Weak Intermetallic Bonding. A Rare Example of Molecular Stacking in a Neutral Square-planar Second-row Transition-metal Complex. *X*-Ray Crystal Structures of [Rh(cod)(Cl)(dmpH)] and [Rh(CO)$_2$(Cl)(pzH)] (cod = cyclo-octa-1,5-diene; dmpH = 3,5-dimethylpyrazole; pzH = pyrazole)

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The molecular geometry of [Rh(cod)(Cl)(dmpH)] (cod = cyclo-octa-1,5-diene; dmpH = 3,5-dimethylpyrazole) is normal in all respects with the heterocycle almost perpendicular to the Rh co-ordination plane and intermolecular Rh · · · Rh 4.49 Å; by contrast the crystal structure of [Rh(CO)$_2$(Cl)(pzH)] (pzH = pyrazole) provides a classic example of molecular 'stacking', with Rh–Rh long at 3.4522(4) Å along the one-dimensional chain.

We are interested in complex formation between transition-metal centres and pyrazole, $C_3N_2H_4$, or the derived anion $C_3N_2H_3^-$, particularly in relation to (a) dynamic character resulting from site exchange of M between adjacent N-atoms,[1,2] (b) occurrence of bridged homo-[3] and hetero-[4] binuclear geometries arising from *exo*-bidentate ligation simultaneously involving both N-atoms. Relevance of the properties of mononuclear pyrazole complexes in both contexts has led us to synthesize a family of square-planar Rh^I derivatives in which a pyrazole group acts as a neutral, two-electron ligand *via* co-ordination through N. As a result we have observed temperature-dependent lineshapes for both

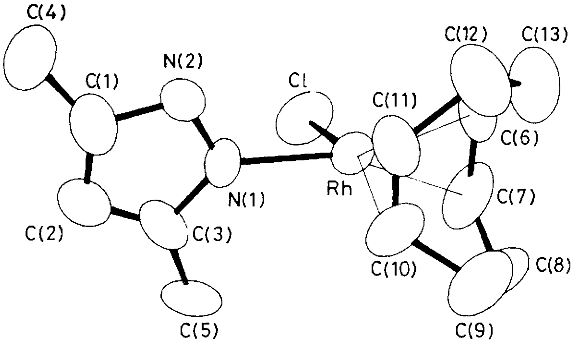

Figure 1. Molecular structure of [Rh(cod)(Cl)(dmpH)] (**2**). Rh–N 2.109(9), Rh–Cl 2.372(3), Rh–C(6) 2.126(13), Rh–C(7) 2.159(11), Rh–C(10) 2.104(12), Rh–C(11) 2.096(11) Å.

pzH (or dmpH) and cod signals (pzH = pyrazole; dmpH = 3,5-dimethylpyrazole; cod = cyclo-octa-1,5-diene) in ^{1}H n.m.r. spectra of the complexes [Rh(cod)(Cl)(pzH)] (**1**), [Rh(cod)(Cl)(dmpH)] (**2**), and [Rh(cod)(pzH)$_2$]PF$_6$ (**3**), conforming to behaviour described qualitatively in 1974 by Borkett and Bruce[5] for [Rh(CO)$_2$(Cl)(pzH)] (**4**). We are attempting to define more rigorously the dynamic character of this group of molecules, and at the same time we have extended our earlier[1–4] *X*-ray studies to determine the solid-state geometry of appropriate examples. In so doing we have discovered a fundamental distinction between the crystal structure of compound (**2**) and that of (**4**), the latter accommodating a one-dimensional chain arrangement of the type which produces anisotropic electrical and optical effects in crystals of a restricted range of related third-row transition-metal (mainly Pt and Ir) complexes.[6]

[Rh(cod)(Cl)(pzH)] [Rh(cod)(pzH)$_2$]PF$_6$
(**1**) (**3**)

Crystal data for (**2**): RhClN$_2$C$_{11}$H$_{16}$, $M = 342.7$, orthorhombic, space group $P2_12_12_1$, $a = 13.512(3)$, $b = 17.875(4)$, $c = 12.217(3)$ Å, $D_c = 1.54$ g cm^{-3}, $Z = 8$, Mo-$K_{\alpha 1}$ radiation ($\lambda = 0.71069$ Å), $\mu = 12.9$ cm^{-1}, 2450 independent observable reflections with $I > 3\sigma(I)$ refined to a conventional R of 0.046. For (**4**): RhClO$_2$N$_2$C$_5$H$_4$, $M = 262.5$, monoclinic, space group $P2_1/n$, $a = 11.622(4)$, $b = 6.885(2)$, $c = 10.443(4)$ Å, $\beta = 100.69(3)°$, $D_c = 2.12$ g cm^{-3}, $Z = 4$, Mo-$K_{\alpha 1}$ radiation (λ 0.71069 Å), $\mu = 22.9$ cm^{-1}, 1251 independent observable reflections with $I > 3\sigma(I)$ giving a conventional R of 0.029.†

The molecular geometry of complex (**2**) is shown in Figure 1 and is unremarkable in all respects: a square environment about the Rh atom is defined by Cl, the chelating diolefin, and a N-bound dimethylpyrazole molecule. As in all related compounds which have been structurally characterized[1,7] (Table VI of ref. 1), the plane of the heterocycle is almost perpendicular to the Rh co-ordination plane ($\theta = 103.7°$). There are two distinct molecules in the unit cell which show marginal differences in bond distances and angles, and are separated by Rh $\cdots$ Rh′ 4.487 Å. In striking contrast, the molecular packing in crystals of compound (**4**) is dominated (Figure 2) by stacking of square metal-centred units along one axis, forming slightly zig-zag (177.3°) chains of metal atoms with Rh–Rh 3.4522(4) Å. The close intermolecular approach is made possible by rotation of the pyrazole heterocycle [compared with the orientation in (**2**)] to only 13.1° away from coincidence with the metal co-ordination plane. Individual stacks are spaced at 4.96 and 5.74 Å from one another but are staggered so that Rh $\cdots$ Rh distances are >7 Å. The structure of compound (**4**), which deposits as deep red crystals from bright yellow solutions, thus provides crystallographic support for the conclusion based on u.v.–visible spectroscopy[8] that intermolecular metal–metal interactions exist in the solid state in certain chloro(dicarbonyl)-rhodium–amine complexes.

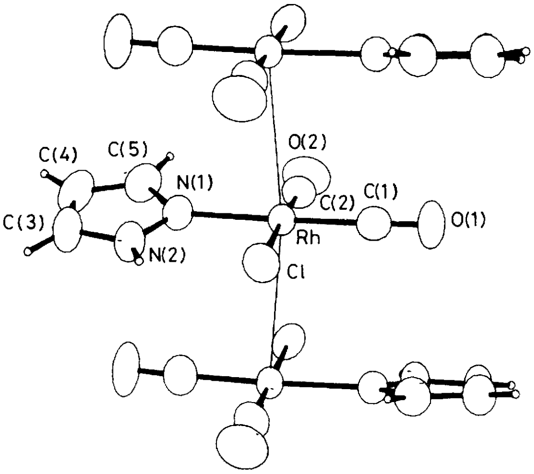

Figure 2. Stacking arrangement in crystalline [Rh(CO)$_2$(Cl)-(pzH)] (**4**). Rh–Rh 3.452(0), Rh–N 2.090(4), Rh–Cl 2.364(1), Rh–C(1) 1.840(7), Rh–C(2) 1.835(6) Å.

[Rh(CO)$_2$(acac)] [M(cod)(μ-pz)]$_2$
(**5**) (**6**) M = Rh
(**7**) M = Ir

[Rh(CO)$_2$(μ-pz)]$_2$
(**8**)

The Rh–Rh distance in (**4**) is longer by only *ca.* 0.2 Å than that in [Rh(CO)$_2$(acac)] [(**5**) acacH = acetylacetone], for which intrinsic semiconductor behaviour has been suggested on the basis of conductivity measurements.[9] Columnar chain-structures like those of compounds (**4**) and (**5**) remain very rare for Rh (and other lighter transition elements) although a number of Ir examples are known of which [Ir(CO)$_3$Cl] has received most attention.[9,10] We have shown that Ir analogues of compounds (**2**) and (**4**) are unstable with respect to dimer formation,[3] giving di-iridium(I) complexes with Ir$_2$ separation *ca.* 3.2 Å. We have also suggested[11] on the basis of crystallographic evidence that in the binuclear complexes [M(cod)(μ-pz)]$_2$ [(**6**) M = Rh; (**7**) M = Ir] there is some degree of interaction between the (formally non-bonded) metal centres; such a situation resembles that proven to obtain in related 'face-to-face' Rh$^{\text{I}}$ dimers, for which direct spectroscopic evidence for ground-state non-zero Rh–Rh bond-order has recently been obtained by Gray and co-workers.[12] Under appropriate conditions the mononuclear complex (**4**) can be induced to dimerize giving [Rh(CO)$_2$-(μ-pz)]$_2$ (**8**); the influence on one another of weakly interacting metal centres in these and related compounds is being investigated further.

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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