Oxidative-addition Reactions of MeI or CH_2I_2 to $[M_2(\mu\text{-pz})(\mu\text{-SBu}^t)(CO)_2\{P(OMe)_3\}_2]$ (M = Rh or Ir) Complexes. X-Ray Structure of $[Ir_2(\mu\text{-pz})(\mu\text{-SBu}^t)(\mu\text{-CH}_2)I_2(CO)_2\{P(OMe)_3\}_2]$ (pz = pyrazolate)†

M. Teresa Pinillos, Anabel Elduque, José A. López, Fernando J. Lahoz and Luis A. Oro*
Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-Consejo Superior de Investigaciones Científicas, 50009 Zaragoza, Spain

The heterobridged binuclear complexes of general formula $[M_2(\mu\text{-pz})(\mu\text{-SBu}^t)(CO)_2\{P(OMe)_3\}_2]$ (pz = pyrazolate; M = Rh, **1**; or Ir, **2**) react with methyl iodide to give $[M_2(\mu\text{-pz})(\mu\text{-SBu}^t)(Me)I(CO)_2\{P(OMe)_3\}_2]$ (M = Rh, **3**; or Ir, **4**). Reaction of the diiridium complexes **2** or $[Ir_2(\mu\text{-dmpz})(\mu\text{-SBu}^t)(CO)_2\{P(OMe)_3\}_2]$ (dmpz = 3,5-dimethylpyrazolate) with diiodomethane give $[Ir_2(\mu\text{-pz})(\mu\text{-SBu}^t)(\mu\text{-CH}_2)I_2(CO)_2\{P(OMe)_3\}_2]$ **5** or $[Ir_2(\mu\text{-dmpz})(\mu\text{-SBu}^t)(CH_2I)I(CO)_2\{P(OMe)_3\}_2]$ respectively. The crystal and molecular structure of **5** has been determined by X-ray diffraction methods. Crystals are monoclinic, space group $P2_1/c$, with $a = 11.398(1)$, $b = 16.571(2)$, $c = 16.274(2)$ Å, $\beta = 106.87(1)°$, and $Z = 4$. The molecule is binuclear, with the two metal centres bridged by a pyrazolate anion, a SBu^t group and a methylene carbon atom.

The synthesis of binuclear alkyl or alkylidene compounds is receiving considerable attention because of their structural features and reactivity, particularly as related to homogeneous catalysis.[1,2] In this context, oxidative-addition reactions of MeI or CH_2I_2 to systems containing the $Ir_2(\mu\text{-SR})_2$,[3,4] $Ir_2(\mu\text{-pz})_2$, (pz = pyrazolate)[5–8] $Ir_2(\mu\text{-}C_5H_4NS)_2$[9] and $Ir_2\{\mu\text{-}1,8\text{-}(NH)_2C_{10}H_6\}$[10] moieties have been the subject of detailed investigations. In particular, the nature of the reactions of dihalogenomethanes with diiridium(I) complexes appears to depend critically on the nature of the bridging ligands.[11]

As part of our studies concerning the preparation and properties of bi- and tri-nuclear complexes containing the M(μ-az)(μ-X)M framework, where M is either rhodium or iridium, az an azolate type ligand, and X an anion such as Cl, OH, N_3 or SCN,[12–14] we have recently synthesised the dinuclear Rh–Rh and Ir–Ir complexes of general composition $[M_2(\mu\text{-pz})(\mu\text{-SBu}^t)(L_2)_2]$ (L_2 = diolefin or $COPR_3$).[15,16] In these complexes, the individual metal centres are joined by one exobidentate pyrazolate ligand and one *tert*-butylthiol group, in such a way that the cyclic bridged M(μ-pz)(μ-SBu^t)M core deviates from planarity, adopting a bent conformation which results in a wide range of intermetallic separations.[16]

In this paper, oxidative-addition reactions with methyl iodide or diiodomethane of the mixed-bridged complexes $[M_2(\mu\text{-pz})(\mu\text{-SBu}^t)(CO)_2\{P(OMe)_3\}_2]$ are reported, as well as the X-ray structure of the μ-methylene complex $[Ir_2(\mu\text{-pz})(\mu\text{-SBu}^t)(\mu\text{-CH}_2)I_2(CO)_2\{P(OMe)_3\}_2]$.

Results and Discussion

Addition of Methyl Iodide to $[M_2(\mu\text{-pz})(\mu\text{-SBu}^t)(CO)_2\{P(OMe)_3\}_2]$ *Complexes.*—The oxidative addition of methyl iodide to the recently reported heterobridged dinuclear complexes $[M_2(\mu\text{-pz})(\mu\text{-SBu}^t)(CO)_2\{POMe)_3\}_2]$ (M = Rh, **1**; or Ir, **2**) yields dinuclear compounds of general formulation $[M_2(\mu\text{-pz})(\mu\text{-SBu}^t)(Me)I(CO)_2\{P(OMe)_3\}_2]$ (M = Rh, **3**; or Ir, **4**). The formation of **4** in dichloromethane, at 25 °C, is essentially complete within 1 h compared with 24 h for **3**.

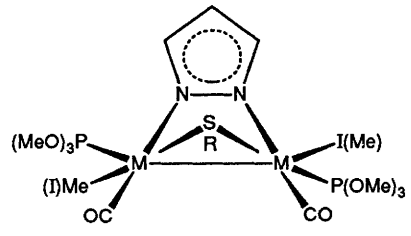


Fig. 1 Proposed structures for complexes $[M_2(\mu\text{-pz})(\mu\text{-SBu}^t)(Me)I(CO)_2\{P(OMe)_3\}_2]$ (M = Rh, **3**; or Ir, **4**)

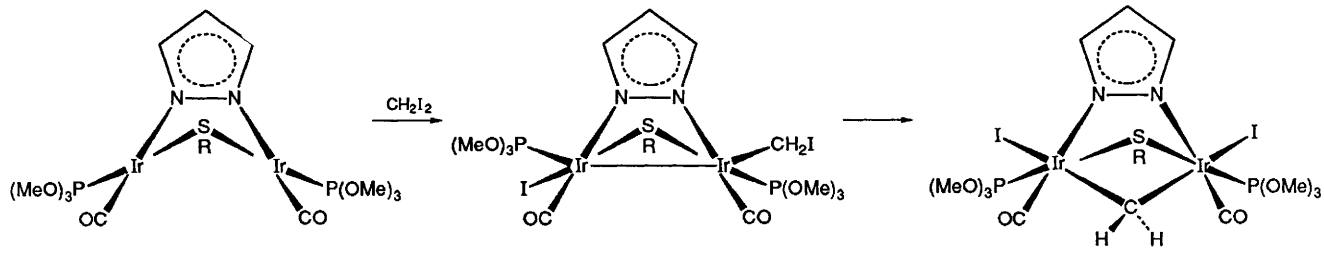
The ^1H and $^{31}P\text{-}\{^1H\}$ NMR spectra of complex **3** provide key information about its structure. The ^1H NMR spectrum which exhibits two doublets of equal intensity at δ 7.54 and 8.33 reveals the presence of distinguishable μ-pz H^3 and H^5 proton signals. The phosphite protons appears as two doublets at δ 3.63 and 3.68 with J(P–H) 11.2 Hz in both cases. The $^{31}P\text{-}\{^1H\}$ NMR spectrum contains one pair of doublets of doublets. The doublet splitting of 144 or 143 Hz is due to rhodium–phosphorus coupling, and that of 4 Hz could be assigned to phosphorus–phosphorus coupling. It is of interest that the two $^{103}Rh\text{–}^{31}P$ coupling constants have similar values, within the range described for other rhodium(II) complexes.[17] Thus, the reaction of complex **1** with methyl iodide can be interpreted as a one-electron oxidative addition at each rhodium centre and concurrent formation of a rhodium–rhodium single bond. In addition, the pair of doublets of doublets separated by 38.1 indicates that the phosphorus ligands should be *trans* to very different ligands.

Two of the possible isomeric structures for complex **3** are represented in Fig. 1.

The ^1H and $^{31}P\text{-}\{^1H\}$ NMR spectra of the iridium compound **4** are very similar to those of the rhodium complex **3**. The three protons of the pyrazolate ligand are inequivalent, so that they appear as two doublets (δ 7.58 and 8.40) and a pseudo-triplet at

† μ-*tert*-Butylthio-μ-methylene-μ-pyrazolato-κN^1:κN^2-bis[carbonyliodo(trimethyl phosphite)iridium].

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.



2 6 5

Scheme 1 R = Bu^t

δ 6.18. The protons of the phosphite ligands appear as two doublets at δ 3.54 and 3.64. The ^{31}P-{^{1}H} NMR spectrum consists of two doublets (δ 28.6 and 67.1) with 5 Hz coupling, indicative of two chemically inequivalent phosphorus ligands.

These spectroscopic data provide good evidence that complexes **3** and **4** have identical structures and the close relationship of the oxidative-addition chemistry of the heterobridged compounds [M_2(μ-pz)(μ-SBu^t)(CO)$_2${P(OMe)$_3$}$_2$] (M = Rh or Ir) with methyl iodide. In contrast, a different reactivity has been reported, under similar conditions, for the related homobridged compounds [M_2(μ-SBu^t)$_2$(CO)$_2$L$_2$] (M = Rh[18] or Ir[3]).

Addition of Diiodomethane to [Ir$_2$(μ-pz)(μ-SBu^t)(CO)$_2${P(OMe)$_3$}$_2$].—Addition of diiodomethane to [Ir$_2$(μ-pz)(μ-SBu^t)(CO)$_2${P(OMe)$_3$}$_2$], in dichloromethane solution at 25 °C, yields yellow crystalline [Ir$_2$(μ-pz)(μ-SBu^t)(μ-CH$_2$)I$_2$(CO)$_2${P(OMe)$_3$}$_2$] **5** in good yield after a reaction time of 1 h.

The ^{31}P-{^{1}H} NMR spectrum of complex **5** shows a singlet at δ 64.2 arising from a symmetrical compound. This is confirmed by the ^{1}H NMR spectrum, which shows two pyrazolate resonances [δ 6.08 (t) and 8.37 (d)] and one doublet for the methyl groups of the trimethyl phosphite ligands (δ 3.73). The spectroscopic data are in accordance with the structure found in the solid state by X-ray diffraction methods (see below).

While the preparative procedure for complex **5** was being optimized, the unsymmetrical compound [Ir$_2$(μ-pz)(μ-SBu^t)(CH$_2$I)I(CO)$_2${P(OMe)$_3$}$_2$] **6** was detected in solution. In dichloromethane, the reaction of **2** and diiodomethane at 25 °C, yields, after a reaction time of 30 min, a mixture of **5** and **6**, as evidenced by ^{31}P-{^{1}H} and ^{1}H NMR spectra. The ^{31}P-{^{1}H} NMR spectrum contains the resonance attributed to the μ-methylene complex **5** and two new doublets at δ 85.0 and 78.2 indicating an unsymmetrical structure for complex **6**. Similarly the corresponding ^{1}H NMR spectrum includes the signals of the unsymmetric complex **6**. The pyrazolate region of **6** consists of two doublets at δ 8.15 and 8.28 and one pseudo-triplet at δ 6.17. The methyl protons of the co-ordinated trimethyl phosphite ligands appear as two doublets at δ 3.61 and 3.71. The methylene resonance occurs at δ 1.27 as one singlet.

The spectroscopic data provide the basis of a consistent interpretation of the reaction involving [Ir$_2$(μ-pz)(μ-SBu^t)(CO)$_2${P(OMe)$_3$}$_2$] and diiodomethane as shown in Scheme 1: the initial product having two doublets in its ^{31}P-{^{1}H} NMR spectrum can be formulated as an iodo (iodomethyl) derivative. The peak separations of the phosphorus ligands could indicate that these ligands are *trans* to different groups. This complex [Ir$_2$(μ-pz)(μ-SBu^t)(CH$_2$I)I(CO)$_2${P(OMe)$_3$}$_2$] is thus assigned structure **6** (see Scheme 1), with a single iridium–iridium bond. The migration of the CH_2 group leads to the formation of the symmetric iridium(III)–iridium(III) complex **5**. A similar mechanism has been proposed from studies with digold[19] and diiridium complexes.[8]

Qualitative studies of oxidative-addition reactions of homobridged dinuclear complexes of pyrazolate and its methyl-substituted derivatives indicated that the processes were slowed down as the number of methyl substituents increased. So we turned our attention to the synthesis of heterobridged dinuclear complexes with dimethylpyrazolate in place of pyrazolate, in the hope that intermediate iodo(iodomethyl) species might be isolated.

Thus, the reaction of the complexes [IrCl(cod)(Hdmpz)] (cod = cycloocta-1,5-diene, Hdmpz = 3,5-dimethylpyrazole), [Ir(acac)(cod)] (acac = acetylacetonate) and KSBu^t affords the mixed-bridged compound [Ir$_2$(μ-dmpz)(μ-SBu^t)(cod)$_2$] **7**. Treatment of a dichloromethane solution of **7** with carbon monoxide at 1 atm (101 325 Pa) resulted in the formation of the carbonyl derivative [Ir$_2$(μ-dmpz)(μ-SBu^t)(CO)$_4$] but this was not isolated as a solid due to its tendency to form oils. It shows four representative ν(CO) bands at 2070, 2045, 1995 and 1990 cm^{-1}.

The room-temperature addition of trimethyl phosphite or triphenylphosphine to a dichloromethane solution of [Ir$_2$(μ-dmpz)(μ-SBu^t)(CO)$_4$] leads to the evolution of carbon monoxide and the essentially quantitative production of the complexes *cis*-[Ir$_2$(μ-dmpz)(μ-SBu^t)(CO)$_2$L$_2$] [L = P(OMe)$_3$, **8**; or PPh$_3$, **9**]. The *cis* dimeric structure of **8** and **9**, with the sulphur atom *trans* to the phosphorus-donor ligands, is assigned on the basis of the ^{31}P-{^{1}H} and ^{1}H NMR spectra, and by analogy with the rhodium complex [Rh$_2$(μ-pz)(μ-SBu^t)(CO)$_2${P(OMe)$_3$}$_2$] recently characterized by X-ray methods.[1,15]

Reaction of [Ir$_2$(μ-dmpz)(μ-SBu^t)(CO)$_2${P(OMe)$_3$}$_2$] and diiodomethane, at 25 °C, for 2 h leads to the formation of the orange microcrystalline compound [Ir$_2$(μ-dmpz)(μ-SBu^t)(CH$_2$I)I(CO)$_2${P(OMe)$_3$}$_2$] **10**. The spectroscopic properties of this compound are in agreement with its formulation as an iodo(iodomethyl) complex. In the ^{1}H NMR spectrum the two methyl groups of the pyrazolate ligand are inequivalent and occur at δ 1.96 and 2.26; the H^4 proton appears at δ 5.46. The ^{31}P-{^{1}H} NMR spectrum shows two doublets at δ 83.6 and 78.4 [J(P–P) = 9 Hz]. The spectrum is consistent with an unsymmetrical diiridium complex, and the peak separation suggests that the two phosphorus ligands are *trans* to different groups. No further oxidative isomerization of the iodo(iodomethyl) diiridium(II) compound **10** to [Ir$_2$(μ-dmpz)(μ-SBu^t)(μ-CH$_2$)I$_2$(CO)$_2${P(OMe)$_3$}$_2$] was observed even by refluxing in chloroform for 1 h.

X-Ray Structure of [Ir$_2$(μ-pz)(μ-SBu^t)(μ-CH$_2$)I$_2$(CO)$_2${P(OMe)$_3$}$_2$] **5**.—The molecular structure of this binuclear complex is shown in Fig. 2, together with the atomic numbering scheme; selected bond distances and angles are given in Table 1. In this molecule the two metal centres are maintained together by a triple bridge formed by a pyrazolate group, bound through the two N atoms, a SBu^t ligand linked through the S atom, and a methylene group coming from the added diiodomethane. The intermetallic separation is 3.2990(6) Å, excluding any but the weakest metal–metal interaction. Both iridium atoms complete their coordination spheres with three additional terminal ligands: a carbonyl group, a trimethyl phosphite and a iodine atom. Each iridium centre lies in a distorted-octahedral environment, both octahedra sharing the face S, C(1), N (from pyrazolate). The iodide ligands, one on each iridium in a

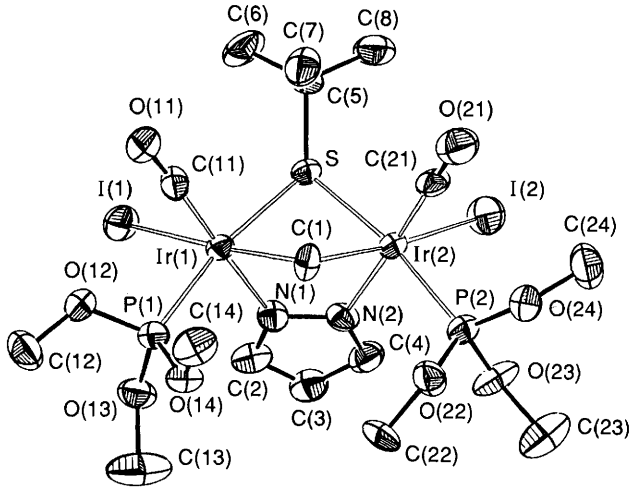


Fig. 2 View of the molecular structure of $[Ir_2(\mu\text{-pz})(\mu\text{-SBu}^t)(\mu\text{-CH}_2)\text{-}I_2(CO)_2\{P(OMe)_3\}_2]$ **5**

Table 1 Selected bond lengths (Å) and angles (°) for the complex $[Ir_2(\mu\text{-pz})(\mu\text{-SBu}^t)(\mu\text{-CH}_2)I_2(CO)_2\{P(OMe)_3\}_2]$ **5**

Ir(1)···Ir(2)	3.2990(6)		
Ir(1)–I(1)	2.8015(8)	Ir(2)–I(2)	2.7808(8)
Ir(1)–S	2.431(2)	Ir(2)–S	2.425(2)
Ir(1)–P(1)	2.263(2)	Ir(2)–P(2)	2.261(2)
Ir(1)–N(1)	2.080(6)	Ir(2)–N(2)	2.069(6)
Ir(1)–C(1)	2.109(9)	Ir(2)–C(1)	2.102(9)
Ir(1)–C(11)	1.878(9)	Ir(2)–C(21)	1.849(9)
C(11)–O(11)	1.114(12)	C(21)–O(21)	1.131(12)
N(1)–N(2)	1.373(11)	S–C(5)	1.861(10)
N(1)–C(2)	1.338(11)	C(5)–C(6)	1.538(15)
N(2)–C(4)	1.334(11)	C(5)–C(7)	1.536(12)
C(2)–C(3)	1.387(15)	C(5)–C(8)	1.536(18)
C(3)–C(4)	1.418(14)		
I(1)–Ir(1)–S	94.07(5)	I(2)–Ir(2)–S	91.15(5)
I(1)–Ir(1)–P(1)	90.98(5)	I(2)–Ir(2)–P(2)	93.87(6)
I(1)–Ir(1)–N(1)	90.7(2)	I(2)–Ir(2)–N(2)	90.9(2)
I(1)–Ir(1)–C(1)	172.3(2)	I(2)–Ir(2)–C(1)	169.8(2)
I(1)–Ir(1)–C(11)	89.2(3)	I(2)–Ir(2)–C(21)	92.2(3)
S–Ir(1)–P(1)	169.99(7)	S–Ir(2)–P(2)	171.48(6)
S–Ir(1)–N(1)	79.5(2)	S–Ir(2)–N(2)	80.1(2)
S–Ir(1)–C(1)	79.1(3)	S–Ir(2)–C(1)	79.3(2)
S–Ir(1)–C(11)	98.9(3)	S–Ir(2)–C(21)	98.4(3)
P(1)–Ir(1)–N(1)	91.8(2)	P(2)–Ir(2)–N(2)	92.9(2)
P(1)–Ir(1)–C(1)	95.3(2)	P(2)–Ir(2)–C(1)	95.2(2)
P(1)–Ir(1)–C(11)	89.8(3)	P(2)–Ir(2)–C(21)	88.3(3)
N(1)–Ir(1)–C(1)	84.6(3)	N(2)–Ir(2)–C(1)	83.9(3)
N(1)–Ir(1)–C(11)	178.4(3)	N(2)–Ir(2)–C(21)	176.6(4)
C(1)–Ir(1)–C(11)	95.4(3)	C(1)–Ir(2)–C(21)	92.9(4)
Ir(1)–S–Ir(2)	85.58(7)	Ir(1)–C(1)–Ir(2)	103.2(4)
Ir(1)–N(1)–N(2)	116.9(5)	Ir(2)–N(2)–N(1)	118.4(5)
Ir(1)–N(1)–C(2)	134.9(6)	Ir(2)–N(2)–C(4)	132.7(6)
Ir(1)–C(11)–O(11)	176.2(7)	Ir(2)–C(21)–O(21)	175.8(9)

terminal mode, are mutually *trans* to the bridging methylene. The other *trans* ligands are for both metals: phosphite to thiolate, and carbonyls to the N atoms of the bridging pyrazolate.

The whole molecule recalls the related triply heterobridged $[Ir_2(\mu\text{-pz})(\mu\text{-SBu}^t)(\mu\text{-L})I_2(CO)_2\{P(OMe)_3\}_2]$ complex[16] (L = dimethyl acetylenedicarboxylate) with formal substitution of the acetylene ligand (L) for the methylene group. Comparing these two analogous molecules, two main differences arise. First, the shorter metal–metal distance observed in **5**, 3.2990(6) Å, compared to that reported for the alkyne derivative, 3.626(2) Å, is probably due to the bonding requirements of the bridging methylene (no methylene bridge is known with an intermetallic separation longer than 3.464 Å[11]). Another variation involves the special distribution of bridging planes; whereas in $[Ir_2(\mu\text{-pz})(\mu\text{-SBu}^t)(\mu\text{-L})I_2(CO)_2\{P(OMe)_3\}_2]$ the thiolate and alkyne (L = dimethyl acetylenedicarboxylate) bridges are almost coplanar, with the pyrazolate nearly perpendicular to them,[16] in **5** the dihedral angles between bridges show similar values: Ir_2S with Ir_2C and Ir_2N_2 are 139.1(2) and 102.2(1)°, that between methylene and pyrazolate is 118.6(3)°. A comparable bridge disposition has been observed in the binuclear complex $[Ir_2(\mu\text{-pz})(\mu\text{-SBu}^t)(\mu\text{-L})(CO)_2\{P(OMe)_3\}_2]$ (L = dimethyl acetylenedicarboxylate) where a clear Ir–Ir bond is present.[16]

All the bridging ligands are bonded to the metals in a symmetrical way. The Ir–S bond distances, 2.431(2) and 2.425(2) Å, compare well with those in $[Ir_2(\mu\text{-SBu}^t)_2(\mu\text{-CH}_2)I_2(CO)_2\{P(OMe)_3\}_2]$ (average 2.43 Å),[4] although the *trans* ligands are different. As far as we know, the above-mentioned complex is the unique case previously described where a methylene bridges two non-bonded iridium atoms. The Ir–C bond length reported for this complex, average 2.107(8) Å, is identical to that observed in **5**, 2.105(9) Å. However the value of the Ir–C–Ir angle is higher in **5**, 103.2(4)°, corresponding to a longer intermetallic distance.

Interestingly, the metal–nitrogen bond distances, involving the flexible pyrazolate ligand, do not differ essentially from those in the related complexes $[Ir_2(\mu\text{-pz})(\mu\text{-SBu}^t)(\mu\text{-L})(CO)_2\text{-}\{P(OMe)_3\}_2]$ and $[Ir_2(\mu\text{-pz})(\mu\text{-SBu}^t)(\mu\text{-L})I_2(CO)_2\{P\text{-}(OMe)_3\}_2]$[16] in spite of the very different intermetallic distances, 2.614(2)–3.626(2) Å.

All the terminal ligands exhibit metal–donor atom bond distances similar to those observed in related complexes,[3,15,16] with no remarkable features.

The above-mentioned data confirm the marked flexibility of the '$Ir_2(\mu\text{-pz})(\mu\text{-SBu}^t)$' framework. These bridging ligands can straddle a wide range of intermetallic separations (2.614–3.626 Å)[16] to hold two iridium centres in oxidation state I, II or III.

Experimental

All solvents were dried, distilled, and stored under a nitrogen atmosphere. The reactants were of commercial origin and used without further purification. All the preparations were carried out under nitrogen using standard Schlenk techniques.

Elemental analyses were carried out with a Perkin-Elmer 240B microanalyser. Proton and ^{31}P NMR spectra were carried out in $CDCl_3$ solution at room temperature on a Varian XL200 spectrometer; ^{31}P chemical shifts are positive downfield from external 85% H_3PO_4 in D_2O. Infrared spectra were recorded on a Perkin-Elmer spectrophotometer with the use of Nujol mulls or in solution in NaCl cells.

The complexes $[M_2(\mu\text{-pz})(\mu\text{-SBu}^t)(CO)_2\{P(OMe)_3\}_2]$ (M = Rh, **1**; or Ir, **2**) were prepared according to literature methods.[15,16]

Preparations.—$[Rh_2(\mu\text{-pz})(\mu\text{-SBu}^t)(Me)I(CO)_2\{P(OMe)_3\}_2]$ **3**. To a solution of $[Rh_2(\mu\text{-pz})(\mu\text{-SBu}^t)(CO)_2\{P(OMe)_3\}_2]$ (0.1 g, 0.150 mmol) in dichloromethane (10 cm^3) was added methyl iodide (9.4 μl, 0.150 mmol). The mixture was stirred for 24 h, at room temperature, until the IR spectrum showed no starting material. Concentration of the solution to *ca.* 1 cm^3 followed by dilution with diethyl ether (20 cm^3) afforded a brown solid which was filtered off, washed with hexane and dried under vacuum (yield 65%) (Found: C, 23.6; H, 3.6; N, 3.2. Calc. for $C_{16}H_{33}IN_2O_8P_2Rh_2S$: C, 23.7; H, 3.7; N, 3.4%). NMR ($CDCl_3$): ^1H, δ 1.60 (s, SBu^t), 1.64 (s, CH_3), 3.63 [d, J(P–H) = 11.2, POMe], 3.68 [d, J(P–H) = 11.2], 6.22 [pt, J(H–H) = 1.9, pz],

7.54 [d, J(H–H) = 1.9, pz] and 8.33 [d, J(H–H) = 1.9 Hz, pz]; ^{31}P-{^{1}H} δ 68.3 [dd, J(Rh–P) = 144, J(P–P) = 4] and 106.4 [dd, J(Rh–P) = 143, J(P–P) = 4 Hz]. IR (CH_2Cl_2): 2070br cm^{-1} [ν(CO)].

$[Ir_2(\mu\text{-pz})(\mu\text{-SBu}^t)(Me)I(CO)_2\{P(OMe)_3\}_2]$ **4**. Methyl iodide (7.3 μl, 0.118 mmol) was added to a solution of $[Ir_2(\mu\text{-pz})(\mu\text{-SBu}^t)(CO)_2\{P(OMe)_3\}_2]$ (0.1 g, 0.118 mmol) in dichloromethane (20 cm^3). The mixture was allowed to react for 1 h, at room temperature, during which a yellow solution was formed. Then the solution was concentrated under reduced pressure to *ca.* 5 cm^3 and hexane (20 cm^3) was added to give a yellow precipitate which was filtered off, washed with hexane and dried under vacuum (yield 60%) (Found: C, 19.4, H, 3.3; N, 2.7. Calc. for $C_{16}H_{33}IIr_2N_2O_8P_2S$: C, 19.4; H, 3.4; N, 2.8%). NMR ($CDCl_3$): ^{1}H, δ 1.33 (s, CH_3), 1.60 (s, SBu^t), 3.54 [d, J(P–H) = 11.3, POMe], 3.64 [d, J(P–H) = 11.3, POMe], 6.18 [pt, J(H–H) = 2.2, pz], 7.58 [d, J(H–H) = 2.2, pz] and 8.40 [d, J(H–H) = 2.2 Hz, pz]; ^{31}P-{^{1}H}, δ 28.6 [d, J(P–P) = 5] and 67.1 [d, J(P–P) = 5 Hz]. IR (CH_2Cl_2): 2040br cm^{-1} [ν(CO)].

$[Ir_2(\mu\text{-pz})(\mu\text{-SBu}^t)(\mu\text{-}CH_2)I_2(CO)_2\{P(OMe)_3\}_2]$ **5**. The complex $[Ir_2(\mu\text{-pz})(\mu\text{-SBu}^t)(CO)_2\{P(OMe)_3\}_2]$ (0.054 g, 0.063 mmol) and diiodomethane (30.88 μl, 0.382 mmol) were stirred in dichloromethane (20 cm^3) at room temperature for 1 h. After the reaction was judged complete (IR spectroscopy), the solvent was evaporated, under reduced pressure, to 1 cm^3 and hexane (10 cm^3) was added to give a pale yellow precipitate which was filtered off, washed with hexane and dried under vacuum (yield 70%) (Found: C, 17.1; H, 2.8; N, 2.4. Calc. for $C_{16}H_{32}I_2Ir_2N_2O_8P_2S$: C, 17.3; H, 2.8; N, 2.5%). NMR ($CDCl_3$): δ 1.48 (s, SBu^t), 2.42, 2.49 (CH_2), 3.73 [d, J(P–H) = 10.7, POMe], 6.08 [t, J(H–H) = 2.2, pz] and 8.37 [d, J(H–H) = 2.2 Hz, pz]; ^{31}P-{^{1}H}, δ 64.2 (s). IR (CH_2Cl_2): 2045br cm^{-1} [ν(CO)].

Reaction of $[Ir_2(\mu\text{-pz})(\mu\text{-SBu}^t)(CO)_2\{P(OMe)_3\}_2]$ *with diiodomethane*. The reaction was carried out at room temperature. In a typical procedure, complex **2** (0.054 g, 0.063 mmol) was dissolved in $CDCl_3$ (1 cm^3) and diiodomethane (30.8 μl, 0.382 mmol) was added. The solution was placed in a nitrogen-purged NMR tube; 30 min after mixing the compound the ^{1}H NMR spectrum showed the presence of $[Ir_2(\mu\text{-pz})(\mu\text{-SBu}^t)(\mu\text{-}CH_2)I_2(CO)_2\{P(OMe)_3\}_2]$ **5** (60%) and $[Ir_2(\mu\text{-pz})(\mu\text{-SBu}^t)(CH_2I)I(CO)_2\{P(OMe)_3\}_2]$ **6** (40%).

$[Ir_2(\mu\text{-dmpz})(\mu\text{-SBu}^t)(cod)_2]$ **7**. An acetone solution (20 cm^3) of [IrCl(cod)(Hdmpz)] (0.1 g, 0.23 mmol), prepared *in situ* by treating $[Ir_2(\mu\text{-Cl})_2(cod)_2]$ (0.8 g, 0.12 mmol) with Hdmpz (0.2 g, 0.24 mmol) was added to a solution of [Ir(acac)(cod)] (0.92 g, 0.24 mmol) in acetone (15 cm^3). The mixture was allowed to react for 1 h, at room temperature, until a red suspension was formed. This suspension was treated with a methanol solution (15 cm^3) of $KSBu^t$ (0.23 mmol; prepared by treating $HSBu^t$ with potassium hydroxide). The mixture immediately became purple. After stirring for 1 h the solvent was removed *in vacuo* and the purple solid residue taken up in dichloromethane (20 cm^3) was filtered off. The filtrate was reduced to 5 cm^3, and hexane (10 cm^3) was added to precipitate a purple solid which was washed with hexane and dried under vacuum (yield 85%) (Found: C, 37.9; H, 4.3; N, 3.6. Calc. for $C_{25}H_{40}Ir_2N_2S$: C, 38.1; H, 4.1; N, 3.6%). ^{1}H NMR ($CDCl_3$): δ 1.46 (s, SBu^t), 2.04 (s, dmpz) and 5.80 (s, dmpz); two broad peaks centred at 2.16 and 4.02 (cod).

$[Ir_2(\mu\text{-dmpz})(\mu\text{-SBu}^t)(CO)_2\{P(OMe)_3\}_2]$ **8**. Carbon monoxide was bubbled through a solution of complex **7** (0.1 g, 0.127 mmol) in dichloromethane (15 cm^3) for 20 min. Trimethyl phosphite (30.1 μl, 0.254 mmol) was then added to give an orange solution with evolution of carbon monoxide. Evaporation of this solution to *ca.* 1 cm^3 and addition of hexane (10 cm^3) gave the complex as a crystalline solid which was filtered off, washed with cold hexane (3 cm^3) and vacuum dried (yield 80%) (Found: C, 23.1; H, 4.1; N, 3.4. Calc. for $C_{17}H_{34}Ir_2N_2O_8P_2S$: C, 23.4; H, 3.9; N, 3.2%). NMR ($CDCl_3$): ^{1}H, δ 1.76 (s, SBu^t), 2.19 (s, dmpz), 3.72 [d, J(P–H) = 10.9 Hz, POMe] and 5.77 (s, dmpz); ^{31}P-{^{1}H}, δ 109.1 (s). IR (CH_2Cl_2): 1980br cm^{-1} [ν(CO)].

Table 2 Final atomic coordinates ($\times 10^4$; $\times 10^5$ for Ir and I) for the non-hydrogen atoms for $[Ir_2(\mu\text{-pz})(\mu\text{-SBu}^t)(\mu\text{-}CH_2)I_2(CO)_2\{P(OMe)_3\}_2]$ **5**

Atom	*X/a*	*Y/b*	*Z/c*
Ir(1)	35 820(3)	46 793(2)	23 550(2)
Ir(2)	19 599(3)	54 867(2)	35 258(2)
I(1)	30 610(6)	35 583(4)	10 087(4)
I(2)	−4 549(6)	52 435(5)	35 237(5)
S	2 073(2)	4 130(1)	2 995(1)
P(1)	4 795(2)	5 392(1)	1 738(1)
P(2)	1 948(2)	6 812(1)	3 853(1)
O(11)	5 741(7)	3 660(5)	3 248(4)
O(12)	5 901(6)	4 849(4)	1 667(4)
O(13)	4 132(6)	5 698(4)	816(4)
O(14)	5 374(5)	6 196(4)	2 185(4)
O(21)	2 958(8)	5 177(5)	5 402(5)
O(22)	3 063(6)	7 334(4)	3 774(4)
O(23)	755(6)	7 255(4)	3 316(5)
O(24)	2 130(6)	7 019(4)	4 828(4)
N(1)	2 050(6)	5 356(4)	1 720(4)
N(2)	1 402(6)	5 706(5)	2 218(4)
C(1)	3 727(7)	5 500(5)	3 370(6)
C(2)	1 443(9)	5 494(6)	896(6)
C(3)	380(9)	5 928(6)	832(6)
C(4)	404(9)	6 052(6)	1 699(6)
C(5)	2 583(9)	3 325(6)	3 819(6)
C(6)	2 678(11)	2 556(6)	3 313(7)
C(7)	3 794(9)	3 493(7)	4 516(6)
C(8)	1 548(10)	3 236(7)	4 242(8)
C(11)	4 938(8)	4 051(6)	2 942(5)
C(12)	6 798(10)	5 145(7)	1 254(7)
C(13)	4 140(15)	6 472(9)	451(9)
C(14)	6 304(9)	6 186(6)	3 027(6)
C(21)	2 547(9)	5 272(5)	4 688(6)
C(22)	3 170(14)	7 585(8)	2 947(9)
C(23)	571(12)	8 107(7)	3 486(9)
C(24)	1 241(11)	6 832(8)	5 273(8)

$[Ir_2(\mu\text{-dmpz})(\mu\text{-SBu}^t)(CO)_2(PPh_3)_2]$ **9**. The complex was prepared by using the procedure described for **8** with complex **7** (0.1 g, 0.127 mmol), CO (15 min) and PPh_3 (0.7 g, 0.254 mmol) (yield 85%) (Found: C, 48.8; H, 4.2; N, 2.3. Calc. for $C_{47}H_{46}Ir_2N_2O_2P_2S$: C, 49.0; H, 4.0; N, 2.4%). NMR ($CDCl_3$): ^{1}H, δ 1.53 (s, SBu^t), 2.35 (s, dmpz); 5.34 (s, dmpz) and 7.35 (m, PPh); ^{31}P-{^{1}H}, δ 18.8 (s). IR (CH_2Cl_2): 1960 and 1940 cm^{-1} [ν(CO)].

$[Ir_2(\mu\text{-dmpz})(\mu\text{-SBu}^t)(CH_2I)I(CO)_2\{P(OMe)_3\}_2]$ **10**. A solution of $[Ir_2(\mu\text{-dmpz})(\mu\text{-SBu}^t)(CO)_2\{P(OMe)_3\}_2]$ **8** (0.05 g, 0.057 mmol) in acetone (20 cm^3) was treated with diiodomethane (13.84 μl, 0.171 mmol) at room temperature for 20 min to give a yellow-orange solution. Concentration of the solution to 1 cm^3 under vacuum and addition of hexane (20 cm^3) gave the complex as a microcrystalline solid (yield 70%) (Found: C, 19.5; H, 3.0; N, 2.5. Calc. for $C_{18}H_{36}I_2Ir_2N_2O_8P_2S$: C, 19.7; H, 3.2; N, 2.5%). NMR ($CDCl_3$): ^{1}H, δ 1.24 (s, CH_2), 1.75 (s, SBu^t), 1.96 (s, dmpz), 2.26 (s, dmpz), 3.71 [m, P(OMe)] and 5.46 (s, dmpz); ^{31}P-{^{1}H}, δ 83.6 [d, J(P–P) = 9] and 78.4 [d, J(P–P) = 9 Hz]. IR (CH_2Cl_2): 2035br cm^{-1} [ν(CO)].

Crystal Structure Determination of $[Ir_2(\mu\text{-pz})(\mu\text{-SBu}^t)(\mu\text{-}CH_2)I_2(CO)_2\{P(OMe)_3\}_2]$ **5**.—Crystals were obtained as transparent yellow prismatic blocks by slow diffusion of diethyl ether into a dichloromethane solution of the product at −20 °C.

Crystal data. $C_{16}H_{32}I_2Ir_2N_2O_8P_2S$, M = 1112.69, monoclinic, space group $P2_1/c$ (no. 14), a = 11.398(1), b = 16.571(2), c = 16.274(2) Å, β = 106.87(1)°, U = 2941.5(6) Å^3 (by least-squares refinement of the 2θ values of 61 accurately measured reflections in the range 20–35°), Z = 4, λ = 0.710 69 Å, D_c = 2.513 g cm^{-3}, F(000) = 2048, μ(Mo-Kα) = 112.98 cm^{-1}, approximate crystal dimensions 0.36 × 0.47 × 0.46 mm.

Data collection and processing. Four-circle Siemens AED

diffractometer, ω–2θ scan mode, graphite-monochromated Mo-Kα radiation. 8141 Reflections were measured in the range $3 \leqslant 2\theta \leqslant 45°$ ($-h$, $\pm k$, $\pm l$). Of 3824 independent reflections (R_{int} 0.048), 3546 having $I \geqslant 3\sigma(I)$ were considered observed and used in the analysis. The stability of the crystal was checked by measuring three reflections every hour, but no significant variation was observed. A correction for the absorption effects was applied, using the ψ-scan method with 14 reflections[20] (minimum and maximum transmission factors 0.0147 and 0.0579).

Structure solution and refinement. The structure was solved by standard Patterson and Fourier methods. Full-matrix least-squares refinement was carried out with anisotropic thermal parameters for all non-hydrogen atoms. In the last stage the hydrogen atoms were refined riding on the corresponding carbon atoms with a common isotropic thermal parameter, starting from found positions for the methylene and pyrazolate ligands, and from calculated positions for the remaining hydrogens. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$, with the weight defined as $w = 1.3884/[\sigma^2(F_o) + 0.0005F_o^2]$. Final R and R' values were 0.033 and 0.037. The SHELX system of computer programs was used.[21] Atomic scattering factors, corrected for anomalous dispersion, were taken from ref. 22. Final atomic coordinates for the non-hydrogen atoms are given in Table 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Acknowledgements

We thank the Dirección General de investigación Científica y Técnica (Spain) for financial support (project PB 89-0058).

References

1 J. P. Collman and L. S. Hegedus, *Principles and Applications of Organotransition Metal Complexes*, University Science Books, Mill Valley, CA, 1980.
2 W. A. Hermann, *Adv. Organomet. Chem.*, 1982, **20**, 159.
3 M. El Amane, A. Maisonnat, F. Dahan and R. Poiblanc, *New J. Chem.*, 1988, **12**, 661.
4 M. El Amane, A. Maisonnat, F. Dahan, R. Pince and R. Poiblanc, *Organometallics*, 1985, **4**, 773.
5 A. W. Coleman, D. T. Eadie, S. R. Stobart, M. J. Zaworotko and J. L. Atwood, *J. Am. Chem. Soc.*, 1982, **104**, 922.
6 R. D. Brost, D. O. K. Fjeldsted and S. R. Stobart, *J. Chem. Soc., Chem. Commun.*, 1989, 488.
7 D. G. Harrison and S. R. Stobart, *J. Chem. Soc., Chem. Commun.*, 1986, 285.
8 R. D. Brost and S. R. Stobart, *J. Chem. Soc., Chem. Commun.*, 1989, 498.
9 M. A. Ciriano, F. Viguri, L. A. Oro, A. Tiripicchio and M. Tiripicchio-Camellini, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 444.
10 M. J. Fernández, J. Modrego, F. J. Lahoz, J. A. López and L. A. Oro, *J. Chem. Soc., Dalton Trans.*, 1990, 2587.
11 R. J. Puddephatt, *Polyhedron*, 1988, **7**, 767 and refs. therein.
12 L. A. Oro, M. T. Pinillos, C. Tejel, C. Foces-Foces and F. H. Cano, *J. Chem. Soc., Dalton Trans.*, 1986, 1087.
13 F. H. Cano, C. Foces-Foces, L. A. Oro, M. T. Pinillos and C. Tejel, *Inorg. Chim. Acta*, 1987, **128**, 75.
14 M. T. Pinillos, A. Elduque and L. A. Oro, *J. Organomet. Chem.*, 1988, **338**, 411.
15 C. Claver, Ph. Kalck, M. Ridmy, A. Thorez, L. A. Oro, M. T. Pinillos, M. C. Apreda, F. H. Cano and C. Foces-Foces, *J. Chem. Soc., Dalton Trans.*, 1988, 1523.
16 M. T. Pinillos, A. Elduque, L. A. Oro, F. J. Lahoz, F. Bonati, A. Tiripicchio and M. Tiripicchio-Camellini, *J. Chem. Soc., Dalton Trans.*, 1990, 989.
17 L. A. Oro, D. Carmona, P. L. Pérez, M. Esteban, A. Tiripicchio and M. Tiripicchio-Camellini, *J. Chem. Soc., Dalton Trans.*, 1985, 973.
18 A. Mayanza, J. J. Bonnet, J. Galy, Ph. Kalck and R. Poiblanc, *J. Chem. Res.*, 1980, (*S*) 146, (*M*) 2101.
19 H. H. Murray III, J. P. Fackler, jun. and D. A. Tocher, *J. Chem. Soc., Chem. Commun.*, 1985, 1278.
20 A. C. T. North, D. C. Phillips and F. S. Mathews, *Acta Crystallogr., Sect. A*, 1968, **24**, 351.
21 G. M. Sheldrick, SHELX 76, Program for crystal structure determination, University of Cambridge, 1976.
22 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4.

Received 12*th October* 1990; *Paper* 0/04591H