Trinuclear Pyrazolate Complexes. Crystal Structure of $[(OC)_2Rh(\mu\text{-pz})_2Pd(\mu\text{-pz})_2Rh(CO)_2]$†

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The preparation and properties of trinuclear complexes containing pyrazolate and chloride as bridging ligands are reported. Representative formulae are $[L_2M(\mu\text{-Cl})(\mu\text{-pz})Pd(\mu\text{-Cl})(\mu\text{-pz})ML_2]$ [M = Rh, L_2 = diolefin or $(CO)_2$; M = Ir, L_2 = diolefin; M = Pd, L_2 = $\eta^3\text{-}C_3H_5$ or $\eta^3\text{-}C_4H_7$]. These complexes react with the pyrazolate anion to give trinuclear homobridged compounds of formula $[L_2M(\mu\text{-pz})_2Pd(\mu\text{-pz})_2ML_2]$. The crystal structure of the carbonyl derivative $[(OC)_2Rh(\mu\text{-pz})_2\text{-}Pd(\mu\text{-pz})_2Rh(CO)_2]$ has been determined by single-crystal *X*-ray methods. Crystals are monoclinic, space group $P2_1/c$ with cell constants a = 8.928 1(5), b = 11.796 1(6), c = 10.391 6(5) Å, β = 94.727(4)°, and Z = 2. The intermetallic distance palladium–rhodium is equal to 3.578 9(6) Å.

Binuclear platinum metal pyrazolate (pz) complexes have attracted considerable interest in recent years.[1] In these complexes two identical or different metal centres are, generally, joined by two pyrazolate ligands, co-ordinated in an exobidentate fashion. With few exceptions the '$M(\mu\text{-pz})_2M'$' core formed is in a boat configuration. Much work has been done with metallocycles containing the $M(\mu\text{-pz})_2M$ ring. Various exchange reactions can be carried out on the terminal ligands leaving the central $M(\mu\text{-pz})_2M$ ring intact;[2] oxidative additions to one[3] or both metal atoms[4] can also take place. The puckered nature of the central ring in these complexes results in a wide range of intermetallic separations (Rh–Rh 2.581—3.568, Ir–Ir 2.623—3.290 Å).[2b,5]

Interestingly, while binuclear structures are, generally, observed for pyrazolate-bridged complexes, higher nuclearity is found for related chemistry involving imidazolate[6] and tri- or tetra-azolate ligands.[7]

As suggested by Trofimenko[1] in his recent review, controlled extension of the '$M(\mu\text{-pz})_2M'$' core to form well defined tri- or tetra-nuclear compounds may constitute an interesting area of research. These oligomeric compounds are rare; as far as we know few examples have been described.[8,9] In this paper we report the preparation of homo- and hetero-trinuclear complexes containing the metallocycles $M(\mu\text{-pz})_2M'(\mu\text{-pz})_2M$, as well as the *X*-ray structure of the complex $[(OC)_2Rh(\mu\text{-pz})_2\text{-}Pd(\mu\text{-pz})_2Rh(CO)_2]$.

Results and Discussion

Pyrazole (Hpz) displaces acetonitrile from $[PdCl_2(NCMe)_2]$[10] to form $[PdCl_2(Hpz)_2]$ (**1**). A *trans* stereochemistry is indicated by far-i.r. absorption at 375 cm^{-1} assigned to the Pd–Cl stretching vibration (B_{3u} under D_{2h} symmetry).[11] Interest in this mononuclear complex mainly originates from its capacity to act as a metallo-ligand in the preparation of homo- or hetero-trinuclear species.

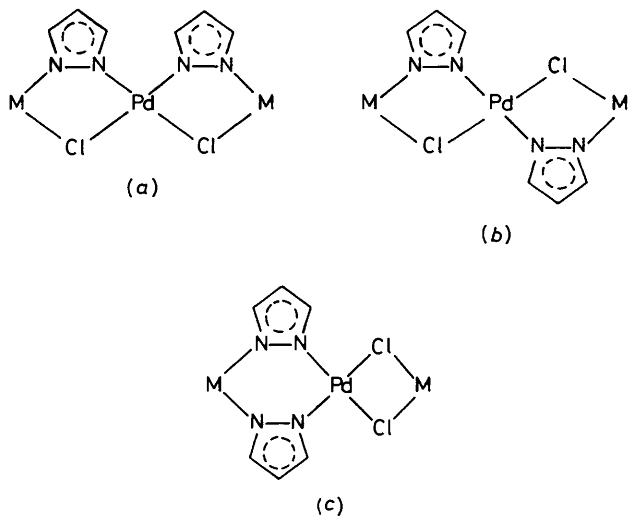

Figure 1. Structures of the possible geometric isomers of the compounds $[PdM_2(\mu\text{-Cl})_2(\mu\text{-pz})_2(\text{diolefin})_2]$ (M = Rh or Ir)

The reaction of [M(acac)(diolefin)] (acac = acetylacetonate) complexes {M = Rh, diolefin = cyclo-octa-1,5-diene (cod)[12] or tetrafluorobenzo[5,6]bicyclo[2.2.2]octa-2,5,7-triene (tfbb);[13] M = Ir, diolefin = cod[14]} with $[PdCl_2(Hpz)_2]$ leads to the isolation in good yields of $[PdM_2(\mu\text{-Cl})_2(\mu\text{-pz})_2(\text{diolefin})_2]$ complexes [equation (1)]. Molecular weight measurements

$$[PdCl_2(Hpz)_2] + 2[M(acac)(\text{diolefin})] \longrightarrow [PdM_2(\mu\text{-pz})_2(\mu\text{-Cl})_2(\text{diolefin})_2] + 2\text{Hacac} \quad (1)$$

confirm the trinuclear formulation. Compounds of the type $[PdM_2(\mu\text{-Cl})_2(\mu\text{-pz})_2(\text{diolefin})_2]$ can exist in three geometrical isomers (Figure 1) where one nitrogen is bound to each rhodium or iridium atom in a *cis* (*a*) or *trans* (*b*) arrangement, or one rhodium or iridium is bound to two nitrogen atoms in a *cis* arrangement (*c*). According to the ^1H n.m.r. spectra of the isolated compounds only one of the possible isomers is produced in the present process. Taking into account the *trans* geometry present in complex (**1**), we think that (*b*) is the most probable structure for this new family of trinuclear compounds. These materials are air-stable in the solid, however partial

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† 1,1,3,3-Tetracarbonyl-1,2;1,2;2,3;2,3-tetra-μ-pyrazolato-*NN'*-palladium-1,3-dirhodium.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

Table 1. Analytical data[a] for the trinuclear compounds

Compound	Analyses (%) C	H	N	M[b]	Colour	Yield (%)	ν(CO)/cm^{-1}
(1) $[PdCl_2(Hpz)_2]$	22.70 (23.00)	2.50 (2.55)	17.70 (17.85)	310 (313)	Orange	95	
(2) $[(cod)Rh(\mu\text{-}Cl)(\mu\text{-}pz)Pd(\mu\text{-}Cl)(\mu\text{-}pz)Rh(cod)]$	36.20 (36.00)	4.05 (4.10)	7.65 (7.65)	806 (734)	Yellow	91	
(3) $[(tfbb)Rh(\mu\text{-}Cl)(\mu\text{-}pz)Pd(\mu\text{-}Cl)(\mu\text{-}pz)Rh(tfbb)]$	37.55 (37.15)	2.10 (1.90)	6.00 (5.80)		Yellow	73	
(4) $[(cod)Ir(\mu\text{-}Cl)(\mu\text{-}pz)Pd(\mu\text{-}Cl)(\mu\text{-}pz)Ir(cod)]$	28.60 (28.95)	3.40 (3.30)	6.20 (6.15)		Orange-red	66	
(5) $[(OC)_2Rh(\mu\text{-}Cl)(\mu\text{-}pz)Pd(\mu\text{-}Cl)(\mu\text{-}pz)Rh(CO)_2]$	18.90 (19.10)	0.90 (0.95)	9.05 (8.90)	743 (629)	Orange	76	2 082, 2 020[c]
(6) $[(\eta^3\text{-}C_3H_5)Pd(\mu\text{-}Cl)(\mu\text{-}pz)Pd(\mu\text{-}Cl)(\mu\text{-}pz)Pd(\eta^3\text{-}C_3H_5)]$	23.60 (23.75)	2.65 (2.65)	9.40 (9.25)	660 (606)	Yellow-orange	76	
(7) $[(\eta^3\text{-}C_4H_7)Pd(\mu\text{-}Cl)(\mu\text{-}pz)Pd(\mu\text{-}Cl)(\mu\text{-}pz)Pd(\eta^3\text{-}C_4H_7)]$	26.60 (26.50)	3.20 (3.20)	8.90 (8.85)	621 (634)	Yellow-orange	60	
(8) $[(cod)Rh(\mu\text{-}pz)_2Pd(\mu\text{-}pz)_2Rh(cod)]$	42.50 (42.20)	4.60 (4.55)	14.30 (14.05)	796 (797)	Yellow	60	
(9) $[(tfbb)Rh(\mu\text{-}pz)_2Pd(\mu\text{-}pz)_2Rh(tfbb)]$	42.00 (41.85)	2.50 (2.35)	10.75 (10.85)		Yellow	77	
(10) $[(cod)Ir(\mu\text{-}pz)_2Pd(\mu\text{-}pz)_2Ir(cod)]$	35.00 (34.50)	3.80 (3.70)	11.10 (11.50)		Orange-yellow	60	
(11) $[(OC)_2Rh(\mu\text{-}pz)_2Pd(\mu\text{-}pz)_2Rh(CO)_2]$	28.00 (27.75)	1.90 (1.75)	16.25 (16.20)	660 (692)	Yellow	87	2 080, 2 015[d]
(12) $[(OC)_2Ir(\mu\text{-}pz)_2Pd(\mu\text{-}pz)_2Ir(CO)_2]$	22.40 (22.05)	1.40 (1.40)	13.05 (12.85)		Yellow	60	2 075, 1 995[d]
(13) $[(\eta^3\text{-}C_3H_5)Pd(\mu\text{-}pz)_2Pd(\mu\text{-}pz)_2Pd(\eta^3\text{-}C_3H_5)]$	32.00 (32.30)	3.15 (3.30)	16.30 (16.75)		White	92	
(14) $[(\eta^3\text{-}C_4H_7)Pd(\mu\text{-}pz)_2Pd(\mu\text{-}pz)_2Pd(\eta^3\text{-}C_4H_7)]$	34.25 (34.45)	3.80 (3.75)	16.20 (16.05)	640 (697)	White	62	

[a] Required values are given in parentheses. [b] In chloroform. [c] In diethyl ether. [d] In pentane.

Table 2. Proton n.m.r. chemical shifts * and coupling constants (Hz) for the trinuclear compounds in $CDCl_3$ at 293 K

Compound	Pyrazolate H^3	H^5	H^4	cod or η^3-allyl		
(2)	7.42(d, 2.2)	6.91(d, 2.2)	6.04(t, 2.2)	>CH 4.44(br) 4.32(br)	$>CH_2$ 2.56(br) 2.53(br) 1.94(br) 1.90(br)	
(4)	7.50(d, 1.8)	7.14(d, 1.8)	6.11(t, 1.8)	>CH 4.18(br) 4.01(br)	$>CH_2$ 2.31(m) 1.70(m)	
(5)	7.47(d, 2.0)	7.44(d, 2.0)	6.17(t, 2.0)			
(6)	7.60(d, 2.2)	7.36(d, 2.2)	6.12(t, 2.2)	H_{anti} 3.16(d, 12.5) 3.05(d, 12.5)	H_{syn} 4.06(br) 4.08(br)	H 5.65(m)
(7)	7.63(d, 2.1)	7.38(d, 2.1)	6.13(t, 2.1)	H_{anti} 3.05(s) 2.90(s)	H_{syn} 3.80(s) 3.83(s)	CH_3 2.17(s)
(8)	7.35(d, 2)	6.92(d, 2)	6.03(d, 2)	>CH 4.32(br) 4.16(br)	$>CH_2$ 2.69(m) 2.12(m)	
(10)	7.57(d, 2)	6.93(d, 2)	6.14(t, 2)	>CH 4.12(br) 3.90(br)	$>CH_2$ 2.55(m) 1.85(m)	
(11)	7.52(d, 2.2)	6.82(d, 2.2)	6.15(t, 2.2)			
(12)	7.63(d, 2.2)	6.89(d, 2.2)	6.21(t, 2.2)			
(14)	7.43(d, 1.7) 7.45(d, 1.7)	6.71(d, 1.7) 6.74(d, 1.7)	6.05(t, 1.7) 6.06(t, 1.7)	H_{anti} 3.05(s) 3.01(s)	H_{syn} 3.72(s)	CH_3 2.31(s)

* Position of the centre of the doublet (d), triplet (t), or multiplet (m). The chemical shifts are relative to $SiMe_4$. The coupling constants are given in parentheses.

decomposition was noted in chloroform solution over a period of hours, for some samples, particularly those involving iridium centres.

Attempts to prepare binuclear complexes of general formula $[(Hpz)ClPd(\mu\text{-}Cl)(\mu\text{-}pz)M(diolefin)]$ by treating $[PdCl_2(Hpz)_2]$ with [M(acac)(diolefin)] (1:1 mol ratio) were unsuccessful due to the formation of the stable trinuclear compounds described above.

Bubbling of carbon monoxide through a hexane suspension of $[(cod)Rh(\mu\text{-}Cl)(\mu\text{-}pz)Pd(\mu\text{-}Cl)(\mu\text{-}pz)Rh(cod)]$ (**2**) gives rise to the displacement of cod and to the formation of the tetracarbonyl derivative $[(OC)_2Rh(\mu\text{-}Cl)(\mu\text{-}pz)Pd(\mu\text{-}Cl)(\mu\text{-}pz)Rh\text{-}$

$(CO)_2]$ (**5**). The 200-MHz ^1H n.m.r. spectrum of (**5**) exhibited three well separated μ-pz signals (H^{3-5}), and its i.r. spectrum (diethyl ether) shows two ν(CO) absorptions at 2 082 and 2 020 cm^{-1}, as expected for *cis*-dicarbonyl structures.[15] Carbonylation of (**2**) is best carried out using non-polar solvents; if the reaction is performed in a polar solvent traces of metal may be produced. The complex [(cod)Ir(μ-Cl)(μ-pz)Pd(μ-Cl)(μ-pz)Ir(cod)] (**4**) also reacts with carbon monoxide to form, presumably, $[(OC)_2Ir(\mu\text{-}Cl)(\mu\text{-}pz)Pd(\mu\text{-}Cl)(\mu\text{-}pz)Ir(CO)_2]$ [ν(CO) 2 075 and 2 005 cm^{-1}], but the material isolated did not give satisfactory microanalyses.

Another family of homotrinuclear complexes has been derived from two palladium precursors. The reaction of $[Pd(acac)(\eta^3\text{-allyl})]$ (allyl = C_3H_5 or C_4H_7) complexes with $[PdCl_2(Hpz)_2]$ yielded yellow-orange solids with elemental analyses, molecular weights, and ^1H n.m.r. spectra consistent with the general formula $[(\eta^3\text{-allyl})Pd(\mu\text{-}Cl)(\mu\text{-}pz)Pd(\mu\text{-}Cl)(\mu\text{-}pz)Pd(\eta^3\text{-allyl})]$.

Our interest in this area is focused on proposing an easy method for building a multinuclear framework with the possibility of varying the metal centres and their environment. The synthesis and some properties of binuclear complexes containing the '$M_2(\mu\text{-}pz)(\mu\text{-}X)$' core have recently been described where X is a simple anion such as Cl[16] or N_3[17] in which single atoms are the bridging groups. Some structural studies on these complexes show that the central $M_2(\mu\text{-}pz)(\mu\text{-}X)$ ring is nearly planar, which favours a stacking arrangement of square-planar metal units involving nearly linear chains of metal atoms along one axis.[18,19] The intramolecular M ··· M separations reported are generally longer than those found for binuclear systems containing a '$M_2(\mu\text{-}pz)_2$' core, in which the co-ordination planes of the two metals are inclined with respect to each other. In this context we have studied the exchange of the bridging chloride ligands in complexes (**2**)—(**7**) by the pyrazolate group.

The addition of K(pz) to acetone solutions of compounds of the type [(diolefin)M(μ-Cl)(μ-pz)Pd(μ-Cl)(μ-pz)M(diolefin)] gives rise to yellow $[(diolefin)M(\mu\text{-}pz)_2Pd(\mu\text{-}pz)_2M(diolefin)]$ [M = Rh, diolefin = cod (**8**) or tfbb (**9**); M = Ir, diolefin = cod (**10**)] containing four pyrazolate anions as bridging ligands. The formulation of these complexes is substantiated by microanalytical results, molecular-weight measurements, and also by the appearance of distinguishable μ-pz, H^3, and H^5 proton signals in their ^1H n.m.r. spectra.

Complexes (**8**) and (**10**) undergo diolefin substitution with carbon monoxide, at room temperature, in dichloromethane to give $[(OC)_2M(\mu\text{-}pz)_2Pd(\mu\text{-}pz)_2M(CO)_2]$ [M = Rh (**11**) or Ir (**12**)]. These preparations yielded well formed single crystals of the products, which were of high purity, even though in moderate yields. Complexes (**11**) and (**12**) are obtained pure and in higher yields by addition of the pyrazolate anion to solutions of $[PdCl_2(Hpz)_2]$ and the appropriate $[M(acac)(CO)_2]$ (M = Rh or Ir) complex in acetone (Experimental section).

In order to confirm the proposed formulation an *X*-ray structural determination of complex (**11**) was undertaken (see below).

The homotrinuclear complexes (**6**) and (**7**) react with the pz anion to give colourless solids analysing as $[(\eta^3\text{-allyl})Pd(\mu\text{-}pz)_2Pd(\mu\text{-}pz)_2Pd(\eta^3\text{-allyl})]$ [allyl = C_3H_5 (**13**) or C_4H_7 (**14**)]. A molecular-weight determination on complex (**14**) supports their formulation as trinuclear complexes. Interestingly, the ^1H n.m.r. spectrum of (**14**) [(**13**) is not soluble enough] is more complex than would be expected from a molecule with a centre of symmetry at the central palladium atom [symmetry found in complex (**11**), see Figure 2]. The ^1H n.m.r. spectrum of this compound shows two different *anti*-hydrogens and two different pyrazolate groups. Rotation of the η^3-allyl groups has been suggested as a possible dynamic process which would account for ^1H n.m.r. spectra of related binuclear pyrazolate palladium complexes.[20]

Table 3. Selected bond lengths (Å) and angles (°) for complex (**11**)

Pd–Rh	3.578 9(6)	N(2)–C(3)	1.335(11)
Pd–N(2)	1.988(6)	C(3)–C(4)	1.393(13)
Pd–N(12)	1.992(7)	C(4)–C(5)	1.354(14)
Rh–N(1)	2.063(7)	C(5)–N(1)	1.352(12)
Rh–N(11)	2.062(6)	N(11)–N(12)	1.343(9)
Rh–C(6)	1.854(11)	N(12)–C(13)	1.348(11)
Rh–C(7)	1.835(13)	C(13)–C(14)	1.355(16)
C(6)–O(6)	1.116(15)	C(14)–C(15)	1.374(15)
C(7)–O(7)	1.163(16)	C(15)–N(11)	1.337(13)
N(1)–N(2)	1.358(9)		
N(1)–Rh–C(6)	90.3(4)	N(1)–N(2)–C(3)	107.8(6)
C(6)–Rh–C(7)	89.1(5)	N(2)–C(3)–C(4)	109.6(8)
C(7)–Rh–N(11)	91.4(5)	C(3)–C(4)–C(5)	104.8(8)
N(11)–Rh–N(1)	89.2(3)	N(1)–C(5)–C(4)	110.1(8)
N(2)–Pd–N(12)	90.1(3)	N(12)–N(11)–C(15)	107.9(7)
N(2)–Pd–N(12^I)	89.9(3)	N(11)–N(12)–C(13)	107.9(7)
Rh–C(6)–O(6)	177.7(13)	N(12)–C(13)–C(14)	109.6(9)
Rh–C(7)–O(7)	178.2(13)	C(13)–C(14)–C(15)	105.2(10)
N(2)–N(1)–C(5)	107.7(7)	N(11)–C(15)–C(14)	109.5(10)

Symmetry operation: I $-x, -y, -z$.

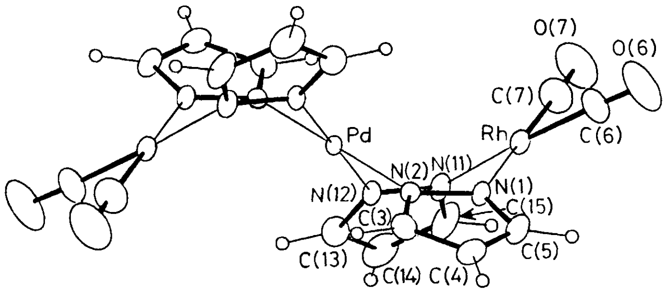
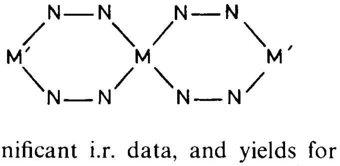


Figure 2. ORTEP drawing of complex (**11**) showing the atomic numbering

The tetracarbonyl complexes (**5**) and (**11**) present a markedly different reactivity towards phosphorus donor ligands. Addition of PPh_3 to a solution of (**5**) in dichloromethane produces a fragmentation of the trinuclear framework to yield the previously known complexes $[PdCl_2(PPh_3)_2]$[21] and $[Rh_2(\mu\text{-}pz)_2(CO)_2(PPh_3)_2]$[2b] [4 equiv. of PPh_3 were required for completion of the reaction]. In contrast, complex (**11**) reacts with PPh_3 to give $[(Ph_3P)(OC)Rh(\mu\text{-}pz)_2Pd(\mu\text{-}pz)_2Rh(CO)(PPh_3)]$;[22] these results demonstrate the high stability of the six-membered cyclic core shown below.



Analytical, significant i.r. data, and yields for all the new complexes prepared are collected in Table 1, ^1H n.m.r. data in Table 2.

Description of the Structure.—The solid state structure of complex (**11**) is shown in Figure 2[23] together with the atomic numbering scheme. Selected bond distances and angles are given in Table 3. The three metals are in a square-planar environment. The central palladium atom is bound to four nitrogen atoms of four pyrazolate ligands; the two terminal rhodium atoms are bound to two nitrogen atoms from two pyrazolate ligands and to two carbon atoms from terminal carbonyls. The two units are related through a centre of symmetry where the palladium atom is located. The Rh–N distances are similar to those found in related pyrazolate complexes;[2b,c] the Pd–N distances are slightly shorter than those observed for pyrazolate palladium compounds,[7b,17,24] and related square-planar palladium complexes,[25] with Pd–N bonds. The palladium–rhodium distance, equal to 3.5789(6) Å, excludes any metal–metal interaction. The six-membered ring [Rh,N(1),N(2),Pd,N(11),N(12)] shows a distorted boat conformation. The angle between the planes Rh,C(6),C(7) and Rh,N(1),N(11) is 2.8(4)°.

Recent studies on binuclear μ-pyrazolate dirhodium or diiridium complexes have demonstrated the high flexibility of the six-membered cyclic core $M(N{-}N)_2M$ since the metal–metal distances range from 2.581(1)[5a] to 3.57 Å.[2b] It is noteworthy that, although for analogous binuclear pyrazolate complexes Ir–Ir distances are, generally, shorter than Rh–Rh separations, the shortest intermetallic distances so far reported are found in the binuclear triply bridged rhodium complexes $[Rh_2(\mu\text{-}pz)_2\{\mu\text{-}P(C_6F_4)Ph_2\}Br(CO)\{P(o\text{-}BrC_6F_4)Ph_2\}]$ 2.581(1) Å[5a] and $[Rh_2(\mu\text{-}pz)_2(\mu\text{-}dppm)I_2(CO)_2]$ 2.612(3) Å[4c] [dppm = bis(diphenylphosphino)methane]. In this context, the flexibility of our trinuclear complexes is under investigation.

Experimental

Measurements.—Elemental analyses were carried out with a Perkin-Elmer 240 B microanalyser. Infrared spectra (range 4 000—200 cm^{-1}) were recorded on a Perkin-Elmer 599 spectrophotometer using Nujol mulls between polyethylene sheets or dichloromethane solutions in sodium chloride windows. Molecular weights were determined with a Knauer osmometer using chloroform solutions. Proton n.m.r. spectra were recorded in $CDCl_3$ solutions at room temperature on a Varian XL 200 spectrophotometer, using $SiMe_4$ as internal standard.

Syntheses.—The reactions were carried out at room temperature. Prior to use, solvents were purified by standard methods.

$[PdCl_2(Hpz)_2]$ (**1**). A solution of pyrazole (263 mg, 3.86 mmol) in dichloromethane (15 cm^3) was added dropwise to a solution of $[PdCl_2(NCMe)_2]$ (500 mg, 1.93 mmol) in dichloromethane (50 cm^3). During the addition a white solid precipitated and slowly redissolved to give an orange solution. After stirring for 30 min the solution was evaporated under reduced pressure to *ca.* 1 cm^3, and slow addition of hexane (30 cm^3) gave an orange microcrystalline solid, which was filtered off, washed with hexane, and air dried.

$[(diolefin)Rh(\mu\text{-}Cl)(\mu\text{-}pz)Pd(\mu\text{-}Cl)(\mu\text{-}pz)Rh(diolefin)]$ (**2**) *and* (**3**). To a suspension of [Rh(acac)(diolefin)] (diolefin = cod or tfbb) (0.3 mmol) in methanol (25 cm^3) was added $[PdCl_2(Hpz)_2]$ (47 mg, 0.15 mmol). The starting materials dissolved and the yellow complexes precipitated immediately from the solution. The resulting suspension was stirred for 30 min and the products were isolated after partial evaporation of the solvent to *ca.* 10 cm^3. The solids were filtered off, washed with hexane, and air dried.

$[(cod)Ir(\mu\text{-}Cl)(\mu\text{-}pz)Pd(\mu\text{-}Cl)(\mu\text{-}pz)Ir(cod)]$ (**4**). To a suspension of [Ir(acac)(cod)] (100 mg, 0.25 mmol) in methanol (20 cm^3) kept under a nitrogen atmosphere was added dropwise a solution of $[PdCl_2(Hpz)_2]$ (39 mg, 0.125 mmol) in methanol (15 cm^3). The resulting suspension was stirred for 2 h; during this time the starting material dissolved and an orange-red powder was precipitated. After partial evaporation of the solvent to *ca.* 10 cm^3, the solid was filtered off, washed with hexane, and vacuum-dried.

Complexes (**2**)—(**4**) were also prepared by this procedure, using acetone as solvent. In this case, the expected complexes precipitated after 30 min. The resulting suspensions were stirred for 1 h. Partial evaporation of the solvent to *ca.* 10 cm^3 and addition of hexane (30 cm^3) gave the complexes which were isolated as above.

$[(OC)_2Rh(\mu\text{-}Cl)(\mu\text{-}pz)Pd(\mu\text{-}Cl)(\mu\text{-}pz)Rh(CO)_2]$ (**5**). Dry carbon monoxide was bubbled slowly for 1 h through a suspension of $[(cod)Rh(\mu\text{-}Cl)(\mu\text{-}pz)Pd(\mu\text{-}Cl)(\mu\text{-}pz)Rh(cod)]$ (150 mg, 0.2 mmol) in deoxygenated hexane (20 cm^3). During this time, the starting material dissolved and an orange solid was precipitated. This was filtered off, washed with cold hexane, and vacuum dried.

$[(\eta^3\text{-}allyl)Pd(\mu\text{-}Cl)(\mu\text{-}pz)Pd(\mu\text{-}Cl)(\mu\text{-}pz)Pd(\eta^3\text{-}allyl)]$ (**6**) and (**7**). To a solution of acetylacetone (31 μl, 0.3 mmol) and potassium hydroxide (0.3 mmol) in methanol (20 cm^3) was added $[Pd_2(\mu\text{-}Cl)_2(\eta^3\text{-}allyl)_2]$ (allyl = C_3H_5 or C_4H_7) (0.15 mmol). The resulting mixture was stirred for 30 min and vacuum evaporated to dryness. The residue was extracted with dichloromethane (20 cm^3), filtered through Kieselguhr (to remove the potassium chloride formed), and vacuum evaporated to dryness. The residue, containing pure $[Pd(acac)(\eta^3\text{-}allyl)]$, was dissolved in methanol (20 cm^3) to give a pale yellow solution, and solid $[PdCl_2(Hpz)_2]$ (47 mg, 0.15 mmol) was added. The expected complexes precipitated immediately as yellow-orange solids. After vacuum evaporation to *ca.* 10 cm^3 they were filtered off, washed with methanol, and vacuum dried.

$[(diolefin)Rh(\mu\text{-}pz)_2Pd(\mu\text{-}pz)_2Rh(diolefin)]$ (**8**) *and* (**9**). Solid $[PdCl_2(Hpz)_2]$ (50 mg, 0.16 mmol) was added to a solution of [Rh(acac)(diolefin)] (diolefin = cod or tfbb) (0.32 mmol) in acetone (30 cm^3) to give yellow solutions of complexes (**2**) and (**3**). After stirring 30 min [compound (**8**)] or 10 min [(**9**)] a solution of pyrazole (21.8 mg, 0.32 mmol) and potassium hydroxide (0.32 mmol) in methanol (10 cm^3) was added dropwise. Stirring was continued for 30 min, and during this time the expected products precipitated as microcrystalline yellow solids. The complexes were isolated after partial evaporation of the solvent to *ca.* 15 cm^3 and then water (2 cm^3) was added to complete the precipitation. The compounds were filtered off, washed with methanol–water (10:1), and air dried.

$[(cod)Ir(\mu\text{-}pz)_2Pd(\mu\text{-}pz)_2Ir(cod)]$ (**10**). To a solution of [Ir(acac)(cod)] (128 mg, 0.32 mmol) in acetone (15 cm^3) kept under a nitrogen atmosphere was added dropwise a solution of $[PdCl_2(Hpz)_2]$ (50 mg, 0.16 mmol) in acetone (10 cm^3). After stirring for 30 min a solution of pyrazole (21.8 mg, 0.32 mmol) and potassium hydroxide (0.32 mmol) in methanol (10 cm^3) was added dropwise. Stirring was continued for 30 min, and during this time (**10**) precipitated as an orange-yellow solid. The complex was isolated after partial evaporation of the solvent to *ca.* 10 cm^3, and was filtered off, washed with cold methanol, and vacuum dried.

$[(OC)_2Rh(\mu\text{-}pz)_2Pd(\mu\text{-}pz)_2Rh(CO)_2]$ (**11**). A solution of $[PdCl_2(Hpz)_2]$ (50 mg, 0.16 mmol) in acetone (15 cm^3) was added slowly to a solution of $[Rh(acac)(CO)_2]$ (83 mg, 0.32 mmol) in acetone (15 cm^3), kept under a nitrogen atmosphere to give a yellow solution. After stirring for 15 min, a solution of pyrazole (22 mg, 0.32 mmol) and potassium hydroxide (0.32 mmol) in methanol (10 cm^3) was added. Stirring was continued for 30 min and then the yellow suspension was evaporated to dryness under vacuum. The residue was extracted with dichloromethane (30 cm^3), dried with anhydrous magnesium sulphate, and then filtered off. Concentration of the filtrate to dryness and addition of methanol (10 cm^3) rendered the complex which was filtered off, washed with cold methanol, and vacuum dried.

$[(OC)_2Ir(\mu\text{-}pz)_2Pd(\mu\text{-}pz)_2Ir(CO)_2]$ (**12**). To a solution of $[Ir(acac)(CO)_2]$ (100 mg, 0.28 mmol) in acetone (30 cm^3) kept

Table 4. Final atomic coordinates

Atom	*X/a*	*Y/b*	*Z/c*
Pd	0	0	0
Rh	0.224 54(7)	0.108 33(5)	0.273 82(5)
N(1)	0.284 7(8)	0.116 5(6)	0.086 5(7)
N(2)	0.199 3(7)	0.071 8(5)	−0.015 1(6)
C(3)	0.274 5(10)	0.083 9(8)	−0.120 1(8)
C(4)	0.410 4(10)	0.138 8(8)	−0.087 1(10)
C(5)	0.413 0(10)	0.155 6(9)	0.042 0(9)
N(11)	0.013 9(7)	0.167 7(6)	0.210 9(7)
N(12)	−0.062 8(7)	0.132 4(5)	0.101 6(6)
C(13)	−0.188 3(10)	0.195 9(8)	0.083 3(10)
C(14)	−0.191 8(12)	0.272 3(9)	0.180 4(13)
C(15)	−0.063 9(11)	0.252 0(9)	0.259 8(11)
C(6)	0.417 4(12)	0.062 4(11)	0.330 4(10)
O(6)	0.535 0(11)	0.038 3(13)	0.364 4(10)
C(7)	0.172 7(16)	0.100 0(12)	0.440 8(12)
O(7)	0.136 7(13)	0.093 0(12)	0.545 5(8)

under a nitrogen atmosphere was added dropwise a solution of $[PdCl_2(Hpz)_2]$ (43.8 mg, 0.56 mmol) in acetone (10 cm^3). After stirring for 10 min, a solution of pyrazole (19 mg, 0.28 mmol) and potassium hydroxide (0.28 mmol) in methanol (10 cm^3) was added. Stirring was continued for 10 min and then the yellow solution was evaporated to dryness under vacuum. The residue was extracted with pentane to give a yellow solution together with a small amount of black solid, which was removed by filtration. The filtrate was evaporated to dryness to give pure complex (**12**).

Complexes (**11**) and (**12**) can also be prepared by bubbling carbon monoxide through a suspension of the corresponding diolefin complex (0.1 mmol) in hexane (50 cm^3). The resulting yellow solutions were evaporated under reduced pressure to *ca.* 10 cm^3 and cooled to −30 °C overnight to give the complexes as yellow crystals.

$[(\eta^3\text{-allyl})Pd(\mu\text{-pz})_2Pd(\mu\text{-pz})_2Pd(\eta^3\text{-allyl})]$ (**13**) and (**14**). The solid compound $[PdCl_2(Hpz)_2]$ (50 mg, 0.16 mmol) was added to a solution of $[Pd(acac)(\eta^3\text{-allyl})]$ (allyl = C_3H_5 or C_4H_7) (0.32 mmol) [obtained as for complexes (**5**) and (**6**)] to give yellow-orange solutions. After stirring for 10 min a solution of pyrazole (21.7 mg, 0.32 mmol) and potassium hydroxide (0.32 mmol) in methanol (10 cm^3) was added dropwise. Stirring was continued for 30 min and then the expected complexes precipitated. Water (2 cm^3) was added to complete the precipitation of the compounds. The solids were filtered off, washed with methanol–water (10:1), and vacuum dried.

Crystallography.—Crystal data. $C_{16}H_{12}N_8O_4PdRh_2$, monoclinic, space group $P2_1/c$, $Z = 2$, $M = 692.5$, $F(000) = 664$, $a = 8.928\,1(5)$, $b = 11.796\,1(6)$, $c = 10.391\,6(5)$ Å, $\beta = 94.727(4)°$ (determined by least-squares fit of the angular positions of 89 reflections with θ up to 45°, Cu-K_α radiation, $\lambda = 1.541\,8$ Å), $U = 1\,090.7(1)$ Å^3, $D_c = 2.109$ g cm^{-3}, $\mu = 195.12$ cm^{-1} [empirical absorption correction applied,[26] maximum and minimum factors were 1.757 and 0.533].

A rectangular prismatic crystal 0.53 × 0.17 × 0.17 mm was used to collect 1 859 independent intensities on a Philips PW 1100 diffractometer, up to θ = 65°; bisecting geometry, oriented graphite monochromator for Cu-K_α radiation with ω—2θ scans of width 1.6° and detector apertures of 1.0 × 1.0°. The two standard reflections monitored showed no significant variations. A total of 1 791 reflections were considered as observed $[I > 3\sigma(I)]$.

Solution and refinement. The structure was solved by Patterson methods, completed through the DIRDIF system[27] and refined by one-block-matrix least-squares procedures operated on $F_{obs.}$. Hydrogen atoms were obtained from a difference synthesis and fixed in the refinement. Weights were applied so as to give no trends in $<w\Delta^2F>$ *vs.* $<F_o>$ and $<\sin\theta/\lambda>$, through the use of functions of the type $w = K/f([F_o])g(\sin\theta/\lambda)$. The last difference synthesis gave a residual electron density equal to 1.63 e A^{-3} near the Pd atom. The final *R* and *R′* were 0.056 and 0.071 respectively. Final atomic co-ordinates for non-hydrogen atoms are given in Table 4. Scattering factors were taken from ref. 28. All calculations were done on a VAX 11/750 computer, mostly using the *X*-RAY 76 system.[29]

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

References

1 S. Trofimenko, *Chem. Rev.*, 1972, **72**, 497; *Prog. Inorg. Chem.*, 1986, **34**, 115.
2 (*a*) K. A. Beveridge, G. W. Bushnell, S. R. Stobart, J. L. Atwood, and M. J. Zaworotko, *Organometallics*, 1983, **2**, 1447; (*b*) R. Usón, L. A. Oro, M. A. Ciriano, M. T. Pinillos, A. Tiripicchio, and M. Tiripicchio-Camellini, *J. Organomet. Chem.*, 1981, **205**, 247; (*c*) R. Usón, L. A. Oro, M. A. Ciriano, D. Carmona, A. Tiripicchio, and M. Tiripicchio-Camellini, *ibid.*, 1982, **224**, 69.
3 A. Tiripicchio, F. J. Lahoz, L. A. Oro, and M. T. Pinillos, *J. Chem. Soc., Chem. Commun.*, 1984, 936.
4 (*a*) A. W. Coleman, D. T. Eadie, S. R. Stobart, M. J. Zaworotko, and J. L. Atwood, *J. Am. Chem. Soc.*, 1982, **104**, 922; (*b*) G. W. Bushnell, M. J. Decker, D. T. Eadie, S. R. Stobart, R. Vefghi, J. L. Atwood, and M. J. Zaworotko, *Organometallics*, 1985, **4**, 2106; (*c*) L. A. Oro, M. T. Pinillos, A. Tiripicchio, and M. Tiripicchio-Camellini, *Inorg. Chim. Acta*, 1985, **99**, L13.
5 (*a*) F. Barceló, P. Lahuerta, M. A. Ubeda, C. Foces-Foces, F. H. Cano, and M. Martínez-Ripoll, *J. Chem. Soc., Chem. Commun.*, 1985, 43; (*b*) J. L. Atwood, K. A. Beveridge, G. W. Bushnell, K. R. Dixon, D. T. Eadie, S. R. Stobart, and M. J. Zarowotko, *Inorg. Chem.*, 1984, **23**, 4050.
6 A. Tiripicchio, M. Tiripicchio-Camellini, R. Usón, L. A. Oro, M. A. Ciriano, and M. T. Pinillos, *J. Organomet. Chem.*, 1982, **224**, 207.
7 (*a*) L. A. Oro, M. T. Pinillos, and C. Tejel, *J. Organomet. Chem.*, 1985, **280**, 261; (*b*) A. Tiripicchio, F. J. Lahoz, L. A. Oro, M. T. Pinillos, and C. Tejel, *Inorg. Chim. Acta*, 1985, **100**, L5.
8 A. L. Bandini, G. Banditelli, G. Minghetti, and F. Bonati, *Can. J. Chem.*, 1979, **57**, 3237.
9 K. S. Chong, S. J. Rettig, A. Storr, and J. Trotter, *Can J. Chem.*, 1981, **59**, 996.
10 F. R. Hartley, S. G. Murray, and C. A. McAuliffe, *Inorg. Chem.*, 1979, **5**, 1394.
11 G. E. Coates and C. Parkin, *J. Chem. Soc.*, 1963, 421.
12 F. Bonati and G. Wilkinson, *J. Chem. Soc.*, 1964, 3156.
13 D. M. Roe and A. G. Marsey, *J. Organomet. Chem.*, 1971, **28**, 273.
14 S. B. Robinson and B. L. Shaw, *J. Chem. Soc.*, 1965, 4997.
15 R. Usón, L. A. Oro, C. Claver, and M. A. Garralda, *J. Organomet. Chem.*, 1976, **105**, 365.
16 W. C. Deese, D. A. Johnson, and A. W. Cordes, *Inorg. Chem.*, 1981, **20**, 1519; B. M. Louie, S. J. Rettig, A. Storr, and J. Trotter, *Can. J. Chem.*, 1985, **63**, 688.
17 F. H. Cano, C. Foces-Foces, L. A. Oro, M. T. Pinillos, and C. Tejel, *Inorg. Chim. Acta*, 1987, **128**, 75.
18 L. A. Oro, M. T. Pinillos, C. Tejel, C. Foces-Foces, and F. H. Cano, *J. Chem. Soc., Chem. Commun.*, 1984, 1687; *J. Chem. Soc., Dalton Trans.*, 1986, 1087.
19 (*a*) L. A. Oro, M. T. Pinillos, C. Tejel, C. Foces-Foces, and F. H. Cano, *J. Chem. Soc., Dalton Trans.*, 1986, 2193; (*b*) L. A. Oro, M. T. Pinillos, C. Tejel, M. C. Apreda, C. Foces-Foces, and F. H. Cano, *ibid.*, 1988, 1927.
20 S. Trofimenko, *Inorg. Chem.*, 1971, **10**, 1372.
21 H. A. Tayim, A. Bouldoukian, and F. Awad, *J. Inorg. Nucl. Chem.*, 1970, **32**, 3799.
22 L. A. Oro, M. T. Pinillos, C. Tejel, M. C. Apreda, C. Foces-Foces, and F. H. Cano, unpublished work.

23 C. K. Johnson, ORTEP, Report ORNL-3794, Oak Ridge National Laboratory, Tennessee, 1965.

24 G. W. Henslee and J. D. Oliver, *J. Cryst. Mol. Struct.*, 1977, **7**, 137.

25 H. C. Freeman and M. R. Snow, *Acta Crystallogr.*, 1965, **18**, 843.

26 N. Walker and D. Stuart, DIFABS, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.

27 P. T. Beurskens, W. P. Bosman, H. M. Doesburg, R. O. Gould, Th. E. M. Van den Hark, P. A. J. Prick, J. H. Noordik, G. Beurskens, V. Parthasarathi, H. J. Bruins Slot, and R. C. Haltiwanger, DIRDIF System, Crystallography Laboratory, Toernooivel, Nijmegen, 1983.

28 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.

29 J. M. Stewart, P. A. Machin, C. W. Dickinson, H. L. Ammon, H. Heck, and H. Flack. 'The *X*-RAY system,' Technical report TR-446, Computer Science Center, University of Maryland, 1976.

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