Synthesis and Characterization of the Alkoxycarbonyl Complexes $[(C_5Me_5)M(\mu\text{-pz})(\mu\text{-I})_2RhI(CO_2R)(CO)]$ (M = Rh, R = Me or Et; M = Ir, R = Me; pz = pyrazolate). Molecular Structure of $[(C_5Me_5)Ir(\mu\text{-pz})(\mu\text{-I})_2RhI(CO_2Me)(CO)]$†

Daniel Carmona, Fernando J. Lahoz, and Luis A. Oro*
Departamento de Quimica Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-Consejo Superior de Investigaciones Científicas, 50009 Zaragoza, Spain
Josefa Reyes
Departamento de Química Inorgánica, Centro Politécnico Superior de Ingenieros Industriales, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza, 50009 Zaragoza, Spain
Mª Pilar Lamata
Departamento de Química Inorgánica, Escuela Universitaria Superior de Ingenieria Técnica Industrial, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza, Corona de Aragón 35, 50009 Zaragoza, Spain

The alkoxycarbonyl complexes $[(C_5Me_5)M(\mu\text{-pz})(\mu\text{-I})_2RhI(CO_2R)(CO)]$ [M = Rh, R = Me, (**4**), or Et, (**5**); M = Ir, R = Me, (**6**); pz = pyrazolate] were prepared by treating the corresponding dicarbonyl complex $[(C_5Me_5)ClM(\mu\text{-pz})_2Rh(CO)_2]$ [M = Rh, (**1**), or Ir, (**3**)] with molecular iodine in methanol [(**4**), (**6**)] or ethanol [(**5**)] and in the presence of sodium salts (*i.e.* $NaBPh_4$, $NaI{\cdot}2H_2O$). The molecular structure of compound (**6**) was determined by *X*-ray diffraction: monoclinic space group *C*2/*c* with $a = 28.574(3)$, $b = 8.688(1)$, $c = 19.321(2)$ Å, $\beta = 96.44(1)°$, and $Z = 8$. The structure was refined to $R = 0.037$ for 2 789 observed reflections [$F \geqslant 5.0\sigma(F)$] and 236 parameters. The complex is dinuclear with the two metals, bridged by two iodides and a pyrazolate ligand. The rhodium exhibits distorted-octahedral co-ordination involving three terminal ligands: an iodide, a carbonyl, and a methoxycarbonyl group formed during the preparative reaction.

We have recently prepared the dinuclear complexes $[(C_5Me_5)XM(\mu\text{-pz})_2Rh(CO)_2]$ [M = Rh, X = Cl, (**1**);[1] or I, (**2**);[2] M = Ir, X = Cl, (**3**);[2] pz = pyrazolate], in which a saturated d^6 rhodium(III) or iridium(III) centre is connected by two pyrazolate groups to a $Rh^I(CO)_2$ entity. These dicarbonyl compounds react with tertiary diphosphines or diarsines (L–L) to yield cationic complexes of stoicheiometry $[(C_5Me_5)M(\mu\text{-pz})_2(\mu\text{-CO})Rh(L\text{–}L)]^+$, *via.* the intermediates $[(C_5Me_5)M(\mu\text{-pz})_2(\mu\text{-CO})Rh(CO)(L\text{–}L)]^+$. These reactions have to be accomplished in the presence of an halogen scavenger (*i.e.* sodium or silver salts).[2–4] We consider of interest the oxidative-addition reactions of complexes (**1**)—(**3**) owing to the potential catalytic activity of the rhodium(I) centre. Preliminary studies show that the addition of halogens or alkyl halides to these compounds affords complex mixtures of products which we have not been able to separate and characterize. However, in the presence of sodium salts, clean formation of the alkoxycarbonyl complexes $[(C_5Me_5)M(\mu\text{-pz})(\mu\text{-I})_2RhI(CO_2R)(CO)]$ [M = Rh, R = Me, (**4**), or Et, (**5**); M = Ir, R = Me, (**6**)] by oxidative addition of iodine to complexes (**1**) and (**3**) in methanol or ethanol was observed. This reaction is the main subject of this paper.

Alkoxycarbonyl complexes are intermediates in synthetically and catalytically important processes[5] and are, usually, prepared by nucleophilic addition of alkoxide anions to metal carbonyl compounds.[6] Reaction of alcohols with metal carbonyls is a less common synthetic route to alkoxycarbonyl complexes. Due to the weak nucleophilicity of the alcohols the route is restricted to strongly activated metal carbonyl compounds.[7,8] Frequently, a proton acceptor, such as NEt_3, is needed to shift this latter reaction towards the products.[8]

We now report the synthesis and characterization of the new alkoxycarbonyl complexes (**4**)—(**6**), as well as the molecular structure determination of complex (**6**).

Results and Discussion

Reaction of $[(C_5Me_5)ClM(\mu\text{-pz})_2Rh(CO)_2]$ [M = Rh, (**1**), or Ir, (**3**)] with excess of iodine in methanol or ethanol and in the presence of 1 equivalent of $NaBPh_4$ or $NaI{\cdot}2H_2O$ gave dark solutions from which dark red solids slowly precipitate. These solids were characterized as the alkoxycarbonyl complexes $[(C_5Me_5)M(\mu\text{-pz})(\mu\text{-I})_2RhI(CO_2R)(CO)]$ [M = Rh, R = Me, (**4**), or Et (**5**); M = Ir, R = Me, (**6**)] by elemental analysis, i.r., ^1H n.m.r., and ^{13}C n.m.r. [complex (**4**)] spectroscopies and by the determination of the molecular structure of compound (**6**) by diffractometric methods (see below). The i.r. spectra show one terminal ν(C≡O) band (2 085—2 070 cm^{-1}) and two strong absorptions in the 1 710—1 690 and 1 065—1 045 cm^{-1} regions, which are attributed to ν(C=O) and ν(C–O) of an alkoxycarbonyl group, respectively. The frequencies of the ν(C≡O) bands are higher than that found for the related bis(alkoxycarbonyl) complex of rhodium(III) $[Rh(C_5Me_5)(CO_2Me)_2(CO)]$.[8a] The ν(C=O) absorptions of the alkoxycarbonyl ligand

---

† Carbonyl-2κ*C*-di-μ-iodo-iodo-2κ*I*-methoxycarbonyl-2κ*C*-1(η^5)-pentamethylcyclopentadienyl-μ-pyrazolato-1:2κ^2N^1 : N^2-iridiumrhodium.

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

Table 1. Relevant i.r. bands[a] and ^{1}H n.m.r. data[b] for complexes (**4**)—(**6**)

				^{1}H N.m.r.				
	I.r. (cm^{-1})					pz		
Complex	ν(C≡O)	ν(C=O)	ν(C–O)	C_5Me_5	OMe	H^4	$H^{3/5}$	$H^{5/3}$
(**4**) [$(C_5Me_5)Rh(\mu\text{-pz})(\mu\text{-I})_2RhI(CO_2Me)(CO)$]	2 085	1 690	1 055	1.97 (s)	3.75 (s)	6.22 (t) $^3J_{HH}$ = 2.2	7.64 (d)	8.38 (d)
(**5**) [$(C_5Me_5)Rh(\mu\text{-pz})(\mu\text{-I})_2RhI(CO_2Et)(CO)$]	2 070	1 690	1 045	1.96 (s)	1.25 (t)[c] 4.24 (dq)[d] $^3J_{HH}$ = 7.1 $^3J_{RhH}$ = 3.4	6.20 (*t*) $^3J_{HH}$ = 2.2	7.63 (d)	8.36 (d)
(**6**) [$(C_5Me_5)Ir(\mu\text{-pz})(\mu\text{-I})_2RhI(CO_2Me)(CO)$]	2 075	1 710	1 060	1.89 (s)	3.76 (s)	6.17 (t) $^3J_{HH}$ = 2.2	7.67 (d)	8.46 (d)

[a] In Nujol mulls. [b] Measured in $CDCl_3$ at room temperature; chemical shifts relative to $SiMe_4$ as external standard; *J* in Hz. Abbreviations: s = singlet, d = doublet, t = triplet, and q = quartet. [c] OCH_2CH_3. [d] OCH_2CH_3.

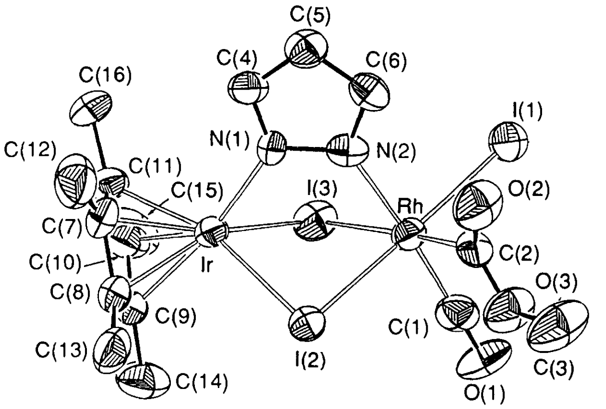

Figure. ORTEP drawing of complex (**6**) showing the atomic numbering

for complexes (**4**) and (**5**) (1 690 cm^{-1}) fall in the upper range of observed ν(C=O) frequencies for alkoxycarbonyl complexes (1 580—1 703 cm^{-1})[6,7a,b] and for complex (**6**) (1 710 cm^{-1}) is slightly higher than the usual values reported. These values are indicative of a low d_π–p_π back bonding from the metal and are congruent with oxidation of the rhodium during the reaction.

Besides the expected resonances for the co-ordinated C_5Me_5 and pz ligands, which indicated that the product contained one pz group per C_5Me_5 ligand, the ^{1}H n.m.r. spectra of complexes (**4**)—(**6**) show the presence of a singlet at δ 3.75 for (**4**) and 3.76 for (**6**) assigned to methoxy groups and a doublet of quartets and a triplet centred at δ 4.24 and 1.25 respectively, for (**5**) attributed to an ethoxy group (Table 1).

The presence of the methoxy group in complex (**4**) was confirmed by ^{13}C n.m.r. spectroscopy. The ^{13}C-{^{1}H} spectrum enables possible structures which contained ketonic carbonyl groups[9] to be ruled out since the two low-field resonances at 174.0 and 182.0 p.p.m. split into doublets by ^{103}Rh–^{13}C coupling. In the ^{13}C (^{1}H-coupled) n.m.r. spectrum the signal at 174.0 p.p.m. is additionally split into quartets ($^3J_{HC}$ = 4.2 Hz) and, consequently, we assign this resonance to the carbonyl group of the methoxycarbonyl ligand.

There are several dinuclear geometries which account for the spectral data depending on the terminal (on the iridium or on the rhodium) or the bridging position of the iodide ligands, as well as on the relative disposition of the ligands around the rhodium. Therefore, a stucture determination of compound (**6**) was undertaken.

The geometry of the molecule is shown in the Figure and the bond distances and angles in Table 2. Crystals of (**6**) consist of discrete molecules of the heterodinuclear complex with a bridging pyrazolate group accompanied by two bridging iodide ligands. The metal–metal separation 3.604(1) Å excludes any significant intermetallic interaction. The pseudo-octahedral co-ordination of the iridium atom is completed by an η^5-co-ordinated C_5Me_5 group. The separation between the iridium and the centroid of the cyclopentadienyl ring is 1.773(6) Å while the Ir–C(ring) distances range from 2.132(11) to 2.187(12) Å. These values compare well with those reported.[10–12] The methyl substituents are bent away from the iridium atom; displacements for C(12), C(13), C(14), C(15), and C(16) are 0.13(2), 0.04(1), 0.10(2), 0.15(2), and 0.16(2) Å, respectively.

The octahedral co-ordination around the rhodium atom is completed by an iodine [I(1)] *trans* to the bridging iodine ligand I(2) [I(1)–Rh–I(2) 177.3(1)°] and the carbon atoms of the carbonyl and methoxycarbonyl ligands *trans* to the N(2) atom of the bridging pyrazolate ligand [N(2)–Rh–C(1) 175.6(5)°] and the other bridging iodine I(3) [I(3)–Rh–C(2) 175.7(3)°], respectively.

The methoxycarbonyl-metal group Rh–C(2)–O(2)–O(3) is essentially planar. The least-squares plane through these atoms makes a dihedral angle of 78.3(5)° with the co-ordination plane defined by I(1), I(2), I(3), and C(2). The metal–carbon bond length of the methoxycarbonyl ligand, 2.088(11) Å, is longer than those found in the bis(methoxycarbonyl)rhodium(III) compound [$Rh(C_5Me_5)(CO_2Me)_2(CO)$], 2.041(5) Å,[8c] and in the iridium(III) complex [$IrH(CO_2Me)\{Ph_2P(CH_2)_2SEt\}_2$]$BPh_4$, 2.01(2) Å,[7e] and comparable with those reported for the iridium(III) methoxycarbonyl complexes [$IrI_2(CO_2Me)(CO)(bipy)$] (bipy = 2,2′-bipyridine)[13] and [$IrCl(CO_2Me)(dmpe)_2$]SFO_3 (dmpe = $Me_2PCH_2CH_2PMe_2$),[14] 2.05(2) and 2.073(8) Å, respectively. The relatively large metal–carbon bond in (**6**) along with the short C(2)–O(2) bond distance, 1.145(15) Å,[6] and the high ν(C=O) frequency (see above) indicate a very low d_π–p_π interaction in the methoxycarbonylrhodium group.[13,15]

The Rh–C(2)–O(2) angle of 122.1(9)° is very close to the expected for an ideal sp^2 hybridization of the carbon and lies at the lower end of the range of values found for other methoxycarbonyl transition-metal derivatives (124—133°).[6,7e,8e,16]

The distances Ir–I(2) 2.722(1) Å and Ir–I(3) 2.737(1) Å are comparable to those found for the Ir–I(bridging) distances in the pentamethylcyclopentadienyl iridium dimer [$\{IrI(C_5Me_5)\}_2(\mu\text{-I})_2$] [average 2.710(4) Å].[17] There are two different Rh–I distances: the bridging Rh–I(3) distance [2.816(1) Å] and the other bridging Rh–I(2) and the terminal Rh–I(1) distances, 2.646(1) and 2.654(1) Å, respectively. The latter bond distances compare well with the values of 2.648(1) and 2.630(1) Å found

Table 2. Selected bond lengths (Å) and angles (°) for the complex $[(C_5Me_5)Ir(\mu\text{-pz})(\mu\text{-I})_2RhI(CO_2Me)(CO)]$ (**6**)*

Ir–N(1)	2.095(8)	Rh–N(2)	2.081(9)
Ir–N(2)	2.722(1)	Rh–I(2)	2.646(1)
Ir–I(3)	2.737(1)	Rh–I(3)	2.816(1)
Ir–C(7)	2.155(13)	Rh–I(1)	2.654(1)
Ir–C(8)	2.187(12)	Rh–C(1)	1.885(15)
Ir–C(9)	2.139(12)	Rh–C(2)	2.088(11)
Ir–C(10)	2.132(11)	Ir••• Rh	3.604(1)
Ir–C(11)	2.152(12)	G*••• Ir	1.773(6)
N(1)–N(2)	1.363(13)	C(1)–O(1)	1.115(18)
N(1)–C(4)	1.318(15)	C(2)–O(2)	1.145(15)
N(2)–C(6)	1.318(16)	C(2)–O(3)	1.276(15)
C(4)–C(5)	1.379(18)	C(3)–O(3)	1.447(19)
C(5)–C(6)	1.407(17)		
C(7)–C(8)	1.426(19)	C(7)–C(12)	1.504(20)
C(8)–C(9)	1.439(18)	C(8)–C(13)	1.480(16)
C(9)–C(10)	1.447(16)	C(9)–C(14)	1.502(21)
C(10)–C(11)	1.429(21)	C(10)–C(15)	1.487(20)
C(7)–C(11)	1.445(18)	C(11)–C(16)	1.489(19)
G*–Ir–N(1)	133.7(3)	N(1)–Ir–I(2)	84.5(2)
G*–Ir–I(2)	125.2(2)	N(1)–Ir–I(3)	84.4(2)
G*–Ir–I(3)	127.2(2)	I(2)–Ir–I(3)	86.1(1)
N(2)–Rh–I(3)	85.2(3)	I(3)–Rh–I(2)	86.0(1)
N(2)–Rh–I(2)	85.2(3)	I(3)–Rh–C(1)	92.1(4)
N(2)–Rh–C(1)	175.6(5)	I(3)–Rh–C(2)	175.7(3)
N(2)–Rh–C(2)	93.7(4)	I(3)–Rh–I(1)	95.2(1)
N(2)–Rh–I(1)	92.4(3)	C(1)–Rh–C(2)	88.8(5)
I(2)–Rh–C(1)	91.1(4)	C(1)–Rh–I(1)	91.4(4)
I(2)–Rh–C(2)	89.8(3)	C(2)–Rh–I(1)	89.0(3)
I(2)–Rh–I(1)	177.3(1)		
N(2)–N(1)–C(4)	107.8(8)	Ir–N(1)–N(2)	123.3(7)
N(1)–N(2)–C(6)	108.9(9)	Ir–N(1)–C(4)	128.9(7)
N(1)–C(4)–C(5)	110.6(10)	Rh–N(2)–N(1)	121.5(7)
C(4)–C(5)–C(6)	103.8(11)	Rh–N(2)–C(6)	129.6(8)
N(2)–C(6)–C(5)	109.0(11)		
Rh–C(2)–O(2)	122.1(9)	Ir–I(2)–Rh	84.3(1)
Rh–C(2)–O(3)	109.9(8)	Ir–I(3)–Rh	80.9(1)
O(2)–C(2)–O(3)	128.0(12)		
C(2)–O(3)–C(3)	113.9(11)		

G* represents the centroid of the η^5-pentamethylcyclopentadienyl ligand.

for the bridging Rh–I distances and of 2.647(1) Å for one of the terminal Rh–I distances in the dinuclear complex $[(\eta^5\text{-}C_5Me_5)Rh(\mu\text{-I})(\mu\text{-dppy})Rh_2I_2(CO)]$[dppy = 2-(diphenylphosphino)pyridine].[18] The Rh–I(1) and Rh–I(2) bond distances in complex (**6**) are also comparable with the two terminal Ir–I values of 2.672(2) and 2.684(2) Å reported for the mononuclear iridium(III) complex $[IrI_2(CO_2Me)(CO)(bipy)]$,[13] in which the iodide ligands are mutually *trans* to each other, as are I(1) and I(2) in complex (**6**). The bridging Rh–I(3) length, 2.816(1) Å, compares well with the values of 2.865 and 2.851 Å reported for the bridging Rh–I distances in the trinuclear cluster $[Rh_3\{\mu\text{-PPh}(CH_2PPh_2)_2\}_2(CO)_3I_2]^+$,[19] and with one of the terminal Rh–I bond distances in the dirhodium compound $[(C_5Me_5)Rh(\mu\text{-I})(\mu\text{-dppy})RhI_2(CO)]$, 2.812(1) Å.[18] The difference between the bridging Rh–I distances in complex (**6**) indicates a stronger structural *trans* effect of the methoxycarbonyl group[6] as compared to the iodide ligand.

The structural features of the terminal carbonyl group and of the bridging pyrazolate ligand are normal, the Ir–N(1) and Rh–N(2) bond distances of 2.095(8) and 2.081(9) Å being comparable with those found in other pyrazolate-bridged iridium(III)[20] and rhodium(III)[1,3,21] compounds.

There are three possible geometrical isomers for compounds (**4**)—(**6**) (all are chiral and give rise to three enantiomeric pairs) depending on the terminal group which is *trans* to the N(2) atom in the rhodium environment. The one in which the carbonyl ligand is *trans* to the N(2) atom corresponds to the stereochemistry actually determined from the present structural study for complex (**6**).

Complex (**4**) could also be prepared by treating in methanol the iodide complex $[(C_5Me_5)IRh(\mu\text{-pz})_2Rh(CO)_2]$ (**2**) with stoicheiometric amounts of iodine, although in lower yield (44%). It was also obtained by treating the chloride complex $[(C_5Me_5)ClRh(\mu\text{-pz})_2Rh(CO)_2]$ (**1**) in methanol with equimolar amounts of iodine. In this case complex (**4**) was contaminated by another structurally related compound most probably the monochloride di-iodide $[(C_5Me_5)Rh(\mu\text{-pz})RhClI_2(CO_2Me)]$ [^1H n.m.r. (200 MHz; solvent $CDCl_3$, standard $SiMe_4$): δ 1.83 (15 H, s, C_5Me_5), 3.72 (3 H, s, OMe), 6.29 (1 H, br s, H^4 of pz), 7.74 (1 H, br s, $H^{3/5}$ of pz), and 8.30 (1 H, br s, $H^{5/3}$ of pz)].

The formation of alkoxycarbonyl complexes starting from the dicarbonyl complexes $[(C_5Me_5)ClM(\mu\text{-pz})_2M'(CO)_2]$ through the aforementioned route was found to be critically dependent on the nature of the metal M′ and of the alcohol. Thus in the reaction of $[(C_5Me_5)ClM(\mu\text{-pz})_2Ir(CO)_2]$ [M = Rh, (**7**) or Ir, (**8**)][2] with excess of iodine, in methanol, in the presence of sodium salts the only characterized products were the pentamethylcyclopentadienyl iodide dimers $[\{MI(C_5Me_5)\}_2(\mu\text{-I})_2]$ (M = Rh[22] or Ir[23]). Reaction of the dirhodium complex $[(C_5Me_5)ClRh(\mu\text{-pz})_2Rh(CO)_2]$ (**1**) with iodine and $NaI{\cdot}2H_2O$ in n-propanol, Pr^iOH, or phenol gives $[\{RhI(C_5Me_5)\}_2(\mu\text{-I})_2]$ among other unidentified products.

On the other hand, we have attempted the reactions of (**1**) with Br_2, MeI, and CH_2I_2 in methanol. On monitoring the reaction by i.r. spectroscopy, the disappearance of the ν(CO) bands of the starting material and formation of one new ν(CO) band at *ca.* 2 050 cm^{-1} were observed. The residue obtained was shown to be a mixture of inseparable compounds.

In summary, the alkoxycarbonyl complexes (**4**)—(**6**) were formed by nucleophilic attack of methanol [(**4**), (**6**)] or ethanol [(**5**)] on the dinuclear carbonyl rhodium compounds (**1**)—(**3**) previously oxidized by iodine [complexes (**1**)—(**3**) are indefinitely stable in alcohols]. The reaction is not general; thus, dinuclear complexes related to (**1**)—(**3**), but with iridium carbonyl moieties, under the same conditions, exhibit decomposition reactions leading to $[\{MI(C_5Me_5)\}_2(\mu\text{-I})_2]$ among other unidentified products. On the other hand, complex (**1**), under the same conditions, is not susceptible to nucleophilic attack by other alcohols such as n-propanol, Pr^iOH, or phenol.

Experimental

Infrared spectra were recorded on a Perkin-Elmer 577 spectrophotometer (range 4 000—200 cm^{-1}) using Nujol mulls between polyethylene sheets, or dichloromethane solutions between NaCl plates. The C, H, and N analyses were carried out with a Perkin-Elmer 240B microanalyzer. Carbon-13 and ^1H n.m.r. spectra were recorded on a Varian XL200 spectrometer [50.3 (^{13}C) and 200.0 (^1H) MHz]. Solvents were dried and distilled before use.

Preparation of Complexes $[(C_5Me_5)M(\mu\text{-pz})(\mu\text{-I})_2RhI(CO_2R)(CO)]$ [M = Rh, R = Me, (**4**), or Et, (**5**); M = Ir, R = Me, (**6**)].—To a suspension of the corresponding complex $[(C_5Me_5)ClM(\mu\text{-pz})_2Rh(CO)_2]$ (0.50 mmol) in ROH (10 cm^3) was added the NaA salt (A = I^- or BPh_4^-) (0.55 mmol) and I_2 (2.50 mmol) in ROH (10 cm^3). The reaction mixture was stirred for 20 h. During this time a red solid precipitated which was filtered off, washed with ROH, and air-dried. The complexes were recrystallized from dichloromethane–hexane. Complex (**4**)

Table 3. Fractional atomic co-ordinates ($\times 10^4$) for the non-hydrogen atoms of the complex [(C_5Me_5)Ir(μ-pz)(μ-I)$_2$RhI(CO_2Me)(CO)] (**6**)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Ir*	11 565(1)	9 281(5)	47 543(2)
I(1)*	6 904(3)	39 274(10)	72 122(5)
I(2)*	19 264(2)	21 092(10)	55 321(4)
I(3)*	6 914(3)	34 972(10)	51 303(5)
Rh*	13 093(3)	30 839(10)	63 576(4)
N(1)	990(3)	41(11)	5 705(4)
N(2)	1 068(3)	822(11)	6 319(5)
C(1)	1 539(4)	5 113(18)	6 321(7)
C(2)	1 801(4)	2 688(13)	7 223(6)
C(3)	2 453(6)	3 617(20)	7 883(9)
C(4)	825(4)	−1 330(13)	5 840(6)
C(5)	793(4)	−1 491(14)	6 543(7)
C(6)	955(4)	−71(14)	6 826(6)
C(7)	1 232(5)	−1 125(15)	4 151(7)
C(8)	1 578(4)	−45(15)	3 984(6)
C(9)	1 339(4)	1 333(16)	3 726(6)
C(10)	839(4)	1 040(19)	3 703(6)
C(11)	770(4)	−470(17)	3 967(6)
C(12)	1 346(6)	−2 753(17)	4 375(8)
C(13)	2 095(4)	−261(17)	4 076(7)
C(14)	1 564(5)	2 723(18)	3 440(8)
C(15)	457(5)	2 072(21)	3 391(8)
C(16)	306(5)	−1 254(18)	3 960(8)
O(1)	1 671(3)	6 312(11)	6 276(6)
O(2)	1 785(3)	1 621(12)	7 567(5)
O(3)	2 095(3)	3 797(12)	7 297(5)

* Co-ordinates $\times 10^5$.

(Found: C, 21.8; H, 2.5; N, 3.0. $C_{16}H_{21}I_3N_2O_3Rh_2$ requires C, 21.9; H, 2.4; N, 3.2%). Yield 86%. ^{13}C N.m.r. [(H coupled), $CDCl_3$, 25 °C, $SiMe_4$]: δ 182.0 (d, $^1J_{RhC} = 55.2$, CO), 174.0 (dq, $^1J_{RhC} = 31.9$, $^3J_{HC} = 4.2$, *C*O_2Me), 145.1 (dt, $^1J_{HC} = 189.6$, $^2J_{RhC} \approx {}^2J_{HC} = 6.7$, $C^{3/5}$ of pz), 138.8 (dt, $^1J_{HC} = 180.5$, $^2J_{RhC} \approx {}^3J_{HC} = 7.6$, $C^{5/3}$ of pz), 106.8 (dt, $^1J_{HC} = 176.3$, $^3J_{HC} = 8.4$, C^4 of pz), 96.2 (d, $^1J_{RhC} = 8.0$, C_5Me_5) 56.0 (q, $^1J_{HC} = 147.2$, OMe), and 10.9 p.p.m. (q, $^1J_{HC} = 129.6$ Hz, C_5Me_5). Complex (**5**) (Found: C, 22.9; H, 2.3; N, 3.1. $C_{17}H_{23}I_3N_2O_3Rh_2$ requires C, 22.9; H, 2.6; N, 3.2%). Yield 70%. Complex (**6**) (Found: C, 19.9; H, 2.2; N, 2.8; $C_{16}H_{21}I_3IrN_2O_3Rh$, requires C, 19.9; H, 2.2; N, 2.9%). Yield 75%.

Complex (**4**) was also obtained starting from [(C_5Me_5)IRh(μ-pz)$_2$Rh(CO)$_2$] (**2**) (197.5 mg, 0.30 mmol) and I_2 (76.1 mg, 0.30 mmol) in MeOH. Yield 44%.

Reaction of the Complexes [(C_5Me_5)ClM(μ-pz)$_2$Ir(CO)$_2$] [M = Rh, (**7**), *or* Ir, (**8**)] *with* I_2 *and Sodium Salts.*—To a solution of I_2 (0.80 mmol) and NaA (A = I^- or BPh_4^-) (0.13 mmol) in MeOH was added a suspension of the corresponding complex [(C_5Me_5)ClM(μ-pz)$_2$Ir(CO)$_2$] (0.11 mmol) in MeOH. After stirring for 15 h the precipitate formed was identified as the corresponding iodide complex [{MI(C_5Me_5)}$_2$(μ-I)$_2$] by microanalyses and by comparison of the spectroscopic properties with those previously reported.[22,23]

Reaction of the Complex [(C_5Me_5)ClRh(μ-pz)$_2$Rh(CO)$_2$] *with* I_2 *and Sodium Salts in* ROH (R = Pr^i, Pr^n, *or* Ph).—To a suspension of the complex [(C_5Me_5)ClRh(μ-pz)$_2$Rh(CO)$_2$] (0.35 mmol) in the corresponding ROH was added NaA (A = I^- or BPh_4^-) (0.37 mmol), in the same solvent. After stirring for 20 min a solution of I_2 (1.75 mmol) in ROH was added. The mixture was stirred for 24 h. The precipitated solid was identified as the rhodium(III) iodide complex [{RhI(C_5Me_5)}$_2$(μ-I)$_2$].[22]

X-Ray Structural Determination of the Complex [(C_5Me_5)Ir(μ-pz)(μ-I)$_2$RhI(CO_2Me)(CO)] (**6**).—*Crystal data* $C_{16}H_{21}I_3IrN_2O_3Rh$, *M* = 965.19, monoclinic, space group *C*2/*c*, *a* = 28.574(3), *b* = 8.688(1), *c* = 19.321(2) Å, β = 96.44(1)°, *U* = 4 766.2(9) Å^3 (refined from 54 centred reflections, $20 \leqslant 2\theta \leqslant 32°$), Mo-$K_\alpha$ radiation (λ = 0.710 69 Å), *Z* = 8, D_c = 2.690 g cm^{-3}, crystal dimensions 0.491 × 0.291 × 0.091 mm, *F*(000) = 3 488.

Data collection and processing. Four-circle Siemens AED diffractometer. Data collected at room temperature, ω—2θ scan ($3 \leqslant 2\theta \leqslant 46°$). 7 140 Data measured giving 2 789 unique with $F \geqslant 5\sigma(F)$ used for structure solution and refinement. An empirical absorption correction (μ = 101.05 cm^{-1}) was applied (minimum and maximum values for the absorption correction factors 0.729 and 1.779).[24]

Solution and refinement of the structure. The structure was solved by direct methods (Rh, Ir, and I atoms) and refined by full-matrix least squares for 236 parameters. All remaining atoms of the molecule were located in Fourier difference maps, except hydrogen atoms of the methyl groups. The hydrogen atoms were placed at their calculated positions and introduced in the final structure-factor calculations. The maximum peak in the final Δ*F* had 1.43 e Å^{-3} close to I(1). The final *R* and *R′* values were 0.037 and 0.041 respectively. Weighting scheme $w = 2.0599/[\sigma^2(F_o) + 0.000\,518F_o^2]$. The SHELX system of computer programs was used.[25] Atomic scattering factors, corrected for anomalous dispersion, were taken from ref. 26. Final atomic co-ordinates for the non-hydrogen atoms are given in Table 3.

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

Acknowledgements

We thank the Dirección General de Investigación Cientifica y Técnica for financial support (Grant 87-0289).

References

1 L. A. Oro, D. Carmona, J. Reyes, C. Foces-Foces, and F. H. Cano, *J. Chem. Soc., Dalton Trans.*, 1986, 31.
2 D. Carmona, J. Ferrer, F. J. Lahoz, L. A. Oro, J. Reyes, and M. Esteban, unpublished work.
3 L. A. Oro, D. Carmona, J. Reyes, C. Foces-Foces, and F. H. Cano, *Inorg. Chim. Acta*, 1986, **112**, 35.
4 L. A. Oro, D. Carmona, and J. Reyes, *J. Organomet. Chem.*, 1986, **302**, 417.
5 I. Wender and P. Pino (Editor), 'Organic Synthesis *via* Metal Carbonyls,' Wiley, New York, 1977, vol. 2; G. W. Parshall, 'Homogeneous Catalysis,' Wiley-Interscience, New York, 1980.
6 P. C. Ford and A. Rikicki, *Adv. Organomet. Chem.*, 1988, **28**, 139.
7 (*a*) H. C. Clark, K. R. Dixon, and W. J. Jacobs, *J. Am. Chem. Soc.*, 1969, **91**, 1346; (*b*) S. D. Ibekwe and K. A. Taylor, *J. Chem. Soc. A*, 1970, 1; (*c*) H. Kurosawa, *Inorg. Chem.*, 1975, **14**, 2148; (*d*) D. L. Thorn, *Organometallics*, 1982, **1**, 197; (*e*) A. del Zotto, A. Mezzetti, G. Dolcetti, P. Rigo, and N. B. Pahor, *J. Chem. Soc., Dalton Trans.*, 1989, 607; (*f*) M. A. Esteruelas, L. A. Oro, R. M. Claramunt, C. López, J. L. Lavandera, and J. Elguero, *J. Organomet. Chem.*, 1989, **366**, 245.
8 (*a*) J. E. Byrd and J. Halpern, *J. Am. Chem. Soc.*, 1971, **93**, 1643; (*b*) M. Wada and K. Oguro, *Inorg. Chem.*, 1976, **15**, 2346; (*c*) P. L. Burk, D. van Engen, and K. S. Campo, *Organometallics*, 1984, **3**, 493; (*d*) M. A. Lilga and J. A. Ibers, *ibid.*, 1985, **4**, 590; (*e*) H. Werner, L. Hofmann, and R. Zolk, *Chem. Ber.*, 1987, **120**, 379.
9 M. Cowie and S. K. Dwight, *Inorg. Chem.*, 1980, **19**, 2500.
10 P. M. Maitlis, *Chem. Soc. Rev.*, 1981, **10**, 1.
11 S. L. Grundy, A. J. Smith, H. Adams, and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, 1984, 1747.
12 L. A. Oro, D. Carmona, M. P. Puebla, M. P. Lamata, C. Foces-Foces, and F. H. Cano, *Inorg. Chim. Acta*, 1986, **112**, L11.

13 V. G. Albano, P. L. Bellon, and M. Sansoni, *Inorg. Chem.*, 1969, **8**, 298.
14 R. L. Harlow, J. B. Kinney, and T. Kerskovitz, *J. Chem. Soc., Chem. Commun.*, 1980, 813.
15 L. Garlaschelli, M. C. Malatesta, S. Martinengo, F. Demartin, M. Manassero, and M. Sansoni, *J. Chem. Soc., Dalton Trans.*, 1986, 777.
16 A. Sen, J-T. Chen, W. M. Vetter, and R. R. Whittle, *J. Am. Chem. Soc.*, 1987, **109**, 148.
17 M. R. Churchill and S. A. Julis, *Inorg. Chem.*, 1970, **18**, 1215.
18 G. Bruno, S. Lo Schiavo, E. Rotondo, C. G. Arena, and F. Faraone, *Organometallics*, 1989, **8**, 886.
19 A. L. Balch, R. R. Guimerans, and M. M. Olmstead, *J. Organomet. Chem.*, 1984, **268**, C38.
20 L. A. Oro, D. Carmona, M. P. Puebla, M. P. Lamata, C. Foces-Foces, and F. H. Cano, *Inorg. Chim. Acta*, 1986, **112**, L11.
21 L. A. Oro, D. Carmona, M. P. Lamata, M. C. Apreda, C. Foces-Foces, F. H. Cano, and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, 1984, 1823; L. A. Oro, D. Carmona, M. P. Lamata, C. Foces-Foces, and F. H. Cano, *Inorg. Chim. Acta*, 1985, **97**, 19; M. P. Lamata, D. Carmona, L. A. Oro, M. C. Apreda, C. Foces-Foces, and F. H. Cano, *Inorg. Chim. Acta*, 1989, **158**, 131.
22 J. W. Kang, K. Moseley, and P. M. Maitlis, *J. Am. Chem. Soc.*, 1969, **91**, 5970.
23 D. S. Gill and P. M. Maitlis, *J. Organomet. Chem.*, 1975, **87**, 359.
24 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.
25 G. M. Sheldrick, SHELX 76, 'Program for Crystal Structure Determination,' University of Cambridge, 1976.
26 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.

Received 14*th May* 1990; *Paper* 0/02099K