Binuclear Rhodium and Iridium Complexes containing Pentamethylcyclopentadienyl and Pyrazolate Ligands

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The preparation of the methoxo- and hydroxo-bridged pentamethylcyclopentadienyliridium(III) complexes $[\{(C_5Me_5)Ir\}_2(\mu\text{-}Pz)_2(\mu\text{-}OH)][BF_4]$ [Pz = pyrazolate (pz) or 3-methylpyrazolate (mpz)], $[\{(C_5Me_5)Ir\}_2(\mu\text{-}Pz)(\mu\text{-}OMe)_2][A]$ [A = ClO_4 or BF_4; Pz = pz, mpz, or 3,5-dimethylpyrazolate (dmpz)], and $[\{(C_5Me_5)Ir(Hdmpz)\}_2(\mu\text{-}OH)_2][BF_4]_2$ from $[Ir(C_5Me_5)(Me_2CO)_3][A]_2$ or $[\{(C_5Me_5)Ir\}_2(\mu\text{-}OH)_3][BF_4]\cdot H_2O$ and their characterisation are reported. $[\{(C_5Me_5)Ir\}_2(\mu\text{-}pz)_2(\mu\text{-}OH)][BF_4]$ and $[\{(C_5Me_5)Ir\}_2(\mu\text{-}pz)(\mu\text{-}OMe)_2][BF_4]$ and their rhodium analogues react with HCl yielding the binuclear chloride complexes $[\{(C_5Me_5)M\}_2(\mu\text{-}pz)_2(\mu\text{-}Cl)][BF_4]$ and $[\{(C_5Me_5)M\}_2(\mu\text{-}pz)(\mu\text{-}Cl)_2][BF_4]$ (M = Rh or Ir). Progressive addition of hydrochloric acid to the last rhodium complex leads to the mononuclear compounds $[Rh(C_5Me_5)Cl(Hpz)_2][BF_4]$ and $[Rh(C_5Me_5)Cl_2(Hpz)]$ and, ultimately, to $[\{(C_5Me_5)RhCl\}_2(\mu\text{-}Cl)_2]$. The complexes $[\{(C_5Me_5)M\}_2(\mu\text{-}pz)_2(\mu\text{-}Cl)][BF_4]$ and $[\{(C_5Me_5)M\}_2(\mu\text{-}pz)(\mu\text{-}Cl)_2][BF_4]$ were also prepared from the corresponding neutral complex $[M(C_5Me_5)Cl_2(Hpz)]$; the mixed-metal complex $[(C_5Me_5)Rh(\mu\text{-}pz)(\mu\text{-}Cl)_2Ir(C_5Me_5)][BF_4]$ was also prepared by this route. The di-μ-hydrido-rhodium complex $[\{(C_5Me_5)Rh\}_2(\mu\text{-}pz)(\mu\text{-}H)_2][BF_4]$ reacted with neutral ligands L (CO or Bu^tNC) to give $[\{(C_5Me_5)Rh\}_2(\mu\text{-}pz)L_2][BF_4]$. Spectroscopic studies on these complexes and on the carboxylate complex $[\{(C_5Me_5)Rh\}_2(\mu\text{-}O_2CMe)(\mu\text{-}CO)_2][PF_6]$ (prepared from $[\{(C_5Me_5)Rh\}_2(\mu\text{-}H)_2(\mu\text{-}O_2CMe)][PF_6]$ and CO) indicate that the CO and Bu^tNC ligands are moving between terminal and bridging positions.

We have recently reported the synthesis of binuclear homovalent pentamethylcyclopentadienylrhodium(III) complexes[1] containing pyrazolate[2] or pyrazolate and methoxo- or hydroxo-bridging groups[3] and of heterovalent ($Rh^{III}Rh^{I}$) and heterobinuclear ($Rh^{III}Ir^{I}$, $Rh^{I}Ir^{III}$) complexes.[4–6] However the only binuclear homovalent pentamethylcyclopentadienyliridium(III) complexes containing pyrazolate ligands are $[\{(C_5Me_5)Ir\}_2(\mu\text{-}Pz)(\mu\text{-}H)_2][BF_4]$ [Pz = pyrazolate (pz), 3-methylpyrazolate (mpz), or 3,5-dimethylpyrazolate (dmpz)].[7,†] It seemed of interest to study if the synthetic strategy used for the preparation of the above mentioned heterobridged rhodium complexes containing pyrazolate and methoxo- or hydroxo-bridging ligands could be extended for related pentamethylcyclopentadienyliridium complexes. We also report the preparation of binuclear pentamethylcyclopentadienyl-rhodium or -iridium complexes containing chloro- and pyrazolate-bridging groups as well as the reactivity of the di-μ-hydrido complex $[\{(C_5Me_5)Rh\}_2(\mu\text{-}pz)(\mu\text{-}H)_2][BF_4]$ towards Bu^tNC and CO.

Results and Discussion

When an acetone solution of the unusual di-μ-methoxo-μ-pyrazolate rhodium(III) complex $[\{(C_5Me_5)Rh\}_2(\mu\text{-}pz)(\mu\text{-}OMe)_2][ClO_4]$ (**1a**)[3] was reacted with two equivalents of HCl, it yielded quantitatively the triple-bridged complex $[\{(C_5Me_5)Rh\}_2(\mu\text{-}pz)(\mu\text{-}Cl)_2][ClO_4]$ (**3a**) and two moles of methanol (^1H n.m.r.). Complex (**3a**) was also the main product of the reaction of the μ-hydroxo-di-μ-pyrazolate complex $[\{(C_5Me_5)Rh\}_2(\mu\text{-}pz)_2(\mu\text{-}OH)][ClO_4]$ (**2a**) with two equivalents of HCl (^1H n.m.r.). An intermediate in this reaction, the mono-μ-chloride complex $[\{(C_5Me_5)Rh\}_2(\mu\text{-}pz)_2(\mu\text{-}Cl)]^+$ (**4**), was isolated in 79% yield from the reaction of (**2a**) with one equivalent of HCl in acetone–water (2:1), since its perchlorate salt (**4a**) was insoluble in water. These reactions imply preferential protonation of the methoxo or hydroxo groups and the replacement of the neutral methanol or water by μ-chlorides. They confirm the stability of pyrazolates as *exo*-bidentate ligands.[6,8] Complex (**3a**) reacted further with HCl (one equivalent) to give the mononuclear species $[Rh(C_5Me_5)Cl_2(Hpz)]$ (**5**)[9] and $[Rh(C_5Me_5)Cl(Hpz)_2]^+$ (**6**) as well as dinuclear $[\{(C_5Me_5)RhCl\}_2(\mu\text{-}Cl)_2]$ (**7**),[10] which precipitated from the reaction medium. Addition of more hydrochloric acid led to the formation of complex (**7**) from both complexes (**5**) and (**6**).

In basic media, the pyrazole in complex (**5**) loses it acidic proton and dimerizes with formation of the complex cation (**4**), isolated as its tetraphenylborate salt (**4c**).

The complexes $[\{(C_5Me_5)M\}_2(\mu\text{-}pz)(\mu\text{-}Cl)_2][BF_4]$ (**3b**, M = Rh) and (**8b**, M = Ir) have been prepared by reacting the mononuclear neutral species $[M(C_5Me_5)Cl_2(Hpz)]$ [M = Rh (**5**) or Ir (**9**)‡] with the acetylacetonate complexes $[\{(C_5Me_5)Rh\}_2(\mu\text{-}acac)_2][BF_4]_2$[11] or $[Ir(C_5Me_5)(acac)(MeOH)][BF_4]$.§

Reaction of the acetylacetonato-rhodium or -iridium complex and the corresponding chloride complex of the other metal gave the heterobimetallic related complex $[(C_5Me_5)Rh-$

† Throughout this paper HPz is used to represent a generic pyrazole; Hpz is used for unsubstituted pyrazole itself.

‡ This complex was prepared as described[9] for complex (**5**).

§ This solvated complex was obtained by treating $[Ir(C_5Me_5)(acac)Cl]$[11] with $AgBF_4$ in methanol.

$(\mu\text{-pz})(\mu\text{-Cl})_2Ir(C_5Me_5)][BF_4]$ (**10b**). Other heterobimetallic rhodium–iridium complexes have proven difficult to isolate,[12] in the absence of specific strategies to link the two metal-containing fragments.[5,13]

The ability of the pyrazolate group to participate in triple-bridged d^6 species[3] is also shown by the synthesis of the dinuclear iridium complexes $[\{(C_5Me_5)Ir\}_2(\mu\text{-Pz})_2(\mu\text{-OH})][BF_4]$ [Pz = pz (**11b**) or mpz (**12b**)] and $[\{(C_5Me_5)Ir\}_2(\mu\text{-Pz})(\mu\text{-OMe})_2][A]$ [A = ClO_4, Pz = pz (**13a**), mpz (**14a**), or dmpz (**15a**); A = BF_4, Pz = pz (**13b**), mpz (**14b**), or dmpz (**15b**)]. The dinuclear complexes (**11b**) or (**12b**) were formed by reaction of the solvated complex $[Ir(C_5Me_5)(Me_2CO)_3][BF_4]_2$[14] with pyrazoles (Hpz or Hmpz) and base (KOH or NEt_3) in acetone or by reacting the tri-μ-hydroxo complex $[\{(C_5Me_5)Ir\}_2(\mu\text{-OH})_3][BF_4]\cdot H_2O$* with excess of pyrazole or 3-methylpyrazole (Hmpz). Complexes of formula $[\{(C_5Me_5)Ir\}_2(\mu\text{-Pz})(\mu\text{-OH})_2]^+$ (Pz = pz or mpz) are probably intermediate in the latter reaction, since that pyrazolate complex has been detected by ^1H n.m.r. spectroscopy: δ_H (200 MHz, $CDCl_3$) 1.70 (30 H, s, 2 C_5Me_5), 6.51 [1 H, t, J(HH) 2, 4-CH], 7.84 p.p.m. [2 H, d, J(HH) 2 Hz, 3,5-CH].

All attempts to obtain the triple pyrazolate-bridged complexes $[\{(C_5Me_5)Ir\}_2(\mu\text{-Pz})_3]^+$ have been unsuccessful, as have attempts to make the corresponding rhodium(III) compounds.[3]

The di-μ-methoxo complexes (**13**)—(**15**) were prepared by reacting the mononuclear solvated complex $[Ir(C_5Me_5)(MeOH)_3][ClO_4]_2$ with the corresponding pyrazole and KOH (2:1:3 molar ratio) in methanol or by treating $[\{(C_5Me_5)Ir\}_2(\mu\text{-OH})_3][BF_4]\cdot H_2O$ with one mole of pyrazole, 3-methylpyrazole, or 3,5-dimethylpyrazole (Hdmpz) in methanol. In contrast, reaction of $[Ir(C_5Me_5)(Me_2CO)_3][BF_4]_2$ with Hdmpz and NEt_3 (1:1:1 molar ratio) gave the di-μ-hydroxo complex $[\{(C_5Me_5)Ir(Hdmpz)\}_2(\mu\text{-OH})_2][BF_4]_2$ (**16b**). No 3,5-dimethylpyrazolate derivative of stoicheiometry similar to complexes (**11b**) or (**12b**) was observed. Complex (**16b**) was also prepared by reacting $[\{(C_5Me_5)Ir\}_2(\mu\text{-OH})_3][BF_4]\cdot H_2O$ with Hdmpz and HBF_4 (1:2:1 molar ratio) or by adding tetrafluoroboric acid to complex (**15b**) in the presence of Hdmpz. The last reaction was reversed by treating a methanolic solution of complex (**16b**) with KOH.

Addition of HCl to complex (**13b**) gave the di-μ-chloro complex (**8b**); similarly the dinuclear complex $[\{(C_5Me_5)Ir\}_2(\mu\text{-pz})_2(\mu\text{-Cl})][BF_4]$ (**17b**) was formed on reacting (**11b**) with HCl. Reaction of the mononuclear complex (**9**) with potassium hydroxide yielded $[\{(C_5Me_5)Ir\}_2(\mu\text{-pz})_2(\mu\text{-Cl})]^+$ (**17**), which was isolated as its tetraphenylborate salt (**17c**) on addition of $NaBPh_4$.

Scheme 1 summarizes the above mentioned reactions.

The fully characterised dark blue complex $[\{(C_5Me_5)Ir\}_2(\mu\text{-pz})(\mu\text{-H})_2][BF_4]$, made by reacting $[\{(C_5Me_5)Ir\}_2(\mu\text{-OH})_3][BF_4]\cdot H_2O$ with pyrazole in refluxing propan-2-ol,[7] was inert towards CO and Bu^{t}NC. The related dark green cationic complex $[\{(C_5Me_5)Rh\}_2(\mu\text{-pz})(\mu\text{-H})_2][BF_4]$ (**18b**) could be synthesized in good yield; however, a persistent problem was the presence of impurities, shown by the ^1H n.m.r. spectrum to be the μ-hydroxo-di-μ-pyrazolate complex $[\{(C_5Me_5)Rh\}_2(\mu\text{-pz})_2(\mu\text{-OH})][BF_4]$ (**2b**). Owing to the very similar properties of these two complexes separation was very difficult indeed and could not be accomplished without serious losses. The presence of even more impurities (including hydrido complexes) was observed when the cation $[\{(C_5Me_5)Rh\}_2(\mu\text{-pz})(\mu\text{-H})_2]^+$ was prepared with other counter anions (*e.g.* perchlorate). Other routes to this dihydride did not give better results. However, the impurities did not seem to interfere with the reactions that were carried out on the dihydride and were usually very much easier to remove from the products of those reactions.

The di-μ-hydrido-rhodium complex (**18b**) reacted with neutral ligands, L, according to equation (1). However, stable

$$[\{(C_5Me_5)Rh\}_2(\mu\text{-pz})(\mu\text{-H})_2][BF_4] + 2\,L \longrightarrow [\{(C_5Me_5)Rh\}_2(\mu\text{-pz})L_2][BF_4] + H_2 \quad (1)$$

pure products could only be isolated when L = Bu^{t}NC, (**19b**), or CO, (**20b**). Complex (**19b**) showed only one type of isonitrile and of one C_5Me_5, both in the ^1H and in the ^{13}C n.m.r. spectra at ambient temperatures. This implies that the dinuclear molecule has an effective plane of symmetry. The ^{13}C spectrum of the complex at low temperatures was identical (allowing for some temperature-dependent chemical shift changes) except for the resonance due to the isonitrile –NC, which was a triplet at higher temperatures and a doublet at −65 °C. The splittings are due to coupling to ^{103}Rh (100%, $I = \frac{1}{2}$) and we interpret these data to mean that the complex is fluxional on the n.m.r. time-scale, the two isonitriles being apparently equivalently coupled to both rhodiums at ambient temperature, with a small coupling, J = 39.3 Hz. At −65 °C that signal appears as a doublet with twice the coupling, J = 77.9 Hz, indicating that there the motion is very slow on the n.m.r. time-scale and that the isonitrile is bonded (terminally) to one rhodium. Analogous movements of isonitriles between two metal centres have been described.[16]

Reaction of the di-μ-hydrido-μ-pyrazolate complex (**18b**) with carbon monoxide occurred readily at 1 atm (*ca.* 10^5 N m^{-2}) and ambient temperature. Hydrogen was again displaced and the product was shown by fast-atom bombardment (f.a.b.) mass spectrometry to be again a diligand complex. In this case the i.r. spectrum showed the presence of two carbonyl bands, one at 1 848 cm^{-1}, ascribed to a bridging carbonyl group, and one at 2 006 cm^{-1} which we assign to a terminal carbonyl. However, even at −50 °C the ^{13}C n.m.r. spectrum showed only a single resonance due to the carbonyl, which was a triplet, J = 38.7 Hz, due to coupling to two rhodiums. The remainder of the spectrum was also consistent with this since only one set of C_5Me_5 resonances was observed and the pyrazolate also showed a plane of symmetry. Again we suggest that this molecule undergoes dynamic behaviour, this time exchanging the carbonyls. However here the ground state appears to be an asymmetric one with one bridging and one terminal carbonyl.

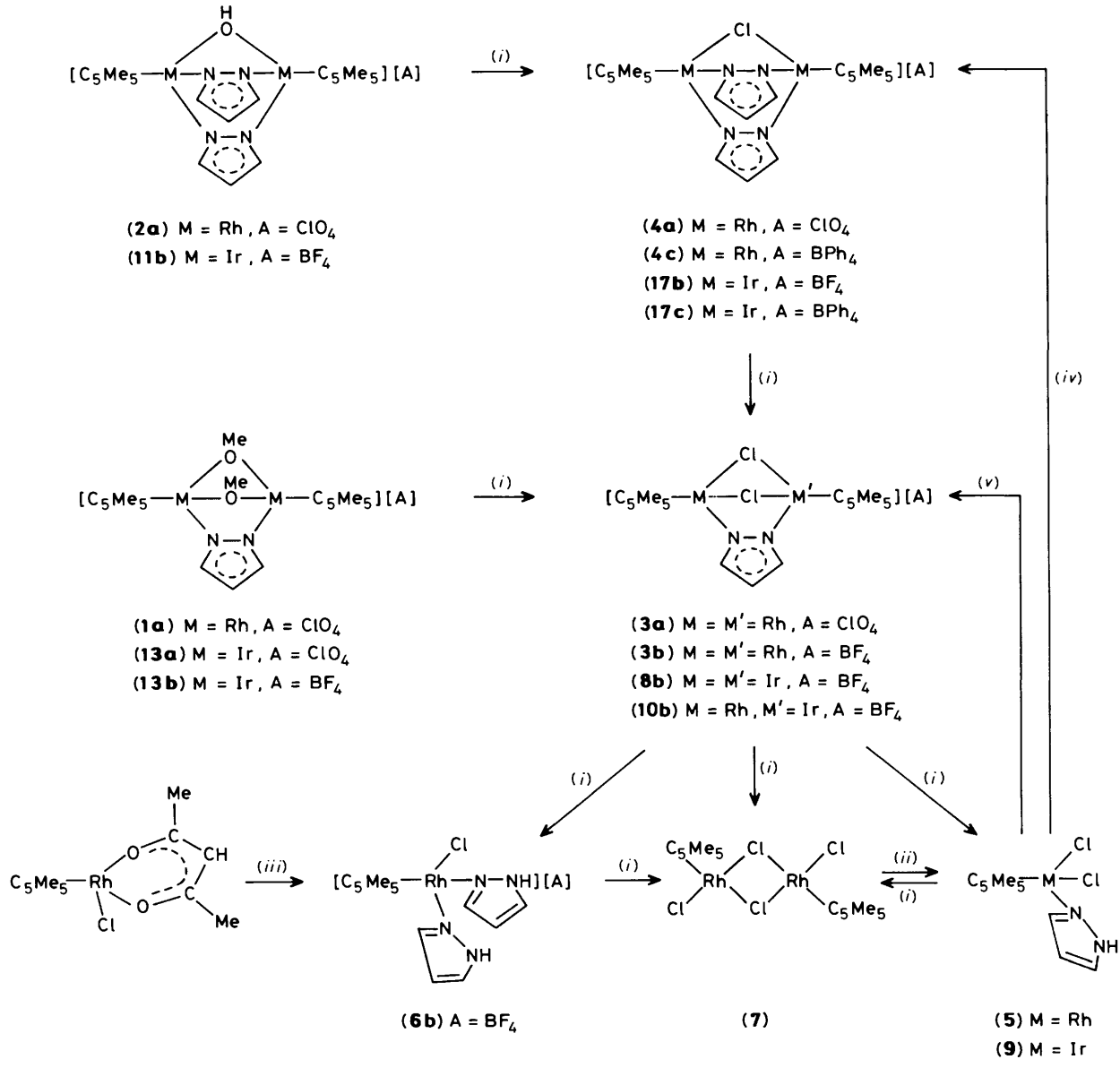
By contrast, although reaction of the μ-acetato-di-μ-hydrido complex with CO gave another diligand complex, (**21d**), equation (2), again shown by the f.a.b. mass spectrum, the

$$[\{(C_5Me_5)Rh\}_2(\mu\text{-H})_2(\mu\text{-}O_2CMe)][PF_6] + 2\,CO \longrightarrow [\{(C_5Me_5)Rh\}_2(\mu\text{-}O_2CMe)(\mu\text{-CO})_2][PF_6] + H_2 \quad (2)$$
(**21d**)

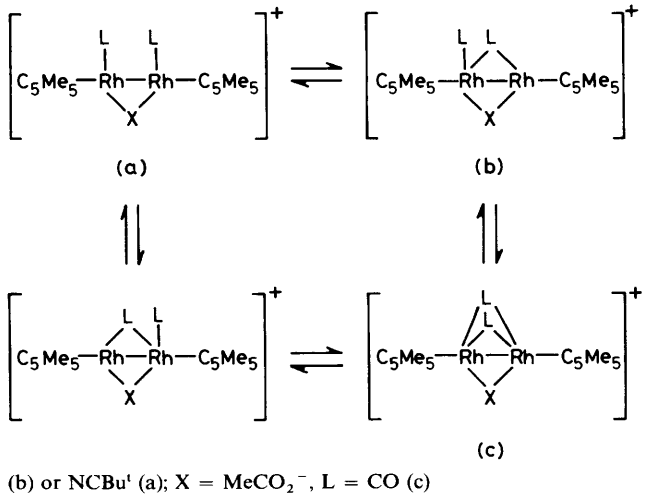
reaction was significantly slower than that of the dihydrido-pyrazolate. Further, whereas in (**20b**) the i.r. spectrum strongly indicated one terminal and one bridging carbonyl, in (**21d**) only one metal carbonyl band was observed, in the bridging region, at 1 840 cm^{-1}. The ^{13}C spectrum at −50 °C confirmed that by showing one carbonyl resonance at 230 p.p.m. as a triplet, J = 40.5 Hz.

Thus the three complexes (**19b**), (**20b**), and (**21d**) show the whole expected range of bridging/terminal behaviour: the di-isocyanide-pyrazolate complex (**19b**) is fluxional and has a ground state having two terminally bound ligands, the acetato-dicarbonyl complex (**21d**) appears to be static with only bridging ligands, and the dicarbonyl-pyrazolate complex (**20b**) is fluxional again with a ground state having one bridging and one terminal carbonyl. The relationships are depicted in Scheme

* Prepared by treating $[\{(C_5Me_5)Ir\}_2(\mu\text{-OH})_3][OH]\cdot nH_2O$[15] with one equivalent of HBF_4 in the presence of excess of $NaBF_4$.



Scheme 1. (*i*) HCl; (*ii*) Hpz; (*iii*) HBF_4, Hpz; (*iv*) KOH, $NaBPh_4$; (*v*) $\frac{1}{2}[\{(C_5Me_5)Rh\}_2(\mu\text{-acac})_2][BF_4]_2$ or $[Ir(C_5Me_5)(acac)(MeOH)][BF_4]$



Scheme 2. X = pyrazolate, L = CO (b) or $NCBu^t$ (a); X = $MeCO_2^-$, L = CO (c)

Table 1. Analytical, i.r. data and yields for the new complexes

Complex	Analysis[a] (%) C	H	N	I.r.[b]/cm^{-1}	Yield (%)
(3a) $[\{(C_5Me_5)Rh\}_2(\mu\text{-pz})(\mu\text{-Cl})_2][ClO_4]$	38.8 (38.7)	4.6 (4.7)	4.4 (3.9)		79
(3b) $[\{(C_5Me_5)Rh\}_2(\mu\text{-pz})(\mu\text{-Cl})_2][BF_4]$	39.3 (39.4)	4.8 (4.7)	4.3 (4.0)		71
(4a) $[\{(C_5Me_5)Rh\}_2(\mu\text{-pz})_2(\mu\text{-Cl})][ClO_4]$	42.2 (41.9)	4.7 (4.9)	7.3 (7.5)		73
(4c) $[\{(C_5Me_5)Rh\}_2(\mu\text{-pz})_2(\mu\text{-Cl})][BPh_4]$	62.3 (62.2)	5.8 (5.9)	5.7 (5.8)		84
(6b) $[Rh(C_5Me_5)Cl(Hpz)_2][BF_4]$	39.2 (38.7)	4.4 (4.7)	11.3 (11.3)	3 270vs[c]	88
(8b) $[\{(C_5Me_5)Ir\}_2(\mu\text{-pz})(\mu\text{-Cl})_2][BF_4]$	31.7 (31.4)	3.8 (3.8)	3.7 (3.2)		47,[d] 65[e]
(9) $[Ir(C_5Me_5)Cl_2(Hpz)]$	33.5 (33.5)	3.9 (4.1)	6.2 (6.0)	3 200vs[c]	88
(10b) $[(C_5Me_5)Rh(\mu\text{-pz})(\mu\text{-Cl})_2Ir(C_5Me_5)][BF_4]$	34.9 (34.9)	4.1 (4.2)	3.6 (3.5)		62,[f] 59[g]
(11b) $[\{(C_5Me_5)Ir\}_2(\mu\text{-pz})_2(\mu\text{-OH})][BF_4]$	34.7 (35.0)	4.0 (4.2)	6.2 (6.3)	3 520w,[h] 520vs[i]	50,[j] 73[k]
(12b) $[\{(C_5Me_5)Ir\}_2(\mu\text{-mpz})_2(\mu\text{-OH})][BF_4]$	37.5 (36.5)	4.7 (4.5)	5.9 (6.1)	3 600w,[h] 525vs[i]	50,[j] 44[k]
(13a) $[\{(C_5Me_5)Ir\}_2(\mu\text{-pz})(\mu\text{-OMe})_2][ClO_4]$	34.0 (34.0)	4.2 (4.4)	3.2 (3.2)	505vs[i]	25
(13b) $[\{(C_5Me_5)Ir\}_2(\mu\text{-pz})(\mu\text{-OMe})_2][BF_4]$	34.7 (34.5)	4.1 (4.5)	3.2 (3.2)	505vs[i]	67
(14a) $[\{(C_5Me_5)Ir\}_2(\mu\text{-mpz})(\mu\text{-OMe})_2][ClO_4]$	34.5 (34.8)	4.3 (4.6)	3.5 (3.1)	505vs[i]	30
(14b) $[\{(C_5Me_5)Ir\}_2(\mu\text{-mpz})(\mu\text{-OMe})_2][BF_4]$	35.1 (35.3)	4.6 (4.7)	3.3 (3.2)	505vs[i]	60
(15a) $[\{(C_5Me_5)Ir\}_2(\mu\text{-dmpz})(\mu\text{-OMe})_2][ClO_4]$	35.7 (35.6)	4.6 (4.8)	3.3 (3.1)	505vs[i]	46
(15b) $[\{(C_5Me_5)Ir\}_2(\mu\text{-dmpz})(\mu\text{-OMe})_2][BF_4]$	35.9 (36.1)	4.5 (4.8)	3.2 (3.1)	510vs[i]	54,[k] 59[l]
(16b) $[\{(C_5Me_5)Ir(Hdmpz)\}_2(\mu\text{-OH})_2][BF_4]_2$	34.5 (34.2)	4.7 (4.6)	5.1 (5.3)	3 580vs,[h] 3 310,[c] 490vs[i]	40,[j] 63,[k] 61[m]
(17b) $[\{(C_5Me_5)Ir\}_2(\mu\text{-pz})_2(\mu\text{-Cl})][BF_4]$	34.5 (34.3)	3.8 (4.0)	6.3 (6.2)		71
(17c) $[\{(C_5Me_5)Ir\}_2(\mu\text{-pz})_2(\mu\text{-Cl})][BPh_4]$	52.8 (52.5)	4.9 (4.9)	5.0 (4.9)		55
(18b) $[\{(C_5Me_5)Rh\}_2(\mu\text{-pz})(\mu\text{-H})_2][BF_4]$	43.0 (43.7)	5.7 (5.6)	4.3 (4.4)		80
(19b) $[\{(C_5Me_5)Rh\}_2(\mu\text{-pz})(Bu^tNC)_2][BF_4]$	50.0 (49.8)	6.5 (6.5)	7.1 (7.0)	2 115vs[n,o]	65
(20b) $[\{(C_5Me_5)Rh\}_2(\mu\text{-pz})(CO)_2][BF_4]$	43.2 (43.8)	5.1 (4.9)	4.4 (4.1)	2 006vs,[p] 1 848vs[q,o]	85
(21d) $[\{(C_5Me_5)Rh\}_2(\mu\text{-}O_2CMe)(\mu\text{-CO})_2][PF_6]$	38.3 (39.2)	4.7 (4.5)		1 840vs[q,o]	85

[a] Calculated values are given in parentheses. [b] Nujol mulls. Typical absorptions bands of the unco-ordinated anions were observed in the expected regions (refs. 4,7,15). [c] ν(NH). [d] Prepared by reacting (**9**) with $[Ir(C_5Me_5)(acac)(MeOH)][BF_4]$. [e] Prepared from (**13b**). [f] Prepared by reacting (**9**) with $[\{(C_5Me_5)Rh\}_2(\mu\text{-acac})_2][BF_4]_2$. [g] Prepared by reacting (**5**) with $[Ir(C_5Me_5)(acac)(MeOH)][BF_4]$. [h] ν(OH). [i] ν(Ir–O–Ir). [j] Prepared from $[Ir(C_5Me_5)(Me_2CO)_3][BF_4]_2$. [k] Prepared from $[\{(C_5Me_5)Ir\}_2(\mu\text{-OH})_3][BF_4]\cdot H_2O$. [l] Prepared from (**16b**). [m] Prepared from (**15b**). [n] ν(CN). [o] In CH_2Cl_2 solution. [p] ν(CO) terminal. [q] ν(CO) bridge.

2, and we propose that the differences are probably caused by the differing steric requirements of the entering ligands, carbonyl and isonitrile, and the volume of space available around the rhodiums which is determined by the compression excercised by the bridging ligand (acetate or pyrazolate).

Unfortunately no crystals useful for *X*-ray determination could be grown of any of these complexes and the ultimate confirmation of the ground-state structures was not feasible.

Experimental

Infrared spectra were recorded on a Perkin-Elmer 1330 spectrophotometer (range 4 000—200 cm^{-1}) using Nujol mulls between polyethylene sheets, or in dichloromethane solutions between NaCl plates. The C, H, and N analyses were carried out with a Perkin-Elmer 240B microanalyzer. ^{1}H N.m.r. spectra were recorded in $CDCl_3$ or $(CD_3)_2CO$ solutions at room temperature on a Varian XL 200 and ^{13}C spectra on a Bruker AB 250 spectrometer, using $SiMe_4$ as internal standard. Mass spectra were measured on a Kratos MS-80 using the f.a.b. mode in which the complex was in a *m*-nitrobenzyl alcohol matrix. Solvents were dried and distilled before use. Analytical, significant i.r. data and yields for all the new complexes prepared are in Table 1; their ^{1}H n.m.r. data are in Table 2.

Preparation of the Di-μ-Chloro Complex (**3a**) *from* (**1a**).—Hydrochloric acid (9.3 cm^3, 0.018 mol dm^{-3}, 0.16 mmol) in

Table 2. ^{1}H N.m.r. spectra[a] for the new complexes

Complex	C_5Me_5	H(3)/H(5)	H(4)	Me(3)/Me(5)	Others
(3a)[b]	1.78 (s, 30)	7.96 (d, 2) *J*(HH) 2	6.44 (t, 1)		
(4a)[b]	1.82 (s, 30)	7.63 (d, 4) *J*(HH) 2	6.16 (t, 2)		
(6b)[b]	1.66 (s, 15)	8.07 (br,s, 2) 7.95 (br,s, 2)	6.58 (br,s, 2)		12.06 (br,s, 2)[c]
(8b)[d]	1.71 (s, 30)	7.81 (d, 2) *J*(HH) 2	6.44 (t, 1)		
(9)[d]	1.60 (s, 30)	7.58 (br,s, 2)	6.36 (br,s, 1)		12.01 (br,s, 1)[c]
(10b)[d]	1.69 (s, 15) 1.74 (s, 15)	7.87 (d, 1) *J*(HH) 2 7.69 (d, 1) *J*(HH) 2	6.45 (t, 1)		
(11b)[d]	1.72 (s, 30)	7.54 (d, 4) *J*(HH) 2	6.16 (t, 2)		
(12b)[d]	1.70 (s, 15) 1.72 (s, 15)	7.39 (d, 2) *J*(HH) 2	5.89 (d, 2)	2.26 (s, 6)	
(13b)[d]	1.61 (s, 30)	7.98 (d, 2) *J*(HH) 2	6.55 (t, 1)		3.32 (s, 6)[e]
(14a)[d]	1.60 (s, 15) 1.61 (s, 15)	7.88 (d, 1) *J*(HH) 2	6.31 (d, 1)	2.55 (s, 3)	3.20 (s, 6)[e]
(15b)[d]	1.60 (s, 30)		6.12 (s, 1)	2.49 (s, 6)	3.15 (s, 6)[e]
(16b)[d]	1.22 (s, 30)		6.13 (s, 2)	2.42 (s, 6) 2.47 (s, 6)	10.85 (br,s, 2)[c]
(17b)[d]	1.75 (s, 30)	7.52 (br,s, 4)	6.16 (br,s, 2)		
(18b)[d]	2.00 (s, 30)	7.23 (d, 2) *J*(HH) 2	5.90 (t, 1)		−10.93 (t, 2)[f] *J*(RhH) 30
(19b)[d]	1.85 (s, 30)	7.17 (d, 2) *J*(HH) 2	6.05 (t, 1)		1.42 (s, 18)[g]
(20b)[d]	1.94 (s, 30)	7.09 (d, 2) *J*(HH) 2	6.04 (t, 1)		
(21d)[d]	1.17 (s, 30)				1.75 (s, 3)[h]

[a] Given as chemical shifts (δ p.p.m.), multiplicity, relative intensity. Coupling constants are in Hz. [b] In $(CD_3)_2CO$. [c] NH protons. [d] In $CDCl_3$. [e] OMe protons. [f] Hydrido ligands. [g] Bu^{t}NC protons. [h] $MeCO_2$ protons.

water was added to a solution of (**1a**) (59.0 mg, 0.08 mmol) in acetone (20 cm^3). The resulting solution was stirred (10 min). After partial vacuum-evaporation, the orange complex, which was precipitated, was filtered off, washed with water and air-dried.

The orange μ-chloro complex (**4a**) was similarly prepared by treating (**2a**) (100.0 mg, 0.14 mmol) with HCl (7.7 cm^3, 0.018 mol dm^{-3}, 0.14 mmol).

Preparation of the Mononuclear Complex (**6b**).—A mixture of $[Rh(C_5Me_5)Cl(acac)]$ (60.0 mg, 0.16 mmol), Hpz (21.9 mg, 0.32 mmol), and an aqueous solution of HBF_4 (32.0 μl, 35% w/w, 0.16 mmol) in methanol (20 cm^3) was stirred (1 h). The resulting solution was concentrated under reduced pressure; addition of diethyl ether led to the precipitation of an orange-yellow complex which was filtered off, washed with diethyl ether and air-dried.

Preparation of the μ*-Chloro Complex* (**4c**) *from* (**5**).—Potassium hydroxide (4.8 cm^3, 0.087 mol dm^{-3}, 0.40 mmol) in methanol was added to a solution of (**5**) (153.6 mg, 0.40 mmol) in chloroform (20 cm^3). The resulting solution was stirred (20 min) and vacuum-evaporated to dryness. The residue was extracted with dichloromethane (15 cm^3) and this solution was vacuum-evaporated to dryness. The residue was dissolved in methanol (20 cm^3) and solid $NaBPh_4$ (68.4 mg, 0.20 mmol) was added. The orange complex which precipitated was filtered off, washed with diethyl ether and air-dried. Recrystallization from CH_2Cl_2–Et_2O led to red crystals.

Preparation of the Mononuclear Complex (**9**).—A mixture of $[\{(C_5Me_5)IrCl\}_2(\mu\text{-}Cl)_2]$ (150.0 mg, 0.19 mmol) and Hpz (25.6 mg, 0.38 mmol) in chloroform (30 cm^3) was stirred (3 h). The solution was concentrated under reduced pressure; addition of diethyl ether led to the precipitation of a yellow solid which was filtered off, washed with diethyl ether and air-dried.

Preparation of the μ*-Chloro Complex* (**3b**) *from* (**5**).—A mixture of (**5**) (63.0 mg, 0.17 mmol) and $[\{(C_5Me_5)Rh\}_2(\mu\text{-}acac)_2][BF_4]_2$ (70.8 mg, 0.09 mmol) in methanol (30 cm^3) was stirred (30 min). The solids dissolved and an orange solid slowly precipitated. The complex was isolated after partial evaporation of the solvent and subsequent addition of diethyl ether.

The yellow di-iridium complex (**8b**) was prepared according to this procedure starting from (**9**) and $[Ir(C_5Me_5)(acac)(MeOH)][BF_4]$. The orange heterobimetallic complex (**10b**) was also prepared by this method from (**9**) and $[\{(C_5Me_5)Rh\}_2(\mu\text{-}acac)_2][BF_4]_2$ or by reacting (**5**) with $[Ir(C_5Me_5)(acac)(MeOH)][BF_4]$ in the above manner.

Preparation of the μ*-Hydroxo Complexes* (**11b**) *and* (**12b**) *from* $[Ir(C_5Me_5)(Me_2CO)_3][BF_4]_2$.—Hpz (15.3 mg, 0.23 mmol) and NEt_3 (31.2 μl, 0.23 mmol) or, respectively, Hmpz (18.5 μl, 0.23 mmol) and a methanolic solution of KOH (2.6 cm^3, 0.087 mol dm^{-3}, 0.23 mmol) were added to solutions of $[Ir(C_5Me_5)(Me_2CO)_3][BF_4]_2$ [prepared *in situ* by treating $[\{(C_5Me_5)IrCl\}_2(\mu\text{-}Cl)_2]$ (60 mg, 0.07 mmol) with $AgBF_4$ (58.6 mg, 0.30 mmol) in acetone (20 cm^3)]. After stirring (45 min), the solutions were vacuum-evaporated to dryness and the yellow residues extracted with dichloromethane (15 cm^3). The resulting

solutions were partially concentrated under reduced pressure. Slow addition of diethyl ether gave yellow microcrystalline solids, which were filtered off and washed with diethyl ether. Recrystallization from dichloromethane–diethyl ether led to yellow crystals.

Preparation of the μ-*Hydroxo Complexes* (**11b**) *and* (**12b**) *from* $[\{(C_5Me_5)Ir\}_2(\mu\text{-}OH)_3][BF_4]\cdot H_2O$.—Hpz (18.4 mg, 0.27 mmol) or Hmpz (21.7 μl, 0.27 mmol) was added, in acetone (5 cm^3), to a solution of $[\{(C_5Me_5)Ir\}_2(\mu\text{-}OH)_3][BF_4]\cdot H_2O$ (73.6 mg, 0.09 mmol) in acetone (20 cm^3). After stirring for 1 h, the solution was partially concentrated under reduced pressure. Slow addition of diethyl ether gave a yellow microcrystalline solid, which was filtered off, washed with diethyl ether and air-dried. The complexes were characterised by comparison of their spectroscopic properties with those of authentic samples prepared from $[Ir(C_5Me_5)(Me_2CO)_3][BF_4]_2$.

*Preparation of the Di-*μ-*methoxo Complexes* (**13a**), (**14a**), *and* (**15a**) *from* $[Ir(C_5Me_5)(MeOH)_3][ClO_4]_2$.—The appropriate ligand HPz (0.09 mmol) and a methanolic solution of KOH (3.4 cm^3, 0.080 mol dm^{-3}, 0.27 mmol) were added to a solution of $[Ir(C_5Me_5)(MeOH)_3][ClO_4]_2$ [prepared *in situ* by treating $[\{(C_5Me_5)IrCl\}_2(\mu\text{-}Cl)_2]$ (0.09 mmol) with $Ag[ClO_4]$ (0.36 mmol) in methanol (20 cm^3)]. The resulting solution was stirred (1 h) and vacuum-evaporated to dryness. The yellow residue was dissolved in methanol (20 cm^3) and stirred (10 min). Addition of diethyl ether gave a yellow solid which was filtered off, washed with diethyl ether and air-dried. Recrystallization from CH_2Cl_2–Et_2O led to yellow crystals.

*Preparation of the Di-*μ-*methoxo Complexes* (**13b**), (**14b**), *and* (**15b**) *from* $[\{(C_5Me_5)Ir\}_2(\mu\text{-}OH)_3][BF_4]\cdot H_2O$.—A mixture of $[\{(C_5Me_5)Ir\}_2(\mu\text{-}OH)_3][BF_4]\cdot H_2O$ (0.16 mmol) and the corresponding pyrazole derivatives HPz (0.16 mmol) in methanol (30 cm^3) was stirred (1 h). The yellow complexes (**13b**) and (**14b**) precipitated spontaneously, whilst the also yellow complex (**15b**) was isolated after partial evaporation of the solvent and subsequent addition of diethyl ether. Recrystallization from CH_2Cl_2–Et_2O led to yellow crystals.

*Preparation of the Di-*μ-*hydroxo Complex* (**16b**).—(*i*) *From* $[Ir(C_5Me_5)(Me_2CO)_3][BF_4]_2$. Hdmpz (16.9 mg, 0.18 mmol) and NEt_3 (24.4 μl, 0.18 mmol) were added to a solution of $[Ir(C_5Me_5)(Me_2CO)_3][BF_4]_2$ [prepared *in situ* by treating $[\{(C_5Me_5)IrCl\}_2(\mu\text{-}Cl)_2]$ (70.0 mg, 0.09 mmol) with $Ag[BF_4]$ (68.4 mg, 0.35 mmol) in acetone (20 cm^3)]. After stirring (30 min) the solution was vacuum-evaporated to dryness and the yellow residue extracted with dichloromethane (15 cm^3). The resulting solution was partially concentrated under reduced pressure. Slow addition of diethyl ether gave a yellow microcrystalline solid, which was filtered off and washed with diethyl ether. Recrystallization from dichloromethane–diethyl ether solutions led to yellow crystals.

(*ii*) *From* $[\{(C_5Me_5)Ir\}_2(\mu\text{-}OH)_3][BF_4]\cdot H_2O$. A mixture of $[\{(C_5Me_5)Ir\}_2(\mu\text{-}OH)_3][BF_4]\cdot H_2O$ (180.0 mg, 0.22 mmol), Hdmpz (42.7 mg, 0.44 mmol), and an aqueous solution of HBF_4 (44.2 μl, 33% w/w, 0.22 mmol) in acetone (20 cm^3) was stirred (5 h). The yellow complex that precipitated spontaneously was isolated after partial evaporation and addition of diethyl ether.

(*iii*) *From* (**15b**). A mixture of (**15b**) (22.5 mg, 0.02 mmol), Hdmpz (2.4 mg, 0.02 mmol), and an aqueous solution of HBF_4 (5.0 μl, 35%, 0.02 mmol) in acetone (20 cm^3) was stirred (30 min). The yellow complex was isolated by partial vacuum-evaporation and subsequent addition of diethyl ether.

*Preparation of the Di-*μ-*methoxo Complex* (**15b**) *from* (**16b**).—KOH (0.9 cm^3, 0.088 mol dm^{-3}, 0.08 mmol), in methanol, was added to a solution of (**16b**) (82.7 mg, 0.08 mmol) in methanol (20 cm^3). The resulting solution was stirred (1 h) and vacuum-evaporated until dryness. The residue was extracted with dichloromethane (15 cm^3). The solution was evaporated to dryness under reduced pressure. The yellow residue was dissolved in methanol (20 cm^3) and stirred (10 min). Addition of diethyl ether gave a yellow solid, which was filtered off, washed with diethyl ether, and air-dried.

The complex was characterized by comparison of its spectroscopic properties with those of an authentic sample prepared from $[\{(C_5Me_5)Ir\}_2(\mu\text{-}OH)_3][BF_4]\cdot H_2O$.

*Preparation of the Di-*μ-*chloro Complex* (**8b**) *from* (**13b**).—Complex (**8b**) was prepared from (**13b**) following the procedure described for the preparation of (**3a**) from (**1a**).

Preparation of the μ-*Chloro Complexes* (**17b**) *and* (**17c**).—Complex (**17b**) was prepared from (**11b**) following the procedure described for the preparation of (**4a**) from (**2a**) and complex (**17c**) was prepared from (**9**) in the same way as (**4c**) was obtained from (**5**).

Preparation of the Hydrido Complex (**18b**) *from* $[\{(C_5Me_5)Rh\}_2(\mu\text{-}OH)_3][BF_4]$.—$[\{(C_5Me_5)Rh\}_2(\mu\text{-}OH)_3][BF_4]$ (164.0 mg, 0.24 mmol) was added to a solution of pyrazole (16.3 mg, 0.24 mmol) in propan-2-ol (90 cm^3) and the yellow-orange solution was heated, whereupon it slowly turned dark green (40 °C, 2 h). Reaction was continued (1 d); the solution was then filtered to remove insoluble impurities, and the solvent was removed *in vacuo*. Diethyl ether was added to the residue and the dark green solid was filtered off, washed with diethyl ether, and air-dried.

The ^1H n.m.r. spectrum showed the presence of an impurity (*ca.* 10%), the properties of which were consistent with it being $[\{(C_5Me_5)Rh\}_2(\mu\text{-}pz)_2(\mu\text{-}OH)][BF_4]$; it was not possible to remove this impurity efficiently.

The di-μ-hydride was quite reactive and decomposed in acetone or tetrahydrofuran (thf) but it was reasonably stable in CH_2Cl_2 or $CHCl_3$. It reacted rapidly with small molecules such as CO, CS_2, Bu^{t}NC, $H_2C{=}CH_2$, or Me_2SO, but only gave stable products with CO and Bu^{t}NC. It reacted with PhC≡CH to give a complicated mixture of products, but it did not react with PhC≡CPh.

Reaction of $[\{(C_5Me_5)Rh\}_2(\mu\text{-}pz)(\mu\text{-}H)_2][BF_4]$ *with* Bu^{t}NC.—t-Butyl isocyanide (0.76 mmol) was added to a solution of $[\{(C_5Me_5)Rh\}_2(\mu\text{-}pz)(\mu\text{-}H)_2][BF_4]$ (150 mg, 0.24 mmol) dissolved in dichloromethane (10 cm^3). The colour of the solution immediately changed from dark green to dark red and H_2 (1 mol equiv.) was evolved as shown by g.c. analysis. After 10 min, the solvent was partially removed *in vacuo* and diethyl ether was added to give a dark red precipitate that was separated by filtration, washed with diethyl ether, and air-dried. It was recrystallized from dichloromethane–diethyl ether to afford dark red crystals. ^{13}C N.m.r. at 25 °C in $CDCl_3$: δ 10.8 (s, $C_5\mathit{Me}_5$), 30.6 [s, $(\mathit{CH}_3)_3CNC$], 58.4 [s, $(CH_3)_3\mathit{C}NC$], 96.7 (s, C_5Me_5), 106.1 (s, pz), 137.3 (s, pz), 149.5 [t, Bu^{t}N*C*, *J*(Rh–C) = 39.3 Hz]. ^{13}C N.m.r. at −65 °C in CD_2Cl_2: δ 10.4 (s, $C_5\mathit{Me}_5$), 30.2 [s, $(\mathit{CH}_3)_3CNC$], 57.6 [s, $(CH_3)_3\mathit{C}NC$], 95.1 (s, C_5Me_5), 105.0 (s, pz), 136.7 (s, pz), 147.3 [d, Bu^{t}N*C*, *J*(Rh–C) = 77.9 Hz]. F.a.b. mass spectrum: $[\{(C_5Me_5)Rh\}_2(\mu\text{-}pz)(Bu^tNC)_2]^+$, *m/e* 709 ($M^+$), 626 ($M^+$ − Bu^{t}NC), 543 (M^+ − 2 Bu^{t}NC).

Reaction of $[\{(C_5Me_5)Rh\}_2(\mu\text{-}pz)(\mu\text{-}H)_2][BF_4]$ *with* CO.—Carbon monoxide was bubbled (2 h, 20 °C) through a solution of $[\{(C_5Me_5)Rh\}_2(\mu\text{-}pz)(\mu\text{-}H)_2][BF_4]$ (150.0 mg, 0.24 mmol) in dichloromethane (25 cm^3). The initially dark green solution turned dark red; the solvent was partially removed *in vacuo* and

diethyl ether was added to give a dark red precipitate which was filtered off and air-dried. ^{13}C-{^1H} N.m.r. in CD_2Cl_2 at −50 °C: δ 9.5 (s, C_5Me_5), 104.6 [d, C_5Me_5, J(Rh–C) = 4.5 Hz], 106.0 (s, pz), 138.6 (s, pz), 210.9 [t, CO, J(Rh–C) = 38.7 Hz]. F.a.b. mass spectrum (*m*-nitrobenzyl alcohol matrix): $[\{(C_5Me_5)Rh\}_2(\mu\text{-}pz)(CO)_2]^+$, *m/e* 599 ($M^+$), 571 ($M^+ - CO$), 543 ($M^+ - 2\ CO$).

Reaction of $[\{(C_5Me_5)Rh\}_2(\mu\text{-}H)_2(\mu\text{-}O_2CMe)][PF_6]$ *with* CO.—$[\{(C_5Me_5)Rh\}_2(\mu\text{-}H)_2(\mu\text{-}O_2CMe)][PF_6]$ (150.0 mg, 0.22 mmol) dissolved in acetone (10 cm^3) was held under CO (3 atm, 16 h) in a Fischer-Porter tube. The initially dark red solution became pale green. The solvent was then partly removed *in vacuo*, and diethyl ether was added to yield a pale green precipitate which was filtered off, washed with diethyl ether and air-dried. ^{13}C N.m.r. in CD_2Cl_2 at −50 °C: δ 8.6 (s, C_5Me_5), 21.1 (s, $MeCO_2$), 107.7 (s, C_5Me_5), 176.6 (s, $MeCO_2$), 230.0 [t, CO, J(Rh–C) = 40.5 Hz]. F.a.b. mass spectrum: $[\{(C_5Me_5)Rh\}_2(\mu\text{-}O_2CMe)(\mu\text{-}CO)_2][PF_6]$, *m/e* 591 ($M^+$), 563 ($M^+ - CO$), 535 ($M^+ - 2\ CO$).

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