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Preliminary communication

HETEROBIMETALLIC (Ru—Co) COMPLEXES WITH CHELATING AND BRIDGING $Ph_2PCH_2PPh_2$ (dppm) LIGANDS

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Summary

Reaction of the heterobinuclear complex $(CO)_4Ru(\mu\text{-}PPh_2)Co(CO)_3$ with $Ph_2PCH_2PPh_2$ (dppm) affords the dppm chelate $(dppm)(CO)_2Ru(\mu\text{-}PPh_2)Co(CO)_3$ (1) and the dppm bridged molecule $(CO)_3Ru(\mu\text{-}PPh_2)(\mu\text{-}dppm)Co(CO)_2$ (2) both of which have been characterised by X-ray diffraction: 1 is the first binuclear Ru—Co complex containing a chelating dppm ligand and 2 the first heterobinuclear μ-dppm (Ru—Co) compound.

An extensive chemistry of homobimetallic complexes has developed from the use of the ditertiary phosphine $Ph_2PCH_2PPh_2$ (dppm), a ligand with unique bridging properties [1]. Until recently however heterobimetallics with μ-dppm ligands were rare [2] and their potentially interesting chemistry was only beginning to be explored [2,3]. The development of facile, rational routes to dppm bridged mixed metal systems largely by Shaw, Chaudret and co-workers [2] has focussed new attention on such systems. We now describe the synthesis and structural characterisation of the first Ru—Co heterobimetallic dppm complexes $(dppm)(CO)_2Ru(\mu\text{-}PPh_2)Co(CO)_3$ (1) and $(CO)_3Ru(\mu\text{-}PPh_2)(\mu\text{-}dppm)Co(CO)_2$ (2). Complex 1 has an unusual unsymmetrical structure with a chelating dppm ligand coordinated only to the ruthenium atom. Characterisation of 2, the first heterobinuclear complex containing both $\mu\text{-}PPh_2$ and μ-dppm ligands suggests the possible use of dppm to further stabilise polynuclear phosphido complexes.

We have previously shown that phosphine mono and di-substitution on $(CO)_4Ru(\mu\text{-}PPh_2)Co(CO)_3$ (3) occurs site specifically at the ruthenium atom

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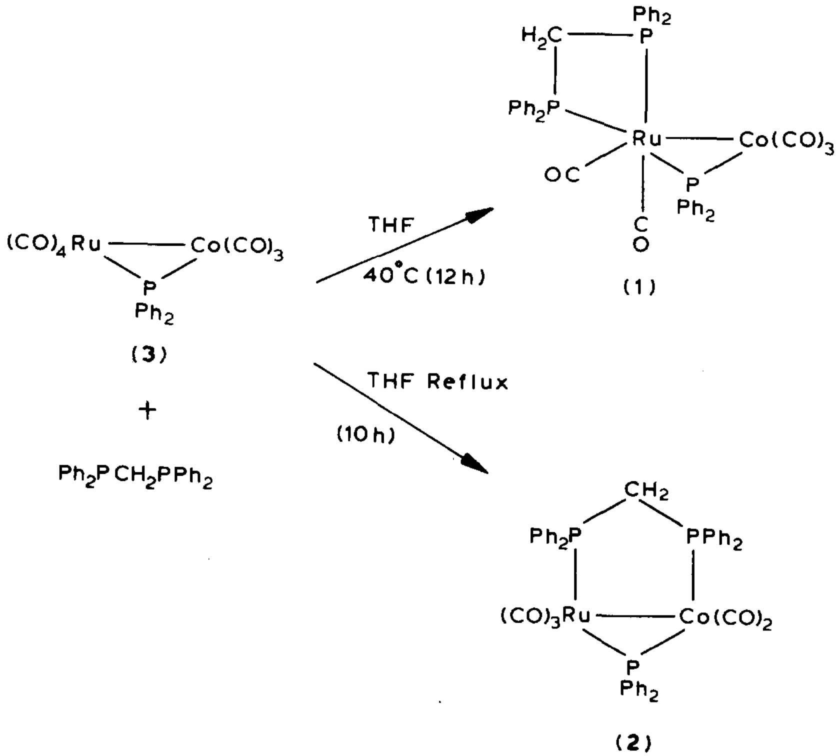
giving (L)$(CO)_3Ru(\mu\text{-}PPh_2)Co(CO)_3$ and $(L)_2(CO)_2Ru(\mu\text{-}PPh_2)Co(CO)_3$ (L = phosphine) [4]. The propensity of dppm to bridge dimetal centres led us to attempt heterodisubstitution with this ligand.

When a solution of light red 3 [5]' (0.54 g, 1 mmol) in dry THF (60 ml) was heated with dppm (1 equiv), thin layer chromatography and IR monitoring showed the disappearance of 3 and the growth of two dark red complexes. Reaction at 313 K for 12 h, followed by silica-gel column chromatography of the reaction mixture (eluant: hexane/ether 9/1) afforded as the major product 1 (0.2 g; 23%), which was recrystallised from hexane/CH_2Cl_2 (Scheme 1).



SCHEME 1

The same reaction carried out under reflux for 10 h, gave, after similar work up and recrystallisation, 3 (0.55 g, 63%). Spectroscopic data: 1: IR (C_6H_{12}); 2019s, 1985vs, 1952m, 1939m, 1934m, 1913w. ^1H NMR ($CDCl_3$, 303 K 60 MHz, δ 7.9—7.1 (m, Ph), 4.70 (t, CH_2, ^2J(PH) 10 Hz; ^{31}P NMR (CD_2Cl_2, 223 K, 32.38 MHz), δ 187.33 (dd, μ-PPh_2), −12.47 (dd, Ru—*P*Ph_2(*trans*)), −29.02 (dd, Ru—*P*Ph_2(cis); ^2J(μ-P—P) 131.8 Hz, ^2J(μ-P—P) 22.0 Hz, ^2J(P—P) 43.9 Hz. 2: IR (C_6H_{12}); 2046w, 1984s, 1956vs, 1907m. ^1H NMR ($CDCl_3$, 303 K, 250 MHz), δ 7.77—7.13 (m, Ph), 4.48 (t, CH_2, ^2J(P—H) 10.2 Hz); ^{31}P NMR ($CDCl_3$, 223 K, 32.38 MHz), 203.5 (dd, μ-PPh_2), 47.4 (dd, Co—*P*Ph_2), 24.3 (dd, Ru—*P*Ph_2); ^2J(μ-P—Co*P*) 107.4 Hz, ^2J(μ-P—Ru*P*) 92.8 Hz, ^2J(Co*P*—Ru*P*) 78.0 Hz. The isomeric nature of 1 and 2 prompted X-ray structure

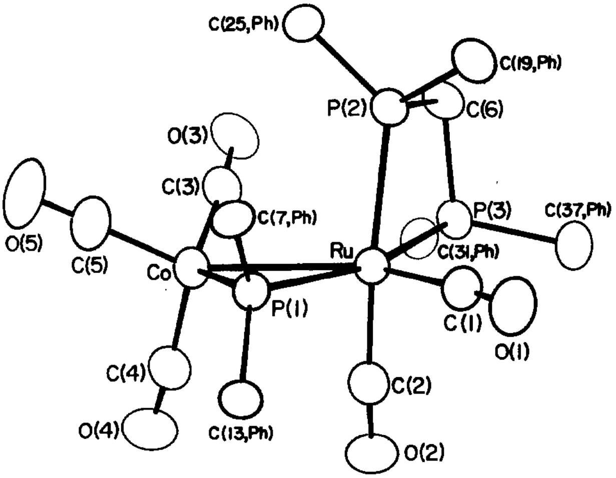


Fig. 1. A perspective view of the molecular structure of the molecule $(dppm)(CO)_2Ru(\mu\text{-}PPh_2)Co(CO)_3$ showing the atomic numbering.

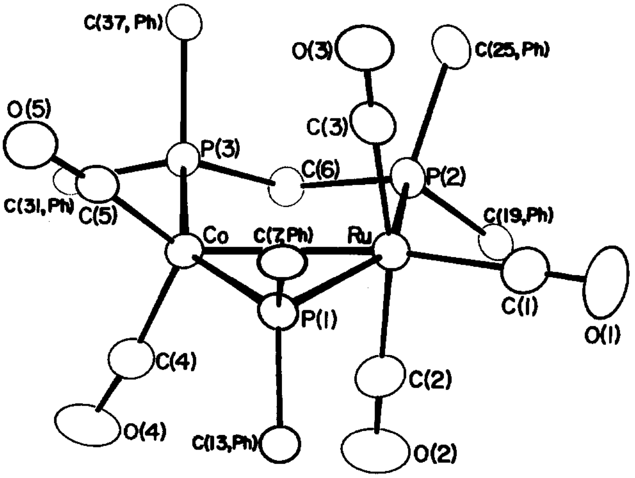


Fig. 2. The molecular structure of $(CO)_3Ru(\mu\text{-}PPh_2)(\mu\text{-}dppm)Co(CO)_2$ drawn to illustrate the dppm and PPh_2 bridges.

determinations*. ORTEP plots of the structures of 1 and 2 are shown in Fig. 1 and 2. In 1 the metal atoms are linked only by an Ru—Co bond (Ru—Co 2.7858(7) Å) and a μ-PPh_2 group with the dppm ligand coordinated to the

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*Crystal data: 1: dark red prisms, $RuCoP_3O_5C_{42}H_{32}$, M = 869.64. Monoclinic, space group $P2_1/c$, a 16.398(2), b 11.239(1), c 21.182(2) Å, β 90.68(1)°, U 3903.5(7) $Å^3$, Z = 4, $\mu(Mo\text{-}K_\alpha)$ 9.88 cm^{-1}, λ 0.71069 Å, $F(000)$ = 1760, T = 293±1 K. The structure solution and refinement were based on 4115 observed ($I \geqslant 3\sigma(I)$) reflections (6158 measured) from a Syntex $P2_1$ diffractometer. Final R and R_w values are 0.033 and 0.037, all non-hydrogen atoms being refined with anisotropic thermal parameters. One disordered phenyl group (C(14)—C(18)) was refined with site occupancies of 2/3 and 1/3. 2: red prisms, $RuCoP_3O_5C_{42}H_{32}$, M = 869.64, monoclinic, space group $P2_1/n$, a 11.590(1), b 27.458(4), c 12.620(2) Å, β 101.54(1)°, U 3935.0(9) $Å^3$, Z = 4, $\mu(Mo\text{-}K_\alpha)$ 9.80 cm^{-1}, λ 0.71069 Å, $F(000)$ = 1760, T = 293±1 K, 2918 observed ($I > 3\sigma(I)$) reflections (4250 measured intensities), θ—2θ scans, $P2_1$ diffractometer, R = 0.037, R_w = 0.041; all non-hydrogen atoms were refined with anisotropic coefficients, hydrogen atoms with isotropic parameters. The atomic coordinates for both structures 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.

quasi-octahedral ruthenium atom as a bidentate chelate. In the isomer 2 the metal atom stereochemistries are remarkably similar to those in 1 but the dppm ligand bridges the two metal centres, with one phosphorus atom occupying the site vacated by C(3)—O(3) on cobalt and with a CO group (C(3)—O(3)) in the axial site occupied by P(2) in 1. Thus the net structural change from 1 → 2 is an exchange of one CO group on Co for a phosphine on Ru. There are several other structural features relevant to the relationship between 1 and 2: (i) with a P(2)—Ru—P(3) angle of only ≈70° the RuP_2C four membered ring in 1 is clearly strained. (ii) Comparison of the Ru—P(2) bond length in 1 (2.437(1) Å) with the significantly shorter Ru—P(3) distances in 1 (2.366(1) Å) and 2 (2.359(2) Å) suggests that the Ru—P(2) link in 1 is relatively weak and hence likely subject to dissociation. Although the intramolecular isomerisation of 1 to 2 was not directly observed on heating 1 alone, infrared monitoring showed that this conversion did occur when 1 equivalent of dppm and 1 were heated together. These results tend to suggest, in agreement with earlier work on monodentate phosphines that sites *cis*-equatorial and *trans*-equatorial to the μ-PPh_2 group in 3 need to be occupied by phosphorus ligands in order for substitution on the cobalt atom to proceed. The only transformation related to that of 1 → 2 of which we are aware is the isomerisation of $(CO)_5W[\mu\text{-}C(Me)(OMe)]Pt(dppm)$ to $(CO)_4W[\mu\text{-}C(Me)(OMe)](\mu\text{-}dppm)Pt(CO)$ [3a].

Finally we note that the Ru—Co bond in 2 is supported by both μ-PPh_2 and μ-dppm ligands. Although useful chemistry has recently been accomplished on phosphido bridged polynuclear complexes [6,7] fragmentation and reactivity at the bridge are complicating factors [7]. We are currently examining the reaction chemistry of mixed bridge bimetallics such as 2 to evaluate the additional stability imparted by the dppm moiety.

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References

1 For a selection of references see: (a) R.J. Puddephatt, K.A. Azam, R.H. Hill, M.P. Brown, C.D. Nelson, R.P. Moulding, K.R. Seddon, and M.C. Grossel, J. Am. Chem. Soc., 105 (1983) 5642; (b) C.T. Hunt, and A.L. Balch, Inorg. Chem., 21 (1982) 1641; (c) C.P. Kubiak, C. Woodcock, and R. Eisenberg, ibid., 19 (1980) 2733; (d) D.M. Hoffman, and R. Hoffmann, ibid., 20 (1981) 3543; (e) J.A.E. Gibson, and M. Cowie, Organometallics, 3 (1984) 984; (f) K.W. Lee, W.T. Pennington, A.W. Cordes, and T.L. Brown, ibid., 3 (1984) 404.

2 (a) D.M. McEwan, P.G. Pringle, and B.L. Shaw, J. Chem. Soc. Chem. Commun., (1982) 1240; (b) P.G. Pringle, and B.L. Shaw, J. Chem. Soc. Dalton Trans., (1983) 889; (c) A.T. Hutton, P.G. Pringle, and B.L. Shaw, Organometallics, 2 (1983) 1889; (d) J.A. Iggo, D.P. Markham, B.L. Shaw, and M. Pett-Thorton, J. Chem. Soc. Chem. Commun., (1985) 432; (e) B. Delavaux, B. Chaudret, F. Dahan and R. Poilblanc, Organometallics, 4 (1985) 935; (f) B. Chaudret, S. Sabo and D. Gervais, J. Organomet. Chem., 258 (1983) C19.

3 (a) M.R. Awang, J.C. Jeffrey, and F.G.A. Stone, J. Chem. Soc. Dalton Trans., (1983) 2091; (b) J.C. Jeffrey, A.G. Orpen, W.T. Robinson, F.G.A. Stone, and M.J. Went, J. Chem. Soc. Chem. Commun., (1984) 396; (c) B. Chaudret, F. Dahan, and S. Sabo, Organometallics, 4 (1985) 1490; (d) B. Delavaux, B. Chaudret, N.J. Taylor, S. Arabi and R. Poilblanc, J. Chem. Soc. Chem. Commun., (1985) 805.

4 R. Regragui, P.H. Dixneuf, N.J. Taylor, and A.J. Carty, Organometallics, 5 (1986) 1.

5 R. Regragui, P.H. Dixneuf, N.J. Taylor, and A.J. Carty, Organometallics, 3 (1984) 1020.

6 See for example: (a) D. Nucciarone, N.J. Taylor, and A.J. Carty, Organometallics, 3 (1984) 177; (b) L. Chen, D.J. Kocunz, and D.W. Meek, ibid., 4 (1985) 598; (c) W.C. Mercer, R.R. Whittle, E.W. Burkhardt and G.L. Geoffroy, ibid., 4 (1985) 68; (d) J.P. Collman, R.K. Rothrock, R.G. Finke, E.J. Moore, and F. Rose-Munch, Inorg. Chem., 21 (1982) 146; (e) Y.F. Yu, C.N. Chau, A. Wojcicki, M. Calligaris, G. Nardin, and G. Balducci, J. Am. Chem. Soc., 106 (1984) 3704.

7 (a) A.D. Horton, M.J. Mays and P.R. Raithby, J. Chem. Soc. Chem. Commun., (1985) 247; (b) R. Regragui, P.H. Dixneuf, N.J. Taylor, and A.J. Carty, Organometallics, 3 (1984) 814; (c) W.F. Smith, N.J. Taylor, and A.J. Carty, J. Chem. Soc. Chem. Commun., (1976) 896; (d) G.J. Geoffroy, S. Rosenberg, P.M. Shulman and R.R. Whittle, J. Am. Chem. Soc., 106 (1984) 1519; (e) Y.F. Yu, J. Galluci and A. Wojcicki, ibid., 105 (1983) 4826; (f) H. Werner and R. Zolk, Organometallics, 4 (1985) 601; (g) J.S. McKennis and E.P. Kyba, Organometallics, 2 (1983) 1249.