Reactivity of Binuclear Heterobridged Iridium Complexes with $SnCl_2$†

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The complex $[Ir_2(\mu\text{-pz})(\mu\text{-SBu}^t)(CO)_2\{P(OMe)_3\}_2]$ **1** (pz = pyrazolate) reacts with HgX_2 (X = Cl or I) (1:2 molar ratio) to give the oxidation compounds $[Ir_2(\mu\text{-pz})(\mu\text{-SBu}^t)X_2(CO)_2\{P(OMe)_3\}_2]$ (X = Cl **2** or I **3**). The addition of $SnCl_2$ to solutions of **2** or **3** leads to the trihalogenotin iridium complexes $[Ir_2(\mu\text{-pz})(\mu\text{-SBu}^t)(SnCl_2X)_2(CO)_2\{P(OMe)_3\}_2]$ (X = Cl **4** or I **5**]. Treating **1** with $SnCl_2$ affords the adduct $[Ir_2(\mu\text{-pz})(\mu\text{-SBu}^t)(\mu\text{-SnCl}_2)(CO)_2\{P(OMe)_3\}_2]$ **6**. The formulation of the compounds has been deduced by elemental analysis, IR, ^{31}P and ^{119}Sn NMR spectroscopy. The structure of one isomer of **4** (**4a**) has been determined by X-ray diffraction methods: triclinic, space group $P\bar{1}$, with a = 11.896(2), b = 12.863(2), c = 13.943(3) Å, α = 69.27(1), β = 68.21(1), γ = 66.47(1) °, and Z = 2. The complex is binuclear with the metal atoms bridged by a pyrazolate and a SBu^t ligand. The Ir–Ir distance, 2.7221(6) Å, indicates the presence of a metal–metal bond.

There is considerable interest in the synthesis of transition-metal–tin complexes because of the use of such species in the catalytic transformations of organic compounds.[1,2] In particular, the reactivity of mononuclear rhodium or iridium compounds with tin halides has been thoroughly investigated[3–7] but, in contrast, related chemistry involving binuclear rhodium or iridium complexes has been less studied.[8–12]

Recently we reported the preparation of binuclear complexes containing the $M(\mu\text{-pz})(\mu\text{-SBu}^t)M$ framework (M = Rh or Ir, pz = pyrazolate). For these complexes, some crystal structures show that the $M(\mu\text{-N–N})(\mu\text{-S})M$ core is a bent configuration. The nature of the central ring results in a wide range of intermetallic separations.[13–16]

In pursuance of our interest in the chemistry of bi- and polynuclear rhodium or iridium complexes, we report here the ability of $[Ir_2(\mu\text{-pz})(\mu\text{-SBu}^t)X_2(CO)_2\{P(OMe)_3\}_2]$ (X = Cl or I) or $[Ir_2(\mu\text{-pz})(\mu\text{-SBu}^t)(CO)_2\{P(OMe)_3\}_2]$ compounds to give the trihalogenotin derivatives $[Ir_2(\mu\text{-pz})(\mu\text{-SBu}^t)(SnCl_2X)_2(CO)_2\{P(OMe)_3\}_2]$ or the Ir_2Sn adduct $[Ir_2(\mu\text{-pz})(\mu\text{-SBu}^t)(\mu\text{-SnCl}_2)(CO)_2\{P(OMe)_3\}_2]$, respectively.

Results and Discussion

Reaction of $[Ir_2(\mu\text{-pz})(\mu\text{-SBu}^t)(CO)_2\{P(OMe)_3\}_2]$ **1** with 2 mol equivalents of mercury(II) chloride, in dichloromethane, and at room temperature, leads to the formation of the compound $[Ir_2(\mu\text{-pz})(\mu\text{-SBu}^t)Cl_2(CO)_2\{P(OMe)_3\}_2]$ **2** [equation (1),

$$[Ir_2(\mu\text{-pz})(\mu\text{-SBu}^t)(CO)_2\{P(OMe)_3\}_2] + 2HgX_2 \longrightarrow [Ir_2(\mu\text{-pz})(\mu\text{-SBu}^t)X_2(CO)_2\{P(OMe)_3\}_2] + Hg_2X_2 \quad (1)$$

X = Cl or I]. The reaction was monitored by IR spectroscopy which after 30 min of stirring revealed the absence of any starting material. By work-up of the resulting solution, as described in the Experimental section, complex **2** was obtained as a pale yellow solid. It is noteworthy that complex **2** cannot be obtained by direct reaction of **1** with molecular chlorine which produces a mixture of products which we were unable to isolate in a pure form.

The $^{31}P\text{-}\{^1H\}$ NMR spectrum of complex **2** shows a singlet at δ 59.1, arising from a symmetrical compound. This is confirmed by the ^1H NMR spectrum which shows two pyrazolate resonances at δ 6.35 and 8.20 and one doublet for the methyl groups of the trimethyl phosphite ligands (δ 3.96). The IR spectrum shows a broad signal corresponding to ν(CO) stretching at a wavenumber 85 cm^{-1} higher than that for complex **1** [ν(CO) 1985 cm^{-1} (CH_2Cl_2)].

The complex $[Ir_2(\mu\text{-pz})(\mu\text{-SBu}^t)I_2(CO)_2\{P(OMe)_3\}_2]$ **3** that we had previously prepared[13] by oxidative addition of molecular iodine to **1**, can also be obtained by the process indicated in equation (1), starting from $[Ir_2(\mu\text{-pz})(\mu\text{-SBu}^t)(CO)_2\{P(OMe)_3\}_2]$ **1** and HgI_2. Analytical and spectroscopic data for **2** and **3** are consistent with structures having a symmetrical *cis* geometry as shown in Scheme 1. The reaction implies a two-centre oxidative addition with concurrent iridium–iridium bond formation.

The symmetrical compound $[Ir_2(\mu\text{-pz})(\mu\text{-SBu}^t)Cl_2(CO)_2\{P(OMe)_3\}_2]$ **2** reacts with $SnCl_2$ (1:2 molar ratio) to give an orange complex analysing as $[Ir_2(\mu\text{-pz})(\mu\text{-SBu}^t)(SnCl_3)_2(CO)_2\{P(OMe)_3\}_2]$ **4**, Scheme 1. In solution, this appears to be a mixture of an asymmetric **4a** and a symmetric **4b** isomer. The $^{31}P\text{-}\{^1H\}$ NMR spectrum of **4a** showed two doublets at δ 71.3 and 62.1 (J_{PP} = 23 Hz). This result indicates that this species is unsymmetrical having chemically different phosphorus environments. Also, the ^1H NMR spectrum is in accord with this proposal. Compound **4a** displayed the pyrazolate resonances at δ 6.21, 7.32 and 7.41 and two doublets for the phosphite resonances at δ 3.80 and 3.93. Isomer **4b** was characterized by a singlet in the $^{31}P\text{-}\{^1H\}$ NMR spectrum indicative of the formation of a symmetrical species.

The ^{119}Sn NMR spectrum of $[Ir_2(\mu\text{-pz})(\mu\text{-SBu}^t)(SnCl_3)_2(CO)_2\{P(OMe)_3\}_2]$ also confirms that compound **4** exists, in solution, as a mixture of the two isomers **4a** and **4b**. As expected, compound **4b** displays a doublet (δ −372.2, $^2J_{PSn}$ = 191 Hz) corresponding to two equivalent trichlorostannate groups which are coupled to the nearest phosphorus atom. However, for compound **4a** we only observe a doublet of doublets (δ −355.2, $^2J_{PSn}$ = 258, $^3J_{PSn}$ = 55 Hz). The signal due to the

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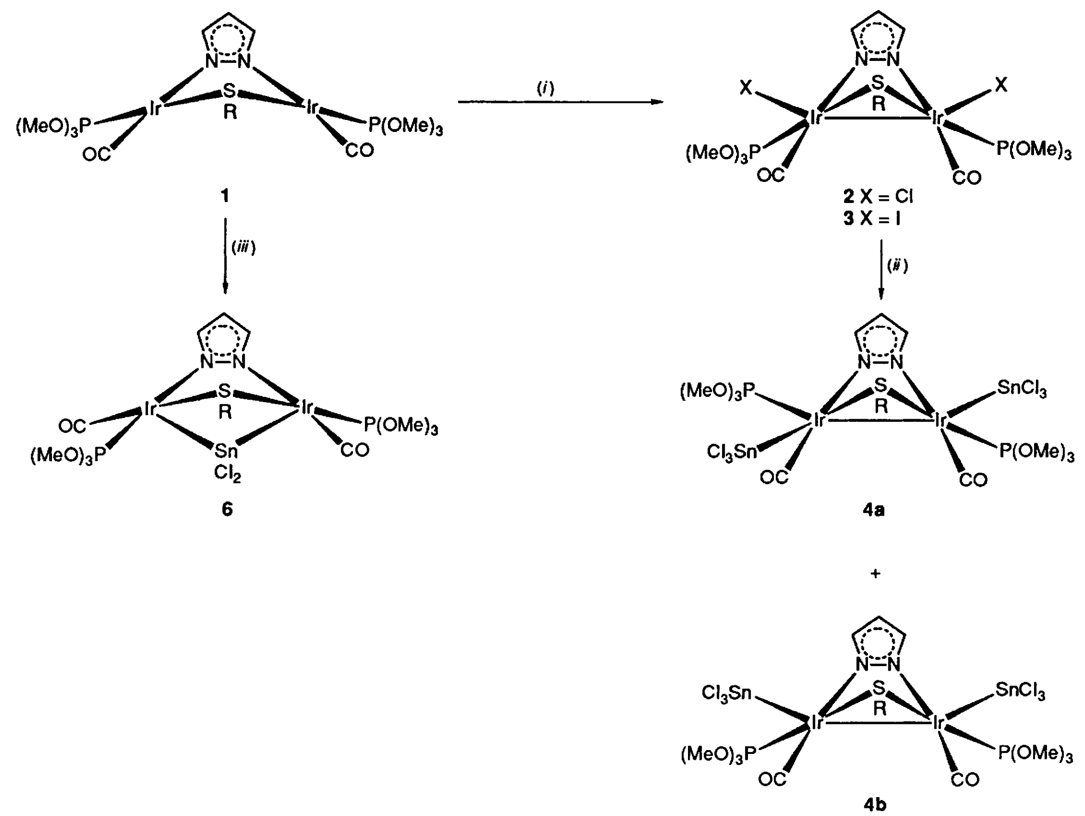
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.



Scheme 1 R = SBu^t. (i) +2HgX$_2$ (X = Cl or I); (ii) +2SnCl$_2$; (iii) +SnCl$_2$

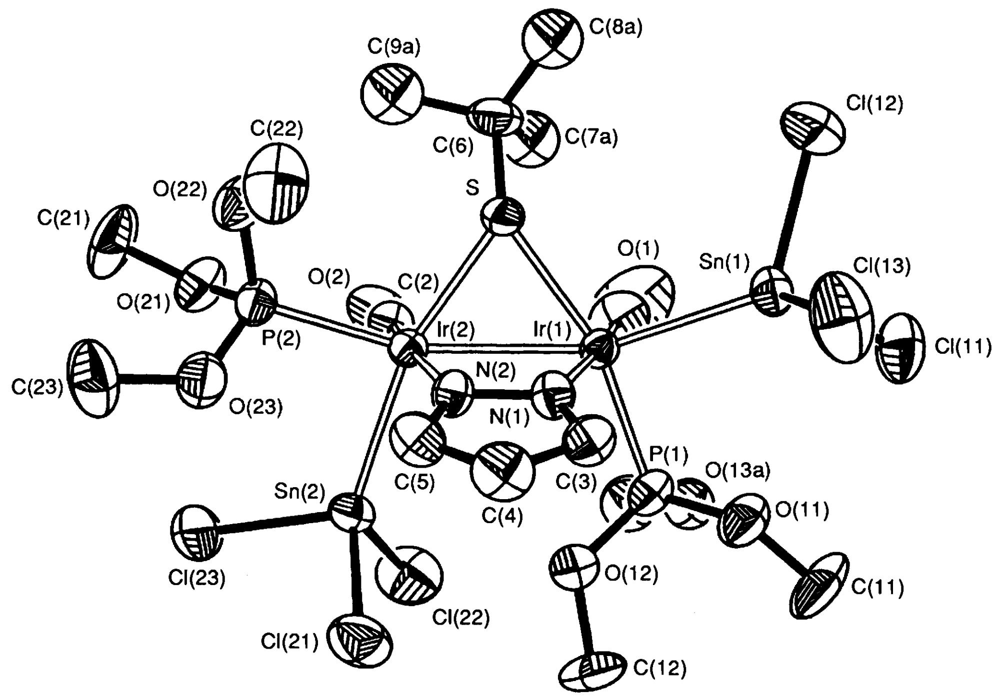


Fig. 1 View of the molecular structure of [Ir$_2$(μ-pz)(μ-SBu^t)(SnCl$_3$)$_2$(CO)$_2${P(OMe)$_3$}$_2$] **4a** with the atomic numbering scheme

second ^{119}Sn site was not detected. This may be due to a long T_1, or a broad signal.

Pure **4a** isomer was obtained by fractional crystallization. The crystal structure of **4a** has been determined by single-crystal X-ray diffraction. The molecular structure is shown in Fig. 1, together with the atomic numbering scheme; selected bond distances and angles are given in Table 1. Within this molecule, the two metal centres are connected by a double bridge formed by a pyrazolate group, bound through the two N atoms, and a SBu^t ligand linked through the S atom. This double bridge maintains an Ir–Ir separation of 2.7221(6) Å, indicative of the presence of a single direct metal–metal bond.[17] This distance compares well with those observed in related iridium complexes such as [Ir$_2$(μ-pz)$_2$Cl$_2$(CO)$_2$(PPh$_3$)$_2$], 2.737(1) Å,[17] or [Ir$_2$(μ-C$_6$H$_4$)(η^5-C$_5$H$_5$)$_2$(CO)$_2$], 2.7166(2) Å,[18] where the existence of an Ir–Ir single bond has been reported.

Table 1 Selected bond lengths (Å) and angles (°) for the complex [Ir$_2$(μ-pz)(μ-SBu^t)(SnCl$_3$)$_2$(CO)$_2${P(OMe)$_3$}$_2$] **4a**

Ir(1)–Ir(2)	2.7221(6)	Ir(2)–Sn(2)	2.593(1)
Ir(1)–Sn(1)	2.636(1)	Ir(2)–S	2.374(2)
Ir(1)–S	2.407(3)	Ir(2)–P(2)	2.288(2)
Ir(1)–P(1)	2.256(4)	Ir(2)–N(2)	2.068(9)
Ir(1)–N(1)	2.088(8)	Ir(2)–C(2)	1.866(10)
Ir(1)–C(1)	1.861(14)	C(2)–O(2)	1.116(13)
C(1)–O(1)	1.117(17)		
N(1)–N(2)	1.347(9)	Sn(1)–Cl(11)	2.356(3)
N(1)–C(3)	1.349(15)	Sn(1)–Cl(12)	2.374(5)
N(2)–C(5)	1.352(15)	Sn(1)–Cl(13)	3.364(4)
C(3)–C(4)	1.404(14)	Sn(2)–Cl(21)	2.337(5)
C(4)–C(5)	1.383(17)	Sn(2)–Cl(22)	2.361(3)
S–C(6)	1.883(16)	Sn(2)–Cl(23)	2.353(3)
Ir(2)–Ir(1)–Sn(1)	153.0(1)	Ir(1)–Ir(2)–Sn(2)	108.7(1)
Ir(2)–Ir(1)–S	54.7(1)	Ir(1)–Ir(2)–S	55.9(1)
Ir(2)–Ir(1)–P(1)	109.3(1)	Ir(1)–Ir(2)–P(2)	155.8(1)
Ir(2)–Ir(1)–N(1)	70.4(2)	Ir(1)–Ir(2)–N(2)	71.0(2)
Ir(2)–Ir(1)–C(1)	101.2(4)	Ir(1)–Ir(2)–C(2)	100.0(3)
Sn(1)–Ir(1)–S	101.2(1)	Sn(2)–Ir(2)–S	163.9(1)
Sn(1)–Ir(1)–P(1)	92.6(1)	Sn(2)–Ir(2)–P(2)	91.5(1)
Sn(1)–Ir(1)–N(1)	95.6(2)	Sn(2)–Ir(2)–N(2)	90.1(2)
Sn(1)–Ir(1)–C(1)	93.9(5)	Sn(2)–Ir(2)–C(2)	86.8(3)
S–Ir(1)–P(1)	162.9(1)	S–Ir(2)–P(2)	102.6(1)
S–Ir(1)–N(1)	80.5(2)	S–Ir(2)–N(2)	80.8(3)
S–Ir(1)–C(1)	98.4(4)	S–Ir(2)–C(2)	99.6(4)
P(1)–Ir(1)–N(1)	88.2(2)	P(2)–Ir(2)–N(2)	96.5(2)
P(1)–Ir(1)–C(1)	90.6(5)	P(2)–Ir(2)–C(2)	94.2(3)
N(1)–Ir(1)–C(1)	170.4(5)	N(2)–Ir(2)–C(2)	169.0(4)
Ir(1)–N(1)–N(2)	109.1(5)	Ir(2)–N(2)–N(1)	109.5(6)
Ir(1)–N(1)–C(3)	140.4(7)	Ir(2)–N(2)–C(5)	141.6(7)
N(2)–N(1)–C(3)	109.9(8)	N(1)–N(2)–C(5)	107.9(8)
Ir(1)–C(1)–O(1)	175(2)	Ir(2)–C(2)–O(2)	176(1)
Ir(1)–S–Ir(2)	69.4(1)		
Ir(1)–S–C(6)	121.7(4)	Ir(2)–S–C(6)	117.3(4)
Ir–Sn–Cl(av.)	119.5(3)	Cl–Sn–Cl(av.)	98(1)

Each metal centre completes its co-ordination sphere by being bonded to three terminal ligands: a carbonyl, a trimethyl phosphite ligand and a trichlorostannate group. Considering the existence of the metal–metal bond the iridium atoms lie in an octahedral environment, severely distorted due to the simultaneous presence of the intermetallic bond and the two bridging ligands. This distortion from the proposed ideal O_h symmetry is clearly shown in the *cis* bond angles observed between the bridging ligands [*i.e.* S–Ir(1)–Ir(2) 54.7(1) or N(1)–Ir(1)–Ir(2) 70.4(2)°].

Noteworthy is the different relative disposition of the ligands around the two metal centres. Thus, the SBu^t ligand is situated *trans* to the P(OMe)$_3$ group in Ir(1), and to SnCl$_3$ in the Ir(2) co-ordination sphere. The P(OMe)$_3$ group is opposite to the metal–metal bond in Ir(2), but, around Ir(1), the SnCl$_3$ ligand is *trans* to this particular bond. In both metal environments the carbonyl groups are *trans* to the bridging pyrazolate ligand.

This different arrangement of the same ligands, around two electronically identical metal centres, makes it possible to argue for the structural *trans* effect of the intermetallic bond. As expected, the Ir–Sn bond distances are different: Ir(1)–Sn(1), 2.636(1) Å, in a pseudo-*trans* situation to the Ir(2) atom [Ir(2)–Ir(1)–Sn(1) 153.0(1)°], is significantly longer than Ir(2)–Sn(2) 2.593(1) Å, *trans* to the SBu^t ligand. In the related complex [Ir(SnCl$_3$)(C$_7$H$_8$)(PMe$_2$Ph)$_2$][19] the Ir–Sn distance is 2.5867(6) Å, comparable to the shortest distance observed in **4a**. Both Ir–Sn lengths in **4a** are shorter than the suggested value for a single Ir–Sn bond, 2.75 Å.[20]

As in [Ir(SnCl$_3$)(C$_7$H$_8$)(PMe$_2$Ph)$_2$],[19] in complex **4a** the tin atom displays a distorted-tetrahedral environment, showing Ir–Sn–Cl angles larger than the ideal value [average 119.5(3)°] and smaller for Cl–Sn–Cl [average 98(1)°].

The Ir(1)–P(1) and Ir(2)–P(2) bond distances are 2.256(4) and 2.288(2) Å, respectively. Again, as observed for the Ir–Sn separation, the high structural *trans* effect of the metal–metal bond causes the largest distance to be opposite to this bond [Ir(1)–Ir(2)–P(2) 15.8(1)°]. A similar behaviour for the Ir–P distance has been observed for the dinuclear complex [Ir$_2$(μ-SBu^t)$_2${C$_2$(CN)$_2$}(CO)$_2${P(OMe)$_3$}$_2$],[21] where a P atom is *trans* to the SBu^t group [2.252(4) Å], while the longest Ir–P distance corresponds to the P(OMe)$_3$ group *trans* to the metal–metal bond [2.301(4) Å].

The disordered group μ-SBu^t shows Ir(1)–S and Ir(2)–S distances, 2.407(3) and 2.374(2) Å, comparable to those reported in symmetric dinuclear complexes, as in [Ir$_2$(μ-SBu^t)$_2$I$_2$(CO)$_2$(PPhMe$_2$)$_2$][22] [2.38(5) Å], or in asymmetric complexes as in [Ir$_2$(μ-SBu^t)(μ-CO)(SBu^t)(CO)$_2$(PMe$_3$)$_3$][23] [2.371(4) and 2.400(4) Å].

The structural parameters of the bridging pyrazolate or terminal carbonyl ligands are normal when compared with those of related dinuclear complexes containing both ligands similarly bonded.[13,16,17,24]

A similar complex to **4** formulated as [Ir$_2$(μ-pz)(μ-SBu^t)(SnCl$_2$I)$_2$(CO)$_2${P(OMe)$_3$}$_2$] **5** may be prepared by treatment of [Ir$_2$(μ-pz)(μ-SBu^t)I$_2$(CO)$_2${P(OMe)$_3$}$_2$] **3** with SnCl$_2$, Scheme 1. Complex **5** has analogous spectroscopic characteristics to those of **4**. However, the ^{31}P NMR spectrum of a CDCl$_3$ solution of this compound, before its isolation, shows the presence of three different isomers (see Experimental section).

The reactions of SnCl$_2$ with the diiridium(II) complex **2** or **3** involve the insertion of Sn^{II} into the iridium–halide bond and the formation of the trihalogenotin derivatives [Ir$_2$(μ-pz)(μ-SBu^t)(SnCl$_2$X)$_2$(CO)$_2${P(OMe)$_3$}$_2$].

The presence of an iridium–iridium bond in complexes **4** and **5** suggested the possibility of SnCl$_2$ insertion to give an Ir–Sn–Ir bridge. However the desired reaction does not appear to occur at least under moderate conditions. Thus, complexes **4** and **5** were unaffected by stirring, in dichloromethane, with SnCl$_2$ (Ir:Sn = 1:10).

Interestingly, reaction of the diiridium(I) compound [Ir$_2$(μ-pz)(μ-SBu^t)(CO)$_2${P(OMe)$_3$}$_2$] **1** with SnCl$_2$, in methanol, gives a violet solution from which a dark blue complex, formulated as [Ir$_2$(μ-pz)(μ-SBu^t)(μ-SnCl$_2$)(CO)$_2${P(OMe)$_3$}$_2$] **6**, is obtained on addition of hexane. The dark colour of this compound could be indicative of the presence of metal–metal interactions.[25]

The IR spectrum shows that the ν(CO) band (2015 cm^{-1}) is at 30 cm^{-1} to higher wavenumber than that of **1**; this suggests that the presence of Sn lowers the π back donation from the carbon atom of the carbonyl ligands to the iridium centres. Also, the presence of two doublets at δ 81.9 ($^3J_{PP}$ = 6 Hz) and at 72.5 ($^3J_{PP}$ = 6 Hz) in the ^{31}P NMR spectrum, and of a doublet of doublets [δ = −388.6; $^2J_{P(trans)Sn}$ = 222 and $^2J_{P(cis)Sn}$ = 144 Hz] in the ^{119}Sn NMR spectrum, indicates the formation of an unsymmetrical compound containing chemically different phosphorus ligands. We propose the molecular structure presented in Scheme 1 in which the SnCl$_2$ group bridges both iridium centres, and the terminal ligands adopt a *trans* geometry.

In conclusion, the series of reactions presented show the ability of the tin(II) chloride to act as a bridging ligand between two metal centres or to originate the formation of a SnX$_3$ group by an insertion process into a metal–halogen bond.

Experimental

Elemental analyses were carried out with a Perkin-Elmer 240B microanalyser. Infrared spectra were recorded on a Perkin-Elmer 783 spectrophotometer, ^{1}H NMR spectra in CDCl$_3$ solution at room temperature on a Varian XL 200 spectrometer. The ^{1}H chemical shifts were reported with respect to SiMe$_4$.

The $^{31}\mathrm{P}$ and $^{119}\mathrm{Sn}$ NMR spectra were recorded in $\mathrm{CDCl_3}$ solution at room temperature on a Bruker WH400 spectrometer. The $^{31}\mathrm{P}$ chemical shifts were referenced to external 85% $\mathrm{H_3PO_4}$, without correction for susceptibility. The $^{119}\mathrm{Sn}$ chemical shifts were referenced *via* $\mathrm{SiMe_4}$ to the absolute frequency 37.290 662 MHz for neat $\mathrm{SnMe_4}$.[26] All preparations were carried out under nitrogen on a vacuum line using Schlenk techniques. Solvents were purified by standard methods prior to use. The reactants were of commercial origin and used without further purification. The complex $[\mathrm{Ir_2(\mu{-}pz)(\mu{-}SBu^t)(CO)_2\{P(OMe)_3\}_2}]$ **1** was prepared according to literature methods.[13]

Preparations.—$[\mathrm{Ir_2(\mu{-}pz)(\mu{-}SBu^t)Cl_2(CO)_2\{P(OMe)_3\}_2}]$ **2**. Solid mercury(II) chloride (32 mg, 0.12 mmol) was added to a solution of $[\mathrm{Ir_2(\mu{-}pz)(\mu{-}SBu^t)(CO)_2\{P(OMe)_3\}_2}]$ (50 mg, 0.06 mmol) in dichloromethane (20 cm^3). After 30 min of stirring the initial compound was consumed, and a white precipitate of mercury(I) chloride was formed. The solution was filtered through Kieselguhr to remove the mercury(I) chloride, and the filtrate was concentrated under reduced pressure to 2 cm^3. Addition of hexane (15 cm^3) gave a pale yellow solid which was filtered off, washed with hexane and dried under vacuum (yield 60%) (Found: C, 19.4; H, 3.2; N, 2.9. Calc. for $\mathrm{C_{15}H_{30}Cl_2Ir_2N_2O_8P_2S}$: C, 19.6; H, 3.2; N, 3.0%). IR ($\mathrm{CH_2Cl_2}$): 2070 (br) cm^{-1} [ν(CO)]. NMR ($\mathrm{CDCl_3}$): $^1\mathrm{H}$, δ 1.75 (s, SBu^t), 3.96 [d, P(OMe)$_3$, $^3J_{PH}$ 11.6], 6.35 (t, pz, $^3J_{HH}$ 2.2) and 8.20 (d, pz, $^3J_{HH}$ 2.2 Hz); $^{31}\mathrm{P}\text{-}\{^1\mathrm{H}\}$, δ 59.1 (s).

$[\mathrm{Ir_2(\mu{-}pz)(\mu{-}SBu^t)I_2(CO)_2\{P(OMe)_3\}_2}]$ **3**. To a solution of $[\mathrm{Ir_2(\mu{-}pz)(\mu{-}SBu^t)(CO)_2\{P(OMe)_3\}_2}]$ (100 mg, 0.12 mmol) in dichloromethane (15 cm^3) was added solid mercury(II) iodide (108 mg, 0.24 mmol). The colour of the solution changed from yellow to orange and a yellow precipitate of mercury(I) iodide was formed. After 30 min of stirring the solution was filtered through Kieselguhr to remove the precipitate. Then the solvent was evaporated to 2 cm^3 and hexane (10 cm^3) was added to give an orange solid. This was filtered off, washed with hexane and dried under vacuum (yield: 75%) (Found: C, 16.2; H, 2.6; N, 2.4. Calc. for $\mathrm{C_{15}H_{30}I_2Ir_2N_2O_8P_2S}$: C, 16.4; H, 2.7; N, 2.5%). IR ($\mathrm{CH_2Cl_2}$): 2040 (br) cm^{-1} [ν(CO)]. NMR ($\mathrm{CDCl_3}$): $^1\mathrm{H}$, δ 1.65 (s, SBu^t), 3.73 [d, P(OMe)$_3$, $^3J_{PH}$ 11.1], 6.16 (t, pz, $^3J_{HH}$ 1.7) and 7.53 (d, pz, $^3J_{HH}$ 1.7); $^{31}\mathrm{P}\text{-}\{^1\mathrm{H}\}$, δ 78.4 (s).

$[\mathrm{Ir_2(\mu{-}pz)(\mu{-}SBu^t)(SnCl_3)_2(CO)_2\{P(OMe)_3\}_2}]$ **4**. To a solution of $[\mathrm{Ir_2(\mu{-}pz)(\mu{-}SBu^t)Cl_2(CO)_2\{P(OMe)_3\}_2}]$ (100 mg, 0.11 mmol) in dichloromethane (20 cm^3) was added the stoichiometric amount of tin(II) chloride (41.71 mg, 0.22 mmol). After stirring for 2 h, at room temperature, the colour of the solution changed from yellow to orange. Then the solvent was evaporated to 2 cm^3 and diethyl ether (10 cm^3) was added to give an orange solid which was filtered off, washed with hexane and dried under vacuum (yield 82%) (Found: C, 13.5; H, 2.3; N, 2.0. Calc. for $\mathrm{C_{15}H_{30}Cl_6Ir_2N_2O_8P_2SSn_2}$: C, 13.9; H, 2.3; N, 2.1%). IR ($\mathrm{CH_2Cl_2}$): 2070 (br) cm^{-1} [ν(CO)]. NMR ($\mathrm{CDCl_3}$): $^1\mathrm{H}$, δ 1.61 (s, SBu^t), 3.80 [d, P(OMe)$_3$, $^3J_{PH}$ 11.6], 3.93 [d, P(OMe)$_3$, $^3J_{PH}$ 11.6], 6.21 (t, pz, $^3J_{HH}$ 2.2), 7.32 (d, pz, $^3J_{HH}$ 2.2) and 7.41 (d, pz, $^3J_{HH}$ 2.2 Hz); $^{31}\mathrm{P}\text{-}\{^1\mathrm{H}\}$, δ 71.3 (d, $^3J_{PP}$ 23 Hz) and 62.1 (d, $^3J_{PP}$ 23 Hz).

NMR spectra from the reaction of $[\mathrm{Ir_2(\mu{-}pz)(\mu{-}SBu^t)Cl_2(CO)_2\{P(OMe)_3\}_2}]$ *with* $\mathrm{SnCl_2}$ *in* $\mathrm{CDCl_3}$ *solution.* Major species ($\mathrm{CDCl_3}$): $^{31}\mathrm{P}\text{-}\{^1\mathrm{H}\}$, δ 71.3 (d, $^3J_{PP}$ 23, $^3J_{SnP} = 56$), 63.0 (d, $^3J_{PP}$ 23, $^2J_{SnP}$ 259 Hz); $^{119}\mathrm{Sn}\text{-}\{^1\mathrm{H}\}$, δ −355.2 (dd, $^2J_{PSn}$ 258, $^3J_{PSn}$ 55 Hz). Minor species ($\mathrm{CDCl_3}$): $^{31}\mathrm{P}\text{-}\{^1\mathrm{H}\}$, δ 58.6 (s); $^{119}\mathrm{Sn}\text{-}\{^1\mathrm{H}\}$, δ −372.2 (d, $^2J_{PSn}$ 191 Hz).

$[\mathrm{Ir_2(\mu{-}pz)(\mu{-}SBu^t)(SnCl_2I)(CO)_2\{P(OMe)_3\}_2}]$ **5**. Tin(II) chloride (43.60 mg, 0.23 mmol) was added to a solution of $[\mathrm{Ir_2(\mu{-}pz)(\mu{-}SBu^t)I_2(CO)_2\{P(OMe)_3\}_2}]$ (130 mg, 0.12 mmol) in dichloromethane (20 cm^3). The solution was stirred, at room temperature, for 1 h. During that period the colour changed from orange to red. Evaporation of the solvent to 2 cm^3 and addition of hexane (15 cm^3) gave a solid which was filtered off, washed with hexane and dried under vacuum (yield 65%) (Found: C, 12.3; H, 2.2; N, 2.0. Calc. for $\mathrm{C_{15}H_{30}Cl_4I_2Ir_2N_2O_8P_2SSn_2}$: C, 12.2; H, 2.1; N, 1.9%). IR ($\mathrm{CH_2Cl_2}$): 2040 (br) cm^{-1} [ν(CO)]. $^{31}\mathrm{P}\text{-}\{^1\mathrm{H}\}$ NMR ($\mathrm{CDCl_3}$): δ 77.2 (d, $^3J_{PP}$ 8) and 71.7 (d, $^3J_{PP}$ 8 Hz).

NMR spectra from the reaction of $[\mathrm{Ir_2(\mu{-}pz)(\mu{-}SBu^t)I_2(CO)_2\{P(OMe)_3\}_2}]$ *with* $\mathrm{SnCl_2}$ *in* $\mathrm{CDCl_3}$ *solution.* Major species ($\mathrm{CDCl_3}$): $^{31}\mathrm{P}\text{-}\{^1\mathrm{H}\}$, δ 77.2 (d, $^3J_{PP}$ 8) and 71.7 (d, $^3J_{PP}$ 8 Hz). Minor species ($\mathrm{CDCl_3}$): $^{31}\mathrm{P}\text{-}\{^1\mathrm{H}\}$, δ 79.8 (d, $^3J_{PP}$ 8) and 69.5 (d, $^3J_{PP}$ 8 Hz). $^{31}\mathrm{P}\text{-}\{^1\mathrm{H}\}$, δ 78.4 (d, $^3J_{PP}$ 8) and 70.8 (d, $^3J_{PP}$ 8 Hz).

trans-$[\mathrm{Ir_2(\mu{-}pz)(\mu{-}SBu^t)(\mu{-}SnCl_2)(CO)_2\{P(OMe)_3\}_2}]$ **6**. To a solution of $[\mathrm{Ir_2(\mu{-}pz)(\mu{-}SBu^t)(CO)_2\{P(OMe)_3\}_2}]$ (100 mg, 0.12 mmol) in methanol (15 cm^3) was added the stoichiometric amount of tin(II) chloride (22.75 mg, 0.12 mmol); the colour of the solution changed from yellow to violet. The progress of the reaction was followed by IR spectroscopy. After 30 min of stirring the solvent was evaporated to 2 cm^3 and hexane (20 cm^3) was added to give a dark blue solid. This was filtered off, washed with hexane and dried under vacuum (yield 85%) (Found: C, 14.4; H, 2.7; N, 2.6. Calc. for $\mathrm{C_{15}H_{30}Cl_2Ir_2N_2O_8P_2SSn}$: C, 14.4; H, 2.9; N, 2.7%). IR ($\mathrm{CH_2Cl_2}$): 2015 (br) cm^{-1} [ν(CO)]. NMR ($\mathrm{CDCl_3}$): $^{31}\mathrm{P}\text{-}\{^1\mathrm{H}\}$, δ 81.9 (d, $^3J_{PP}$ 6, $^2J_{SnP}$ 125) and 72.5 (d, $^3J_{PP}$ 6, $^2J_{SnP}$ 220); $^{119}\mathrm{Sn}\text{-}\{^1\mathrm{H}\}$, δ −388.6 [dd, $^2J_{P(trans)Sn}$ 222, $^2J_{P(cis)Sn}$ 144 Hz].

Crystal Structure Determination of $[\mathrm{Ir_2(\mu{-}pz)(\mu{-}SBu^t)(SnCl_3)_2(CO)_2\{P(OMe)_3\}_2}]$.—Crystals were obtained as transparent yellow-orange prismatic blocks by slow diffusion of diethyl ether into a concentrated solution of compound **4** in dichloromethane.

Crystal data. $\mathrm{C_{15}H_{30}Cl_6Ir_2N_2O_8P_2SSn_2}$, $M = 1294.96$, triclinic, space group $P\bar{1}$, $a = 11.896(2)$, $b = 12.863(2)$, $c = 13.943(3)$ Å, $\alpha = 69.27(1)$, $\beta = 68.21(1)$, $\gamma = 66.47(1)^\circ$, $U = 1762.5(6)$ Å^3 (by least-squares refinement of the 2θ values of 46 accurately measured reflections in the range 20–35°), $Z = 2$, $\lambda = 0.710\,69$ Å, $D_c = 2.44$ g cm^{-3}, $F(000) = 1200$, μ(Mo-Kα) = 95.50 cm^{-1}, approximate crystal dimensions 0.15 × 0.13 × 0.10 mm.

Data collection and processing. Four-circle Siemens AED diffractometer, ω–2θ scan mode, graphite-monochromated Mo-Kα radiation; 6547 reflections measured. Of 5826 independent reflections, 4570 having $F \geq 5.0\sigma(F)$ were considered observed and used in the analysis. Three standard reflections were measured every hour; no variation was observed. An empirical correction for the absorption effects was applied[27] (minimum and maximum correction factors 0.889 and 1.222).

Structure solution and refinement. The structure was solved by Patterson and Fourier methods, and refined by full-matrix least squares first with isotropic and then with anisotropic thermal parameters for all non-hydrogen atoms, except those involved in disorder. A preliminary attempt at refinement including anisotropic parameters for all atoms revealed the existence of two zones in the molecule where thermal parameters were anomalously high, and where, additionally, the highest residuals of electron density were located. From geometrical considerations, a model of disorder for the methyl groups of the SBu^t ligand was clearly established on the basis of the presence of two disordered '(CH$_3$)$_3$' moieties [C(7a), C(8a), C(9a) and C(7b), C(8b), C(9b)], both bonded to C(6) and rotated around the S–C(6) bond *ca.* 45° with respect to each other. A complementary occupancy factor was refined for these atoms [0.71(2) for C(7a)–C(9a) and 0.29(2) for C(7b)–C(9b)], but no constraint was imposed for positional or thermal parameters. The second area of disorder involved the methoxy groups of a phosphite ligand [P(1)]. From the residual density map only one methoxy group [O(13), C(13)] could be modelled, and was included in the refinement with a fixed occupancy factor [0.675 for O(13a) and C(13a), 0.325 for O(13b) and C(13b)]. No attempt was made to locate hydrogen atoms. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$, with $w = 0.9249/[\sigma^2(F) + 0.000\,76F^2]$. Final

Table 2 Final atomic coordinates (× 10^4) for the non-hydrogen atoms for complex **4a**

Atom	*X/a*	*Y/b*	*Z/c*
Ir(1)[a]	11 502(3)	81 615(3)	73 656(3)
Ir(2)[a]	29 010(3)	60 007(3)	74 347(3)
Sn(1)[a]	−11 361(6)	96 035(6)	79 855(6)
Sn(2)[a]	51 151(6)	61 841(6)	71 031(5)
Cl(11)	−1 579(3)	11 607(3)	7 128(3)
Cl(12)	−2 952(3)	9 346(3)	7 881(4)
Cl(13)	−1 958(4)	9 805(4)	9 758(3)
Cl(21)	5 543(3)	6 542(3)	8 443(3)
Cl(22)	5 902(3)	7 497(3)	5 554(3)
Cl(23)	6 933(3)	4 564(3)	6 808(3)
S	679(2)	6 366(2)	7 813(2)
P(1)	2 113(3)	9 473(2)	7 104(2)
P(2)	3 635(2)	4 013(2)	8 020(2)
O(1)	1 210(15)	8 977(10)	5 071(8)
O(2)	3 746(8)	5 972(9)	5 144(6)
O(11)	1 262(7)	10 391(6)	7 791(6)
O(12)[b]	3 395(7)	8 854(6)	7 412(7)
O(13a)[b]	2 266(13)	10 350(11)	5 962(10)
O(13b)[b]	2 773(23)	10 131(18)	5 998(17)
O(21)[b]	4 416(7)	3 430(6)	7 053(5)
O(22)	2 628(7)	3 326(6)	8 627(6)
O(23)	4 469(7)	3 665(6)	8 800(6)
N(1)	1 465(7)	7 442(6)	8 876(6)
N(2)	2 321(7)	6 368(6)	8 905(6)
C(1)	1 148(13)	8 652(11)	5 940(10)
C(2)	3 394(9)	5 974(8)	6 005(7)
C(3)	1 211(9)	7 752(8)	9 781(8)
C(4)	1 945(10)	6 824(10)	10 419(8)
C(5)	2 635(10)	5 987(9)	9 836(8)
C(6)	120(10)	6 017(10)	6 898(9)
C(7a)[b]	311(18)	6 774(18)	5 782(15)
C(7b)[b]	927(39)	5 948(37)	5 811(33)
C(8a)[b]	−1 309(18)	6 168(17)	7 514(16)
C(8b)[b]	−1 234(41)	6 928(40)	6 905(37)
C(9a)[b]	890(20)	4 758(18)	6 818(17)
C(9b)[b]	−44(56)	4 754(49)	7 593(47)
C(11)	1 237(15)	11 600(10)	7 571(12)
C(12)	4 158(13)	9 514(12)	7 451(13)
C(13a)[b]	3 207(19)	9 955(18)	5 005(17)
C(13b)[b]	1 973(39)	10 912(36)	5 296(35)
C(21)	4 840(15)	2 236(10)	7 060(11)
C(22)	1 741(13)	3 496(11)	9 650(10)
C(23)	5 178(13)	2 467(11)	9 258(11)

[a] Atomic coordinates × 10^5. [b] Atom involved in disorder (see text for description).

R and *R*′ values were 0.032 and 0.034. The SHELX system of computer programs was used.[28] Atomic scattering factors, corrected for anomalous dispersion, were taken from ref. 29. Final atomic coordinates for the non-hydrogen atoms are given in Table 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

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