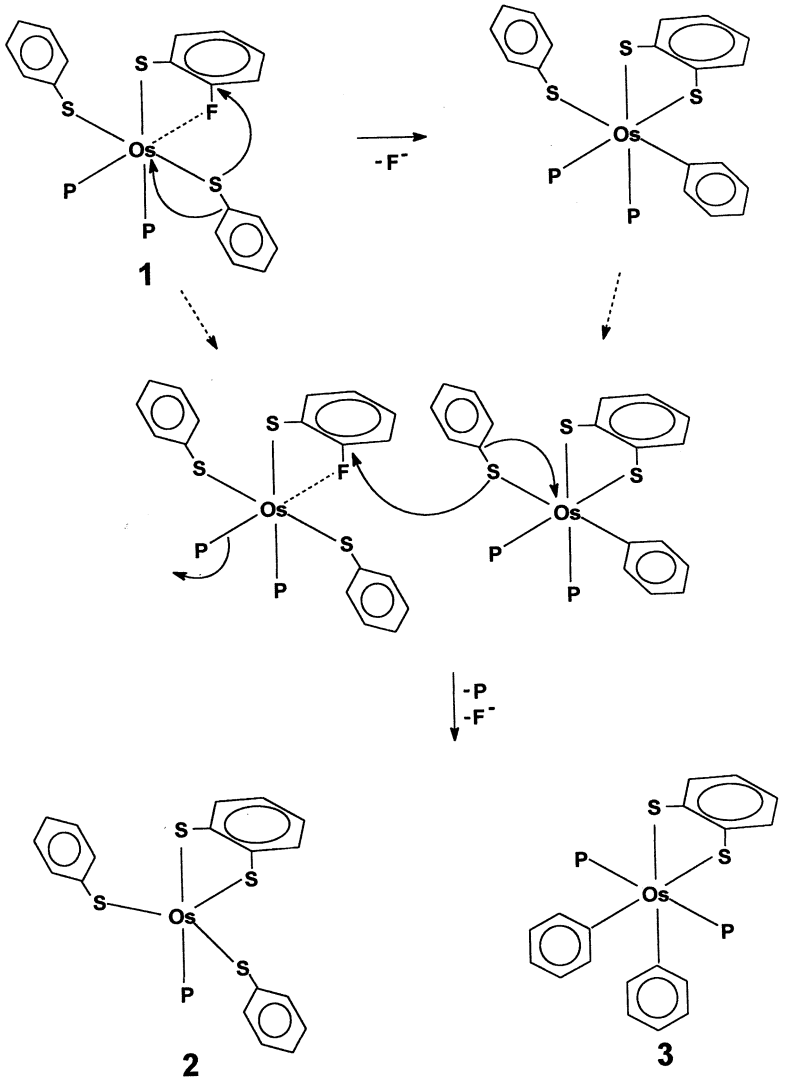
Surprisingly, there are no polymetallic examples known for osmium with SC$_6$F$_5$ ligands. Octahedral, square pyramid and trigonal pyramid are the geometries found for monometallic osmium complexes.

As its ruthenium analogue, the structure of [Os(SX)$_3$(PMe$_2$Ph$_2$)$_2$] (Fig. 5) is closely octahedral with an Os–F–C interaction which occupies the vacant site of this, formally penta coordinated, osmium(III) complex.

Thermolysis of [Os(SX)$_3$(PMe$_2$Ph$_2$)$_2$] provides an interesting rearrangement–oxidative reaction from which [Os(SX)$_2$(*o*-S$_2$C$_6$F$_4$)(PMe$_2$Ph)] (Fig. 6) and [Os(C$_6$F$_5$)$_2$-(*o*-S$_2$C$_6$F$_4$)(PMe$_2$Ph)$_2$] have been isolated.

To rationalise the outcome from this reaction one has to consider phosphine dissociation, cleavage of an *ortho* carbon–fluorine bond at a thiolate ligand, intermolecular transfer of a sulfur atom—and therefore carbon–sulfur splitting—as well as oxidation of the metal centre. An Os–F–C interaction is expected to induce an activated *ortho* carbon–fluorine bond bearing an electrophilic carbon atom. Such interactions are known to render C–F bonds highly susceptible to nucleophilic attack and therefore, the *ortho*-carbon atom can be envisaged as the centre of the nucleophilic attack by a thiolate sulfur atom.

The mechanism of this process has not been established but the following diagram shows some of the possible reactions involved. Compounds **1**, **2** and **3** have been isolated.



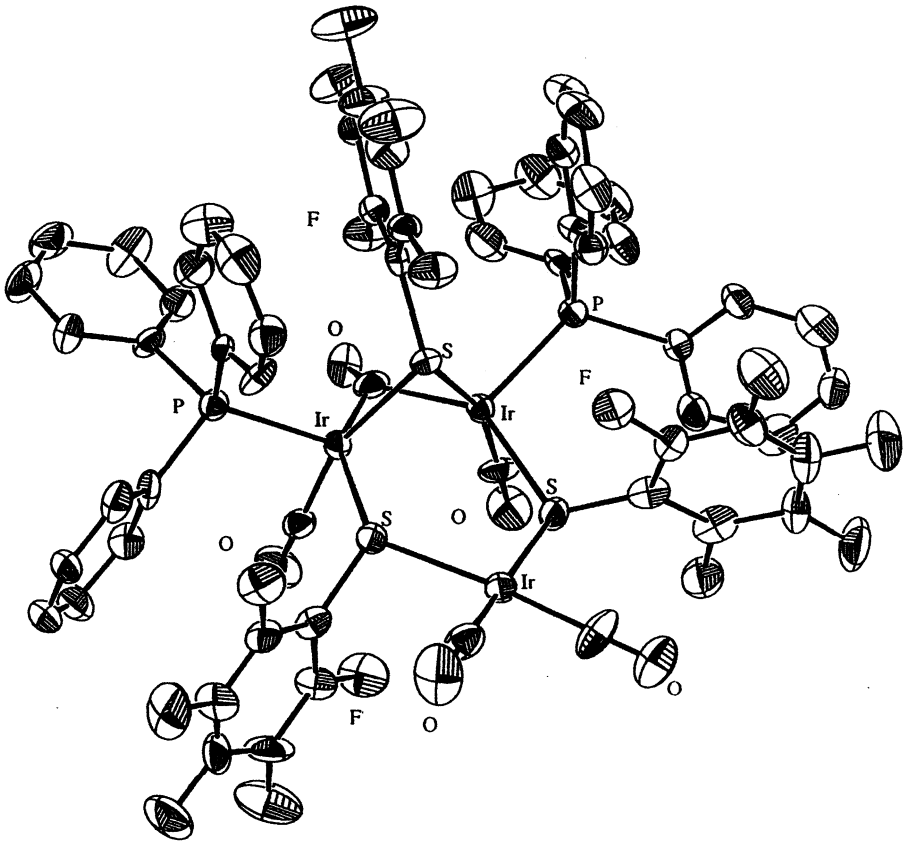


Fig. 12. X-ray diffraction structure of $[Ir_3(\mu\text{-}SX)_3(\mu\text{-}CO)(CO)_3(PPh_3)_3]$. Reprinted from Ref. [53] with permission from RSC.

Treatment of $[Os(SX)_3(L)_2]$ L = PMe_2Ph, $PMePh_2$, PEt_2Ph and $PEtPh_2$ with carbon monoxide in the presence of amalgamated zinc afford the octahedral complexes $[Os(SX)_2(CO)_2(L)_2]$. The *trans-trans-trans* isomer is isolated for all four complexes but other different configurations are also present in solution. The X-ray diffraction structure, shown in Fig. 7, has been determined.

3. Rh and Ir compounds

Table 2 collects the known derivatives of $(SC_6F_5)^- = SX$ with rhodium and iridium metal centres.

3.1. Rhodium

Instead of the straightforward substitution expected, metathetical reaction of $[\{Rh(\mu\text{-}Cl)Cl(Cp^*)\}_2]$ with $Pb(SC_6F_5)_2$ gave the ionic, triply bridged, complex

Table 3
Palladium and platinum compounds with $(SC_6F_5)^-$

Palladium compounds	Ref.[a]
Monometallic	
$[Pd(SX)(\eta^3\text{-}C_3H_5)(PPh_3)]$	[55]
$[Pd(SX)(\eta^3\text{-}C_3H_5)(P(C_6H_4F\text{-}4)_3)]$	[55]
$[Pd(SX)(\eta^3\text{-}C_3H_5)(P(C_6H_4Cl\text{-}4)_3)]$	[55]
$[Pd(SX)(\eta^3\text{-}C_3H_5)(P(C_6H_4(Me)\text{-}4)_3)]$	[55]
$[Pd(SX)(\eta^3\text{-}C_3H_5)(P(C_6H_4(CF_3)\text{-}4)_3)]$	[55]
$[Pd(SX)(\eta^3\text{-}C_3H_5)(P(C_6H_4(OMe)\text{-}4)_3)]$	[55]
$[Pd(SX)_2(PPh_3)_2]$	[56–58]
$[Pd(SX)_2(L1)]$	[59]
$[Pd(SX)_2(L2)]$	[28,59]
$[Pd(SX)_2(L3)]$	[59]
$[Pd(SX)_2(L4)]$	[59]
$[Pd(SX)_2(dppm)]$	[60]
$[Pd(SX)_2(SEt_2)_2]$	[61]
$[Pd(SX)_2(Et_2NC_2H_4NEt_2)]$	[62]
$[Pd(SX)_4]^{2-}$	[57,58,63]
$[Pd(SX)_4](Me_2(H)NC_2H_4N(H)Me_2)$	[**62**]
Bimetallic	
$[\{Pd(\mu\text{-}SX)(dppm)\}_2]$	[60]
$[\{Pd(\mu\text{-}SX)Cl(PPh_3)\}_2]$	[28]
$[\{Pd(\mu\text{-}SX)(SX)(PPh_3)\}_2]$	[56,**64**,**65**]
$[\{Pd(\mu\text{-}SX)(\eta^3\text{-}C_3H_5)\}_2]$	[**66**]
$[\{Pd(\mu\text{-}SX)(\eta^3\text{-}C_4H_7)\}_2]$	[67]
$[(dppm)Pd(\mu\text{-}SX)_2Pd(X)_2]$	[68]
$[(dppe)Pd(\mu\text{-}SX)_2Pd(X)_2]$	[68]
$[(X)_2Pd(\mu\text{-}SX)_2Pd(\mu\text{-}SX)_2]_2^2$	[69]
$[(PPh_3)Pd(\mu\text{-}SX)(\mu\text{-}dppm)Pd(SX)]$	[**70**,71]
$[(PCy_3)Pd(\mu\text{-}SX)(\mu\text{-}dppm)Pd(SX)]$	[70,71]
$[(XS)Pd(\mu\text{-}CO)(\mu\text{-}dppm)Pd(SX)]$	[70,71]
$[(PPh_3)Pd(\mu\text{-}SX)(\mu\text{-}dppm)Pd(PPh_3)]^+$	[**70**,71]
$[(PMePh_2)Pd(\mu\text{-}SX)(\mu\text{-}dppm)Pd(PMePh_2)]^+$	[70,71]
$[(AsPh_3)Pd(\mu\text{-}SX)(\mu\text{-}dppm)Pd(AsPh_3)]^+$	[70,71]
$[(SbPh_3)Pd(\mu\text{-}SX)(\mu\text{-}dppm)Pd(SbPh_3)]^+$	[70,71]
Hetero-bimetallic	
$[(dppm)Pd(\mu\text{-}SX)_2Pt(X)_2]$	[68]
$[(dppe)Pd(\mu\text{-}SX)_2Pt(X)_2]$	[68]
$[(dppm)Pt(\mu\text{-}SX)_2Pd(X)_2]$	[68]
$[(dppe)Pt(\mu\text{-}SX)_2Pd(X)_2]$	[68]
$[(PPh_3)_2Pt(\mu\text{-}SX)_2Pd(X)_2]$	[68]
$[(dppe)Pt(\mu\text{-}SX)_2Pd(X)(PPh_3)]^+$	[68]
$[(dppe)Ni(\mu\text{-}SX)_2Pd(X)_2]$	[68]
Trimetallic	
$[X_2Pd(\mu\text{-}SX)_2Pd(\mu\text{-}SX)_2PdX_2]^2$	[69]
Hetero-trimetallic	
$[X_2Pt(\mu\text{-}SX)_2Pd(\mu\text{-}SX)_2PtX_2]^2$	[69]
$[X_2Pd(\mu\text{-}SX)_2Pt(\mu\text{-}SX)_2PdX_2]^2$	[69]

Table 3 (*Continued*)

Palladium compounds	Ref.[a]
Tetrametallic	
$[X_2Pd(\mu\text{-}SX)_2Pd(\mu\text{-}SX)_2Pd(\mu\text{-}SX)_2PdX_2]^2$	[69]
Hetero-tetrametallic	
$[X_2Pt(\mu\text{-}SX)_2Pd(\mu\text{-}SX)_2Pd(\mu\text{-}SX)_2PtX_2]^2$	[69]
$[X_2Pd(\mu\text{-}SX)_2Pt(\mu\text{-}SX)_2Pt(\mu\text{-}SX)_2PdX_2]^2$	[**69**]
Octametallic	
$[(\{Pd(\mu\text{-}SX)(\mu\text{-dppm})Pd)(\mu\text{-}SX)\}_4]$	[**70**]
Polymeric	
$[Pd(SX)_2]_n$	[56,58,72]

Platinum compounds	Ref.[a]
Monometallic	
$[Pt(SX)Cl(PEt_3)_2]$	[56]
$[Pt(SX)Cl(CH_2{=}CHC_6H_4(N(CH_3)_2)\text{-}2)]$	[**73**]
$[Pt(SX)_2(PPh_3)_2]$	[58,68]
$[Pt(SX)_2(SEt_2)_2]$	[61,**74**]
$[Pt(SX)_2(PBu_3)_2]$	[58,**75**]
$[Pt(SX)_2(dppm)]$	[68]
$[Pt(SX)_2(dppe)]$	[68]
$[Pt(SX)_2(L1)]$	[59]
$[Pt(SX)_2(L2)]$	[59]
$[Pt(SX)_2(L3)]$	[59]
$[Pt(SX)_2(L4)]$	[59]
$[Pt(SX)_2(L5)]$	[76]
$[Pt(SX)_2(L6)]$	[76]
$[Pt(SX)_2(L7)]$	[76]
$[Pt(SX)_2(L8)]$	[76]
$[Pt(SX)_2(COD)]$	[77,78]
$[Pt(SX)_2(P(Ph_2)(C_6F_5)_2)_2]$	[79]
$[Pt(SX)_2(P(Ph_2)_2(C_6F_5))_2]$	[79]
$[Pt(SX)_2(Ph_2PC_6F_4(SX)\text{-}2)]$	[**79**]
$[Pt(SX)_2(Ph(C_6F_5)PC_6F_4(SX)\text{-}2)]$	[79]
$[Pt(SX)_4]^{2-}$	[56–58]
Bimetallic	
$[\{Pt(\mu\text{-}SX)(SX)(P(Ph_2)_2(C_6F_5))\}_2]$	[**79**]
$[\{Pt(\mu\text{-}SX)(SX)(P(Ph_2)(C_6F_5)_2)\}_2]$	[79]
$[\{Pt(\mu\text{-}SX)(SX)_2\}_2]$	[78,80]
$[\{Pt(\mu\text{-}SX)(SC_6HF_4)_2\}_2]$	[78,80]
$[\{Pt(\mu\text{-}SC_6HF_4)(SX)_2\}_2]$	[78,80]
$[(dppm)Pt(\mu\text{-}SX)_2Pt(X)_2]$	[68]
$[(dppe)Pt(\mu\text{-}SX)_2Pt(X)_2]$	[68]
$[(PPh_3)_2Pt(\mu\text{-}SX)_2Pt(X)_2]$	[68]
Hetero-bimetallic	
$[(dppe)Ni(\mu\text{-}SX)_2Pt(X)_2]$	[68]
Trimetallic	
$[\{PtX_2(\mu\text{-}SX)_2\}_2Pt]$	[69]

Table 3 (*Continued*)

Palladium compounds	Ref.[a]
Hetero-trimetallic	
$[\{IrCl(\mu\text{-}SX)_2(Cp^*)\}_2Pt]$	[54]
Tetrametallic	
$[X_2Pt(\mu\text{-}SX)_2Pt(\mu\text{-}SX)_2Pt(\mu\text{-}SX)_2PtX_2]^2$	[69]
Polymeric	
$[Pt(SX)_2]_n$	[58,73,81]

[a] Bold references indicate that the X-ray diffraction structure is known.

$[(Cp^*)Rh(\mu\text{-}SX)_3Rh(Cp^*)][(Cp^*)Rh(SX)_3]$. Fig. 8 shows the X-ray diffraction structure of this unusual rhodium ionic pair.

NMR spectra indicate that in solution this complex participates in a novel equilibrium described by the following reaction:

$$[(Cp^*)Rh(\mu\text{-}SX)_3Rh(Cp^*)][(Cp^*)Rh(SX)_3] \rightleftharpoons 3[Rh(SX)_2(Cp^*)]$$

This reaction is solvent-dependent and it is possible to control the species present in a given system simply by the use of a medium with the right polarity.

3.2. Iridium

In contrast with its rhodium analogue, the reaction of $[\{Ir(\mu\text{-}Cl)Cl(Cp^*)\}_2]$ with $Pb(SC_6F_5)_2$ affords the neutral monomeric complex $[Ir(SX)_2(Cp^*)]$. The structure of this compound has been determined as shown in the Fig. 9.

$[Ir(SX)_2(Cp^*)]$ is a coordinatively unsaturated complex which acts as a metallo-ligand on reaction with $K_2[PtCl_4]$, to afford the hetero-trimetallic compound $[\{IrCl(\mu\text{-}SX)_2(Cp^*)\}_2Pt]$ in which the platinum metal is coordinated to four sulphur atoms as shown in the Fig. 10.

The four closest Pt–F distances (2.993–3.075 Å) are less than the anticipated van der Waals distance between Pt and F of ca. 3.3 Å and represents a relatively strong interaction between such atoms, at least in the solid state.

$[\{Ir(\mu\text{-}Cl)COD\}_2]$ reacts with XSH/NEt_3 to give the binuclear Ir(I) compound $[\{Ir(\mu\text{-}SX)COD\}_2]$ which after exposure to carbon monoxide yields $[\{Ir(\mu\text{-}$

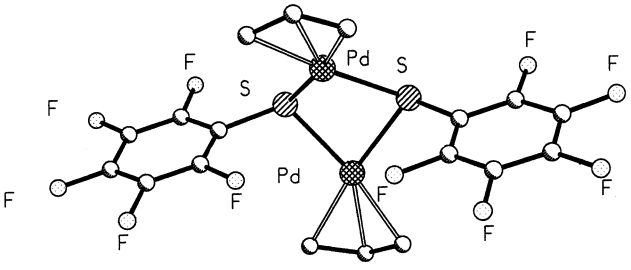


Fig. 13. X-ray diffraction structure of $[\{Pd(\mu\text{-}SX)(\eta^3\text{-}C_3H_5)\}_2]$ [67].

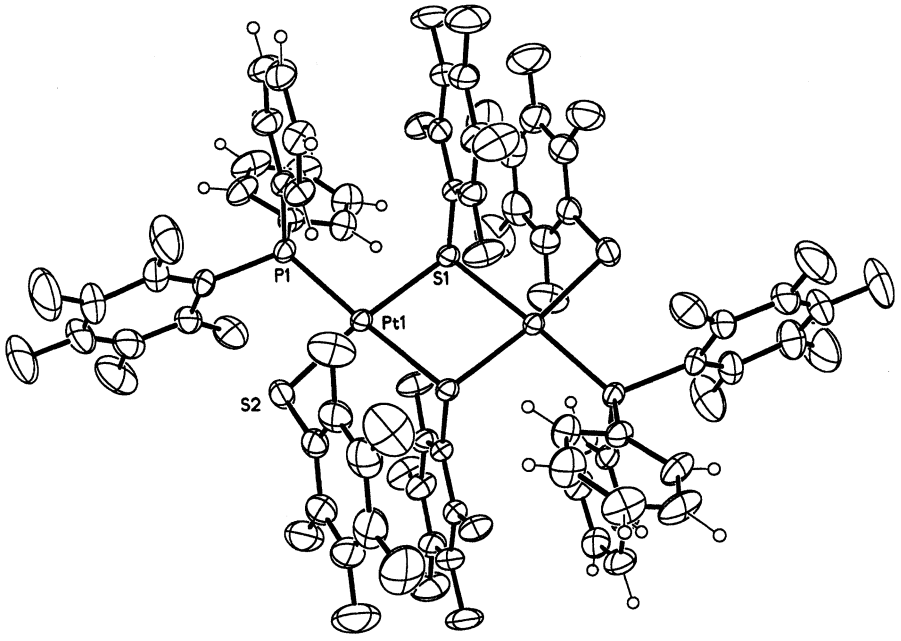


Fig. 14. X-ray diffraction structure of $[(Pt(\mu\text{-}SX)(SX)(PPh_2(C_6F_5))\}_2]$ [79].

$SX)(CO)_2\}_2]$ [53]. In contrast, the reaction of $[\{Ir(\mu\text{-}Cl)(COD)\}_2]$ with pure XSH gives a mixture of the dimer above and the unusual mixed valence [(COD)Cl(SX)Ir(μ-SX)Ir(COD)] also characterised by X-ray diffraction (Fig. 11).

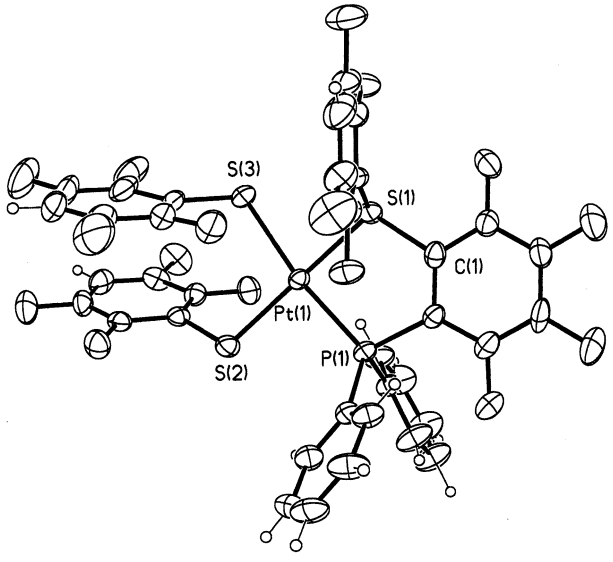


Fig. 15. X-ray diffraction structure of $[Pt(SX)_2(o\text{-}(Ph_2P)(XS)C_6F_4)]$ [79].

Treatment of $[\{Ir(\mu\text{-}SX)(CO)_2\}_2]$ with triphenylphosphine affords not only the expected mononuclear $[Ir(SX)(CO)(PPh_3)_2]$ but also the interesting trinuclear compound $[Ir_3(\mu\text{-}SX)_3(CO)_4(PPh_3)_3]$ whose X-ray structure in Fig. 12 shows a molecule with two distinct environments around the sulfur atoms. Thus two of the bridging S atoms are pyramidal as expected but the third S atom is nearly planar.

The examples above are evidence indicating the complexity of the relationships between structure, metal and ligand which are no fully understood yet.

4. Pd and Pt compounds

Table 3 collects the palladium and platinum derivatives of $(SC_6F_5)^- = SX$

4.1. Palladium

Chloro-bridged allylic compounds $[\{Pd(\mu\text{-}Cl)(\eta^3\text{-allyl})\}_2]$, allyl $= CH_2CHCH_2$ [66] or $CH_2C(CH_3)CH_2$ [67] react with $M(SC_6F_5)_n$, M = Tl or Pb, to give the corresponding $[\{Pd(\mu\text{-}SX)(allyl)\}_2]$ complexes. According to their ^{19}F-NMR spectra at variable temperature, these complexes show a fluxional behaviour which can be attributed to an equilibrium between isomers arising from the relative orientations of both the SX and the allylic ligands. The energy involved for inversion of configuration at the sulfur atoms, in bimetallic transition metal complexes bearing bridging thiolates, spans the 10.7–18.4 kcal mol^{-1} range whereas that corresponding to the rotation of the allyl ligands has been found in the interval between 11.0 and 17.4 kcal mol^{-1}. Since both intervals are practically coincident, differentiation between both processes is extremely difficult. What is clear however is that both phenomena are present. The structure of $[\{Pd(SX)(\eta^3\text{-}C_3H_5)\}_2]$ is shown in Fig. 13.

4.2. Platinum

Reactions of $[Pt(SX)_2(COD)]$ with $[Pt(SX)_4]^{2-}$ gave $[(SX)_2Pt(\mu\text{-}SX)_2Pt(SX)_2]^{2-}$ [79,80] which, since it is fully fluorinated and homoleptic, becomes a distinguished member in the family of the platinum complexes. Similar compounds with mixed ligands have shown that exchange between terminal and bridging moieties is a dynamic process that depends on the temperature.

A very interesting process also involving carbon–fluorine bond activation, is the dimerisation of $[Pt(SX)_2(PPh_2(C_6F_5))_2]$ which spontaneously forms the bimetallic compound $[(Pt(\mu\text{-}SX)(SX)(PPh_2(C_6F_5))\}_2]$. This dimer rearranges itself to afford the new ligand *ortho*-$(Ph_2P)C_6F_4(XS)$ in the complex $[Pt(SX)_2(o\text{-}(Ph_2P)C_6F_4(XS))]$ (Figs. 14 and 15).

Very little is known regarding fluorocarbon activation at platinum centres and a great deal of work remains, fortunately, to be done.

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