

## Orthometallation Reaction at a Binuclear Pyrazolyl(pz) Bridged Rhodium Compound: Synthesis and Crystal Structure Determination of $\text{Rh}_2(\mu\text{-pz})_2[\mu\text{-P}(\text{C}_6\text{F}_4)\text{Ph}_2]\text{Br}(\text{CO})(\text{pcBr})$ , $\text{pcBr} = \text{P}(o\text{-BrC}_6\text{F}_4)\text{Ph}_2$

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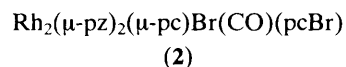
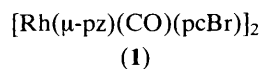
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The complex  $[\text{Rh}(\mu\text{-pz})(\text{CO})(\text{pcBr})]_2$  [pz = pyrazolyl, pcBr =  $\text{P}(o\text{-BrC}_6\text{F}_4)\text{Ph}_2$ ] undergoes orthometallation in refluxing toluene to give a new binuclear compound containing a rhodium–rhodium bond,  $\text{Rh}_2(\mu\text{-pz})_2(\mu\text{-pc})\text{Br}(\text{CO})(\text{pcBr})$  [pc =  $\text{P}(\text{C}_6\text{F}_4)\text{Ph}_2$ ], which has been structurally characterized by X-ray crystallography; the complex has two pyrazolyl groups and one orthometallated phosphine bridging the two inequivalent rhodium atoms, and one phosphine ligand chelating one of the rhodium atoms *via* P and the bromine atom from the *o*-bromotetrafluorophenyl group.

Two centre oxidative addition reactions to rhodium(I) and iridium(I) compounds have only been reported for some bimetallic systems<sup>1</sup> to give binuclear metal–metal bonded  $\text{Rh}^{\text{II}}$  and  $\text{Ir}^{\text{II}}$  complexes. In particular binuclear  $\text{Rh}^{\text{I}}$  and  $\text{Ir}^{\text{I}}$  pyrazolyl bridged compounds undergo two centre oxidative

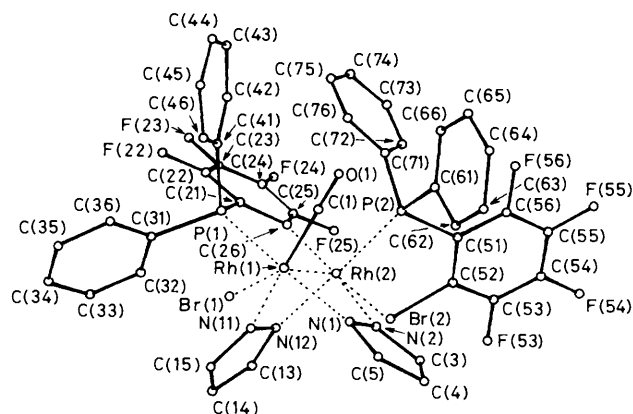
addition although the nature of the reaction products depends on steric and electronic factors.<sup>2</sup> This communication reports the preparation and crystal structure of a new pyrazolyl bridged metal–metal bonded  $\text{Rh}^{\text{II}}$  compound with some interesting structural features.

The thermal reaction of  $[\text{Rh}(\mu\text{-pz})(\text{CO})(\text{pcBr})]_2^\dagger$  (**1**), [pcBr =  $\text{P}(o\text{-BrC}_6\text{F}_4)\text{Ph}_2$ ], in refluxing toluene gives a complex mixture from which  $\text{Rh}_2(\mu\text{-pz})_2(\mu\text{-pc})\text{Br}(\text{CO})(\text{pcBr})$  (**2**), [pc =  $\text{P}(\text{C}_6\text{F}_4)\text{Ph}_2$ ], is isolated in *ca.* 10% yield. Compound (**2**) has



pz = pyrazolyl  
pc =  $\text{P}(\text{C}_6\text{F}_4)\text{Ph}_2$   
pcBr =  $\text{P}(o\text{-BrC}_6\text{F}_4)\text{Ph}_2$

<sup>†</sup> Prepared by treating  $[\text{Rh}(\mu\text{-pz})(\text{CO})]_2$  (ref. 10) in  $\text{CH}_2\text{Cl}_2$  with a stoichiometric amount of pcBr.  $\nu(\text{CO})$  1985  $\text{cm}^{-1}$  ( $\text{CHCl}_3$ ). <sup>31</sup>P n.m.r.  $\delta$  +46.9 p.p.m., <sup>1</sup>J(Rh–P) 161 Hz ( $\delta > 0$  for resonances downfield from 85%  $\text{H}_3\text{PO}_4$  in  $\text{D}_2\text{O}$ , in  $\text{CDCl}_3$ , measured with a Varian XL-200 spectrometer).



**Figure 1.** A view of compound (2)  $\text{Rh}_2(\mu\text{-pz})_2(\mu\text{-pc})\text{Br}(\text{CO})(\text{pcBr})$  with the atomic numbering. Selected bond distances (Å) and angles ( $^\circ$ ) are: Rh(1)–Rh(2) 2.581(1), Rh(1)–Br(1) 2.561(2), Rh(2)–Br(2) 2.660(1), Rh(1)–P(1) 2.271(2), Rh(2)–P(2) 2.283(3), Rh(1)–C(1) 1.845(13), Rh(2)–C(26) 2.005(8), Rh(1)–N(1) 2.061(9), Rh(1)–N(11) 2.038(10), Rh(2)–N(2) 2.091(8), Rh(2)–N(12) 2.051(10), P(1)–C(21) 1.823(10), P(2)–C(51) 1.845(9), Br(2)–C(52) 1.884(13); Rh(1)–P(1)–C(21) 108.6(4), P(1)–Rh(1)–Rh(2) 91.8(1), Rh(1)–Rh(2)–C(26) 94.7(2), Rh(2)–P(2)–C(51) 107.8(3), Rh(2)–Br(2)–C(52) 97.6(3), Rh(1)–Rh(2)–P(2) 107.0(1), Rh(1)–Rh(2)–Br(2) 155.0(1), P(2)–Rh(2)–Br(2) 86.8(1).

been characterized by elemental analysis, i.r. and  $^{31}\text{P}$  n.m.r. spectroscopy,† and crystal structure determination.§

The crystal structure of (2) (Figure 1) shows a binuclear dirhodium unit, triply bridged by two pyrazolyl groups and one pcBr ligand in which orthometallation has occurred at the tetrafluorophenyl ring by labilization of the C–Br bond. One carbonyl group and one bromine atom complete the co-ordination sphere around Rh(1) and one phosphine group

† Satisfactory elemental analysis was obtained.  $\nu(\text{CO})$  2060  $\text{cm}^{-1}$  ( $\text{CHCl}_3$ ).  $^{31}\text{P}$  n.m.r.  $\delta_1 +55.4$  p.p.m.,  $^1J(\text{Rh}–\text{P})$  139 Hz;  $\delta_2 +31.2$ ,  $^1J(\text{Rh}–\text{P})$  106.

§ *Crystal data:*  $\text{Rh}_2\text{C}_{43}\text{H}_{26}\text{N}_4\text{OF}_8\text{Br}_2\text{P}_2 \cdot \text{CH}_2\text{Cl}_2 \cdot \text{H}_2\text{O}$ ;  $M = 1297.206$ , triclinic, space group  $P1$ ,  $a = 14.1211(8)$ ,  $b = 18.1396(8)$ ,  $c = 10.2393(4)$  Å,  $\alpha = 91.588(5)$ ,  $\beta = 111.166(3)$ ,  $\gamma = 84.834(5)$ °,  $U = 2435.9(2)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_c = 1.769$   $\text{g cm}^{-3}$ , Cu- $K_\alpha$  radiation, crystal dimensions  $0.14 \times 0.11 \times 0.30$  mm<sup>3</sup>. The structure was solved by a combination of Patterson and Fourier methods and refined to  $R = 0.057$  using 5022 unique reflections [ $F^2 > 3\sigma(F^2)$ ] measured on a PW1100 Philips diffractometer. A total of 676 parameters were refined, all vibrational parameters were treated anisotropically for the non H atoms. 32 Parameters of 14 H atoms were fixed in the final cycles of refinement. 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.

chelates to Rh(2) *via* P and the Br atom bonded to the tetrafluorophenyl group.

The Rh–Rh distance, 2.581(1) Å in this compound is longer than that reported for any tetracarboxylate bridged dirhodium(II,II) compounds;<sup>3</sup> however it is in the range of metal–metal bond lengths observed for other rhodium(II) complexes with binucleating nitrogen donor ligands<sup>4</sup> and for some biscarboxylate bridged dirhodium(II,II) compounds,  $\text{Rh}_2(\text{O}_2\text{CMe})_2(\text{dmg})_2(\text{PPh}_3)_2$  (dmg = dimethylglyoximate),<sup>5</sup> Rh–Rh 2.618(5);  $\text{Rh}_2(\text{O}_2\text{CH})_2(\text{phen})_2\text{Cl}_2$  (phen = 1,10-phenanthroline),<sup>6</sup> Rh–Rh 2.576; or  $\text{Rh}_2(\text{O}_2\text{CMe})_2[\text{P}(\text{C}_6\text{H}_4)\text{Ph}_2]_2 \cdot 2\text{MeCO}_2\text{H}$ ,<sup>7</sup> Rh–Rh 2.508(1) Å. In the last compound there are two orthometallated triphenylphosphine units bridging the two rhodium atoms, and the orthometallation occurs by a thermal reaction in the presence of  $\text{PPh}_3$ . In our case both metal–metal bond formation and cyclometallation occur in the reaction process.

The pcBr phosphine linked to Rh(2) shows a rather unusual co-ordination mode. It chelates *via* its P and Br atoms, this Rh–Br distance being longer than the one observed for the other bromine atom in the molecule; Rh(2)–Br(2) 2.660(1), Rh(1)–Br(1) 2.561(2) Å. Other examples are known of such halogenocarbon binding in rhodium and iridium complexes,  $\text{RhClBr}[\text{OP}(\text{C}_6\text{F}_4)\text{Ph}_2][(\eta^2\text{-pcBr})]$ <sup>8</sup> and  $\{\text{Ir}(\text{cyclo-octa-1,5-diene})[\eta^2\text{-P}(o\text{-BrC}_6\text{H}_4)\text{Ph}_2]\}\text{SbF}_6$ .<sup>9</sup>

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## References

- 1 J. Powell, A. Kuksis, S. C. Nyburg, and W. N. G. Winnie, *Inorg. Chim. Acta*, 1982, **64**, L211 and references therein.
- 2 K. A. Beveridge, G. W. Bushnell, S. R. Stobart, J. L. Atwood, and M. J. Zawarotko, *Organometallics*, 1983, **2**, 1447; G. W. Bushnell, D. O. K. Fjeldsted, S. R. Stobart, and M. J. Zawarotko, *J. Chem. Soc., Chem. Commun.*, 1983, 580.
- 3 F. A. Cotton and R. A. Walton, 'Multiple Bonds between Metal Atoms,' Wiley, New York, 1982.
- 4 L. A. Oro, D. Carmona, P. L. Perez, N. Esteban, A. Tiripicchio, and M. T. Camellini, *J. Chem. Soc., Dalton Trans.*, in the press; L. A. Oro, M. J. Fernandez, J. Modrego, C. Foces-Foces, and F. H. Cano, *Angew. Chem., Int. Ed. Engl.*, in the press.
- 5 J. Halpern, E. Kimura, J. Molin-Case, and C. S. Wong, *J. Chem. Soc., Chem. Commun.*, 1971, 1207.
- 6 H. Pasternak and F. Pruchnik, *Inorg. Nucl. Chem. Lett.*, 1976, **12**, 591.
- 7 A. R. Chakravarty, F. A. Cotton, and D. A. Tocher, *J. Chem. Soc., Chem. Commun.*, 1984, 501.
- 8 M. Aguiló, J. C. Besteiro, M. Font-Altaba, P. Lahuerta, C. Miravittles, and X. Solans, *Acta Crystallogr. Sect. A*, in the press.
- 9 M. J. Burk, R. H. Crabtree, and E. M. Holt, *Organometallics*, 1984, **3**, 638.
- 10 R. Usón, L. A. Oro, M. A. Ciriano, M. T. Pinillos, A. Tiripicchio, and M. T. Camellini, *J. Organomet. Chem.*, 1981, **205**, 247.