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New *ortho*-Metallated Dirhodium(II) Compounds

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ortho-Metallation reactions involving a multiply bonded dimetal unit are rare. However, there are several reports [1–5] of *ortho*-metallated triarylphosphines bridging a single rhodium-to-rhodium bond. Stereochemically the products of such reactions seem to be very favourable. As far as we are aware, similar reactions have not been reported for mixed alkyl–aryl phosphines. The extension of the synthetic route to the latter class of phosphine ligands is the subject of this report.

Experimental

$Rh_2(O_2CCH_3)_4$ and $Rh_2(O_2CC(CH_3)_3)_4$ were prepared by literature methods [6]. All other reagents were obtained from normal commercial suppliers.

$Rh_2(O_2CCH_3)_2[PhMeP(C_6H_4)]_2\cdot 2CH_3CO_2H$

$Rh_2(O_2CCH_3)_4\cdot 2MeOH$ (0.26 g, 0.52 mmol) was refluxed with PPh_2Me (0.24 g, 1.22 mmol) in glacial acetic acid for 45 min. During this time the colour of the solution changed from orange to deep red. Acetic acid and unreacted diphenylmethylphosphine were removed *in vacuo*. The resulting red gum was dissolved in the minimum amount of CH_2Cl_2 and was eluted down a column of silica gel (60–120 mesh). A mauve band was eluted with hexane/dichloromethane/diethyl ether (40/40/20) and a red band with methanol (100%). The mauve band was collected and the solvent removed under reduced pressure. The residue was treated with water (3 X 20 cm^3) and then the fine mauve powder filtered off and air dried; yield 0.15 g (35%). *Anal.* Calc. for $C_{34}H_{38}O_8P_2Rh_2$: C, 48.6; H, 4.6; P, 7.4. Found: C, 47.9; H, 4.7; P, 8.1%. ^{31}P NMR ($CDCl_3$, 162 MHz): AA′XX′ centred at δ4.64 ppm.

$Rh_2(O_2CC(CH_3)_3)_2[PhMeP(C_6H_4)]_2\cdot 2(CH_3)_3CCO_2H$

$Rh_2(O_2CC(CH_3)_3)_4$ (0.14 g, 0.24 mmol) was refluxed for 45 min in pivalic acid (10 cm^3) to which PPh_2Me (0.15 g, 0.78 mmol) was added. The deep red reaction mixture was cooled and the volatile components removed under vacuum. The red gum was redissolved in CH_2Cl_2 (3 cm^3) and loaded on a column of silica gel (60–120 mesh). The product was eluted as a mauve band using hexane/dichloromethane/diethyl ether (40/40/20). The solvent was removed and the product treated with water (3 X 50 cm^3) to remove any excess pivalic acid. The mauve solid was filtered off and dried in air for 8 h; yield 0.11 g (54%). *Anal.* Calc. for $C_{46}H_{62}O_8P_2Rh_2$: C, 54.9; H, 6.2; P, 6.2. Found: C, 55.0; H, 6.7; P, 5.6%. ^{31}P NMR ($CDCl_3$, 162 MHz): AA′XX′ centred at δ8.66 ppm.

Results and Discussion

Reaction of $Rh_2(O_2CR)_4$ (R = Me, CMe_3) in RCO_2H with a slight excess of PPh_2Me gave mauve powders which analysed (C,H,P) well as $Rh_2(O_2CR)[PhMeP(C_6H_4)]_2\cdot 2RCO_2H$. The ^{31}P NMR spectrum of each compound was observed to be an AA′XX′ pattern at 25 °C and therefore it was deemed very unlikely that we had prepared simple axial adducts of the dirhodiumtetracarboxylate core [7]. In addition we were able to oxidise both compounds electrochemically at potentials significantly removed from those at which the compounds $Rh_2(O_2CR)_4\cdot 2PPh_2Me$ are observed to be oxidised. The compound $Rh_2(O_2CCH_3)_2[PhMeP(C_6H_4)]_2\cdot 2CH_3CO_2H$ was oxidised in CH_2Cl_2/0.1 M $TBABF_4$ solution at +0.92 V, while the related pivalato derivative could be oxidised at +0.89 V. In contrast, the axial adducts of dirhodium tetraacetate are generally oxidised at potentials greater than 1 V. It is also worth noting that both these compounds are easier to oxidise than is the related triphenylphosphine compound $Rh_2(O_2CCH_3)_2[Ph_2P(C_6H_4)]_2\cdot 2CH_3CO_2H$ (+1.04 V) [2], a result which is expected from consideration of the relative electronic effects of the various bridging ligands.

Although we have been unable to obtain a crystalline sample of either of the carboxylic acid adducts, conclusive proof for the correctness of our deductions about the formulation of our products is provided by the preliminary X-ray structure determination of the readily prepared pyridine adduct**

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**Preliminary crystal data for $Rh_2(O_2CC(CH_3)_3)_2[PhMeP(C_6H_4)]_2\cdot 2C_5H_5N\cdot 2CHCl_3$: $M = 1203.50$; monoclinic, space group $C2/c$, $a = 38.238(9)$, $b = 12.312(4)$, $c = 23.253(5)$ Å; $\beta = 111.67(2)°$, $U = 10172(4)$, $D_c = 1.57$ g cm^{-3}, μ(Mo Kα) = 10.62 cm^{-1}, $Z = 8$, $\lambda = 0.71073$ Å; crystal dimensions 0.2 × 0.18 × 0.3 mm^3. The data were corrected for Lorentz, polarisation and absorption effects. The structure was solved by

(continued overleaf)

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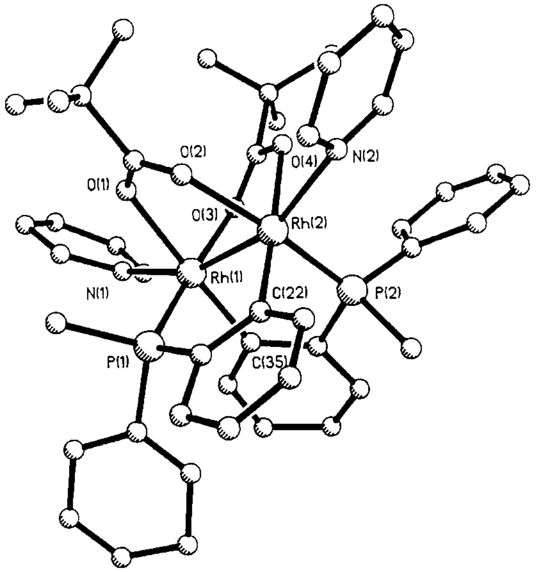

Fig. 1. The molecular structure of the molecule $Rh_2(O_2CC(CH_3)_3)_2[PhMeP(C_6H_4)]_2 \cdot 2C_5H_5N$. Important parameters: Rh(1)–Rh(2) 2.535(5), Rh(1)–O(1) 2.164(24), Rh(1)–O(3) 2.072(28), Rh(1)–P(1) 2.204(12), Rh(1)–C(35) 2.029(36), Rh(1)–N(1) 2.271(32), Rh(2)–O(2) 2.168(23), Rh(2)–O(4) 2.195(27), Rh(2)–P(2) 2.192(11), Rh(2)–C(22) 1.996(35), Rh(2)–N(2) 2.306(34) Å; N(1)–Rh(1)–Rh(2) 160.2(7), N(2)–Rh(2)–Rh(1) 160.1(8)°.

$Rh_2(O_2CC(CH_3)_3)_2[PhMeP(C_6H_4)]_2 \cdot 2C_5H_5N$. This compound is obtained as its dichloroform solvate by the slow evaporation of a chloroform/pyridine solution of $Rh_2(O_2CC(CH_3)_3)_2[PhMeP(C_6H_4)]_2 \cdot 2(CH_3)_3CO_2H$.

The structure consists of a dinuclear rhodium core bridged by cisoid pivalate groups and two diphenylmethylphosphine ligands in which *ortho*-metallation has occurred at one of the phenyl rings of each phosphine (see Fig. 1). The axial sites are occupied by pyridine molecules. The rhodium–rhodium bond, 2.535(5) Å, is somewhat shorter than that observed in $Rh_2(O_2CCH_3)_2[Ph_2P(C_6H_4)]_2 \cdot 2C_5H_5N$, 2.556(2) Å [2]. Despite the lower steric requirements of the $[PhMeP(C_6H_4)]^-$ bridging ligands, the geometry about the rhodium ions is still significantly distorted. For example, the Rh–Rh–N bonds are significantly non-linear, 160.2(7) and 160.1(8)°, and the torsion angles about the rhodium-to-rhodium bond fall in the range 11.9–18.0°.

Investigations are continuing to extend further the range of compounds available.

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References

1 A. R. Chakravarty, F.A. Cotton and D. A. Tocher, *J. Chem. Soc., Chem. Commun.*, (1984) 501.
2 A. R. Chakravarty, F. A. Cotton, D. A. Tocher and J. H. Tocher, *Organometallics, 4* (1985) 8.
3 F. A. Cotton and K. Dunbar, *J. Am. Chem. Soc., 109* (1987) 3142.
4 F. A. Cotton, K. Dunbar and M. G. Verbruggen, *J. Am. Chem. Soc., 109* (1987) 5498.
5 F. Barcelo, F. A. Cotton, P. Lahuerta, M. Sanau, W. Schwotzer and M. A. Ubeda, *Organometallics, 6* (1987) 1105.
6 G. A. Rempel, P. Legzdins, H. Smith and G. Wilkinson, *Inorg. Synth., 13* (1972) 90.
7 E. B. Boyar and S. D. Robinson, *J. Chem. Soc., Dalton Trans.*, (1985) 629.

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direct methods and refined by full-matrix least-squares. The poor quality of the crystal (2148 reflections with $I > 3\sigma(I)$ out of 7133 unique reflections measured) and the presence of two extensively disordered molecules of $CHCl_3$ in the asymmetric unit result in a high residual, $R = 0.1102$; however, the important structural features of the molecule are not in doubt. Problems associated with the structure determination will be discussed in detail in the full paper.