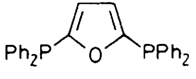
Rhodium Complexes of 2,5-Bisdiphenylphosphinofuran, a Ligand selective for Binuclear Chelation

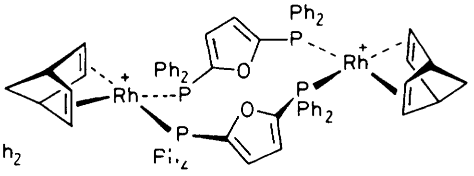
John M. Brown and Lewis R. Canning
Dyson Perrins Laboratory, South Parks Road, Oxford OX1 3QY, U.K.

2,5-Bisdiphenylphosphinofuran forms a series of rhodium complexes which are binuclear with two of the ligands co-ordinated mutually *cis* or *trans*; the *trans*-complexes show evidence for interligand interaction.

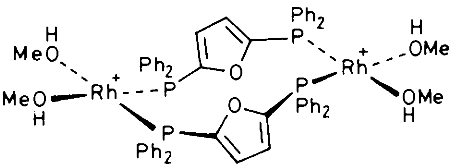
The potential of homo- and hetero-nuclear bimetallic complexes in catalysis is of considerable current interest,[1] and ligands which promote the formation of binuclear species[2] are thus highly desirable. We have begun the systematic synthesis of bisphosphines with especially favourable orientations for a defined intermetallic separation and report here preliminary observations on rhodium complexes of 2,5-bisdiphenylphosphinofuran (**1**). This is prepared easily from dilithiofuran[3] and chlorodiphenylphosphine in hexane.



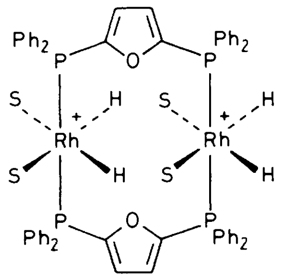
(**1**)



(**2**)



(**3**)



(**4**) S = MeOH

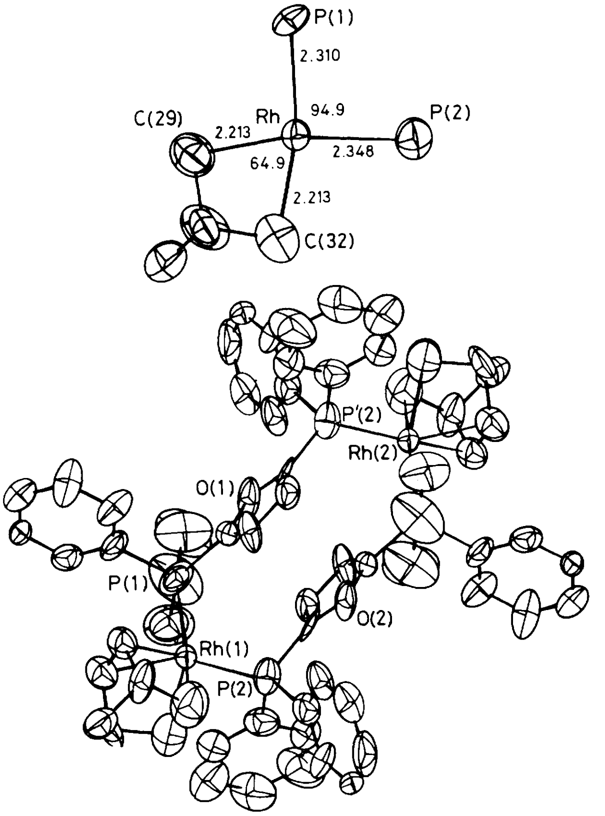
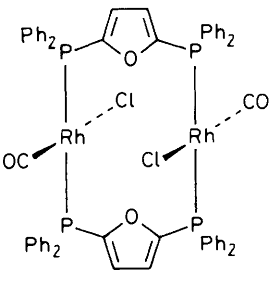


Figure 1. The molecular structure of the cationic portion of complex (**2**).

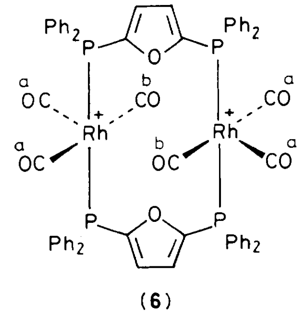
Ligand (**1**) reacts with bisbicyclo[2.2.1]heptadienerhodium(I) tetrafluoroborate in CH_2Cl_2 to give a complex (**2**), recrystallised from dichloromethane–ethanol as orange prisms, whose structure was defined by *X*-ray crystallography.†

Difficulty was encountered during refinement because the solvent is disordered, and because it is partly lost from the lattice during data-collection. At the current *R*-value of 0.105 the structure is clearly centrosymmetric with two rhodium nuclei flanked by pairs of *cis*-disposed ligands. The local environment of rhodium is very similar to that observed in corresponding mononuclear *cis*-chelate complexes.[4] (Figure 1).

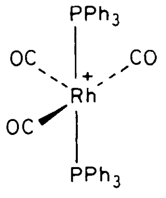
In cold methanol solution complex (**2**) reacts with hydrogen to give solvate (**3**) [δ(P) +41.1 p.p.m., *J*(PRh) 209.7 Hz] which on further warming under hydrogen gives the *trans*-disposed tetrahydride (**4**) [δ(P) +23.2 p.p.m., *J*(PRh) 124.0 Hz; δ(H) −21.1, *J*(PH) 16.9, *J*(RhH) 22.7 Hz]; both complexes revert to (**2**) on reaction with bicyclo[2.2.1]heptadiene.[5]



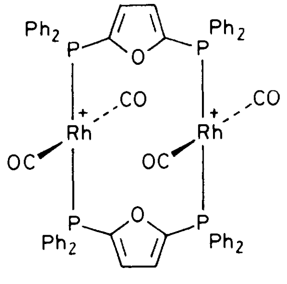
(**5**)



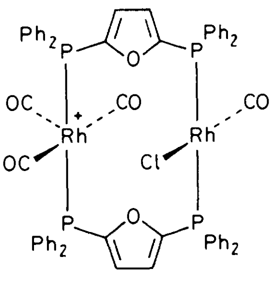
(**6**)



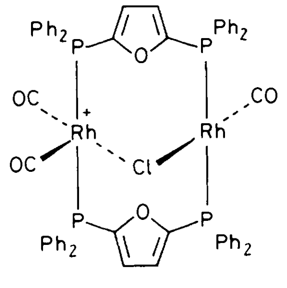
(**7**)



(**8**)



(**9**)



(**10**)

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† *Crystal data:* $C_{70}H_{60}O_2P_4Rh_2B_2F_8·4C_2H_5OH$, orthorhombic, space group *Pbca'*, *a* = 17.211(8), *b* = 19.269(6), *c* = 20.795(8) Å, *Z* = 4, *R* = 0.105 for 1804 independent reflections having $I > 3\sigma(I)$. Solvent disorder precluded further 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.

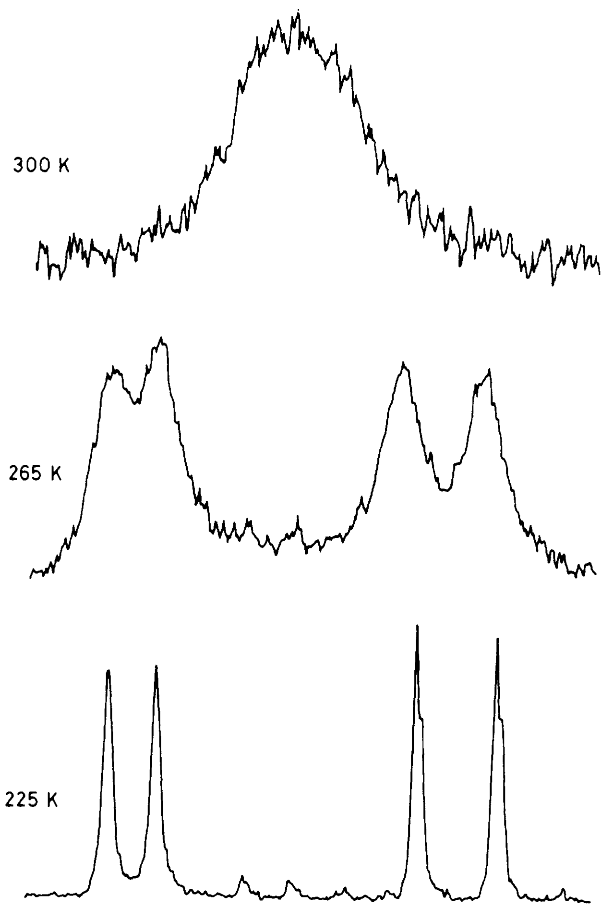

Figure 2. Temperature dependence of the ^{31}P n.m.r. spectrum of complex (**9**) in CD_2Cl_2.

With tetracarbonyl-μ-dichlorodirhodium, a yellow complex is formed which possesses more than one isomeric form in solution; the major species is presumed to be (**5**) [δ(P) + 12.3 p.p.m., J(PRh) 129.0 Hz] by precedent,[6] with some *cis*-isomer present. In CH_2Cl_2 solution it reacts with $AgBF_4$ (2 equiv.) under a CO atmosphere to give complex (**6**) which is not stable in the absence of CO. The ^{13}C n.m.r. spectrum of isotopically enriched complex in CD_2Cl_2 is a singlet δ 184.1 p.p.m. at room temperature but at −65 °C two inequivalent ^{13}C signals are observed in the ratio 2:1 with full Rh and P couplings, {δ(P) 19.3 [dq, J(RhP) 74.3, J(PC) 14.8 Hz], $\delta(C_a)$ 183.6 [m, J(RhC) 67.8, J(PC) 14.8 Hz], $\delta(C_b)$ 182.0 p.p.m. [J(RhC) 65.6, J(PC) 14.8, $J(C_aC_b)$ 15 Hz]}. This is consistent with restricted rotation rendering the inner and outer CO's inequivalent.[7] The temperature dependence of the ^{31}P line-shape for the ^{13}C-enriched complex is similar to that of the related complex (**7**),[8] with coalescence of P–C coupling at 248 and 243 K, respectively (Figure 2). Pumping the solution of (**6**) tenaciously gives a new limiting ^{31}P spectrum [δ(P) +11.7 p.p.m., J(PRh) 109 Hz] ascribed to structure (**8**). The spectrum reverts to that of (**6**) on treatment with CO.

If 1 equiv. of $AgBF_4$ is employed in the reaction with (**5**) then a new species (**9**) with quite distinct spectral properties is formed. Its ^{13}C n.m.r. spectrum demonstrates rapid exchange down to −70 °C. The ^{31}P n.m.r. spectrum of unenriched material has two inequivalent nuclei [δ(a) +21.0, $J(P_aRh)$ 75 Hz; δ(b) +16.9, $J(P_bRh)$ 124.0 Hz] at −65 °C, in dynamic interchange at higher temperatures, and coalesced at room temperature. The line-shape/temperature dependence is unaffected by concentration or by added $Bu_4N^+Br^-$, suggesting an intramolecular mechanism whereby formation of the bridged intermediate (**10**)[9] follows dissociation of CO.

Molecular models indicate that the internuclear distance in unstrained *trans*-chelate complexes (**3**) and (**6**) is 6.0 Å. This is sufficient to discourage the formation of stable bridged complexes but close enough to encourage novel modes of ligand activation.

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