Heterobinuclear IrRh, RuRh and RuIr Complexes with Pyrazolate Bridging Ligands: Reactivity towards Chelating Diphosphines; Crystal Structure of $[(C_5Me_5)Ir(\mu\text{-pz})_2(\mu\text{-CO})\text{-}Ir(CO)(dppen)]BPh_4{\cdot}0.5MeOH$ [pz = pyrazolate, dppen = *cis*-1,2-bis(diphenylphosphino)ethylene] *

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Complexes of general formula $[LClM(\mu\text{-pz})_2M'(cod)]$ **1–5** [L = C_5Me_5, M = Rh or Ir; L = *p*-cymene, Me = Ru; M′ = Rh or Ir; pz = pyrazolate; cod = cycloocta-T,5-diene (not all possible combinations)] and $[(MeC_6H_4Pr^i\text{-}p)Ru(\mu\text{–}pz)(\mu\text{-}Cl)_2Rh(cod)]$ **7** were prepared starting from mononuclear acetylacetonate and pyrazole or pyrazolate-containing moieties. Complexes **1–5** react with CO yielding derivatives $[LClM(\mu\text{-pz})_2M'(CO)_2]$ **8–12**. Complexes $[(C_5Me_5)ClRh(\mu\text{-pz})_2Rh(CO)_2]$ **13** and $[(MeC_6H_4Pr^i\text{-}p)ClRu(\mu\text{-pz})_2Ir(CO)_2]$ **12** react with NaX to give $[(C_5Me_5)XRh(\mu\text{-pz})_2Rh(CO)_2]$ (X = I, **14**; or N_3, **15**) and $[(MeC_6H_4Pr^i\text{-}p)\overline{Ru(\mu\text{-pz})_2Ir}X(CO)_2]$ (X = Br, **16**; or I, **17**. The dicarbonyl compound **10** and $[(MeC_6H_4Pr^i\text{-}p)ClRu(\mu\text{-pz})_2M'(CO)_2]$ (M′ = Rh, **11**; or Ir, **12**) react with diphosphines (L–L) or 1,2-bis(diphenylarsino)ethane (dpae) and $NaBPh_4$ or $AgBF_4$ affording cationic complexes $[LM(\mu\text{-pz})_2(\mu\text{-CO})M'(L\text{–}L)]A$ **23–31** [L–L = bis(diphenylphosphino)methane, 1,2-bis(diphenylphosphino)ethane, 1,3-bis(diphenylphosphino)propane, 1,4-bis(diphenylphosphino)butane, *cis*-1,2-bis(diphenylphosphino)ethylene (dppen) or dpae; A = BPh_4 or BF_4 (not all possible combinations)]. In this reaction intermediates $[LM(\mu\text{-pz})_2(\mu\text{-CO})M'(CO)(L\text{–}L)]A$ have been isolated in some cases. The crystal structure of one of these $[(C_5Me_5)Ir(\mu\text{-pz})_2(\mu\text{-CO})Ir(CO)(dppen)]BPh_4{\cdot}0.5MeOH$ **19** has been determined by X-ray diffraction methods. Crystals are monoclinic, space group $P2_1/c$, a = 15.996(2), b = 22.199(4), c = 18.874(3) Å, β = 115.04(1)° and Z = 4. The complex cation consists of two iridium atoms bridged by two pyrazolates and one ketonic carbonyl group. An $\eta^5\text{-}C_5Me_5$ ligand, a chelate dppen and a terminal CO group complete the co-ordination spheres of the iridium atoms, which are separated by 3.440(5) Å.

Pyrazoles have been actively investigated as versatile ligands which can yield binuclear homo- or hetero-metallic complexes with interesting properties.[1] In this context, we have recently reported the preparation of several $Rh^{III}Rh^{I}$ heterovalent[2] and RuRh and RhIr heterobinuclear[3,4] complexes in which one or two pyrazolate groups act as bridging ligands. On the other hand, complexes containing bridging carbonyl ligands are, generally, accompanied by metal–metal bonds.[5] It is only recently that examples in which bridging carbonyls not accompanied by metal–metal bonds (ketonic carbonyls) have been characterized.[6]

In this paper we describe the preparation of binuclear complexes of general formula $[LClM(\mu\text{-pz})_2M'(cod)]$ (pz = pyrazolate, cod = cycloocta-1,5-diene) (L = C_5Me_5; M = Rh, M′ = Ir **1**; M = Ir, M′ = Rh **2** or Ir **3**; L = *p*-cymene; M = Ru, M′ = Rh **4** or Ir **5**) and their corresponding dicarbonyl derivatives $[LClM(\mu\text{-pz})_2M'(CO)_2]$ **8–12**. We also report the reaction of the dicarbonyl compounds $[(C_5Me_5)ClIr(\mu\text{-pz})_2\text{-}Ir(CO)_2]$ **10** and $[(MeC_6H_4Pr^i\text{-}p)ClRu(\mu\text{-pz})_2M'(CO)_2]$ (M′ = Rh **11** or Ir **12**) with tertiary diphosphines or diarsines (L–L) and $NaBPh_4$ or $AgBF_4$ to yield cationic complexes of general stoichiometry $[LM(\mu\text{-pz})_2(\mu\text{-CO})M'(L\text{–}L)]A$ **23–31** (A = BPh_4 or BF_4) which contain a ketonic carbonyl group. This reaction proceeds *via* the ketonic carbonyl intermediate complexes $[LM(\mu\text{-pz})_2(\mu\text{-CO})M'(CO)(L\text{–}L)]A$ which, in some cases, **18–22** have been isolated and characterized. The crystal structure of one of the latter complexes $[(C_5Me_5)Ir(\mu\text{-pz})_2\text{-}(\mu\text{-CO})Ir(CO)(dppen)]BPh_4{\cdot}0.5MeOH$ **19** [dppen = 1,2-bis(diphenylphosphino)ethylene] is also reported.

Part of this work has been previously communicated.[7]

Results and Discussion

Neutral Complexes.—The reaction in acetone of $[M(C_5Me_5)(acac)Cl]$ (M = Rh or Ir, acac = acetylacetonate)[8] with the cationic complexes $[M'(cod)(Hpz)_2]BF_4$ (M′ = Rh or Ir)[9] in the presence of stoichiometric amounts of KOH leads to the formation of the neutral dinuclear complexes $[(C_5Me_5)ClM(\mu\text{-pz})_2M'(cod)]$ (M = Rh, M′ = Ir **1**; M = Ir, M′ = Rh **2** or Ir **3**. Nevertheless, when the ruthenium(II) complex[10] $[Ru(MeC_6H_4Pr^i\text{-}p)(acac)Cl]$ was treated in a similar way with

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* [1,2-Bis(diphenylphosphino)ethylene-1κ*P*,*P*′]-μ-carbonyl-carbonyl-1κ*C*-2(η^5)-pentamethylcyclopentadienyl-di-(μ-pyrazolato-κN^1:N^2)-diiridium tetraphenylborate–methanol (1/0.5).

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

[Rh(cod)(Hpz)$_2$]BF$_4$ and KOH only small amounts of the heterodinuclear complex [(MeC$_6$H$_4$Pr^i-*p*)ClRu(μ-pz)$_2$Rh(cod)] **4** were detected by ^{1}H NMR spectroscopy, among a mixture of products mostly formed by the mononuclear ruthenium complex[10] [Ru(MeC$_6$H$_4$Pr^i-*p*)(acac)(Hpz)]$^+$ and dimeric[11] [{Rh(pz)(cod)}$_2$]. Complex **4** and the homologous [(MeC$_6$H$_4$Pr^i-*p*)ClRu(μ-pz)$_2$Ir(cod)] **5** could be prepared by treating the cationic compound[10] [Ru(MeC$_6$H$_4$Pr^i-*p*)Cl(Hpz)$_2$]BF$_4$ with [M′(acac)(cod)] (M′ = Rh[12] or Ir[13]) and KOH. Complexes **1**–**3** could also be prepared by this latter method as well as the heterovalent Rh^{III}Rh^{I} complex [(C$_5$Me$_5$)ClRh(μ-pz)$_2$Rh(cod)] **6** recently reported by us.[2] We have also prepared **6** by treating the neutral acetylacetonate-pyrazolate complex [Rh(C$_5$Me$_5$)(acac)(pz)] with the mononuclear rhodium(I) compound [RhCl(cod)(Hpz)].[2] We attempted the preparation of **4** by this latter route but a mixture of the complexes [Rh(MeC$_6$H$_4$Pr^i-*p*)(acac)(Hpz)]Cl and [{Rh(pz)(cod)}$_2$] was obtained instead.

Table 1 summarizes all the above reported reactions. The following two points are worth mentioning. (*i*) Reactions of the type (1) provide a general route for the preparation of dinuclear homo- or hetero-metallic compounds of general formula [LClM(μ-pz)$_2$M′(cod)] with two pyrazolate groups acting as bridging ligands. (*ii*) The co-ordinated acac group of the complexes [Ru(MeC$_6$H$_4$Pr^i-*p*)(acac)Cl] or [Ru(MeC$_6$H$_4$Pr^i-*p*)(acac)(pz)] is difficult to abstract by protonation using the Hpz ligand of the rhodium(I) complexes [Rh(cod)(Hpz)$_2$]BF$_4$ or [RhCl(cod)(Hpz)]. However, the isoelectronic rhodium(III) or iridium(III) complexes [M(C$_5$Me$_5$)(acac)Cl] (M = Rh or Ir) and [Rh(C$_5$Me$_5$)(acac)(pz)] react with the aforementioned rhodium(I) pyrazole complexes rendering the expected dinuclear complexes [reactions (2) and (3)].

Following a comparable synthetic strategy we have prepared the heterobridged complex [(MeC$_6$H$_4$Pr^i-*p*)Ru(μ-pz)(μ-Cl)$_2$-Rh(cod)] **7**. Thus, reaction of [Ru(MeC$_6$H$_4$Pr^i-*p*)Cl$_2$(Hpz)] with stoichiometric amounts of dimeric[14] [{Rh(OMe)(cod)}$_2$] gives complex **7** in good isolated yield. Again, attempts to prepare complex **7** by treating [Ru(MeC$_6$H$_4$Pr^i-*p*)(acac)Cl] with [RhCl(cod)(Hpz)] were unsuccessful, the reaction products being the homonuclear complexes [{RhCl(cod)}$_2$] and [Ru(MeC$_6$H$_4$Pr^i-*p*)(acac)(Hpz)]Cl.

All new complexes were characterized by elemental analyses, IR and NMR spectroscopies and, in some cases, molecular-weight measurements (Tables 2 and 3). In particular, the IR spectra show the absence of the N–H, BF$_4$ and acac vibrations of the starting materials and the ^{1}H NMR spectra are consistent with the proposed formulations, showing the inequivalence of the three protons of the pyrazolate groups and the presence of the C$_5$Me$_5$ (or *p*-cymene), pz and cod ligands in the required proportions. Assuming the bridging nature of the pyrazolate groups, two binuclear structures **A** and **B** (Fig. 1) can be proposed for complexes **1**–**5** depending on whether or not the chlorine atom is bridging. The spectral data for these complexes are compatible with both structures and we cannot unequivocally determine the disposition of the chlorine atom, which, in turn, could be different from one complex to another. Nevertheless, the ^{1}H NMR data for the complex [(MeC$_6$H$_4$Pr^i-*p*)Ru(μ-pz)(μ-Cl)$_2$Rh(cod)] **7** are consistent with a triple bridging formulation for it. The spectrum (Table 3) shows only one AB system and one doublet for the four aromatic and isopropyl methyl protons of the *p*-cymene ligand, respectively. That means that at least in solution the two chlorine atoms must be equivalent and therefore a triply bridged structure is likely. Furthermore, the crystal structure of the related complex [(MeC$_6$H$_4$Pr^i-*p*)Ru(μ-pz)(μ-Cl)$_2$Rh(tfbb)] (tfbb = tetrafluorobenzo[5,6]bicyclo[2.2.2]octa-2,5,7-triene) shows that the two chlorines are bridging the metal atoms.[3]

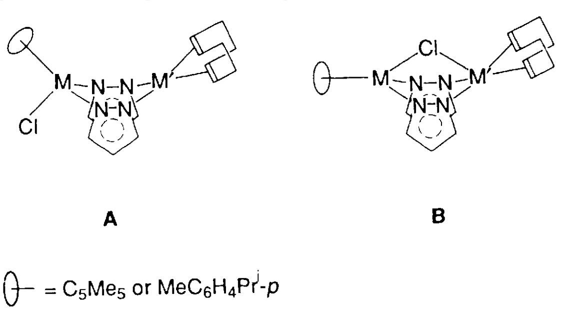


Fig. 1 Proposed structures for complexes **1**–**5**

Carbonylation of complexes **1**–**5** proceeds rapidly at room temperature upon bubbling of CO through dichloromethane or tetrahydrofuran (thf) solutions to give compounds **8**–**12**. The reaction (Scheme 1) results in substitution of the cod ligand by two terminal CO groups.

$$[\text{LClM}(\mu\text{-pz})_2\text{M}'(\text{cod})] + 2\,\text{CO} \longrightarrow [\text{LClM}(\mu\text{-pz})_2\text{M}'(\text{CO})_2] + \text{cod}$$

	L	M	M′
8	C$_5$Me$_5$	Rh	Ir
9	C$_5$Me$_5$	Ir	Rh
10	C$_5$Me$_5$	Ir	Ir
11	MeC$_6$H$_4$Pr^i-*p*	Ru	Rh
12	MeC$_6$H$_4$Pr^i-*p*	Ru	Ir

Scheme 1

The RuIr complex [(MeC$_6$H$_4$Pr^i-*p*)ClRu(μ-pz)$_2$Ir(CO)$_2$] **12** was obtained as a mixture of two isomers **12a** and **12b**. In solution an equilibrium is reached between them (Fig. 2). The structures of **12a** and **12b** were determined by diffractometric methods and previously communicated.[7] We have not observed a similar behaviour for the RuRh compound[7] **11** nor for the isoelectronic complexes **8**–**10**.

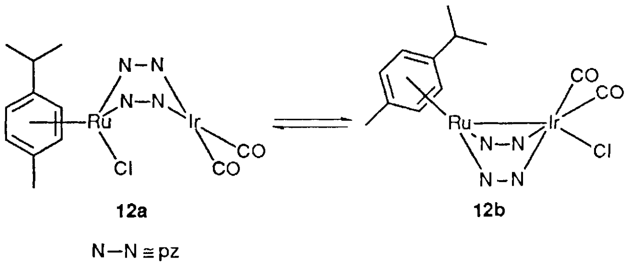


Fig. 2 Equilibrium of isomerization between complexes **12a** and **12b**

We have recently reported the preparation of the related carbonyl dirhodium complex[2] [(C$_5$Me$_5$)ClRh(μ-pz)$_2$Rh(CO)$_2$] **13**. The chlorine atom of this compound can be displaced by iodide or azide on reaction with NaI or NaN$_3$ giving [(C$_5$Me$_5$)IRh(μ-pz)$_2$Rh(CO)$_2$] **14** and [(C$_5$Me$_5$)(N$_3$)Rh(μ-pz)$_2$-Rh(CO)$_2$] **15**, respectively. Analogously, the ruthenium–iridium complex **12** reacts with NaX (X = Br or I) rendering the corresponding [(MeC$_6$H$_4$Pr^i-*p*)$\overline{\text{Ru}(\mu\text{-pz})_2\text{Ir}}$X(CO)$_2$] (X = Br, **16**; or I, **17**). From their spectroscopic properties we propose for **16** and **17** a similar structure to **12b** with a Ru–Ir metal–metal bond.[7]

Table 2 collects analytical and physical data for these new carbonyl complexes. In their IR spectra are present two very strong ν(CO) bands characteristic of a *cis*-dicarbonyl structure. Table 3 lists the proton NMR data. The chemical shifts, multiplicities and intensities are in good agreement with the proposed formulations. In general, the chemical shifts of the protons of the pyrazolate bridging groups are shifted to lower fields relative to the parent diolefinic compounds, as a reflection of the greater π-acceptor character of the CO ligands.

Cationic Complexes.—The dicarbonyl complex [(C$_5$Me$_5$)ClIr(μ-pz)$_2$Ir(CO)$_2$] **10** reacts with the diphosphines 1,3-

Table 1 Preparative routes to complexes **1**–**6**

Reaction number	Starting materials	L	M	M′	Product(s)
(1)	$[MLCl(Hpz)_2][BF_4]$ + $[M'(acac)(cod)]$ + KOH	C_5Me_5	Rh	Ir	**1** $[(C_5Me_5)ClRh(\mu\text{-}pz)_2Ir(cod)]$
		C_5Me_5	Ir	Rh	**2** $[(C_5Me_5)ClIr(\mu\text{-}pz)_2Rh(cod)]$
		C_5Me_5	Ir	Ir	**3** $[(C_5Me_5)ClIr(\mu\text{-}pz)_2Ir(cod)]$
		$MeC_6H_4Pr^i\text{-}p$	Ru	Rh	**4** $[(MeC_6H_4Pr^i\text{-}p)ClRu(\mu\text{-}pz)_2Rh(cod)]$
		$MeC_6H_4Pr^i\text{-}p$	Ru	Ir	**5** $[(MeC_6H_4Pr^i\text{-}p)ClRu(\mu\text{-}pz)_2Ir(cod)]$
		C_5Me_5	Rh	Rh	**6** $[(C_5Me_5)ClRh(\mu\text{-}pz)_2Rh(cod)]$
(2)	$[ML(acac)Cl]$ + $[M'(cod)(Hpz)_2][BF_4]$ + KOH	C_5Me_5	Rh	Ir	**1**
		C_5Me_5	Ir	Rh	**2**
		C_5Me_5	Ir	Ir	**3**
		$MeC_6H_4Pr^i\text{-}p$	Ru	Rh	**4** + $[Ru(MeC_6H_4Pr^i\text{-}p)(acac)(Hpz)]^+$ + $[\{Rh(pz)(cod)\}_2]$
		C_5Me_5	Rh	Rh	**6**
(3)	$[ML(acac)(pz)]$ + $[M'Cl(cod)(Hpz)]$	C_5Me_5	Rh	Rh	**6**
		$MeC_6H_4Pr^i\text{-}p$	Ru	Rh	$[Ru(MeC_6H_4Pr^i\text{-}p)(acac)(Hpz)]Cl$ + $[\{Rh(pz)(cod)\}_2]$

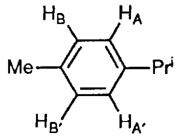
Table 2 Analytical[a] and physical data for the new neutral complexes

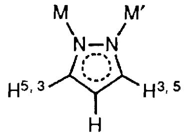
Complex		Analysis (%) C	H	N	Colour	*M*	ν(CO)[b]/cm⁻¹	Yield (%)
1	$[(C_5Me_5)ClRh(\mu\text{-}pz)_2Ir(cod)]$	40.6	5.1	7.9	Yellow	—	—	40[c]
		(40.7)	(4.7)	(7.9)				60[d]
2	$[(C_5Me_5)ClIr(\mu\text{-}pz)_2Rh(cod)]$	40.8	5.0	7.85	Yellow	691	—	72[c]
		(40.7)	(4.7)	(7.9)		(708.1)		70[d]
3	$[(C_5Me_5)ClIr(\mu\text{-}pz)_2Ir(cod)]$	36.3	4.3	7.0	Yellow	764	—	40[c]
		(36.15)	(4.2)	(7.0)		(797.4)		55[d]
4	$[(MeC_6H_4Pr^i\text{-}p)ClRu(\mu\text{-}pz)_2Rh(cod)]$	47.1	5.8	9.3	Yellow	637	—	96
		(46.8)	(5.2)	(9.1)		(615.0)		
5	$[(MeC_6H_4Pr^i\text{-}p)ClRu(\mu\text{-}pz)_2Ir(cod)]$	40.7	4.9	7.9	Orange	—	—	70
		(40.9)	(4.6)	(7.9)				
7	$[(MeC_6H_4Pr^i\text{-}p)Ru(\mu\text{-}pz)(\mu\text{-}Cl)_2Rh(cod)]$	43.9	5.5	5.1	Orange	—	—	81
		(43.2)	(5.3)	(5.0)				
8	$[(C_5Me_5)ClRh(\mu\text{-}pz)_2Ir(CO)_2]$	33.2	3.5	8.5	Yellow	626.4	2080, 2000	45
		(33.0)	(3.2)	(8.5)		(655.9)		
9	$[(C_5Me_5)ClIr(\mu\text{-}pz)_2Rh(CO)_2]$	33.0	3.3	8.5	Yellow	631.9	2080, 2005	50
		(33.0)	(3.2)	(8.5)		(655.9)		
10	$[(C_5Me_5)ClIr(\mu\text{-}pz)_2Ir(CO)_2]$	29.1	2.95	7.6	Yellow	748.1	2100, 1990	30
		(29.0)	(2.8)	(7.5)		(745.2)		
11	$[(MeC_6H_4Pr^i\text{-}p)ClRu(\mu\text{-}pz)_2Rh(CO)_2]$	38.3	3.8	10.0	Yellow	565	2080, 2010	90
		(38.3)	(3.6)	(9.9)		(563.8)		
12a	$[(MeC_6H_4Pr^i\text{-}p)ClRu(\mu\text{-}pz)_2Ir(CO)_2]$	33.1	2.9	8.4	Orange	615	2066, 1994	75[e]
		(33.1)	(3.1)	(8.6)		(653.1)		
12b	$[(MeC_6H_4Pr^i\text{-}p)\overline{Ru(\mu\text{-}pz)_2Ir}Cl(CO)_2]$	33.0	2.8	8.4	Red	—	2076, 2021	—
		(33.1)	(3.1)	(8.6)				
14	$[(C_5Me_5)IRh(\mu\text{-}pz)_2Rh(CO)_2]$	32.55	3.3	8.2	Orange	679.9	2070, 2015	90
		(32.85)	(3.2)	(8.5)		(658.2)		
15	$[(C_5Me_5)(N_3)Rh(\mu\text{-}pz)_2Rh(CO)_2]$	37.5	3.6	17.4	Yellow	619.0	2080, 2010	70
		(37.7)	(3.7)	(17.1)	Orange	(573.2)		
16	$[(MeC_6H_4Pr^i\text{-}p)\overline{Ru(\mu\text{-}pz)_2Ir}Br(CO)_2]$	31.7	2.9	8.25		—	2077, 2020	76
		(31.0)	(2.9)	(8.0)	Orange			
17	$[(MeC_6H_4Pr^i\text{-}p)\overline{Ru(\mu\text{-}pz)_2Ir}I(CO)_2]$	28.8	2.8	7.7		—	2076, 2022	73
		(29.0)	(2.7)	(7.5)				

[a] Required values are given in parentheses. [b] In CH_2Cl_2 solution. All ν(CO) bands are very strong. [c] Prepared according to reaction (2) (Table 1). [d] Prepared according to reaction (1) (Table 1). [e] Yield for **12a** + **12b**.

bis(diphenylphosphino)propane (dppp) or *cis*-1,2-bis(diphenylphosphino)ethylene (dppen), in methanol and in the presence of $NaBPh_4$, affording the cationic dicarbonyl complexes $[(C_5Me_5)Ir(\mu\text{-}pz)_2(\mu\text{-}CO)Ir(CO)(L\text{-}L)]BPh_4$ (L–L = dppp, **18**; or dppen, **19**). Treatment of the ruthenium–iridium complex **12** (mixture of both isomers) with $AgBF_4$ in thf and subsequent addition of dppp or dppen renders the related complexes $[(MeC_6H_4Pr^i\text{-}p)Ru(\mu\text{-}pz)_2(\mu\text{-}CO)Ir(CO)(L\text{-}L)]BF_4$ (L–L = dppp, **20**; or dppen, **21**). The analogous tetraphenylborate compound $[(MeC_6H_4Pr^i\text{-}p)Ru(\mu\text{-}pz)_2(\mu\text{-}CO)Ir(CO)(dppen)]BPh_4$ **22** was prepared by metathesis of the BF_4 anion by treating **21** with excess of $NaBPh_4$ in methanol. Table 4 collects the analytical and physical data for these complexes. Their IR spectra show two strong ν(CO) absorptions in the 2050–2060 and 1650–1660 cm⁻¹ regions, attributable to terminal and bridging carbonyl ligands, respectively. The very low value of the bridging carbonyl band is consistent with a ketonic carbonyl formulation,[15–17] as shown by the structure determination of complex **19** (see below). Table 5 lists the proton and $^{31}P\text{-}\{^1H\}$ NMR data for these complexes. The $^{31}P\text{-}\{^1H\}$ spectra consist of two resonances assignable to two inequivalent co-ordinated phosphorus atoms. In complex **19** the two phosphorus are *trans*

Table 3 Proton NMR data[a] for the neutral complexes





	[or C_5M_5]						cod	
Complex	Me	Pr^i	$H_{AA'}$	$H_{BB'}$	$H^{3,5\,b}$	H^4	Vinyl protons	Aliphatic protons
1		[1.69(s)]			7.70(d), 7.60(d) $^3J(HH) = 1.85$	6.23(t)	4.05(m), 3.60(m)	2.35(m), 1.63(m)
2		[1.71(s)]			7.58(br s), 7.31(br s)	6.10(br s)	4.40(m), 3.92(m)	2.42(m), 1.60(m)
3		[1.65(s)]			7.65(d), 7.49(d) $^3J(HH) = 2.3$	6.16(t)	4.05(m), 3.60(m)	2.42(m), 1.60(m)
4	1.78(s)	1.20(d), 2.50(spt) $^3J(HH) = 6.5$	5.86 $J(H_AH_B) = 5.9$	5.91	7.66(d), 7.34(d) $^3J(HH) = 1.9$	6.07(t)	4.20(m), 3.95(m)	2.50(m), 1.90(m)
5	1.77(s)	1.17(d), 2.30(spt) $^3J(HH) = 6.9$	5.75(s)[c]		7.71(d), 7.48(d) $^3J(HH) = 2.2$	6.14(t)	4.00(m), 3.65(m)	2.30(m), 1.70(m)
7	2.16(s)	1.29(d), 2.95(spt) $^3J(HH) = 6.8$	5.28 $J(H_AH_B) = 6.0$	5.43	7.70(br s), 6.91(br s)	6.14(br s)	4.20(m)	2.25(m), 1.70(m)
8		[1.60(s)]			7.68(d), 7.57(d) $^3J(HH) = 2.05$	6.26(t)	—	—
9		[1.59(s)]			7.63(d), 7.43(d) $^3J(HH) = 2.1$	6.21(t)	—	—
10		[1.59(s)]			7.65(dd), 7.55(dd) $^3J(HH) = 2.2$ $^4J(HH) = 0.7$	6.26(t)	—	—
11	1.78(s)	1.17(d), 2.50(spt) $^3J(HH) = 7.0$	5.56 $J(H_AH_B) = 6.0$	5.61	7.70(d), 7.50(d) $^3J(HH) = 2.0$	6.21(t)	—	—
12a	1.80(s)	1.17(d), 2.59(spt) $^3J(HH) = 6.9$	5.56 $J(H_AH_B) = 6.1$	5.64	7.72(dd), 7.62(dd) $^3J(HH) = 2.2$ $^4J(HH) = 0.7$	6.25(t)	—	—
12b	2.04(s)	1.06(d), 2.58(spt) $^3J(HH) = 7.0$	5.50 $J(H_AH_B) = 5.7$	5.59	7.57(d), 7.42(d) $^3J(HH) = 2.1$	5.97(t)	—	—
14		[1.74(s)]			7.95(d), 7.57(d) $^3J(HH) = 2.15$	6.21(t)	—	—
15		[1.62(s)]			7.59(d), 7.56(d) $^3J(HH) = 2.1$	6.33(t)	—	—
16	2.04(s)	1.06(d), 2.57(spt) $^3J(HH) = 6.8$	5.51 $J(H_AH_B) = 5.7$	5.61	7.58(d), 7.44(d) $^3J(HH) = 2.1$	5.95(t)	—	—
17	2.04(s)	1.05(d), 2.58(spt) $^3J(HH) = 6.9$	5.52 $J(H_AH_B) = 5.8$	5.62	7.58(d), 7.45(d) $^3J(HH) = 2.1$	5.93(t)	—	—

[a] Measured in $CDCl_3$ at room temperature; chemical shifts relative to $SiMe_4$ as external standard, J in Hz. s = Singlet, d = doublet, dd = doublet of doublets, t = triplet, spt = septet and m = multiplet. [b] $^3J(H^3H^4) \approx {}^3J(H^4H^5)$. [c] Four aromatic protons.

to the carbonyl bridging group and to one pyrazolate ligand. We propose the same disposition for the cations of the complexes **18** and **20**–**22**, owing to the similarity of their spectroscopic properties. Consistent with the proposed structure, the two pyrazolate groups are inequivalent and we observe two one-proton resonances assignable to the two magnetically different H^4 protons of the heterocyclic rings. (The $H^{3,5}$ resonances of the pyrazolate anions are obscured by the phenyl protons of the diphosphine ligand.) In this way, the ^1H NMR spectra of the *p*-cymene ruthenium complexes **20**–**22** show two AB systems and two doublets assigned to the aromatic and the isopropyl methyl protons of the *p*-cymene ligand, respectively.[19] Complexes **18**–**22** wil be racemic mixtures of the two possible enantiomers. We have not detected the formation of the non-optically active isomer with the two CO ligands in a *trans* disposition around the iridium atom.

Molecular Structure of $[(C_5Me_5)Ir(\mu\text{-pz})_2(\mu\text{-CO})Ir(CO)(dppen)]BPh_4 \cdot 0.5MeOH$ **19**.—An ORTEP drawing of the complex cation is shown in Fig. 3 and important bond angles and distances are given in Table 6. The cation consists of two iridium atoms bridged by two pyrazolates and one CO group. The co-ordination geometry about Ir(1) closely approximates octahedral whereas that about Ir(2) is the usual pseudo-octahedral 'three-legged piano stool' commonly found for $(C_5Me_5)IrLL'L''$ derivatives. The co-ordination around Ir(1) is completed by a carbonyl group *trans* to a nitrogen atom of one of the bridging pyrazolate ligands [N(1)–Ir(1)–C(2) 169.3(4)°] and the dppen ligand acting as a chelating group *via* the two phosphorus atoms P(1) and P(2), which are *trans* to a nitrogen atom of the other bridging pyrazolate ligand and to the carbon atom of the bridging carbonyl group, respectively [P(1)–Ir(1)–N(3) 177.3(3) and P(2)–Ir(1)–C(1) 176.1(3)°].

An interesting feature of this structure is the existence of a carbonyl ligand bridging the two metal centres, which are not bonded to each other [Ir(1) $\cdots$ Ir(2) 3.440(5) Å]. Its structural parameters [C(1)–O(1) 1.205(15) Å and Ir(1)–C(1)–Ir(2) 111.0(5), Ir(2)–C(1)–O(1) 127.3(9), Ir(1)–C(1)–O(1) 121.7(9)°] are near the values expected for an sp^2-hybridized carbon atom and, consistently, it presents a very low infrared stretching frequency: 1650 cm^{-1}. This type of carbonyl ligand has been called ketonic and the compound considered as a dimetallated ketone.[15–17,20]

There are two different Ir(1)–P bond distances: Ir(1)–P(1) 2.297(4), Ir(1)–P(2) 2.458(3) Å. The difference between these distances indicates a stronger *trans* influence of the ketonic carbonyl group as compared to the pyrazolate ligand. Long metal–ligand bond distances have been found for ligands *trans* to ketonic carbonyl groups,[21–23] often comparable to those observed in linear σ-C–M–ligand systems.[21,24] These observa-

Table 4 Analytical[a] and physical data for the cationic complexes

Complex	Analysis (%) C	H	N	Colour	ν(CO)[b]/cm^{-1}	Yield (%)
18 $[(C_5Me_5)Ir(\mu\text{-pz})_2(\mu\text{-CO})Ir(CO)(dppp)]BPh_4$	56.9 (57.5)	4.8 (4.7)	3.8 (3.9)	Orange	2050, 1660	60
19 $[(C_5Me_5)Ir(\mu\text{-pz})_2(\mu\text{-CO})Ir(CO)(dppen)]BPh_4$	56.8 (57.3)	4.9 (4.5)	3.85 (3.9)	Red	2060, 1650	65
20 $[(MeC_6H_4Pr^i\text{-}p)Ru(\mu\text{-pz})_2(\mu\text{-CO})Ir(CO)(dppp)]BF_4$	—	—	—	Yellow	2050, 1655	—
21 $[(MeC_6H_4Pr^i\text{-}p)Ru(\mu\text{-pz})_2(\mu\text{-CO})Ir(CO)(dppen)]BF_4$	46.9 (48.1)	4.0 (3.8)	4.7 (5.1)	Orange	2055, 1655	85
22 $[(MeC_6H_4Pr^i\text{-}p)Ru(\mu\text{-pz})_2(\mu\text{-CO})Ir(CO)(dppen)]BPh_4$	61.5 (61.25)	4.8 (4.7)	4.0 (4.2)	Orange	2055, 1653	58
23 $[(C_5Me_5)Ir(\mu\text{-pz})_2(\mu\text{-CO})Ir(dppp)]BPh_4$	58.2 (57.5)	4.6 (4.8)	4.0 (4.0)	Orange	1710	50
24 $[(MeC_6H_4Pr^i\text{-}p)Ru(\mu\text{-pz})_2(\mu\text{-CO})Ir(dppp)]BF_4$	47.95 (48.5)	4.5 (4.3)	5.0 (5.1)	Yellow	1710	50
25 $[(MeC_6H_4Pr^i\text{-}p)Ru(\mu\text{-pz})_2(\mu\text{-CO})Ir(dppp)]BPh_4$	62.1 (61.8)	4.7 (5.0)	3.9 (4.2)	Yellow	1705	82
26 $[(MeC_6H_4Pr^i\text{-}p)Ru(\mu\text{-pz})_2(\mu\text{-CO})Ir(dppb)]BPh_4$	61.7 (62.1)	4.8 (5.1)	4.1 (4.2)	Yellow	1705	68
27 $[(MeC_6H_4Pr^i\text{-}p)Ru(\mu\text{-pz})_2(\mu\text{-CO})Ir(dppb)]BF_4$	48.6 (49.0)	4.6 (4.4)	4.7 (5.1)	Yellow	1712	80
28 $[(MeC_6H_4Pr^i\text{-}p)Ru(\mu\text{-pz})_2(\mu\text{-CO})Rh(dppm)]BPh_4$	66.3 (65.8)	5.8 (5.2)	4.3 (4.6)	Orange	1740	58
29 $[(MeC_6H_4Pr^i\text{-}p)Ru(\mu\text{-pz})_2(\mu\text{-CO})Rh(dppm)]BF_4$	51.6 (51.9)	4.2 (4.4)	5.6 (5.8)	Orange	1745	60
30 $[(MeC_6H_4Pr^i\text{-}p)Ru(\mu\text{-pz})_2(\mu\text{-CO})Rh(dppb)]BF_4$	53.7 (53.3)	5.1 (4.8)	5.4 (5.5)	Yellow	1747	50
31 $[(MeC_6H_4Pr^i\text{-}p)Ru(\mu\text{-pz})_2(\mu\text{-CO})Rh(dpae)]BF_4$	47.4 (48.1)	4.4 (4.1)	5.1 (5.2)	Yellow	1750	54

[a] Required values are given in parentheses. [b] In CH_2Cl_2 solution. All ν(CO) bands are very strong.

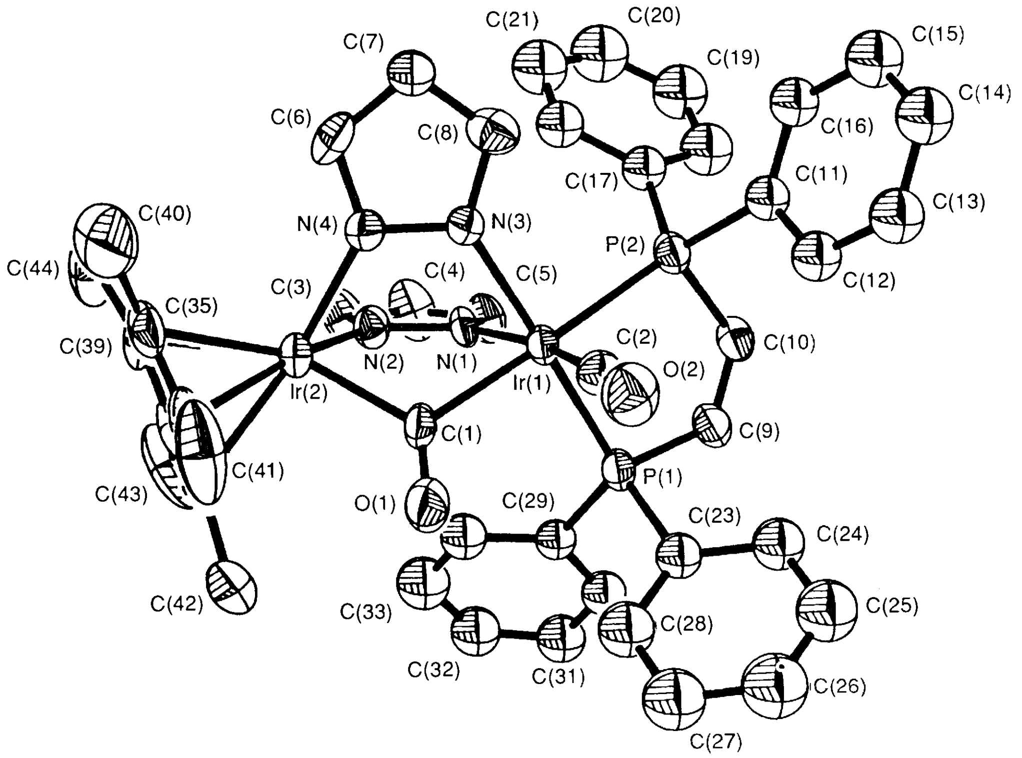


Fig. 3 An ORTEP drawing of the cation of complex **19** with the atomic numbering scheme

tions also support an sp^2 hybridization for the ketonic carbonyl carbon atom and that it forms two σ-covalent (non-dative) bonds to the metal atoms, acting as a CO^{2-} ligand.[15] Consequently, the Ir(1) atom of complex **19** would be formally considered as a six-co-ordinate 18e$^-$ iridium centre and the formation of **19** from **10** implies the oxidation of this atom from +1 to +3. Consistently, the infrared stretching frequency of the terminal CO groups of the cationic complex **19**, 2060 cm^{-1}, is 32 cm^{-1} higher than that found for the neutral diiridium(III) complex $[Ir_2(CO)_2(PPh_3)_2(\mu\text{-pz})_2(\mu\text{-CH}_2)I_2]$, in which the

Table 5 Selected NMR data[a] for the cationic complexes

	^{1}H						^{31}P		
	$MeC_6H_4Pr^i$-*p* [or C_5Me_5]				pz[b]				
Complex	Me	Pr^i	$H_{AA'}$	$H_{BB'}$	$H^{3,5}$	H^4	δ(P)	*J*(Rh–P)	*J*(P–P)
18			[1.47(s)]		*c*	5.93(dt) ^3J(HH) = 2.0 ^5J(PH) = 1.0[d] 6.13(t) ^3J(HH) = 2	−29.8 −30.2	—	—
19			[1.69(s)]		6.34(br s) *c*	5.52(t) ^3J(HH) = 2.3 6.07(m)	17.6 5.1		41.0
20	1.80(s)	0.96(d) ^3J(HH) = 6.7 1.18(d) ^3J(HH) = 7.0	4.62 $J(H_AH_B)$ = 6.3 5.24 $J(H_AH_B)$ = 5.9	4.98 5.65	*c*	5.95(br s) 6.11(br s)	−30.1 −35.3	—	—
21	2.17(s)	1.05(d), 2.72(spt) ^3J(HH) = 6.8 1.17(d) ^3J(HH) = 6.8	5.17 $J(H_AH_B)$ = 5.85 5.38 $J(H_AH_B)$ = 5.9	5.23 5.62	6.38(br s) 7.75(br s) *c*	5.47(t)[e] ^3J(HH) = 2.1 6.12(br s)	11.8 5.1	—	39.5
22	2.08(s)	1.01(d), 2.68(spt) ^3J(HH) = 6.8 1.16(d) ^3J(HH) = 6.6	5.09 $J(H_AH_B)$ = 5.6 5.17 $J(H_AH_B)$ = 5.6	5.17 5.42	6.28(br s) *c*	5.52(t)[f] 6.08(br s)	13.0 5.3	—	39.3
23			[1.56(s)]		*c*	5.77(t) ^3J(HH) = 2.2	−11.4	—	—
24	1.80(s)	0.88(d), 2.45(spt) ^3J(HH) = 7.0	5.48(br s)[g]		*c*	5.84(br s)	−13.0	—	—
26	1.41(s)	0.70(d), 2.05(spt) ^3J(HH) = 7.8	4.81 $J(H_AH_B)$ = 5.9	5.07	*c*	5.90(br s)	−0.5	—	—
27	1.61(s)	0.76(d), 2.18(spt) ^3J(HH) = 6.65	5.20 $J(H_AH_B)$ = 6.4	5.40	*c*	5.88(br s)	−0.9	—	—
28	1.90(s)	0.80(d), 2.43(spt) ^3J(HH) = 7.8	5.00 $J(H_AH_B)$ = 6.0	5.15	*c*	6.18(br s)	−18.9	127	—
29[h]	2.21(s)	0.94(d) *i* ^3J(HH) = 6.8	5.72	5.80	8.10(d), 7.30(d) ^3J(HH) = 2.0	6.21(br s)	−20.9	126	—
30	1.59(s)	0.73(d), 2.45(spt) ^3J(HH) = 6.9	5.22 $J(H_AH_B)$ = 5.7	5.42	*c*	5.87(br s)	34.2	146	—
31	2.01(s)	0.73(d), 2.45(spt) ^3J(HH) = 6.8	5.39 $J(H_AH_B)$ = 5.65	5.45	7.78(br s), 6.88(br s)	6.09(br s)	—	—	—

[a] Measured in $CDCl_3$ (^{1}H) or $CDCl_3$–$CHCl_3$ (1:1 v/v) (^{31}P) at room temperature; chemical shifts relative to $SiMe_4$ (^{1}H) or 85% H_3PO_4 in D_2O (^{31}P) as external standards, *J* in Hz. [b] The labelling of *p*-cymene and pyrazolate protons is the same as in Table 3. [c] Obscured by the phenyl protons. [d] Long-range coupling constants *J*(PH) have recently been documented.[18] [e] Selective decoupling experiments show that the signals at δ 5.47, 6.38 and 7.75 belong to the same pyrazolate group. [f] As above the signals at δ 5.52 and 6.28 belong to the same pyrazolate group. [g] Four aromatic protons. [h] In CD_3COCD_3 solution. [i] Obscured by the methylene protons of the diphosphine.

carbon monoxide terminal groups are also *trans* to bridging pyrazolate anions,[25] and comparable to the values reported for other cationic carbonyl iridium(III) complexes.[26]

The Ir(1)–C(1) bond distance, 2.134(9) Å, is unusually long compared to those found in other ketonic carbonyl di-iridium complexes $[Ir_2Cl_2(\mu\text{-}CO)(\mu\text{-}MeO_2CC{=}CCO_2Me)(dppm)_2]$ [2.02(1) and 1.99(1) Å][16] and $[Ir_2(\mu\text{-}SBu^t)_2(\mu\text{-}CO)(CO)_2(PMe_3)_2I_2]$ [2.00(3) and 2.00(3) Å],[23] which in turn are comparable to the Ir(2)–C(1) bond length [2.038(12) Å].

All the Ir–N bond distances are similar [Ir(1)–N(1) 2.090(8), Ir(1)–N(3) 2.098(10), Ir(2)–N(2) 2.080(9), and Ir(2)–N(4) 2.068(8) Å] and compare well with the Ir^{III}–N (bridging pyrazolate) distances found in other binuclear complexes such as $[\{Ir(C_5Me_5)\}_2(\mu\text{-}H)_2(\mu\text{-}pz)]BF_4$, 2.098(10) and 2.065(11) Å,[27] $[(C_5Me_5)Ir(\mu\text{-}pz)(\mu\text{-}I)_2Rh(CO_2Me)I(CO)]$, 2.095(8) Å,[4] or the methylene complex[25] $[Ir_2(CO)_2(PPh_3)_2(\mu\text{-}pz)_2(\mu\text{-}CH_2)I_2]$, 2.075(13) Å.

The Ir(2) atom is η^5-bonded to a C_5Me_5 ligand and, as a consequence of the asymmetry of co-ordination around the metal, presents different Ir(2)–C(ring) distances, C(36)–Ir(2) being the shortest. In this respect, the C_5Me_5 ring involves two shorter bonds C(37)–C(38) and C(35)–C(39) and three longer ones C(35)–C(36), C(36)–C(37) and C(38)–C(39). Thus, the ring presents some degree of localized 'di-π-olefin-σ' bonding[28] although the differences in the bond lengths are within the accuracy limits.

The structural parameters of the dppen and pz ligands, as well as those of the BPh_4 anion, are normal.

The terminal carbonyl group of the dppp complexes **18** and **20** can be completely released by refluxing them in chloroform during 1 h, rendering the new monocarbonyl derivatives $[(C_5Me_5)Ir(\mu\text{-}pz)_2(\mu\text{-}CO)Ir(dppp)]BPh_4$ **23** and $[(MeC_6H_4Pr^i\text{-}p)Ru(\mu\text{-}pz)_2(\mu\text{-}CO)Ir(dppp)]BF_4$ **24**. In particular, complex **20** looses easily its terminal CO group so that we have not been able to obtain it analytically pure. The process is not reversible. Thus, only unidentified CO-containing decomposition products were detected in the reaction of compound **24** with CO (atmospheric pressure, room temperature) in $CHCl_3$. However, the dppen complexes **19** and **21** retain their terminal CO group after refluxing them in chloroform during 2 h.

The formation of cationic complexes with two pyrazolate and one CO bridging group starting from terminal dicarbonyl derivatives of the type **10** and **12** is more general. Thus, the related complex $[(MeC_6H_4Pr^i\text{-}p)ClRu(\mu\text{-}pz)_2Rh(CO)_2]$ **11** and the aforementioned ruthenium–iridium complex **12** react with the diphosphines bis(diphenylphosphino)methane (dppm),

Table 6 Selected bond lengths (Å) and angles (°) for the complex $[(\mathrm{C_5Me_5})\mathrm{Ir}(\mu\text{-pz})_2(\mu\text{-CO})\mathrm{Ir(CO)(dppen)}]\mathrm{BPh_4}\cdot 0.5\mathrm{MeOH}$ **19**

Ir(1)–P(1)	2.297(4)	Ir(2)–N(2)	2.080(9)	C(1)–O(1)	1.205(15)	C(2)–O(2)	1.128(14)
Ir(1)–P(2)	2.458(3)	Ir(2)–N(4)	2.068(8)	N(1)–N(2)	1.362(11)	N(3)–N(4)	1.372(11)
Ir(1)–N(1)	2.090(8)	Ir(2)–C(1)	2.038(12)	N(1)–C(5)	1.334(15)	N(3)–C(8)	1.351(15)
Ir(1)–N(3)	2.098(10)	Ir(2)–C(35)	2.233(12)	N(2)–C(3)	1.344(14)	N(4)–C(6)	1.337(20)
Ir(1)–C(1)	2.134(9)	Ir(2)–C(36)	2.173(10)	C(3)–C(4)	1.376(18)	C(6)–C(7)	1.379(15)
Ir(1)–C(2)	1.867(11)	Ir(2)–C(37)	2.189(11)	C(4)–C(5)	1.368(16)	C(7)–C(8)	1.352(20)
Ir(1) ··· Ir(2)	3.440(5)	Ir(2)–C(38)	2.204(10)				
		Ir(2)–C(39)	2.271(10)	C(35)–C(36)	1.420(20)	C(35)–C(40)	1.511(24)
				C(36)–C(37)	1.434(21)	C(36)–C(41)	1.506(17)
P(1)–C(9)	1.789(10)	P(2)–C(10)	1.832(14)	C(37)–C(38)	1.397(19)	C(37)–C(42)	1.490(24)
P(1)–C(23)	1.830(12)	P(2)–C(11)	1.858(9)	C(38)–C(39)	1.426(22)	C(38)–C(43)	1.498(21)
P(1)–C(29)	1.819(10)	P(2)–C(17)	1.814(12)	C(35)–C(39)	1.393(18)	C(39)–C(44)	1.543(21)
C(9)–C(10)	1.321(16)			Ir(2)–G*	1.849(6)		
P(1)–Ir(1)–P(2)	84.7(1)	N(1)–Ir(1)–C(2)	169.3(4)	Ir(1)–C(1)–Ir(2)	111.0(5)	Ir(1)–P(1)–C(9)	108.7(4)
P(1)–Ir(1)–N(1)	91.0(2)	N(3)–Ir(1)–C(1)	83.3(4)	Ir(1)–C(1)–O(1)	121.7(9)	Ir(1)–P(2)–C(10)	103.6(4)
P(1)–Ir(1)–N(3)	177.3(3)	N(3)–Ir(1)–C(2)	90.7(4)	Ir(1)–C(2)–O(2)	176.0(10)	P(1)–C(9)–C(10)	121.8(9)
P(1)–Ir(1)–C(1)	95.8(3)	C(1)–Ir(1)–C(2)	85.3(5)	Ir(2)–C(1)–O(1)	127.3(9)	P(2)–C(10)–C(9)	120.9(9)
P(1)–Ir(1)–C(2)	91.8(4)	N(2)–Ir(2)–N(4)	82.7(3)				
P(2)–Ir(1)–N(1)	92.1(2)	N(2)–Ir(2)–C(1)	84.4(4)	Ir(1)–N(1)–N(2)	116.9(7)	Ir(1)–N(3)–N(4)	118.6(6)
P(2)–Ir(1)–N(3)	96.0(3)	N(2)–Ir(2)–G*	131.6(3)	Ir(1)–N(1)–C(5)	133.8(8)	Ir(1)–N(3)–C(8)	132.6(8)
P(2)–Ir(1)–C(1)	176.1(3)	N(4)–Ir(2)–C(1)	85.2(4)	N(2)–N(1)–C(5)	109.3(8)	N(4)–N(3)–C(8)	108.3(9)
P(2)–Ir(1)–C(2)	98.5(3)	N(4)–Ir(2)–G*	131.0(4)	Ir(2)–N(2)–N(1)	122.8(7)	Ir(2)–N(4)–N(3)	120.9(7)
N(1)–Ir(1)–N(3)	86.4(3)	C(1)–Ir(2)–G*	125.5(4)	Ir(2)–N(2)–C(3)	130.7(9)	Ir(2)–N(4)–C(6)	133.6(9)
N(1)–Ir(1)–C(1)	84.1(4)			N(1)–N(2)–C(3)	106.3(9)	N(3)–N(4)–C(6)	105.4(9)
				N(2)–C(3)–C(4)	110.1(11)	N(4)–C(6)–C(7)	111.9(12)
				C(3)–C(4)–C(5)	105.4(11)	C(6)–C(7)–C(8)	104.0(11)
				N(1)–C(5)–C(4)	108.9(11)	N(3)–C(8)–C(7)	110.3(10)

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

$$[(\mathrm{MeC_6H_4Pr^i}\text{-}p)\mathrm{ClRu}(\mu\text{-pz})_2\mathrm{M'(CO)_2}] + \text{L-L} + \mathrm{NaBPh_4}\ (\text{or } \mathrm{AgBF_4}) \longrightarrow$$

$$[(\mathrm{MeC_6H_4Pr^i}\text{-}p)\mathrm{Ru}(\mu\text{-pz})_2(\mu\text{-CO})\mathrm{M'(L\text{-}L)}]\mathrm{A} + \mathrm{NaCl}\ (\text{or AgCl})$$

	M′	L-L	A
25	Ir	dppp	$\mathrm{BPh_4}$
26	Ir	dppb	$\mathrm{BPh_4}$
27	Ir	dppb	$\mathrm{BF_4}$
28	Rh	dppm	$\mathrm{BPh_4}$
29	Rh	dppm	$\mathrm{BF_4}$
30	Rh	dppb	$\mathrm{BF_4}$
31	Rh	dpae	$\mathrm{BF_4}$

Scheme 2

dppp, 1,4-bis(diphenylphosphino)butane (dppb) or the diarsine 1,2-bis(diphenylarsino)ethane (dpae) in thf or methanol and in the presence of $\mathrm{NaBPh_4}$ according to Scheme 2. Treatment of **11** or **12** with $\mathrm{AgBF_4}$ and subsequent addition of the corresponding diphosphine gives the same results. In both cases complexes of general stoichiometry $[(\mathrm{MeC_6H_4Pr^i}\text{-}p)\mathrm{Ru}(\mu\text{-pz})_2(\mu\text{-CO})\mathrm{M'(L\text{-}L)}]\mathrm{A}$ are isolated. The corresponding intermediates $[(\mathrm{MeC_6H_4Pr^i}\text{-}p)\mathrm{Ru}(\mu\text{-pz})_2(\mu\text{-CO})\mathrm{M'(CO)(L\text{-}L)}]\mathrm{A}$ were not detected.

Table 4 collects the analytical and physical data of complexes **23**–**31**. Their IR spectra show a strong ν(CO) absorption in the 1740–1750 $\mathrm{cm^{-1}}$ region when M′ is rhodium, which is shifted to lower energies, 1705–1712 $\mathrm{cm^{-1}}$, for the related ruthenium–iridium compounds. The lower values of this stretching could be attributed to the greater basicity of the iridium atom M′. In all cases the low value for the bridging carbonyl band is consistent with a ketonic carbonyl formulation for it.[15–17] The $^{13}\mathrm{C}\text{-}\{^1\mathrm{H}\}$ NMR spectra of complexes **27**, **29** and **30** show a resonance at δ 210.1, 221.2 and 222.6, respectively, which we assign to the ketonic carbonyl group.[29,30]

Table 5 lists selected NMR data for these complexes which are in good agreement with the proposed formulation. Complex **25** is not soluble enough to make NMR assignments. In these complexes, the two phosphorus nuclei are equivalent and the ^{1}H NMR spectra show that there is only one type of pyrazolate group. The *p*-cymene ruthenium complexes **26**–**31** show only one AB system and one doublet for the aromatic and the isopropyl methyl protons of the *p*-cymene ligand, respectively. All these data indicate that in solution the M′ atom must have a rectangular pyramidal geometry with the carbonyl ligand occupying the apical position as has been found in the homologous dirhodium complex $[(\mathrm{C_5Me_5})\mathrm{Rh}(\mu\text{-pz})_2(\mu\text{-CO})\mathrm{Rh(dppp)}]\mathrm{BPh_4}$.[17]

On the other hand, we have carried out the reaction of the compound $[(\mathrm{MeC_6H_4Pr^i}\text{-}p)\mathrm{ClRu}(\mu\text{-pz})_2\mathrm{Rh(CO)_2}]$ **11** with 1,2-bis(diphenylphosphino)ethane (dppe), dppen and dppp according to Scheme 2 and have spectroscopically detected the formation of the complexes $[(\mathrm{MeC_6H_4Pr^i}\text{-}p)\mathrm{Ru}(\mu\text{-pz})_2(\mu\text{-CO})\mathrm{Rh(dppe)}]^+$ **32** {ν(CO) 1763 $\mathrm{cm^{-1}}$. NMR: ^{1}H, δ 1.98(s), *p*-cymene methyl), 0.64 (d), 2.30 [spt, ^3J(HH) = 7.0, *p*-cymene isopropyl], 5.29, 5.33 [J(AB) = 6.4 Hz, aromatic *p*-cymene protons], 6.04 (br s, $\mathrm{H^4}$) and 7.65 (d), 6.80 [d, ^3J(HH) = 2.0, $\mathrm{H^{3,5}}$ pyrazolate protons]; $^{31}\mathrm{P}\text{-}\{^1\mathrm{H}\}$, δ 64.0 [$^1J$(Rh–P) = 147 Hz] and $[(\mathrm{MeC_6H_4Pr^i}\text{-}p)\mathrm{Ru}(\mu\text{-pz})_2(\mu\text{-CO})\mathrm{Rh(dppp)}]^+$ **33** [ν(CO) 1740 $\mathrm{cm^{-1}}$. NMR: ^{1}H, δ 1.73 (s, *p*-cymene methyl), 0.84 d, ^3J(HH) = 6.6, *p*-cymene isopropyl methyls], 5.48, 5.56 [J(AB) = 5.4, aromatic *p*-cymene protons] and 5.86 (br s, $\mathrm{H^4}$ pyrazolate proton); $^{31}\mathrm{P}\text{-}\{^1\mathrm{H}\}$ δ 22.5 [^1J(Rh–P) = 139.5 Hz]. We have also detected the species $[\mathrm{Rh(dppe)_2}]^+$ [δ(P) 58.0 (d), ^1J(Rh–P) = 133 Hz], $[\mathrm{Rh(dppen)_2}]^+$ [δ(P) 70.85 (d), ^1J(Rh–P) = 134.2 Hz] and $[\mathrm{Rh(dppp)_2(CO)}]^+$ as by-products,[31] probably formed by cleavage of the pyrazolate bridges by the corresponding diphosphine. We have not been able to obtain analytically pure salts of the complexes **32** and **33**. Similarly, the isomers $[(\mathrm{MeC_6H_4Pr^i}\text{-}p)\mathrm{ClRu}(\mu\text{-pz})_2\mathrm{Ir(CO)_2}]$ **12a**, **12b** react with dppe according to Scheme 2 yielding the complexes $[(\mathrm{MeC_6H_4Pr^i}\text{-}p)\mathrm{Ru}(\mu\text{-pz})_2(\mu\text{-CO})\mathrm{Ir(CO)(dppe)}]^+$ [ν(CO) 2050 and 1650 $\mathrm{cm^{-1}}$] $[(\mathrm{MeC_6H_4Pr^i}\text{-}p)\mathrm{Ru}(\mu\text{-pz})_2(\mu\text{-CO})\mathrm{Ir(dppe)}]^+$ [ν(CO) 1728 $\mathrm{cm^{-1}}$] and other unidentified materials.

In summary, the chloride atom of the dicarbonyl complexes $[\mathrm{LClM}(\mu\text{-pz})_2\mathrm{M'(CO)_2}]$ can be partially removed (in the presence of Na^+) or completely (by treatment with $AgBF_4$) and the subsequent addition of chelating diphosphines (or dpae) yields the corresponding cationic complexes $[LM(\mu\text{-pz})_2(\mu\text{-CO})M'(L\text{–}L)]^+$ *via* the intermediates $[LM(\mu\text{-pz})_2(\mu\text{-CO})M'(CO)(L\text{–}L)]^+$. When M′ is iridium the terminal CO group is more strongly retained than when M′ is rhodium, most probably due to the greater basicity of the iridium atom which favours the six-co-ordination. In some cases the species $[M'(L\text{–}L)_2]^+$ and $[M'(L\text{–}L)_2(CO)]^+$ have been detected as decomposition products. The bridging ketonic CO groups could be envisaged as dianionic CO^{2-} ligands,[15] especially in the $[LM(\mu\text{-pz})_2(\mu\text{-CO})M'(CO)(L\text{–}L)]^+$ species and, consequently, in the reaction the starting M'^+ cations are formally oxidized to M'^{3+}.

Experimental

Infrared spectra were recorded on a Perkin-Elmer 783 spectrophotometer (range 4000–200 cm^{-1}) using Nujol mulls between polyethylene sheets, or in dichloromethane solutions between NaCl plates. Molecular weights were measured in $CHCl_3$ with a Perkin-Elmer 115 osmometer. The C, H and N analyses were carried out with a Perkin-Elmer 240B microanalyser. Proton, $^{13}C\text{-}\{^1H\}$ and $^{31}P\text{-}\{^1H\}$ NMR spectra were recorded on a Varian XL200 spectrometer [80.9 (^{31}P), 50.3 (^{13}C) and 200.0 (^1H) MHz]. Solvents were dried and distilled before use.

Preparation of $[(C_5Me_5)ClRh(\mu\text{-pz})_2Ir(cod)]$ **1**.—To a mixture of $[Rh(C_5Me_5)(acac)Cl]$ (100.6 g, 0.27 mmol) and $[Ir(cod)(Hpz)_2]BF_4$ (141.3 mg, 0.27 mmol) in acetone (30 cm^3) was added KOH in methanol (3.0 cm^3, 0.0898 mol dm^{-3}, 0.27 mmol). The resulting suspension was stirred for 48 h and vacuum-evaporated until dryness. The residue was extracted with dichloromethane (30 cm^3). The solution was concentrated under reduced pressure and addition of hexane led to the precipitation of an orange solid which was filtered off, washed with hexane, and vacuum-dried. The complex was recrystallized from dichloromethane–acetone.

Complexes **2** and **3** were prepared analogously.

Reaction of $[Ru(MeC_6H_4Pr^i\text{-}p)(acac)Cl]$ *with* $[Rh(cod)(Hpz)_2]BF_4$ *and* KOH.—To a mixture of $[Ru(MeC_6H_4Pr^i\text{-}p)(acac)Cl]$ (100.0 g, 0.27 mmol) and $[Rh(cod)(Hpz)_2]BF_4$ (117.3 mg, 0.27 mmol) in acetone (20 cm^3) was added KOH (1.05 cm^3, 0.2580 mol dm^{-3}, 0.27 mmol) in MeOH and a yellow precipitate was formed. The resulting suspension was stirred for 20 h and the solid filtered off, washed with diethyl ether, and air-dried. This precipitate was characterized as $[\{Rh(pz)(cod)\}_2]$ by comparison of its spectroscopic properties and analytical data with those of an authentic sample. The resulting filtrate was vacuum-evaporated until dryness. The residue was extracted with dichloromethane (20 cm^3). The solution was concentrated under reduced pressure and the yellow precipitate which formed was filtered off, washed with hexane, and air-dried. This solid was a mixture of products, from which the compounds $[Ru(MeC_6H_4Pr^i\text{-}p)(acac)(Hpz)]BF_4$, $[Ru(MeC_6H_4Pr^i\text{-}p)(acac)Cl]$ and $[(MeC_6H_4Pr^i\text{-}p)ClRu(\mu\text{-pz})_2Rh(cod)]$ were identified.

Preparation of $[MeC_6H_4Pr^i\text{-}p)ClRu(\mu\text{-pz})_2Rh(cod)]$ **4**.—To a mixture of $[Ru(MeC_6H_4Pr^i\text{-}p)Cl(Hpz)_2]BF_4$ (159.2 g, 0.32 mmol) and $[Rh(acac)(cod)]$ (100.0 mg, 0.32 mmol) in thf (30 cm^3) was added KOH (1.25 cm^3, 0.2580 mol dm^{-3}, 0.32 mmol) in methanol. The resulting suspension was stirred for 40 h then the KBF_4 formed was filtered off. The filtrate was evaporated under reduced pressure and addition of diethyl ether gave a yellow precipitate, which was filtered off, washed with Et_2O and air-dried.

The analogue $[(MeC_6H_4Pr^i\text{-}p)ClRu(\mu\text{-pz})_2Ir(cod)]$ **5** and complexes **1**–**3** were also prepared by this method.

Reaction of $[Ru(MeC_6H_4Pr^i\text{-}p)(acac)(pz)]$ *with* $[RhCl(cod)(Hpz)]$.—The addition of $[Ru(MeC_6H_4Pr^i\text{-}p)(acac)(pz)]$ (127.6 mg, 0.32 mmol) to $[RhCl(cod)(Hpz)]$ (100.0 mg, 0.32 mmol) in acetone (30 cm^3) led to the precipitation of a yellow solid which, after 7 h of stirring, was filtered off, washed with diethyl ether and air-dried. This precipitate was characterized as $[\{Rh(pz)(cod)\}_2]$ by comparison of its spectroscopic properties and analytical data with those of an authentic sample. The resulting filtrate was evaporated under reduced pressure and slow addition of diethyl ether gave a yellow solid whose analytical and spectroscopic data are identical to those found for the complex $[Ru(MeC_6H_4Pr^i\text{-}p)(acac)(Hpz)]Cl$.

Preparation of $[MeC_6H_4Pr^i\text{-}p)Ru(\mu\text{-pz})(\mu\text{-Cl})_2Rh(cod)]$ **7**.—A mixture of $[\{Rh(OMe)(cod)\}_2]$ (222.3 mg, 0.46 mmol) and $[Ru(MeC_6H_4Pr^i\text{-}p)Cl_2(Hpz)]$ (343.9 mg, 0.92 mmol) in acetone (40 cm^3) was stirred for 3 h. The resulting solution was partially concentrated under reduced pressure and slow addition of diethyl ether gave an orange solid which was filtered off, washed with diethyl ether and air-dried.

Reaction of $[Ru(MeC_6H_4Pr^i\text{-}p)(acac)Cl]$ *with* $[RhCl(cod)(Hpz)]$.—When $[Ru(MeC_6H_4Pr^i\text{-}p)(acac)Cl]$ (100.0 mg, 0.27 mmol) was added to $[RhCl(cod)(Hpz)]$ (85.0 mg, 0.27 mmol) in methanol (25 cm^3) the slow precipitation of a yellow solid began immediately. The mixture was stirred for 4 h and then the solid was filtered off, washed with diethyl ether and air-dried. This precipitate was characterized as $[\{RhCl(cod)\}_2]$ by comparison of its spectroscopic properties and analytical data with those of an authentic sample. The filtrate was evaporated to *ca.* 2 cm^3 and addition of hexane led to a yellow solid. It was a mixture of products from which $[Ru(MeC_6H_4Pr^i\text{-}p)(acac)(Hpz)]Cl$ and the starting compound $[Ru(MeC_6H_4Pr^i\text{-}p)(acac)Cl]$ were identified.

Preparation of $[(MeC_6H_4Pr^i\text{-}p)ClRu(\mu\text{-pz})_2Rh(CO)_2]$ **11**.—Bubbling of carbon monoxide (atmospheric pressure, room temperature) for 3 h through CH_2Cl_2 or thf solutions (20 cm^3) of compound **4** (0.15 mmol) led to orange solutions which were partially concentrated under reduced pressure. The slow addition of hexane gave complex **11** as an orange-yellow solid which was filtered off, washed with hexane and air-dried.

Preparation of $[(C_5Me_5)IRh(\mu\text{-pz})_2Rh(CO)_2]$ **14**.—A mixture of $[(C_5Me_5)ClRh(\mu\text{-pz})_2Rh(CO)_2]$ (250.3 mg, 0.442 mmol) and $NaI{\cdot}6H_2O$ (228.4 mg, 0.884 mmol) in acetone (40 cm^3) was stirred for 30 h. The resulting orange solution was vacuum-evaporated until dryness. The residue was extracted with dichloromethane (30 cm^3). The solution obtained was partially concentrated under reduced pressure. Slow addition of hexane led to the precipitation of an orange solid which was filtered off, washed with hexane and vacuum-dried. The complex was recrystallized from dichloromethane–hexane. Complex **15** was prepared analogously.

Preparation of $[(C_5Me_5)Ir(\mu\text{-pz})_2(\mu\text{-CO})Ir(CO)(dppp)]BPh_4$ **18**.—To a suspension of complex **10** (320.5 mg, 0.40 mmol) in methanol (25 cm^3) was added successively $NaBPh_4$ (150.6 mg, 0.44 mmol) and dppp (165.8 mg, 0.40 mmol). The solids dissolved and the slow precipitation of an orange solid was observed. The mixture was stirred for 24 h and then the solid formed was filtered off, washed with MeOH and Et_2O, and air-dried. The complex was recrystallized from MeOH–Et_2O. Complex **19** was prepared analogously.

Preparation of $[(MeC_6H_4Pr^i\text{-}p)Ru(\mu\text{-pz})_2(\mu\text{-CO})Ir(CO)(dppen)]BF_4$ **21**.—To a suspension of complex **12** (160.0 mg, 0.24 mmol) in thf (20 cm^3) was added $AgBF_4$ (47.7 mg, 0.24 mmol). The resulting suspension was stirred for 30 min and the AgCl formed filtered off. To the filtrate was added dppen (102.0 mg, 0.26 mmol). The solution was stirred for 3 h and then

Table 7 Fractional atomic coordinates (× 10^4) for the non-hydrogen atoms of complex **19**

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Ir(1)*	44 838(3)	27 985(2)	34 078(2)
Ir(2)*	68 485(3)	29 057(2)	43 421(2)
P(1)	3 675(2)	2 817(1)	4 164(2)
P(2)	3 100(2)	3 274(1)	2 409(2)
O(1)	5 721(5)	2 012(4)	4 681(5)
O(2)	4 022(6)	1 499(4)	3 007(5)
N(1)	5 080(5)	3 633(4)	3 851(4)
N(2)	6 019(6)	3 661(4)	4 183(5)
N(3)	5 261(5)	2 814(4)	2 749(5)
N(4)	6 200(6)	2 879(4)	3 134(5)
C(1)	5 726(7)	2 444(5)	4 296(6)
C(2)	4 168(7)	1 994(5)	3 135(6)
C(3)	6 241(8)	4 234(5)	4 417(7)
C(4)	5 454(9)	4 565(5)	4 255(7)
C(5)	4 739(8)	4 170(5)	3 907(6)
C(6)	6 495(8)	2 943(6)	2 573(8)
C(7)	5 778(8)	2 925(6)	1 836(7)
C(8)	5 021(8)	2 843(5)	1 972(6)
C(9)	2 609(7)	3 205(5)	3 640(6)
C(10)	2 351(7)	3 386(5)	2 911(6)
C(35)	8 266(7)	2 648(6)	4 498(7)
C(36)	7 912(7)	2 227(5)	4 868(8)
C(37)	7 787(8)	2 541(6)	5 480(7)
C(38)	8 028(7)	3 142(6)	5 448(7)
C(39)	8 345(7)	3 209(5)	4 851(8)
C(40)	8 599(10)	2 493(8)	3 881(9)
C(41)	7 811(9)	1 558(6)	4 724(10)
C(42)	7 527(10)	2 242(8)	6 065(9)
C(43)	8 060(10)	3 619(7)	6 020(8)
C(44)	8 769(10)	3 777(6)	4 662(11)
C(11)	2 358(7)	2 824(4)	1 540(6)
C(12)	2 084(8)	2 256(5)	1 660(7)
C(13)	1 523(8)	1 912(5)	1 029(7)
C(14)	1 245(9)	2 128(5)	287(8)
C(15)	1 486(9)	2 695(6)	143(8)
C(16)	2 066(8)	3 057(5)	791(7)
C(17)	3 185(8)	4 016(5)	2 043(6)
C(18)	2 399(9)	4 412(6)	1 755(7)
C(19)	2 521(10)	4 990(6)	1 515(8)
C(20)	3 369(11)	5 171(7)	1 541(9)
C(21)	4 109(10)	4 791(6)	1 799(8)
C(22)	4 022(8)	4 215(5)	2 049(7)
C(23)	3 285(8)	2 078(5)	4 327(6)
C(24)	2 402(8)	1 870(5)	3 822(7)
C(25)	2 157(10)	1 285(6)	3 921(8)
C(26)	2 745(10)	943(7)	4 488(8)
C(27)	3 594(10)	1 129(6)	4 992(8)
C(28)	3 876(9)	1 725(5)	4 904(7)
C(29)	4 178(7)	3 174(4)	5 121(6)
C(30)	3 612(8)	3 303(5)	5 488(7)
C(31)	3 959(8)	3 603(5)	6 205(7)
C(32)	4 849(9)	3 777(5)	6 533(8)
C(33)	5 454(10)	3 630(6)	6 193(8)
C(34)	5 098(8)	3 333(5)	5 486(7)
C(45)	−82(8)	5 022(5)	1 935(7)
C(46)	−648(9)	5 003(6)	1 130(7)
C(47)	−580(10)	5 404(6)	592(9)
C(48)	30(10)	5 863(6)	852(9)
C(49)	571(10)	5 942(7)	1 640(9)
C(50)	507(9)	5 505(5)	2 166(8)
C(51)	−1 211(8)	4 692(5)	2 542(7)
C(52)	−1 389(8)	5 248(5)	2 742(7)
C(53)	−2 225(10)	5 411(7)	2 752(8)
C(54)	−2 878(14)	5 015(9)	2 608(11)
C(55)	−2 698(16)	4 434(11)	2 430(12)
C(56)	−1 892(13)	4 287(9)	2 369(10)
C(57)	596(7)	4 614(4)	3 449(6)
C(58)	401(8)	4 617(5)	4 111(7)
C(59)	1 082(9)	4 607(5)	4 868(8)
C(60)	2 000(9)	4 590(5)	4 999(8)
C(61)	2 230(9)	4 600(5)	4 372(7)
C(62)	1 533(8)	4 615(5)	3 602(7)
C(63)	−119(7)	3 835(5)	2 314(6)
C(64)	−31(7)	3 637(5)	1 646(6)
C(65)	59(8)	3 019(5)	1 501(7)
C(66)	78(8)	2 600(6)	2 010(7)
C(67)	2(9)	2 767(5)	2 690(7)
C(68)	−93(8)	3 376(5)	2 837(7)
B	−186(9)	4 549(6)	2 560(8)
O(3)	5 558(11)	467(7)	4 896(10)
C(69)	5 278(30)	14(19)	5 360(21)

* Atomic co-ordinates expressed × 10^5.

concentrated to *ca.* 1 cm^3. Complex **21** was precipitated by addition of Et_2O, filtered off, washed with Et_2O and air-dried.

Complex **20**, prepared analogously, was contaminated by $[(MeC_6H_4Pr^i\text{-}p)Ru(\mu\text{-}pz)_2(\mu\text{-}CO)Ir(dppp)]BF_4$ **24**. The complex $[(MeC_6H_4Pr^i\text{-}p)Ru(\mu\text{-}pz)_2(\mu\text{-}CO)Ir(CO)(dppen)]BPh_4$ **22** was obtained by treating a solution of **21** (100.0 mg, 0.09 mmol) in methanol (30 cm^3) with $NaBPh_4$ (46.6 mg, 0.14 mmol). The orange solid, which slowly precipitates, was filtered off, washed with MeOH and Et_2O, and air-dried.

Preparation of $[(C_5Me_5)Ir(\mu\text{-}pz)_2(\mu\text{-}CO)Ir(dppp)]BPh_4$ **23**.—A solution of complex **18** (0.30 mmol) in $CHCl_3$ (25 cm^3) was refluxed for 1 h. The solution was partially concentrated under reduced pressure. Addition of hexane led to the precipitation of a yellow solid which was filtered off, washed with hexane and vacuum dried. The complex was recrystallized from dichloromethane–hexane. The homologous complex **24** was prepared analytically pure by refluxing for 1 h in chloroform a mixture of complexes **20** and **24** prepared as described above.

Preparation of $[(MeC_6H_4Pr^i\text{-}p)Ru(\mu\text{-}pz)_2(\mu\text{-}CO)Ir(dppb)]BF_4$ **27**.—Under nitrogen, to a solution of complex **12** (110.0 mg, 0.17 mmol) in methanol (25 cm^3) was added $AgBF_4$ (32.8 mg, 0.17 mmol) in the same solvent. The resulting suspension was stirred for 30 min and then filtered to remove the AgCl formed. To the filtrate, dppb (71.8 mg, 0.17 mmol) was added and the yellow solution was stirred for 5 h. The solvent was concentrated to *ca.* 3 cm^3 and the addition of diethyl ether gave a solid which was filtered off, washed with diethyl ether, and air-dried.

Complexes **29**–**31** were prepared by the same method but the solvent was thf and the reactions were completed in 2 h. {δ_C (50.3 MHz, solvent $CDCl_3$, standard $SiMe_4$): **27**, 210.1 (s, μ-CO); **29**, 221.2 [d, ^1J(Rh–C) 22, μ-CO]; **30**, 222.6 [d, J(Rh–C) 21 Hz, μ-CO]}.

Complexes **25**, **26** and **28** were prepared by treating, under nitrogen, methanolic solutions of $[(MeC_6H_4Pr^i\text{-}p)ClRu(\mu\text{-}pz)_2M'(CO)_2]$ (M′ = Ir or Rh) (0.17 mmol) with $NaBPh_4$ (0.17 mmol) in the presence of 0.17 mmol of the ligands dppp, dppb or dppm, respectively. The starting compounds dissolved and slow precipitation of the products began immediately. The suspensions were stirred for 6 h and then the complexes were filtered off, washed with methanol and diethyl ether, and air-dried.

X-*Ray Structure Determination of* $[(C_5Me_5)Ir(\mu\text{-}pz)_2(\mu\text{-}CO)Ir(CO)(dppen)]BPh_4\cdot 0.5MeOH$ **19**.—*Crystal data* $C_{68}H_{63}BIr_2N_4O_2P_2\cdot 0.5CH_3OH$, M = 1441.98, monoclinic, space group $P2_1/c$, a = 15.996(2), b = 22.199(4), c = 18.874(3) Å, β = 115.04(1)°, U = 6072(2) $Å^3$ (refined from 56 carefully centred reflections, 20 ⩽ 20 ⩽ 35°), Mo-Kα radiation (λ = 0.710 69 Å), Z = 4, D_c = 1.577 g cm^{-3}, crystal dimensions 0.338 × 0.308 × 0.334 mm, $F(000)$ = 2852.

Data collection and processing. Four-circle Siemens AED-2 diffractometer (graphite-monochromated Mo-Kα radiation). Data collected at room temperature, ω–2θ scan technique ($3 \leqslant 2\theta \leqslant 45°$). 8558 Reflections measured, 7427 unique (R_{int} 0.016), 5458 with $F \geqslant 5\sigma(F)$ used for calculations. An absorption correction based on the ψ-scan method ($\mu = 44.61$ cm^{-1}) was applied (minimum and maximum transmission factors 0.275, 0.338).[32]

Structure solution and refinement. The structure was solved by direct and Fourier methods and refined by full-matrix least squares for 476 parameters. All remaining atoms of the molecule were located in Fourier difference maps, except hydrogen atoms. The hydrogens were placed at their calculated positions and introduced in the final structure-factor calculations. A methanol solvent molecule was also included in the refinement to account for the remaining peaks in the Fourier difference map; its occupancy factor was fixed at 0.5. The maximum peak in the final ΔF had 1.38 e Å^{-3} close to C(69). The final R and R' values were 0.035 and 0.036 respectively; weighting scheme $w = 1.0000/[\sigma^2(F) + 0.000\,525\,8F]$. The SHELX system of computer programs was used.[33] Atomic scattering factors, corrected for anomalous dispersion, were taken from ref. 34. Final atomic coordinates for the non-hydrogen atoms are given in Table 7.

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

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