

***trans*-BIS(DIPHENYLPHOSPHINE)CYCLOPROPANE; A LIGAND SELECTIVE FOR BINUCLEAR COMPLEXATION WITH ca. 4.5 Å INTERMETALLIC SEPARATION**

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Summary

trans-1,2-Bis(diphenylphosphino)ethylene was treated with $(\text{CH}_3)_2\text{S}(\text{CH}_2)$ in dimethyl sulphoxide and the product reduced with HSiCl_3 to give *trans*-bis(diphenylphosphino)cyclopropane in 56% overall yield. The new ligand was found to have a strong affinity for AgBF_4 forming a 2/2 complex under conditions where related ligands gave a mixture of 2/2 and 3/2 adducts. This complex could be employed as precursor to a cationic binuclear rhodium carbonyl complex $\text{P}_2\text{Rh}_2^+(\text{CO})_3\text{Cl}$. When synthesis of the corresponding iridium complex was attempted, a soluble yellow adduct of $\text{P}_2\text{Ir}_2(\text{CO})_2\text{Cl}_2$ and AgBF_4 was obtained, assumed to contain an Ir–Ag bond.

Introduction

In previous publications [1,2] we have presented aspects of the complexation chemistry and catalytic reactivity of 2,5-bis(diphenylphosphino)furan, which forms a series of binuclear rhodium and iridium complexes with an internuclear separation of 5.5 Å. In contrast to reports on bis(diphenylphosphino)methane complexes [3], intermetallic bridging by ligands is not observed, and it was therefore of interest to prepare a biphosphine of intermediate P–P separation. Inspection of molecular

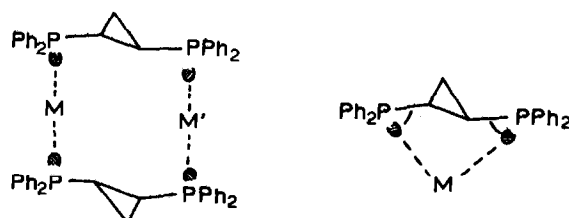


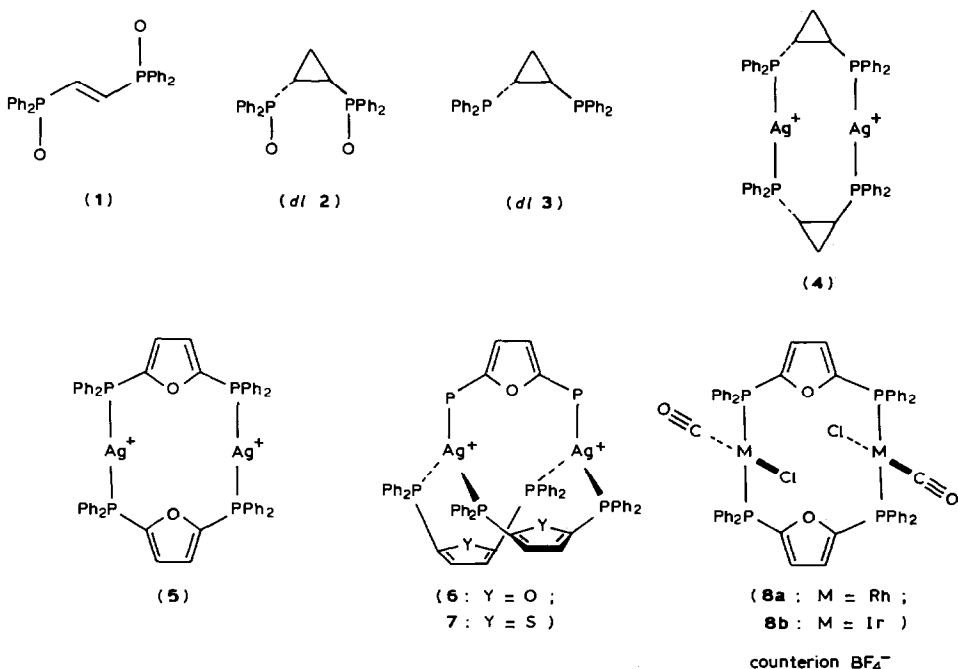
Fig. 1. Mono- and di-nuclear structures derived from ligand 3.

models indicated that a *trans*-disubstituted cyclopropane was suitable in that the phosphorus lone-pairs may be favourably disposed for *trans*-binuclear complexation, but that mononuclear chelation engenders considerable angle strain (Fig. 1).

Results and discussion

Preparation

The synthesis of *trans*-bis(diphenylphosphino)cyclopropane proved straightforward. Commercially available *trans*-1,2-bis(diphenylphosphino)ethylene was first oxidised with H_2O_2 ($(\text{CH}_3)_2\text{CO}$, 50°C [4]) giving the dioxide **1**. Following unsatisfactory trial cyclopropanations with $(\text{CH}_3)_2\text{S}(\text{CH}_2)\text{O}$, dimethylsulphonium methylide [5] ($(\text{CH}_3)_3\text{S}^+ \text{I}^-$, NaH , DMSO , 20°C) proved very effective as a methylene transfer reagent. The resulting phosphine oxide **2** was then reduced (HSiCl_3 , Et_3N , C_7H_8) giving the desired biphosphine **3** as a white crystalline solid, m.p. $156\text{--}157^\circ\text{C}$.



Silver(I) complexation

In early experiments with the new ligand it was adventitiously discovered that a binuclear silver complex **4** of 2/2 stoichiometry was readily formed. This was best studied by ^{31}P NMR spectroscopy. Dissolution of equimolar quantities of biphosphine and AgBF_4 in CH_2Cl_2 or THF gave a single species exhibiting a sharp spectrum below -30°C ($\delta(\text{P})$ 29.5 ppm, $J(^{107}\text{AgP})$ 719, $J(^{109}\text{AgP})$ 829 Hz, THF, -40°C) similar to other phosphine-silver complexes of this stoichiometry [6]. No other species were observed when the ratio of reactants was varied. By contrast, 2,5-bis(diphenylphosphino)furan gave a mixture of the 2/2 complex with AgBF_4 , **5** (δ 3.8 ppm, $J(^{107}\text{AgP})$ 532 Hz, -40°C , CH_2Cl_2) and the corresponding 3/2 addend **6** (δ -7.8 ppm, $J(^{107}\text{AgP})$ 330 Hz, -40°C , CH_2Cl_2) when equimolar

quantities of the reagents were mixed, and the latter could be made the exclusive product, by employing an appropriate excess of biphosphine. With 2,5-bis(diphenylphosphino)thiophene, only the 3/2 adduct **7** ($\delta(\text{P}) -1.3$ ppm; $J(^{107}\text{AgP}) 326$ Hz) was obtained.

Rhodium and iridium carbonyl complexes

Direct reaction between phosphine **3** and an equimolar quantity of $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ in CH_2Cl_2 gave the binuclear carbonyl chloride complex **8a** which rapidly precipitated an insoluble oligomer on standing. The ^{31}P NMR spectrum ($\delta(\text{P}) 30.0$ ppm, $J(\text{PRh}) 129$ Hz) was consistent with the proposed structure.

An entirely different complex was formed when the silver adduct **4** was treated directly with $[(\text{CO})_2\text{RhCl}]_2$, leading to precipitation of one equivalent of AgCl . The soluble yellow complex **9** exhibited an $\text{AA}'\text{MM}'(\text{XY})$ ^{31}P NMR spectrum, indicating that the two phosphorus nuclei of each ligand were in non-identical environments. At high resolution each line of the spectrum showed an additional splitting of ca. 2 Hz. This is presumably due to the chirality of the ligand; two diastereomeric forms of complex **9** with R^*R^* - or R^*S^* -configuration are possible, and these might be expected to have similar but distinguishable spectra. The CO-multiplicity at each nucleus was revealed by ^{13}C O-enrichment, and examination of the ^{31}P spectrum at low temperatures (Fig. 2). The low-field signal is strongly second-order at 36.4 MHz but has the appearance of a triplet at 121.7 MHz. Under a ^{13}C O atmosphere, only very slight broadening was observed at -50°C and it is assumed that rapid

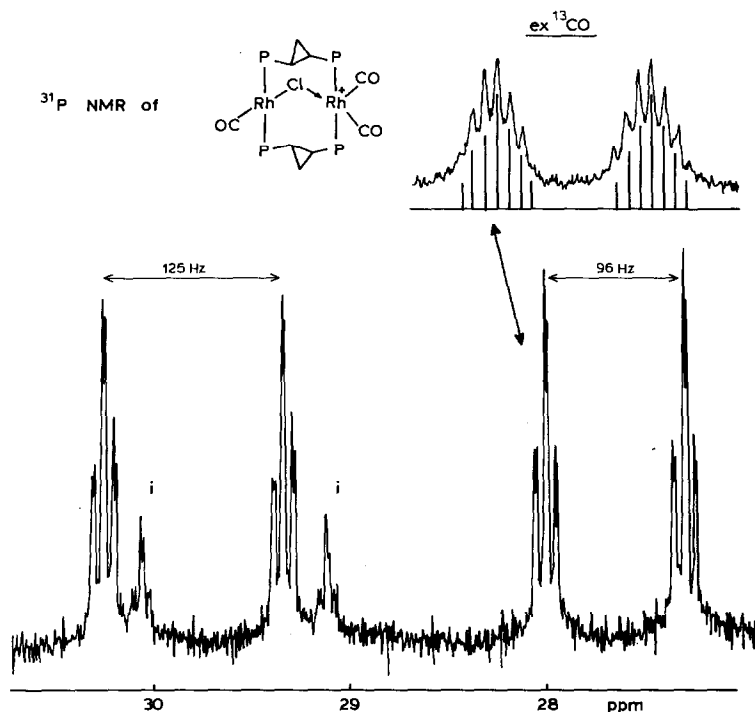
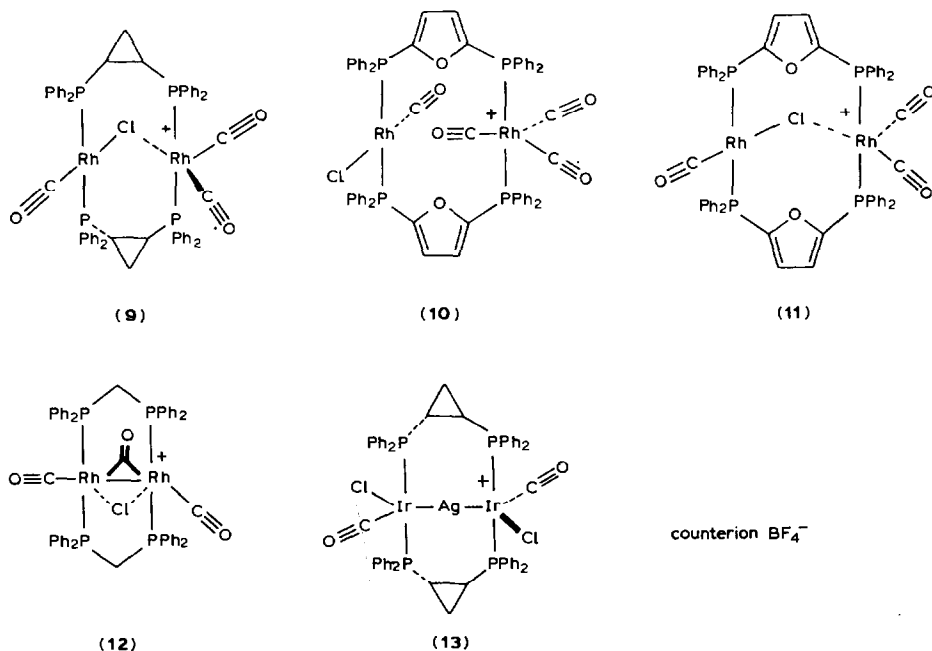


Fig. 2. ^{31}P NMR spectra of complex **9**; the high field region under a ^{13}C O atmosphere at -50°C is inset.

exchange occurred. The coupling constant $J(\text{PRh})$ 124 Hz is typical of a square-planar monocarbonyl environment, however. In contrast, each line of the high-field triplet is further split into a 1/2/1 triplet ($J(\text{PC})$ 15.5 Hz) at -50°C indicating a rhodium dicarbonyl species. Taken together these observations suggest that the complex has structure **9**, with bridging chloride. The two nuclear environments are not exchanging at room temperature, indicating that the bridge is stable. This stands in contrast to the monocation **10** formed in similar manner from $[(\text{CO})_2\text{RhCl}]_2$ and the furanbiphosphine silver complex **5**, previously prepared by a different route [1]. This exchanges CO at low temperature by a dissociative mechanism, equivalencing the two phosphorus environments. It has previously been suggested that the equivalencing process involved a transient intermediate **11** with bridging chloride. This is isostructural with complex **9** and the difference in stability between the two may be attributed to the difference in intermetallic distance, which is about 4.5 Å in the cyclopropane-bridged biphosphine and 5.5 Å in the furan-bridged ligand. In typical structures [7], the RhClRh angle is $90 \pm 10^\circ$, and the $\text{Rh}-\text{Cl}$ bond length 2.40 Å, so that the shorter span is much more favourably disposed to accommodate chloride-bridging (optimum 3.4 Å). In this bis(diphenylphosphino)methane series, the stable cationic carbonyl chloride **12** has a bridging carbonyl group, and a rhodium-rhodium bond [8].



The corresponding iridium chemistry was investigated. A sparingly soluble carbonyl chloride **8b** was prepared by reaction of the biphosphine with (*p*-toluidine) $\text{Ir}(\text{CO})_2\text{Cl}$ [9] or by direct displacement of PPh_3 from Vaska's compound. This reacted with one equivalent of AgBF_4 to form a bright orange soluble compound without precipitation of AgCl . Further AgBF_4 had no effect and the new complex did not react with CO. The new complex exhibited a broadened ^{31}P NMR resonance at 5.5 ppm, 10 ppm downfield from complex **8b**. On standing in solution in CH_2Cl_2 for protracted periods it deposited AgCl very slowly. The structure of

this stable 1/1 adduct is most probably **13**, and this finds precedent in a number of complexes with a stable iridium–silver σ bond [10].

Experimental

All solvents were freshly distilled before use after drying by standard procedures. NMR spectra were recorded on a Bruker WH 90 (^{31}P 36.43 MHz) or WH 300 (^{31}P 121.7 MHz) and chemical shifts are recorded in ppm, downfield from TMS. Infrared spectra were recorded on a Pye–Uvicam SDP-200 spectrophotometer. Mass spectra were recorded by Dr. R.T. Aplin on a ZAB Mass Spectrometer in FAB or FD mode as stated. Microanalyses were recorded by Dr. G. Strauss and his staff.

dl-trans-1,2-Bis(diphenylphosphino)cyclopropane

A commercial sample of *trans*-1,2-diphenylphosphinoethylene (0.49 g, Strem) was dissolved in hot acetone (10 ml) with stirring and H_2O_2 (1 ml, 30% aqueous solution) added in one portion. After 5 min the suspension was cooled and the precipitate of *trans*-1,2-diphenylphosphinoethylene filtered, washed with water, acetone and ether and dried in vacuo, (0.484 g, 91%). Reaction may be carried out on a 2 g scale without loss of yield.

Sodium hydride (0.600 g, 50% suspension in mineral oil) was washed 3 times with pentane and dried in vacuo. DMSO (5 ml, distilled off CaH_2) was added and the suspension heated for 30 min at 70°C , when evolution of H_2 had ceased. The solution was diluted with THF (15 ml) and cooled to -2°C whilst $\text{Me}_3\text{S}^+ \text{I}^-$ (2.547 g, 12.5 mmol) was added over 3 min. To the resulting solution was then added *trans*-1,2-bis(diphenylphosphino)ethylene (1.870 g, 4.37 mmol) and stirring continued for 30 min at 0°C , followed by 2 h at ambient temperature. The resulting suspension was directly transferred to H_2O (50 ml) and the volume then reduced until a white precipitate formed, which was filtered and dried in vacuo. There was thus obtained *trans*-1,2-bis(diphenylphosphino)cyclopropane (1.683 g, 87%, m.p. $268\text{--}270^\circ\text{C}$) NMR (^1H , CDCl_3): δ 7.3–7.8, m, 20H; 2.2, m, 2H; 1.7, m, 2H ppm. (^{31}P , EtOH): δ 31.9 ppm.

To the phosphine oxide (1.683 g, 3.81 mmol) suspended in dry toluene (20 ml) was added NEt_3 (10 ml, freshly distilled) and then a solution of HSiCl_3 (8 ml freshly distilled) in toluene (5 ml). The suspension of bulky precipitate was stirred under reflux for 4 h, and then stood overnight before adding NaOH (24 g, in 80 ml H_2O) cautiously. The toluene layer was separated, washed $3 \times$ with H_2O and solvent removed in vacuo. The residue was recrystallised (acetone/methanol) giving *dl-trans*-1,2-bis(diphenylphosphino)cyclopropane (1.00 g, 64%, mp $156\text{--}157^\circ\text{C}$). Found: C, 78.84; H, 6.02. $\text{C}_{27}\text{H}_{24}\text{P}_2$ calcd.: C, 79.0; H, 5.85%. NMR (^1H , CDCl_3): δ 7.4–7.0, m, 20H; 1.5, m, 2H; 1.15, m, 2H ppm. (^{31}P , C_7H_8): δ -4.9 ppm.

Silver ion complexation

The following experimental conditions are typical: a mixture of *dl-trans*-1,2-bis(diphenylphosphino)cyclopropane (0.198 g) and AgBF_4 (0.25 g, excess) was stirred in CH_2Cl_2 (5 ml) and then filtered by cannula in dry Et_2O (25 ml). The white precipitate of silver complex was collected by filtration, dried in vacuo and stored with exclusion of light (0.255 g, 87%; $\delta(\text{P})$ 29.5 ppm. $J(^{107}\text{AgP})$ 719 Hz, $J(^{109}\text{AgP})$ 829 Hz, THF, -40°C).

Carbonyl chloride chemistry

(a) The silver complex (0.061 g, prepared as above) and dicarbonylrhodium chloride dimer (0.019 g, 0.05 mmol) were stirred together for 5 min in CH_2Cl_2 at 20°C and the solution decanted off AgCl into a large excess of rapidly stirred hexane, giving the product (0.063 g, 100%) as a bright yellow precipitate. Found: C, 54.14; H, 4.28. $\text{C}_{58}\text{H}_{48}\text{BClF}_4\text{O}_3\text{P}_4\text{Rh}_2$ calcd.: C, 55.51, H, 3.92%; $\text{C}_{57}\text{H}_{48}\text{BClF}_4\text{O}_3\text{P}_4\text{Rh}_2 \cdot 0.5\text{CH}_2\text{Cl}_2$ calcd.: C, 54.13; H, 3.87%. Λ_m $105.3 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ (CH_3NO_2 , $10^{-3} M$) (Λ_m $101.2 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ for $\text{Rh}(\text{dppp})_2\text{BF}_4$ (CH_3NO_2 , $10^{-3} M$)). MS (FAB) = 1062 ($M^+ - 3\text{CO}$). NMR (^{31}P , CH_2Cl_2 , -30°C): δ 29.8, dt, with diastereometric splitting, $J(\text{PRh})$ 128 Hz, $J(\text{PP}') \cong 7$ Hz; 27.6, dt, $J(\text{PRh})$ 96 Hz).

(b) A mixture of biphosphine (0.044 g, 0.107 mmol) and rhodium dicarbonyl chloride dimer (0.021 g, 0.107 mmol) were evacuated together in a small Schlenk tube and then placed under argon. CH_2Cl_2 (3 ml) was added by cannula, giving a yellow solution which rapidly precipitated the oligomeric product. There was thus obtained 0.030 g (48%), NMR (^{31}P , CH_2Cl_2): δ 30.0 ppm, $J(\text{PRh})$ 129 Hz).

(c) A mixture of biphosphine (0.052 g, 0.127 mmol) and carbonylchlorobis(tri-phenylphosphine)iridium (0.099 g, 0.127 mmol) in C_7H_8 (3 ml) was stirred at ambient temperature for 16 h. The partially suspended product was encouraged to settle by addition of hexane (6 ml) and excess solvent removed by cannula. The residual yellow solid was washed with a mixture of toluene (3 ml) and hexane (6 ml) twice and then dried in vacuo, giving 0.044 g (52%). NMR (^{31}P , C_7H_8): δ -4.6 ppm.

A sample of the iridium carbonyl chloride thus obtained (0.057 g, 0.043 mmol) was placed in a Schlenk tube together with AgBF_4 (0.017 g, 0.086 mmol). Degassed CH_2Cl_2 (3 ml) was added, immediately giving an orange solution which was filtered into stirred hexane to provide a yellow precipitate, 0.50 g (77%), NMR (^{31}P , CH_2Cl_2): δ +5.5 ppm (brs).

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