A Flexible Framework obtained from Oxidative Additions upon the Binuclear Complex $[Ir_2(\mu\text{-}pz)(\mu\text{-}SBu^t)(CO)_2\{P(OMe)_3\}_2]$: Preparation and *X*-Ray Structures of $[Ir_2(\mu\text{-}pz)(\mu\text{-}SBu^t)(\mu\text{-}L)(CO)_2\{P(OMe)_3\}_2]$ and $[Ir_2(\mu\text{-}pz)(\mu\text{-}SBu^t)(\mu\text{-}L)I_2(CO)_2\{P(OMe)_3\}_2]$ (Hpz = pyrazole, L = dimethyl acetylenedicarboxylate)†

M. Teresa Pinillos, Anabel Elduque, Luis A. Oro,* Fernando J. Lahoz, and Flavio Bonati
Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-Consejo Superior de Investigaciones Científicas, 50009 Zaragoza, Spain
Antonio Tiripicchio* and Marisa Tiripicchio-Camellini
Istituto di Chimica Generale ed Inorganica, Università di Parma, Centro di Studio per la Strutturistica Diffrattometrica del C.N.R., Viale delle Scienze, 43100 Parma, Italy

The formation and properties of the heterobridged complexes $[Ir_2(\mu\text{-}pz)(\mu\text{-}SBu^t)(cod)_2]$ (**1**) (cod = cyclo-octa-1,5-diene, pz = pyrazolate) and $[Ir_2(\mu\text{-}pz)(\mu\text{-}SBu^t)(CO)_2\{P(OMe)_3\}_2]$ (**2**) are reported. Compound (**2**) undergoes stepwise addition of molecular iodine to yield the complexes $[Ir_2(\mu\text{-}pz)(\mu\text{-}SBu^t)I_n(CO)_2\{P(OMe)_3\}_2]$ [n = 2 (**3**) and 4 (**4**)]. Interaction of complex (**2**) with dimethyl acetylenedicarboxylate affords the triply heterobridged complex $[Ir_2(\mu\text{-}pz)(\mu\text{-}SBu^t)(\mu\text{-}MeO_2CC{=}CCO_2Me)(CO)_2\{P(OMe)_3\}_2]$ (**5**). Compound (**5**) undergoes a further oxidative addition with I_2 to form $[Ir_2(\mu\text{-}pz)(\mu\text{-}SBu^t)(\mu\text{-}MeO_2CC{=}CCO_2Me)I_2(CO)_2\{P(OMe)_3\}_2]$ (**6**). Compound (**6**) can be also obtained using mercury(II) iodide as oxidant, and similarly, $[Ir_2(\mu\text{-}pz)(\mu\text{-}SBu^t)(\mu\text{-}MeO_2CC{=}CCO_2Me)Cl_2(CO)_2\{P(OMe)_3\}_2]$ (**7**) using mercury(II) chloride. The structures of (**5**) and (**6**) have been determined by *X*-ray diffraction methods. Crystals of (**5**) are monoclinic, space group $P2_1/n$, with a = 18.040(7), b = 15.986(6), c = 11.085(4) Å, β = 92.68(2)°, and Z = 4. Complex (**6**) is orthorhombic, space group $P2_12_12_1$, with a = 13.522(5), b = 20.871(8), c = 12.649(7) Å, with Z = 4. Both complexes are binuclear with the metal atoms held in proximity by a triple bridge: a pyrazolate anion, a Bu^tS group and a dimethyl acetylenedicarboxylate ligand bonded as a *cis*-dimetallated olefin. The oxidative addition of I_2 to (**5**) originates a remarkable change in the Ir–Ir distance from 2.614(2) to 3.626(2) Å, leaving practically unaltered the bridging framework.

Preparation and properties of some bi- and tri-nuclear complexes containing the $M_2(\mu\text{-}az)(\mu\text{-}X)$ 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 have been previously described.[1–4] For these complexes some crystal structures (only for Rh complexes) show that the $\overline{\text{M–N–N–M–X}}$ ring is almost planar and the Rh–Rh separation about 3.82 Å.

However, this ring was shown to be bent in $[Rh_2(\mu\text{-}pz)(\mu\text{-}SBu^t)(CO)_2\{P(OMe)_3\}_2]$,[5] in which X = SBu^t, with a Rh–Rh separation of 3.4770(9) Å.

On the other hand, preparation and *X*-ray characterization of compounds containing binucleating ligands of general formulae $[Ir_2(\mu\text{-}X\text{–}C\text{–}Y)_2(ligand)_2]$, X–C–Y = 2-hydroxypyridinate,[6] 2-pyridinethiolate,[7] have attracted interest in recent times. Furthermore, oxidative addition reactions to systems containing the $Ir_2(\mu\text{-}SR)_2$[8–12] or $Ir_2(\mu\text{-}pz)_2$[13–15] moieties have been extensively studied.

In this paper, oxidative addition reactions with molecular iodine and/or $MeO_2CC{\equiv}CCO_2Me$ (L) on the mixed bridged complex $[Ir_2(\mu\text{-}pz)(\mu\text{-}SBu^t)(CO)_2\{P(OMe)_3\}_2]$ are reported. Interestingly, the *X*-ray crystal structures of two of the resulting adducts show that the triply bridged binuclear framework '$(IrZ)_2(\mu\text{-}pz)(\mu\text{-}SBu^t)(\mu\text{-}L)$' is remarkably flexible with metal-metal separations of 2.614(2) Å and 3.626(2) Å, when IrZ is $Ir^{II}(CO)\{P(OMe)_3\}$ or $Ir^{III}I(CO)\{P(OMe)_3\}$.

Results and Discussion

We have previously described the preparation of binuclear rhodium(I) complexes with mixed bridging ligands.[5] The synthetic routes can be easily extended to the preparation of Ir complexes by using [IrCl(Hpz)(cod)] and [Ir(acac)(cod)] as reagents [equation (1)].

$$[\mathrm{IrCl(Hpz)(cod)}] + [\mathrm{Ir(acac)(cod)}] \xrightarrow{-\mathrm{Hacac}} [\mathrm{Ir_2(\mu\text{-}pz)(\mu\text{-}Cl)(cod)_2}] \xrightarrow[-\mathrm{KCl}]{\mathrm{KSBu^t}} \underset{(1)}{[\mathrm{Ir_2(\mu\text{-}pz)(\mu\text{-}SBu^t)(cod)_2}]} \qquad (1)$$

The intermediate complex $[Ir_2(\mu\text{-}pz)(\mu\text{-}Cl)(cod)_2]$ shown in equation (1) has not been isolated, but its conversion into (**1**) is consistent with the indicated formulation. Complex (**1**) has been fully characterized by spectroscopic data (see Experimental section). The ^1H n.m.r. data point out the existence of two isomers, probably due to the different relative positions of the Bu^tS and pyrazolate groups.

Bubbling carbon monoxide through a dichloromethane solution of (**1**) probably gives $[Ir_2(\mu\text{-}pz)(\mu\text{-}SBu^t)(CO)_4]$ [ν(CO)-(CH_2Cl_2): 2 060, 2 040, 2 010, and 1 990 cm^{-1}] but attempts to isolate it as a solid were unsuccessful. Addition of two moles of trimethyl phosphite to this solution yields $[Ir_2(\mu\text{-}pz)(\mu\text{-}SBu^t)(CO)_2\{P(OMe)_3\}_2]$ (**2**), which could be isolated as a stable yellow microcrystalline solid. The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum of (**2**) shows a single resonance at δ 110.59 p.p.m. assigned to the equivalent $P(OMe)_3$ ligands. This suggests a *cis* configuration

---

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

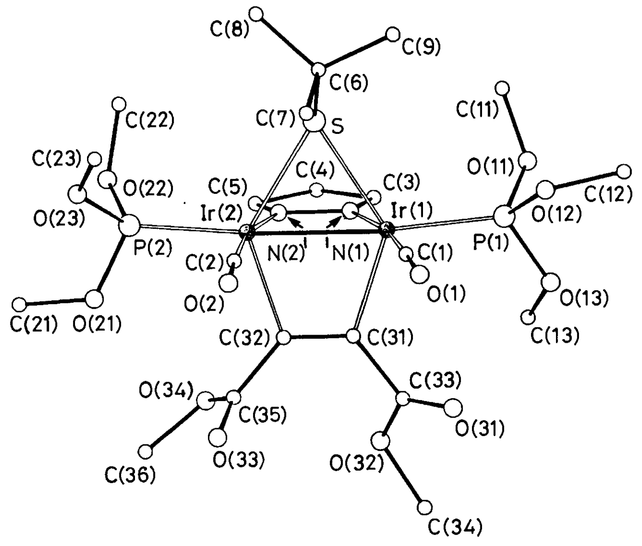

Figure 1. View of the molecular structure of $[Ir_2(\mu\text{-pz})(\mu\text{-SBu}^t)(\mu\text{-}MeO_2CC{=}CCO_2Me)(CO)_2\{P(OMe)_3\}_2]$ (**5**) with the atomic numbering scheme

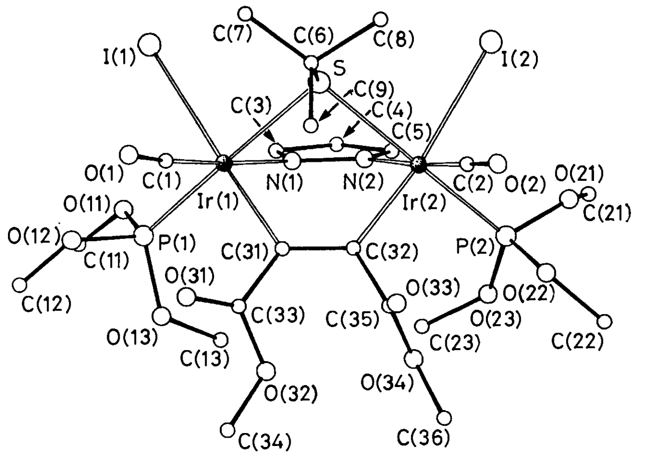

Figure 2. View of the molecular structure of $[Ir_2(\mu\text{-pz})(\mu\text{-SBu}^t)(\mu\text{-}MeO_2CC{=}CCO_2Me)I_2(CO)_2\{P(OMe)_3\}_2]$ (**6**) with the atomic numbering scheme

of the complex as observed for the related dirhodium(I) compound.[5] A similar *cis* arrangement has been also observed in $[Rh_2(\mu\text{-SPh})_2(CO)_2(L)_2]$,[16] whilst a *trans* arrangement has been found in $[Rh_2(\mu\text{-pz})_2(CO)_2\{P(OMe)_3\}_2]$.[17] The *cis* configuration observed in the heterobridged complexes, with the $P(OMe)_3$ ligands bonded to the metal centre in *trans* position relative to the sulphur atom, could be attributed to the steric influence of the t-butyl group.

Compound (**2**) undergoes stepwise addition of molecular iodine, yielding first $[Ir_2(\mu\text{-pz})(\mu\text{-SBu}^t)I_2(CO)_2\{P(OMe)_3\}_2]$ (**3**) and, then, $[Ir_2(\mu\text{-pz})(\mu\text{-SBu}^t)I_4(CO)_2\{P(OMe)_3\}_2]$ (**4**), both stable and orange coloured. The increase of the formal oxidation number from (I) to (II) and, then, to (III) is paralleled by the increase of the carbonyl stretching frequency: from 1 985, to 2 040 and 2 082 cm^{-1} respectively. The n.m.r. spectra of (**4**) show the presence of a small quantity of an isomer which has escaped isolation upon fractional crystallization.

Reaction of $[Ir_2(\mu\text{-pz})(\mu\text{-SBu}^t)(CO)_2\{P(OMe)_3\}_2]$ (**2**) with the electron-withdrawing alkyne dimethyl acetylenedicarboxylate readily forms a pale yellow complex analysed as $[Ir_2(\mu\text{-pz})(\mu\text{-SBu}^t)(\mu\text{-}MeO_2CC{=}CCO_2Me)(CO)_2\{P(OMe)_3\}_2]$ (**5**).

From its ^{31}P n.m.r. spectrum it is evident that the acetylene interacts with both iridium atoms. Two bonding modes are possible for this ligand: the pseudotetrahedral $\mu\text{-}\eta^2$ mode in which the acetylene is disposed perpendicularly to the metal–metal axis,[18] and the *cis*-dimetallated olefinic mode in which the C=C bond is parallel to the metal–metal axis.[19,20] According to ^1H n.m.r. data the –OMe groups are equivalent. This observation is only consistent with the acetylene symmetrically bound as a dimetallated olefin. This reaction implies a one electron oxidative addition to each iridium centre and formation of an iridium–iridium bond.

The results of the structure determination (see below) confirm the proposed bridging mode of the acetylene ligand.

Addition of 1 equivalent of molecular iodine to complex (**5**), in dichloromethane solution, results in the formation of the compound $[Ir_2(\mu\text{-pz})(\mu\text{-SBu}^t)(\mu\text{-}MeO_2CC{=}CCO_2Me)I_2(CO)_2\{P(OMe)_3\}_2]$ (**6**). Complex (**6**) has spectroscopic characteristics similar to those of (**5**). The ν(CO) stretching frequency is *ca.* 30 cm^{-1} higher than in the starting complex (**5**). Therefore, in this reaction, the diamagnetic iridium centres present in complex (**5**) have undergone a further oxidative addition. The *X*-ray structure of (**6**) has also been determined.

It is noteworthy that complex (**6**) cannot be obtained by reaction of (**3**) with dimethyl acetylenedicarboxylate.

An alternative route to prepare complex (**6**) was provided by the following reaction, equation (2). Oxidation of the iridium(II)

$$[Ir_2(\mu\text{-pz})(\mu\text{-SBu}^t)(\mu\text{-}MeO_2CC{=}CCO_2Me)(CO)_2\{P(OMe)_3\}_2] + 2HgI_2 \longrightarrow [Ir_2(\mu\text{-pz})(\mu\text{-SBu}^t)(\mu\text{-}MeO_2CC{=}CCO_2Me)I_2(CO)_2\{P(OMe)_3\}_2] + Hg_2I_2 \quad (2)$$

complex with mercury(II) iodide was monitored by i.r. spectroscopy. After 1 h stirring, the i.r. spectra revealed the absence of any starting material. Workup of the resulting solution, as described in the Experimental section, gave complex (**6**).

A similar complex formulated as $[Ir_2(\mu\text{-pz})(\mu\text{-SBu}^t)(\mu\text{-}MeO_2CC{=}CCO_2Me)Cl_2(CO)_2\{P(OMe)_3\}_2]$ (**7**) has been obtained by oxidation of the binuclear iridium(II) complex (**5**) with mercury(II) chloride. Attempts to synthesize complex (**7**) by reacting complex (**5**) with molecular chlorine were unsuccessful. The reaction produces a mixture of products, which we were unable to isolate in a pure form.

X-Ray Crystal Structures of $[Ir_2(\mu\text{-pz})(\mu\text{-SBu}^t)(\mu\text{-}MeO_2CC{=}CCO_2Me)(CO)_2\{P(OMe)_3\}_2]$ (**5**) *and* $[Ir_2(\mu\text{-pz})(\mu\text{-SBu}^t)(\mu\text{-}MeO_2CC{=}CCO_2Me)I_2(CO)_2\{P(OMe)_3\}_2]$ (**6**).—The structures of the two binuclear complexes (**5**) and (**6**) are shown in Figures 1 and 2 together with the atomic numbering scheme; selected bond distances and angles for them are given in Tables 1 and 2 respectively. In both complexes the two metal centres are connected by a triple bridge formed by a pyrazolate group, bound through the two N atoms, a Bu^tS ligand linked through the S atom, and a $MeO_2CC{=}CCO_2Me$ alkyne, co-ordinated through two *cis*-metallated olefinic carbons. This triple bridge results in a flexible system, allowing Ir–Ir separations of 2.614(2) in (**5**), corresponding to a single metal–metal bond, and 3.626(2) Å in (**6**), excluding any metal–metal interaction. Other common terminal ligands for both complexes are a carbonyl group and a trimethyl phosphite for each metal. In (**6**) each Ir atom is further co-ordinated by an iodine atom.

The thiolate and alkyne bridges in (**5**) are almost coplanar, the dihedral angle between the Ir_2S and Ir_2C_2 planes being 5.7°, with the pyrazolate bridge nearly perpendicular to the other two [dihedral angles formed by this bridge with the thiolate and

Table 1. Selected bond lengths (Å) and angles (°) for the complex $[\mathrm{Ir_2(\mu\text{-}pz)(\mu\text{-}SBu^t)(\mu\text{-}MeO_2CC{=}CCO_2Me)(CO)_2\{P(OMe)_3\}_2}]$ (**5**)

Ir(1)–Ir(2)	2.614(2)		
Ir(1)–N(1)	2.095(11)	Ir(2)–N(2)	2.087(11)
Ir(1)–C(31)	2.131(15)	Ir(2)–C(32)	2.148(13)
Ir(1)–S	2.471(4)	Ir(2)–S	2.459(4)
Ir(1)–P(1)	2.260(5)	Ir(2)–P(2)	2.272(5)
Ir(1)–C(1)	1.834(15)	Ir(2)–C(2)	1.856(14)
C(1)–O(1)	1.15(2)	C(2)–O(2)	1.12(2)
C(31)–C(32)	1.30(2)		
C(31)–C(33)	1.50(2)	C(32)–C(35)	1.48(2)
C(33)–O(31)	1.18(2)	C(35)–O(33)	1.19(2)
C(33)–O(32)	1.32(2)	C(35)–O(34)	1.31(2)
O(32)–C(34)	1.51(2)	O(34)–C(36)	1.50(3)
N(1)–N(2)	1.34(2)	S–C(6)	1.83(2)
N(1)–C(3)	1.35(2)	C(6)–C(7)	1.53(2)
N(2)–C(5)	1.30(2)	C(6)–C(8)	1.57(2)
C(3)–C(4)	1.36(3)	C(6)–C(9)	1.55(2)
C(4)–C(5)	1.46(3)		
P(1)–Ir(1)–Ir(2)	167.9(1)	P(2)–Ir(2)–Ir(1)	168.1(1)
P(1)–Ir(1)–N(1)	97.0(3)	P(2)–Ir(2)–N(2)	95.0(3)
P(1)–Ir(1)–C(31)	111.0(4)	P(2)–Ir(2)–C(32)	109.2(4)
P(1)–Ir(1)–S	117.3(2)	P(2)–Ir(2)–S	117.8(2)
P(1)–Ir(1)–C(1)	90.7(5)	P(2)–Ir(2)–C(2)	94.0(5)
C(1)–Ir(1)–Ir(2)	101.2(5)	C(2)–Ir(2)–Ir(1)	97.8(4)
C(1)–Ir(1)–N(1)	171.4(6)	C(2)–Ir(2)–N(2)	169.0(6)
C(1)–Ir(1)–C(31)	89.5(6)	C(2)–Ir(2)–C(32)	88.5(6)
C(1)–Ir(1)–S	103.4(5)	C(2)–Ir(2)–S	103.4(4)
N(1)–Ir(1)–Ir(2)	71.3(3)	N(2)–Ir(2)–Ir(1)	73.3(3)
N(1)–Ir(1)–C(31)	84.3(5)	N(2)–Ir(2)–C(32)	82.7(5)
N(1)–Ir(1)–S	76.3(3)	N(2)–Ir(2)–S	77.8(3)
C(31)–Ir(1)–Ir(2)	71.9(4)	C(32)–Ir(2)–Ir(1)	72.4(4)
C(31)–Ir(1)–S	129.5(4)	C(32)–Ir(2)–S	130.2(4)
S–Ir(1)–Ir(2)	57.8(1)	S–Ir(2)–Ir(1)	58.2(1)
Ir(1)–C(31)–C(32)	108.9(10)	Ir(2)–C(32)–C(31)	106.6(10)
Ir(1)–C(31)–C(33)	124.7(10)	Ir(2)–C(32)–C(35)	121.8(9)
C(32)–C(31)–C(33)	126.3(13)	C(31)–C(32)–C(35)	131.0(13)
Ir(1)–N(1)–N(2)	109.3(8)	Ir(2)–N(2)–N(1)	106.0(8)
Ir(1)–N(1)–C(3)	142.5(11)	Ir(2)–N(2)–C(5)	144.0(11)
N(2)–N(1)–C(3)	108.2(12)	N(1)–N(2)–C(5)	110.0(12)
Ir(1)–S–Ir(2)	64.0(1)	Ir(2)–S–C(6)	123.2(5)
Ir(1)–S–C(6)	119.2(5)		

Table 2. Selected bond lengths (Å) and angles (°) for the complex $[\mathrm{Ir_2(\mu\text{-}pz)(\mu\text{-}SBu^t)(\mu\text{-}MeO_2CC{=}CCO_2Me)I_2(CO)_2\{P(OMe)_3\}_2}]$ (**6**)

Ir(1) · · · Ir(2)	3.626(2)		
Ir(1)–I(1)	2.771(2)	Ir(2)–I(2)	2.758(2)
Ir(1)–I(3)	2.62(2)	Ir(2)–I(3)	2.59(2)
Ir(1)–N(1)	2.08(2)	Ir(2)–N(2)	2.04(2)
Ir(1)–C(31)	2.06(2)	Ir(2)–C(32)	2.06(2)
Ir(1)–S	2.456(13)	Ir(2)–S	2.455(13)
Ir(1)–P(1)	2.269(6)	Ir(2)–P(2)	2.294(7)
Ir(1)–C(1)	1.81(3)	Ir(2)–C(2)	1.88(3)
C(1)–O(1)	1.18(3)	C(2)–O(2)	1.13(3)
C(31)–C(32)	1.35(3)		
C(31)–C(33)	1.55(3)	C(32)–C(35)	1.49(3)
C(33)–O(31)	1.16(3)	C(35)–O(33)	1.17(3)
C(33)–O(32)	1.35(3)	C(35)–O(34)	1.33(3)
O(32)–C(34)	1.46(3)	O(34)–C(36)	1.54(3)
N(1)–N(2)	1.42(2)	S–C(6)	1.86(4)
N(1)–C(3)	1.33(3)	C(6)–C(7)	1.61(5)
N(2)–C(5)	1.39(3)	C(6)–C(8)	1.57(5)
C(3)–C(4)	1.34(3)	C(6)–C(9)	1.43(5)
C(4)–C(5)	1.33(3)		
P(1)–Ir(1)–I(1)	90.0(2)	P(2)–Ir(2)–I(2)	92.1(2)
P(1)–Ir(1)–N(1)	93.2(6)	P(2)–Ir(2)–N(2)	92.3(5)
P(1)–Ir(1)–C(31)	91.9(5)	P(2)–Ir(2)–C(32)	94.1(5)
P(1)–Ir(1)–S	174.6(4)	P(2)–Ir(2)–S	172.8(3)
P(1)–Ir(1)–C(1)	88.8(8)	P(2)–Ir(2)–C(2)	89.6(7)
C(1)–Ir(1)–I(1)	88.0(8)	C(2)–Ir(2)–I(2)	88.6(7)
C(1)–Ir(1)–N(1)	178.0(9)	C(2)–Ir(2)–N(2)	176.6(8)
C(1)–Ir(1)–C(31)	92.4(9)	C(2)–Ir(2)–C(32)	91.7(8)
C(1)–Ir(1)–S	96.6(9)	C(2)–Ir(2)–S	97.4(8)
N(1)–Ir(1)–I(1)	91.6(5)	N(2)–Ir(2)–I(2)	88.6(5)
N(1)–Ir(1)–C(31)	88.0(7)	N(2)–Ir(2)–C(32)	91.0(7)
N(1)–Ir(1)–S	81.4(6)	N(2)–Ir(2)–S	80.7(6)
C(31)–Ir(1)–I(1)	178.1(5)	C(32)–Ir(2)–I(2)	173.8(5)
C(31)–Ir(1)–S	87.9(6)	C(32)–Ir(2)–S	87.7(6)
S–Ir(1)–I(1)	90.2(3)	S–Ir(2)–I(2)	86.1(3)
Ir(1)–C(31)–C(32)	124(1)	Ir(2)–C(32)–C(31)	123(1)
Ir(1)–C(31)–C(33)	116(1)	Ir(2)–C(32)–C(35)	117(1)
C(32)–C(31)–C(33)	119(2)	C(31)–C(32)–C(35)	119(2)
Ir(1)–N(1)–N(2)	122(1)	Ir(2)–N(2)–N(1)	123(1)
Ir(1)–N(1)–C(3)	131(1)	Ir(2)–N(2)–C(5)	132(2)
N(2)–N(1)–C(3)	106(2)	N(1)–N(2)–C(5)	106(2)
Ir(1)–S–Ir(2)	95.2(5)		
Ir(1)–S–C(6)	115(1)	Ir(2)–S–C(6)	116(1)
Ir(1)–I(3)–Ir(2)	88.2(5)		

alkyne are 94.5(2) and 91.2(3)° respectively]. In contrast, in (**6**) the same dihedral angles show similar values among them: the angles formed by Ir_2S with Ir_2C_2 and Ir_2N_2 are 130.9(6) and 115.2(5), the one between the alkyne and pyrazolate 113.9(6)°.

The co-ordination around each Ir atom in (**5**), involving the S, N, and C atoms from bridges, P from the $P(OMe)_3$ ligand, C from carbonyl and the other metal, is severely distorted octahedral. Even if the metal–metal distance should be considered a metal–metal bond from the observed diamagnetism and the effective atomic number rule, this co-ordination can be better described, ignoring the metal–metal bond, as approximately trigonal bipyramidal. The S, P and one metallated C atom occupy the equatorial sites [bond angles of 111.0(4), 117.3(2) and 129.5(4)° around Ir(1), and 109.2(4), 117.8(2) and 130.2(4)° around Ir(2), with the S–Ir–C angles larger probably for better accommodation of the electron density corresponding to the metal–metal bond] and the C atom from carbonyl group and the N atom from pz in the apical positions [C–Ir(1)–N and C–Ir(2)–N angles of 171.4(6) and 169.0(6)°].

The co-ordination around each Ir atom in (**6**) is slightly distorted octahedral [all bond angles involving *cis* atoms ranging from 81.4(6) to 96.6(9)° around Ir(1), and from 80.7(6) to 97.4(8)° around Ir(2)], as all ligands are not forced to approach the metals for a metal–metal bond formation. The whole molecule can be seen as derived from (**5**) by addition of an iodine atom to each metal centre in *trans* position to the metallated carbons and subsequent readjustment of all ligands taking away the metal atoms.

All the bridging ligands in both complexes are bonded to the metals in a symmetrical way. Even if the formal oxidation state and co-ordination of the metals are different in (**5**) and (**6**), the bond distances involving the metals and the donor atoms of the ligands are comparable in both cases, excepting Ir–C(alkyne) which are slightly longer in (**5**) than in (**6**) [2.131(15) and 2.148(13) Å *vs.* 2.06(2) Å]. All these distances fall in the usual range found in Rh or Ir binuclear complexes containing pyrazolate,[14,15] Bu^{t}S,[9,10] or alkyne ligands.[15,21] This latter ligand (alkyne) could be better described in both complexes as a *cis*-dimetallated olefin as has been reported in [Rh$_2$(μ-PPh$_2$)(μ-MeO$_2$CC=CCO$_2$Me)(cod)$_2$][21] a complex structurally very similar to (**5**) and in the triply bridged Ir complexes [Ir$_2$(μ-pz)$_2$(μ-L)(cod)$_2$] (L = dimethyl acetylenedicarboxylate or methyl propiolate).[15] The C–C bond lengths of 1.30(2) and 1.35(3) Å in (**5**) and (**6**) are comparable to those found in other complexes with a *cis*-dimetallated olefin and very close to a normal double bond distance, 1.337(6) Å.[22] The geometry around C(31) and C(32) is in agreement with a *sp*^{2} hybridization as expected for a dimetallated olefin bonding mode.

In the crystal structure of (**6**) (see Experimental section) an iodine bridge disorderedly substituting the thiolate bridge has been evidenced [Ir(1)–I(3) 2.62(2), Ir(2)–I(3) 2.59(2) Å, and Ir(I)–I(3)–Ir(2) 88.2(5)°]. This bridge, when present, is practically parallel to the Ir$_2$S plane, the dihedral angle being 6.7°.

Experimental

Elemental analyses were carried out with a Perkin-Elmer 240B microanalyser. I.r. spectra were recorded on a Perkin-Elmer 783 spectrophotometer. ^{1}H and ^{31}P n.m.r. spectra were carried out in CDCl$_3$ solution at room temperature on a Varian XL 200 spectrometer. 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 complexes [IrCl(Hpz)(cod)][3] and [Ir(acac)(cod)][23] were prepared according to literature methods.

Preparation of [Ir$_2$(μ-pz)(μ-SBu^t)(cod)$_2$] (**1**).—To a solution of the species [Ir$_2$(μ-pz)(μ-Cl)(cod)$_2$] in acetone (25 cm^3) {prepared by reaction of [IrCl(Hpz)(cod)] (108 mg, 0.27 mmol) with [Ir(acac)(cod)] (107 mg, 0.27 mmol)} was added a mixture of Bu^{t}SH (33.0 μl, 0.27 mmol) and potassium hydroxide (0.27 mmol) in methanol (10 cm^3) to give a dark red solution. The reaction was continued for 2 h at room temperature to afford a purple suspension of (**1**). Then the suspension was evaporated to dryness and the residue extracted with dichloromethane (20 cm^3). Concentration of the filtrate to 2 cm^3 and addition of hexane (20 cm^3) gave complex (**1**) which was filtered off, washed with cold hexane and vacuum dried (yield 81%) (Found: C, 36.5; H, 4.8; N, 3.9. Calc. for $C_{23}H_{36}Ir_2N_2S$: C, 36.5; H, 4.8; N, 3.7%). ^{1}H N.m.r. (CDCl$_3$): major species δ 1.11 (s, SBu^t), 3.25(br) and 4.01 (br, cod), 6.4 (t, pz, $^3J_{HH}$ 2.3) and 7.41 (d, pz, $^3J_{HH}$ 2.3); minor species δ 1.44 (s, SBu^t), 3.50(br) and 4.44(br, cod), 6.2 (t, pz, $^3J_{HH}$ 2.3), and 7.52 (d, pz, $^3J_{HH}$ 2.3 Hz).

Preparation of [Ir$_2$(μ-pz)(μ-SBu^t)(CO)$_2${P(OMe)$_3$}$_2$] (**2**).—Carbon monoxide was bubbled through a solution of (**1**) (100 mg, 0.13 mmol) in dichloromethane (15 cm^3) for 30 min, to give an orange solution probably of the tetracarbonyl complex [Ir$_2$(μ-pz)(μ-SBu^t)(CO)$_4$][i.r.(CH$_2$Cl$_2$): 2 060, 2 040, 2 010, 1 990 cm^{-1}]. Addition of trimethyl phosphite (32 μl, 0.26 mmol) caused evolution of carbon monoxide, and the colour of the solution changed to yellow. After 15 min of stirring, at room temperature, the solvent was evaporated to dryness and the residue crystallized from hexane (20 cm^3) at −20 °C to afford a yellow microcrystalline solid (**2**) (yield 80%) (Found: C, 21.2; H, 3.4; N, 3.2. Calc. for $C_{15}H_{30}Ir_2N_2O_8P_2S$: C, 21.3; H, 3.6; N, 3.3%). I.r. (CH$_2$Cl$_2$): 1 985(br) cm^{-1} [ν(CO)]. ^{1}H N.m.r. (CDCl$_3$): δ 1.62 (s, SBu^t), 3.64 [d, P(OMe)$_3$, $^3J_{HP}$ 12.2], 6.09 (t, pz, $^3J_{HH}$ 2.3), and 7.52 (d, pz, $^3J_{HH}$ 2.3 Hz). ^{31}P-{^{1}H} N.m.r. (80 MHz, CDCl$_3$): δ 110.59(s) p.p.m.

Preparation of [Ir$_2$(μ-pz)(μ-SBu^t)I$_2$(CO)$_2${P(OMe)$_3$}$_2$] (**3**).—To a solution of [Ir$_2$(μ-pz)(μ-SBu^t)(CO)$_2${P(OMe)$_3$}$_2$] (100 mg, 0.12 mmol) in dichloromethane (20 cm^3) was added the stoicheiometric amount of iodine (30 mg, 0.12 mmol); the colour of the solution changed from yellow to orange. The progress of the reaction was followed by i.r. spectra. After 30 min stirring the solvent was evaporated off 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 80%) (Found: C, 16.1; H, 2.5: N, 2.5. Calc. for $C_{15}H_{30}I_2Ir_2N_2O_8P_2S$: C, 16.4; H, 2.7; N, 2.5%). I.r. (CH$_2$Cl$_2$): 2 040(br) cm^{-1} [ν(CO)]. ^{1}H N.m.r. (CDCl$_3$): δ 1.65 (s, SBu^t), 3.73 [d, P(OMe)$_3$, $^3J_{HP}$ 11.1], 6.16 (t, pz, $^3J_{HH}$ 1.7), and 7.53 (d, pz, $^3J_{HH}$ 1.7 Hz). ^{31}P-{^{1}H} N.m.r. (80 MHz, CDCl$_3$): δ 78.46(s) p.p.m.

Preparation of [Ir$_2$(μ-pz)(μ-SBu^t)I$_4$(CO)$_2${P(OMe)$_3$}$_2$] (**4**).—Iodine (60 mg, 0.24 mmol) was added to a solution of [Ir$_2$(μ-pz)(μ-SBu^t)(CO)$_2${P(OMe)$_3$}$_2$] (100 mg, 0.12 mmol) in dichloromethane (15 cm^3). After stirring for 1 h the initial compound (**2**) was consumed. The orange solution was concentrated under reduced pressure to 2 cm^3, and hexane (30 cm^3) was added to give an orange precipitate that was filtered off, washed with hexane and dried under vacuum (yield 80%) (Found: C, 13.4; H, 2.2: N, 2.0. Calc. for $C_{15}H_{30}I_4Ir_2N_2O_8P_2S$: C, 13.3; H, 2.2; N, 2.1%). I.r. (CH$_2$Cl$_2$): 2 082(br) cm^{-1} [ν(CO)]. Major species ^{1}H n.m.r. (CDCl$_3$): δ 1.78 (s, SBu^t), 3.96 [d, P(OMe)$_3$, $^3J_{HP}$ 11.1], 6.39 (t, pz, $^3J_{HH}$ 2.3), and 8.3 (d, pz, $^3J_{HH}$ 2.3). ^{31}P-{^{1}H} N.m.r. (CDCl$_3$): δ 56.77(s). Minor species ^{1}H n.m.r. (CDCl$_3$): δ 1.74 (s, SBu^t), 3.73 [d, P(OMe$_3$), $^3J_{HP}$ 11.1], 6.12 (t, pz, $^3J_{HH}$ 2.3), and 8.21 (d, pz, $^3J_{HH}$ 2.3 Hz). ^{31}P-{^{1}H} N.m.r. (CDCl$_3$): δ 55.34(s) p.p.m.

Preparation of [Ir$_2$(μ-pz)(μ-SBu^t)(μ-MeO$_2$CC=CCO$_2$Me)(CO)$_2${P(OMe)$_3$}$_2$] (**5**).—Dimethyl acetylenedicarboxylate (15 μl, 0.12 mmol) was added to a solution of [Ir$_2$(μ-pz)(μ-SBu^t)(CO)$_2${P(OMe)$_3$}$_2$] (100 mg, 0.12 mmol) in dichloromethane (20 cm^3). The solution was stirred at room temperature for 30 min. During that period the solution lightened to pale yellow. Evaporation of the solvent to 2 cm^3 and addition of hexane (30 cm^3) gave a pale yellow solid which was isolated by filtration, washed with hexane and dried under vacuum (yield 70%) (Found: C, 24.9; H, 3.5: N, 2.9. Calc. for $C_{21}H_{36}Ir_2N_2O_{12}P_2S$: C, 25.5; H, 3.7; N, 2.8%). I.r. (CH$_2$Cl$_2$): 2 040(br) cm^{-1} [ν(CO)]. ^{1}H N.m.r. (CDCl$_3$): δ 1.40(s, SBu^t), 3.71 [s, C$_2$(CO$_2$Me)$_2$], 3.77 [t, P(OMe)$_3$, $^3J_{HP}$ 6.2], 5.69 (t, pz, $^3J_{HH}$ 1.5), and 6.91 (d, pz, $^3J_{HH}$ 1.5 Hz). ^{31}P-{^{1}H} N.m.r. (CDCl$_3$): δ 94.19(s) p.p.m.

Preparation of [Ir$_2$(μ-pz)(μ-SBu^t)(μ-MeO$_2$CC=CCO$_2$Me)I$_2$(CO)$_2${P(OMe)$_3$}$_2$] (**6**).—*Method* (*a*). Iodine (26 mg, 0.10 mmol) was added to a solution of [Ir$_2$(μ-pz)(μ-SBu^t)(μ-MeO$_2$CC=CCO$_2$Me)(CO)$_2${P(OMe)$_3$}$_2$] (**5**) (100 mg, 0.10 mmol) in dichloromethane (20 cm^3); the resulting yellow solution was stirred at room temperature. After 30 min, the i.r. spectra revealed the absence of starting material. Addition of hexane (25 cm^3) to the concentrated solution (1 cm^3) gave a yellow solid, which was filtered off, washed with hexane and vacuum dried (yield 80%) (Found: C, 19.5; H, 3.0; N, 2.1. Calc. for $C_{21}H_{36}I_2Ir_2N_2O_{12}P_2S$: C, 20.3; H, 2.9; N, 2.3%). I.r. (CH$_2$Cl$_2$): 2 070(br) cm^{-1} [ν(CO)]. ^{1}H N.m.r. (CDCl$_3$): δ 1.663 (s, SBu^t), 3.69 [s, C$_2$(CO$_2$CH$_3$)$_2$], 3.73 [d, P(OMe)$_3$, $^3J_{HP}$ 11.3], 6.16 (t, pz, $^3J_{HH}$ 2.3), and 8.24 (d, pz, $^3J_{HH}$ 2.3 Hz). ^{31}P-{^{1}H} N.m.r. (CDCl$_3$): δ 59.9 (s) p.p.m.

Method (*b*).—Solid mercury(II) iodide (92 mg, 0.20 mmol) was added to a solution of [Ir$_2$(μ-pz)(μ-SBu^t)(μ-MeO$_2$CC=CCO$_2$Me)(CO)$_2${P(OMe)$_3$}$_2$] (**5**) (100 mg, 0.10 mmol) in dichloromethane (20 cm^3). The colour of the solution intensified and a yellow precipitate of mercury(I) iodide was formed. After completion of the reaction (monitored by i.r.) the resulting suspension was filtered off through Kieselguhr to remove the mercury(I) iodide. The filtrate was evaporated under vacuum and crystallized from hexane to provide yellow crystalline solid (**6**) (yield 70%).

Preparation of $[Ir_2(\mu\text{-pz})(\mu\text{-SBu}^t)(\mu\text{-MeO}_2CC{\equiv}CCO_2Me)Cl_2(CO)_2\{P(OMe)_3\}_2]$ (**7**).—A solution of $[Ir_2(\mu\text{-pz})(\mu\text{-SBu}^t)(\mu\text{-MeO}_2CC{\equiv}CCO_2Me)(CO)_2\{P(OMe)_3\}_2]$ (**5**) (100 mg, 0.10 mmol) in dichloromethane (20 cm^3) was allowed to react with mercury(II) chloride (55 mg, 0.20 mmol). After 1 h the initial compound (**5**) was consumed. 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 (30 cm^3) gave a pale yellow solid which was isolated by filtration, washed with hexane and dried under vacuum (yield 75%) (Found: C, 23.6; H, 3.2; N, 2.5. Calc. for $C_{21}H_{36}Cl_2Ir_2N_2O_{12}P_2S$: C, 23.8; H, 3.4; N, 2.6%). I.r. (CH_2Cl_2): 2 080(br) cm^{-1} [ν(CO)]. ^{1}H N.m.r. ($CDCl_3$): δ 1.59 (s, SBu^t), 3.67 (s, $C_2(CO_2CH_3)_2$), 3.75 [d, P(OMe)$_3$, $^3J_{HP}$ 11.4], 6.20 (t, pz, $^3J_{HH}$ 2.2), and 8.91(d, pz, $^3J_{HH}$ 2.2 Hz). ^{31}P-{^{1}H} N.m.r. ($CDCl_3$): δ 62.5(s) p.p.m.

Table 3. Experimental data for the *X*-ray diffraction study on (**5**) and (**6**)*

Complex	(**5**)	(**6**)
Molecular formula	$C_{21}H_{36}Ir_2N_2O_{12}P_2S$	$C_{21}H_{36}I_2Ir_2N_2O_{12}P_2S$
M	986.97	1240.78
Crystal system	monoclinic	orthorhombic
Space group	$P2_1/n$	$P2_12_12_1$
a/Å	18.040(7)	13.522(5)
b/Å	15.986(6)	20.871(8)
c/Å	11.085(4)	12.649(7)
β/°	92.68(2)	
U/Å^3	3 193(2)	3 570(3)
Z	4	4
D_c/g cm^{-3}	2.053	2.309
F(000)	1 888	2 312
Crystal dimensions/ mm	0.20 × 0.22 × 0.30	0.25 × 0.28 × 0.35
μ/cm^{-1}	85.12	93.29
2θ range °	6—50	6—46
Reflections measured	$\pm h, k, l$	h, k, l
Unique total data	5 478	2 837
Unique observed data [$I > 2\sigma(I)$]	3 682	2 123
R	0.0441	0.0359
R'	0.0671	0.0462

* Common to both: Mo-K_α radiation, graphite monochromatized (λ = 0.710 73 Å); Philips PW-1100 diffractometer; scan type ω—2θ; one standard reflection per 50 reflections.

Crystal Structure Determinations of Complexes (**5**) *and* (**6**).—The crystallographic data are summarized in Table 3. Unit cell parameters were determined from the θ values of 25 carefully centred reflections, having $10 \leqslant \theta \leqslant 17°$ for both compounds. Data were collected at room temperature, the individual profiles having been analysed according to Lehmann and Larsen.[24] A semiempirical correction for absorption was applied [max. and min. values for the transmission factors were 1.177 and 1.000 for (**5**) and 1.482 and 1.000 for (**6**)].[25]

Both structures were solved by standard 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 of (**5**) excepting oxygen and carbon atoms of the methoxy groups. After isotropic refinement of (**6**) a very low thermal parameter for the S atom and high thermal parameters for the carbon atoms of the t-butyl group were observed, together with the presence of three peaks in the difference Fourier map, each equivalent to about 3 e Å^{-3}, and very close to the S atom. After anisotropic refinement for all the non-hydrogen atoms excepting those of the Bu^{t}S and the carbons of the phosphite and the carboxylate groups, some disorder models for the thiolate group were taken into account in order to explain the anomalous results obtained. Keeping in mind the chemical preparation of (**6**) (oxidative addition of I_2), a disordered bridge was considered involving one iodine atom and the sulphur of the thiolate group. The new refinement with the iodine, I(3), and the atoms of the SBu^t group having an occupancy factor as variable parameter, not only decreased the R value from 0.0403 to 0.0363, but gave quite normal isotropic thermal parameters for all the atoms involved in the bridge [occupancy factor 0.177(8) for I(3), and 0.823(8) for the atoms of the SBu^t group]. In order to have a confirmation of this proposed disorder the structure of another crystal from a different preparation was undertaken and the obtained results were analogous [occupancy factor for I(3) found to be 0.213(5)]. Moreover the elemental analysis found for C and I in the

Table 4. Final atomic co-ordinates (× 10^4) for $[Ir_2(\mu\text{-pz})(\mu\text{-SBu}^t)(\mu\text{-MeO}_2CC{\equiv}CCO_2Me)(CO)_2\{P(OMe)_3\}_2]$ (**5**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ir(1)	5 815(1)	2 577(1)	2 559(1)	C(8)	6 564(13)	−455(10)	2 860(19)
Ir(2)	6 496(1)	1 923(1)	755(1)	C(9)	6 031(11)	420(13)	4 586(15)
S	5 933(2)	1 049(2)	2 292(3)	C(31)	6 126(7)	3 568(9)	1 400(13)
P(1)	5 009(2)	3 031(3)	3 916(4)	C(32)	6 429(8)	3 249(8)	458(12)
P(2)	6 846(2)	1 288(3)	−962(4)	C(33)	6 038(7)	4 483(8)	1 671(13)
O(1)	7 088(7)	3 067(8)	4 225(11)	C(34)	5 755(11)	5 812(9)	830(19)
O(2)	8 037(6)	2 227(8)	1 726(13)	C(35)	6 782(10)	3 655(8)	−569(14)
O(31)	6 145(7)	4 793(7)	2 628(10)	C(36)	6 802(16)	3 868(16)	−2 644(19)
O(32)	5 835(6)	4 878(6)	665(10)	O(11)	4 196(8)	2 618(8)	3 899(12)
O(33)	7 387(7)	3 961(9)	−525(11)	O(12)	5 342(10)	2 885(11)	5 277(15)
O(34)	6 371(7)	3 618(8)	−1 575(10)	O(13)	4 725(8)	3 994(10)	3 897(14)
N(1)	5 027(6)	2 302(7)	1 168(11)	O(21)	7 084(7)	1 924(8)	−1 963(12)
N(2)	5 371(6)	1 973(7)	228(11)	O(22)	6 229(7)	759(8)	−1 674(11)
C(1)	6 602(8)	2 839(9)	3 597(14)	O(23)	7 513(7)	644(9)	−900(12)
C(2)	7 462(8)	2 073(9)	1 366(12)	C(11)	4 139(13)	1 716(15)	3 981(20)
C(3)	4 293(8)	2 341(10)	871(16)	C(12)	4 888(16)	3 074(19)	6 349(27)
C(4)	4 151(10)	2 028(12)	−258(19)	C(13)	4 369(18)	4 323(22)	2 781(30)
C(5)	4 890(9)	1 826(10)	−662(15)	C(21)	7 272(13)	1 640(15)	−3 171(21)
C(6)	6 478(9)	443(10)	3 421(14)	C(22)	5 950(15)	11(18)	−1 133(25)
C(7)	7 261(8)	779(11)	3 713(16)	C(23)	7 869(12)	291(14)	119(21)

Table 5. Final atomic co-ordinates (× 10^4) for $[Ir_2(\mu\text{-pz})(\mu\text{-SBu}^t)(\mu\text{-MeO}_2CC{=}CCO_2Me)I_2(CO)_2\{P(OMe)_3\}_2]$ (**6**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ir(1)	4 999(1)	5 994(1)	288(1)	C(3)	2 832(19)	5 574(9)	758(18)
Ir(2)	4 649(1)	6 357(1)	3 067(1)	C(4)	2 175(19)	5 535(11)	1 549(17)
I(1)	4 946(1)	4 749(1)	−470(1)	C(5)	2 588(20)	5 787(11)	2 404(20)
I(2)	4 383(2)	5 349(1)	4 450(1)	C(31)	5 052(17)	6 907(7)	901(15)
P(1)	4 279(5)	6 346(3)	−1 224(5)	C(32)	4 948(16)	7 045(7)	1 941(14)
P(2)	3 568(5)	6 994(3)	3 987(5)	I(3)*	5 838(12)	5 607(8)	2 048(15)
O(1)	6 969(15)	6 099(8)	−775(15)	S*	5 622(10)	5 605(5)	1 996(11)
O(2)	6 281(15)	6 819(9)	4 493(15)	C(6)*	6 984(25)	5 661(16)	2 157(26)
O(11)	3 399(14)	5 916(8)	−1 568(12)	C(7)*	7 425(32)	5 106(18)	1 409(31)
O(12)	5 004(17)	6 379(8)	−2 161(13)	C(8)*	7 106(28)	5 462(16)	3 349(27)
O(13)	3 850(14)	7 058(7)	−1 242(12)	C(9)*	7 372(25)	6 296(15)	2 044(27)
O(21)	3 048(12)	6 708(9)	4 954(14)	C(11)	2 678(24)	5 991(14)	−2 420(23)
O(22)	4 181(13)	7 525(8)	4 601(14)	C(12)	4 949(38)	6 654(24)	−3 139(37)
O(23)	2 702(14)	7 327(9)	3 436(11)	C(13)	3 000(23)	7 212(13)	−616(24)
O(31)	6 111(12)	7 345(7)	−446(14)	C(21)	2 016(22)	6 526(13)	5 020(21)
O(32)	4 944(15)	7 970(6)	280(12)	C(22)	3 733(23)	8 007(13)	5 215(23)
O(33)	6 052(13)	7 845(8)	2 562(14)	C(23)	2 513(22)	7 439(13)	2 303(21)
O(34)	4 465(13)	8 078(7)	2 440(12)	C(33)	5 476(17)	7 431(9)	156(16)
N(1)	3 653(15)	5 876(7)	1 054(13)	C(34)	5 327(23)	8 491(13)	−356(22)
N(2)	3 544(13)	5 986(8)	2 154(13)	C(35)	5 244(17)	7 692(10)	2 337(16)
C(1)	6 194(20)	6 081(11)	−343(21)	C(36)	4 783(23)	8 766(12)	2 722(21)
C(2)	5 688(21)	6 649(10)	3 934(19)				

* An occupancy factor was refined for this atom (see Experimental section).

with those calculated for the disordered compound (19.54 and 22.15) than for the undisordered compound (20.33 and 20.46%).

In independent cycles of refinement the co-ordinates $-x$, $-y$, $-z$ were used for all the atoms because of the acentric space group. The obtained *R* value worsened remarkably so that the former model was maintained and the reported data refer to it.

In the last cycles of refinement a weighting scheme was used, $w = K/[\sigma^2(F_0) + gF_0{}^2]$, with $K = 0.6108$ and $g = 0.0064$ for (**5**) and, $K = 0.7170$ and $g = 0.0028$ for (**6**). The hydrogen atoms in both complexes (**5**) and (**6**) were placed at their calculated positions and introduced in the final structure factor calculations. The SHELX system of computer programs was used.[26] Atomic scattering factors, corrected for anomalous dispersion, were taken from ref. 27. All calculations were performed on the CRAY X-MP/12 computer of the Centro di Calcolo Elettronico Interuniversitario dell' Italia Nord-Orientale, Bologna. Final atomic co-ordinates for the non-hydrogen atoms of (**5**) and (**6**) are given in Tables 4 and 5 respectively.

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

Acknowledgements

We thank the Consejo Superior de Investigaciones Cientificas–Consiglio Nazionale delle Ricerche agreement for financial support (project 1987/88 no. 8). F. B. thanks the University of Camerino for leave.

References

1 L. A. Oro, M. T. Pinillos, C. Tejel, C. Foces-Foces, and F. H. Cano, *J. Chem. Soc., Chem. Commun.*, 1984, 1687.
2 L. A. Oro, M. T. Pinillos, C. Tejel, C. Foces-Foces, and F. H. Cano, *J. Chem. Soc., Dalton Trans.*, 1986, 1087.
3 F. H. Cano, C. Foces-Foces, L. A. Oro, M. T. Pinillos, and C. Tejel, *Inorg. Chim. Acta*, 1987, **128**, 75.
4 L. A. Oro, M. T. Pinillos, C. Tejel, M. C. Apreda, C. Foces-Foces, and F. H. Cano, *J. Chem. Soc., Dalton Trans.*, 1988, 1927.
5 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.
6 G. R. Rodman and K. R. Mann, *Inorg. Chem.*, 1985, **24**, 3507.
7 M. A. Ciriano, F. Viguri, L. A. Oro, A. Tiripicchio, and M. Tiripicchio-Camellini, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 444; M. A. Ciriano, F. Viguri, J. J. Pérez-Torrente, F. J. Lahoz, L. A. Oro, A. Tiripicchio, and M. Tiripicchio-Camellini, *J. Chem., Soc., Dalton Trans.*, 1989, 25.
8 R. Poilblanc, *Inorg. Chim. Acta*, 1982, **62**, 75.
9 J. J. Bonnet, Ph. Kalck, and R. Poilblanc, *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 551; Ph. Kalck and J. J. Bonnet, *Organometallics*, 1982, **1**, 1211.
10 M. El Amane, A. Maisonnat, F. Dahan, R. Pince, and R. Poilblanc, *Organometallics*, 1985, **4**, 773.
11 M. El Amane, R. Mathieu, and R. Poilblanc, *Nouv. J. Chim.*, 1982, **6**, 191.
12 A. Maisonnat, J. J. Bonnet, and R. Poilblanc, *Inorg. Chem.*, 1980, **19**, 3168.
13 K. A. Beveridge, G. W. Bushnell, K. R. Dixon, D. T. Eadie, and S. R. Stobart, *J. Am. Chem. Soc.*, 1982, **104**, 920; A. W. Coleman, D. T. Eadie, S. R. Stobart, M. J. Zaworotko, and J. L. Atwood, *ibid.*, p. 922; G. W. Bushnell, D. O. Kim Fjeldsted, S. R. Stobart, and M. J. Zaworotko, *J. Chem. Soc., Chem. Commun.*, 1983, 580.
14 J. L. Atwood, K. A. Beveridge, G. W. Bushnell, K. R. Dixon, D. T. Eadie, S. R. Stobart, and M. J. Zaworotko, *Inorg. Chem.*, 1984, **23**, 4050.
15 G. W. Bushnell, M. J. Decker, D. T. Eadie, S. R. Stobart, R. Vefghi, J. L. Atwood, and M. J. Zaworotko, *Organometallics*, 1985, **4**, 2106.
16 J. J. Bonnet, Ph. Kalck, and R. Poilblanc, *Inorg. Chem.*, 1977, **16**, 1514.
17 R. Usón, L. A. Oro, M. A. Ciriano, M. T. Pinillos, A. Tiripicchio and M. Tiripicchio-Camellini, *J. Organomet. Chem.*, 1981, **205**, 247.
18 F. A. Cotton, J. D. Jamerson, and B. R. Stults, *J. Am. Chem. Soc.*, 1976, **98**, 1774.
19 M. Cowie and T. G. Southern, *Inorg. Chem.*, 1982, **21**, 246.
20 J. T. Mague, *Organometallics*, 1986, **5**, 918.
21 T. S. Targos, G. L. Geoffroy and A. L. Rheingold, *Organometallics*, 1986, **5**, 12.
22 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 3, Table 4.2.2.
23 S. B. Robinson and B. L. Shaw, *J. Chem. Soc.*, 1965, 4997.
24 M. S. Lehmann and F. K. Larsen, *Acta Crystallogr., Sect. A*, 1974, **30**, 580.
25 A. C. T. North, D. C. Phillips, and F. C. Mathews, *Acta Crystallogr., Sect. A*, 1968, **24**, 354.
26 G. M. Sheldrick, SHELX Program for crystal structure determination, University of Cambridge, 1976.
27 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.

Received 12*th April* 1989; *Paper* 9/01518C