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MONO- AND DI-NUCLEAR RHODIUM COMPLEXES OF *meso*- AND *dl*-1,1,4,7,10,10-HEXAPHENYL-1,4,7,10-TETRAPHOSPHADECANE. STEREOCHEMICAL CONTROL OF REACTIVITY AND COMPLEXATION GEOMETRY

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Summary

Thermolysis of *meso*- and *dl*-1,1,4,7,10,10-hexaphenyl-1,4,7,10-tetraphosphadecane (200°C, 10 min) followed by fractional crystallisation from ethanol/dichloromethane gives two sharp-melting diastereomers. The higher melting compound, herein shown to be the *meso*-isomer, reacts with 1,5-cyclooctadiene-2,4-pentanedionatorhodium and HBF_4 to give the dinuclear rhodium complex (**3**). This underwent hydrogenation slowly in methanol solution with deposition of rhodium metal and formation of a mononuclear complex (**5**) with four coordinated phosphorus nuclei, also obtained by independent synthesis. This proved to be highly susceptible to oxidation, forming a dioxygen complex (**6**) with P(1) and P(3) mutually *trans*. The lower melting *dl*-isomer likewise formed a dinuclear rhodium complex (**4**) on reaction with 1,5-cyclooctadiene-2,4-pentanedionatorhodium and HBF_4. This reacted more rapidly than complex **3** with hydrogen forming a mononuclear dihydride (**7**) and metallic rhodium. In the presence of cyclohexene, a tetracoordinate phosphinerhodium complex (**9**) was formed. This reacted with oxygen to give dioxygen complex (**10**), although here P(1) and P(4) are mutually *trans*, and with carbon monoxide to give a five-coordinate monocarbonyl (**11**).

The corresponding dirhodium bis-cyclooctadiene complex of 1,1,4,8,11,11-hexaphenyl-1,4,8,11-tetraphosphaundecane (**13**) (a single diastereomer of unknown stereochemistry), reacted with hydrogen in methanol to form a dinuclear solvate without reductive degradation.

Results and discussion

Since the original preparation of, and ligation studies on complexes of 1,1,4,7,10,10-hexaphenyl-1,4,7,10-tetraphosphadecane (Tetraphos) by King and Kapoor [1], there have been numerous cases of its polydentate coordinating be-

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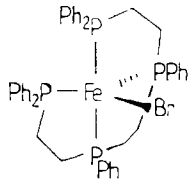
haviour [2]. The existence of stereoisomers was recognised early on [3], and they were separated by fractional crystallisation of the tetrasulphide but not identified. Complexes **1** [4] and **2** [5] are the only Tetraphos derivatives of defined crystal structure and both exhibit *meso*-configuration. This could be due to selective crystallisation, as commercial Tetraphos is a stereoisomeric mixture.



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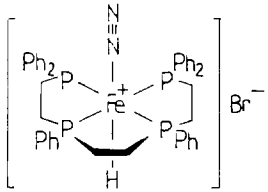

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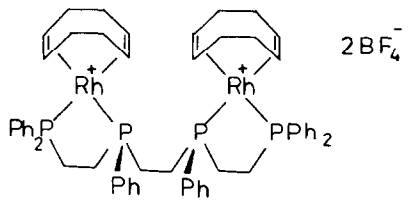
The object of the present work was to prepare binuclear rhodium complexes with defined intermetallic distances, and Tetraphos was considered to be a simple model ligand with the potential for binding at two metal centres. Clearly information on complex stereochemistry would be desirable.

Commercial Tetraphos was heated to 200°C for 10 min under an argon atmosphere. On cooling the melt resolidified and it was separated by fractional crystallisation into a high-melting and a low-melting stereoisomer which had similar but distinct ^{31}P NMR resonances. The commercial sample was a mixture of high-melting isomer **A** and low-melting isomer **B** in ratio 2/1 by this assay. These were separately reacted with cyclooctadieneacetylacetonatorhodium and HBF_4 [6] to give distinct dinuclear complexes of structures **3** and **4** which follow from their ^{31}P and ^{1}H NMR spectra (Table 1). In particular the ^{31}P chemical shifts are in exactly the region which might be predicted if each phosphine forms part of a single 5-ring chelate [7]. Both compounds are crystalline but single crystals suitable for X-ray analysis have not yet been obtained.

Hydrogenation of complex **3** in methanol occurred slowly with complete dissolution and some metal deposition. A single species was then produced whose ^{1}H NMR spectrum showed no trace of Rh–H absorptions. One pair of phosphines was now shifted to very low field consistent with their forming part of two five-ring chelate rings, and the ^{31}P spectrum demonstrated a *trans*-coupling through rhodium [8]. It was successfully simulated using the routines available in the Aspect-2000 software package (Table 1). The overall appearance suggested that the structure was a mononuclear tetracoordinated cation (**5**) and thus independent synthesis was attempted. Literature methods [9] gave species with broad complex spectra with no evidence of P–P coupling. The chelate **5** was synthesised successfully by reaction of the tetraphosphine with bis(bicyclo[2.2.1]heptadiene)dichlorodirhodium in dichloromethane.

Cation **5** reacts rapidly with oxygen in dichloromethane solution, giving a dioxygen complex (**6**) whose ^{31}P spectrum demonstrates that there are four inequivalent phosphines with P(1) and P(3) mutually *trans* (Fig. 1). The same complex was prepared adventitiously by reaction of cyclooctadiene-2,4-pentanedionatorhodium and recrystallised Tetraphos with nitric acid in tetrahydrofuran. This clear preference for one coordination geometry reflects the differing stabilities of the different



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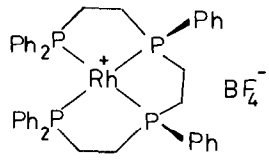

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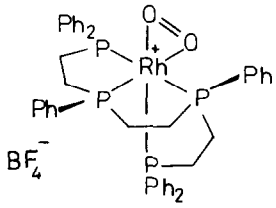


(6)

coordination geometries. The non-planar tetracoordinate forms of *meso*- and *dl*-isomers are illustrated in Fig. 2. Examination of molecular models demonstrates that *dl*-isomer exhibits unfavourable Ph–Ph interactions in the 1,3-*trans* configuration **2A**

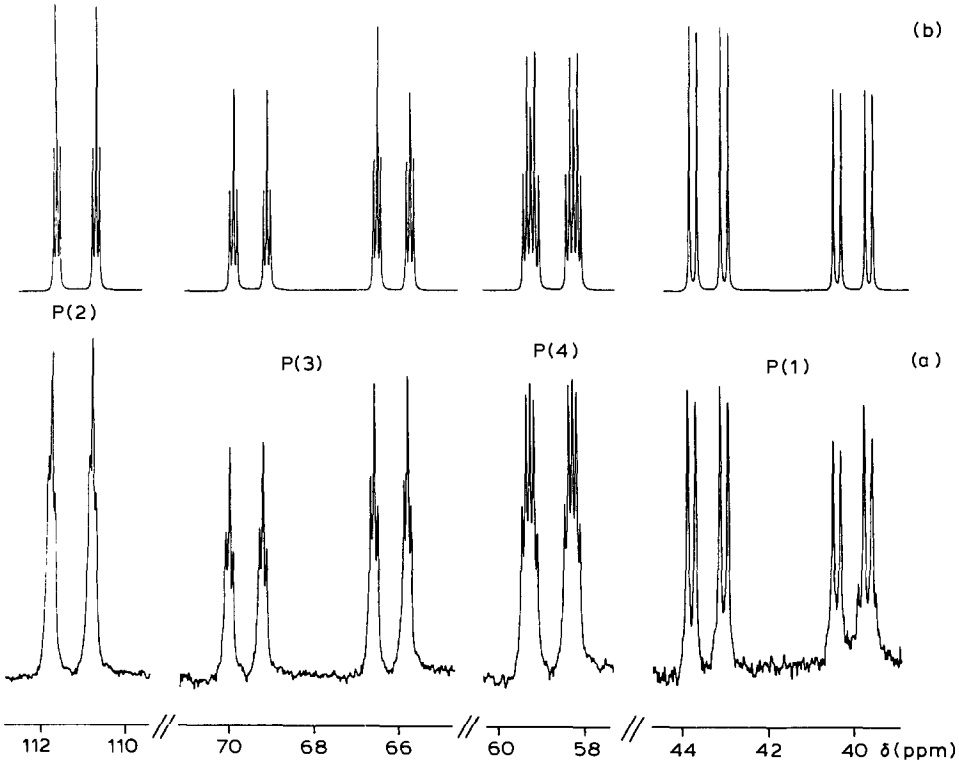


Fig. 1. ^{31}P NMR spectrum of complex **6** in dichloromethane. The upper trace is a simulation based on the parameters recorded in Table 1.

TABLE 1

CHEMICAL SHIFTS OF PHOSPHINE COMPLEXES (Chemical shifts in ppm relative to H_3PO_4 Coupling constants in Hz)

		δ_1 (J(PRh))	δ_2 (J(PRh))	δ_3 (J(PRh))	δ_4 (J(PRh))	J(1,2)	J(1,3)	J(1,4)	J(2,3)	J(2,4)	J(3,4)
A High-melting isomer (*meso*) of tetraphosphine											
Dirhodium cyclooctadiene complex	**(3)**	50.8 (151)	56.0 (149)	–	–	±24	–	–	–	–	[a]
Rhodium complex	**(5)**	52.0 (128)	94.5 (139)	–	–	−27	267	−26	–	[b]	[a]
Rhodium dioxygen complex	**(6)**	42.1 (92)	111.0 (121)	67.3 (96)	58.1 (122)	±3	416	±22	±10	±11	±11
B Low-melting isomer (*dl*) of tetraphosphine											
Dirhodium cyclooctadiene complex	**(4)**	50.6 (152)	55.2 (148)	–	–	±24	–	–	–	–	–
Rhodium dihydride	**(7)**	72.5 (101)	83.2 (br)	–	–	±13	[a]	–	–	[a]	[a]
Rhodium complex	**(8)**	47.6 (138)	105.0 (128)	–	–	−30	255	−25	–	[b]	[a]
Rhodium dioxygen complex	**(10)**	74.2 (119)	52.0 (93)	–	–	±15	[a]	–	–	[a]	[a]
Rhodium carbonyl [a]	**(11)**	67.7 (98)	59.8 (11)	–	–	±11	[a]	–	–	[a]	[a]

[a] J(P(2)C) 43, J(P(1)C) 15 Hz; as J(1, 2). [b] As J(1, 3).

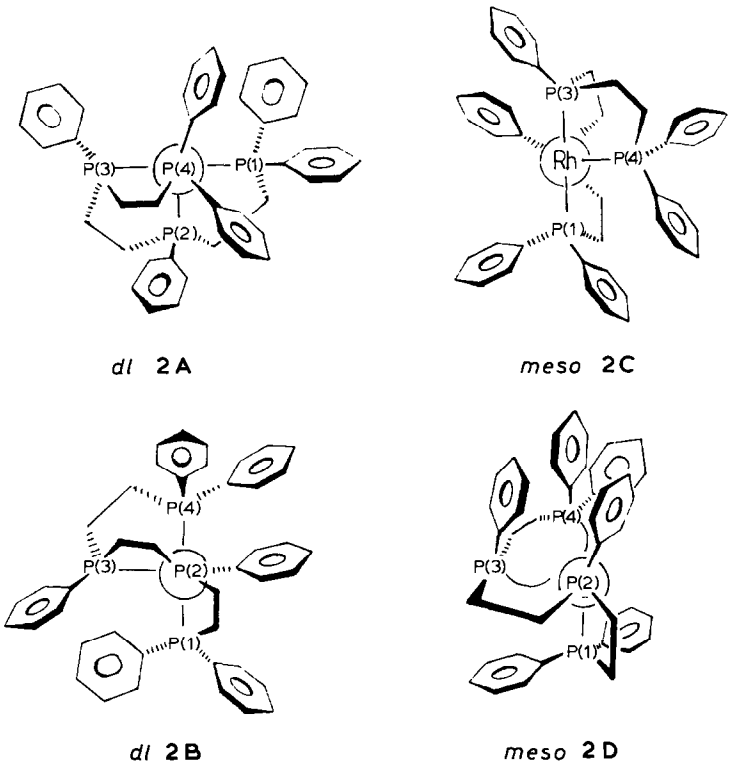


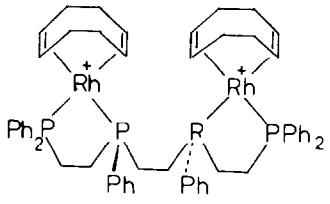
Fig. 2. The stereochemistry of mononuclear *meso*- and *dl*-Tetraphos complexes.

but is relatively unstrained in 1,4-*trans* configuration **2B**. In contrast, the *meso*-isomer adopts a 1,3-*trans* configuration **2C** comfortably but is highly strained, with high non-bonded Ph–Ph interactions in 1,4-*trans*-configuration **2D**. The indication is therefore that the high-melting isomer of Tetraphos has *meso*-stereochemistry.

The second dirhodium complex **4** behaved rather differently on hydrogenation in methanol. The yellow-orange solution darkened slowly, depositing a rhodium mirror. Monitoring reaction by ^{31}P NMR indicated that several products were formed initially with one predominant; the proportion of this increased with time until it was essentially the sole product after 24 h. The presence of just two inequivalent phosphorus environments in the ^{31}P NMR spectrum, the absence of large P–P couplings and the multiplet structure of the ^{1}H spectrum in the hydride region at -7.75 ppm with a 150 Hz proton–phosphorus coupling (proved by heteronuclear decoupling) all indicate the presence of a dihydride with structure **7**. The phosphorus couplings to rhodium and hydrogen are very similar to those observed in *cis*-dihydrobis(bis-1,3-diphenylphosphino)propanerhodium tetrafluoroborate [10], lending further weight to the proposed structure. In the presence of cyclohexene the ^{31}P NMR spectrum was altered to one which partly resembled the tetracoordinate complex **5** but with other species evident. An authentic sample was therefore prepared.

Reaction of the low-melting isomer of Tetraphos (now considered to have

dl-stereochemistry) with bis-norbornadienerhodium tetrafluoroborate gave first a labile species with three mutually *cis*-coordinated phosphines and one norbornadiene, assumed on the basis of its ^{31}P NMR spectrum to have structure **8**. On standing in solution for 24 h, this was gradually converted into the expected product **9**. The ^{31}P NMR spectrum of this complex was successfully simulated, as before (Table 1), and reaction with hydrogen led directly to the dihydride **7**.



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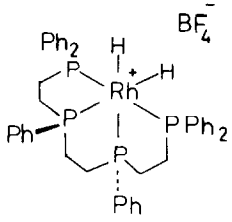

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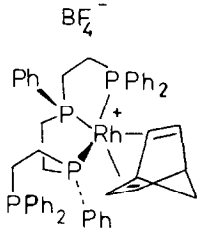

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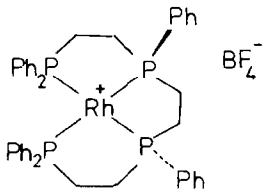

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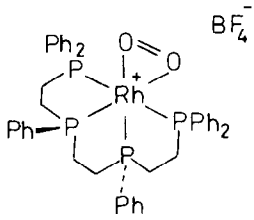

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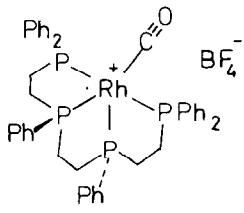


(11)

Passing oxygen through a solution of complex **9** in dichloromethane rapidly gave a dioxygen complex. Here the NMR spectrum (Table 1) exhibits a very simple double-triplet pattern for each pair of phosphines, consistent only with the P(1)P(4)-*trans*-arrangement shown in **10**. A compound of similar structure was prepared by reaction of the square-planar complex with ^{13}CO. The spectral observations (Fig. 3) are in accord only with the geometry depicted in **11**. In this respect the ^{13}C NMR is informative, the double triple triplet appearance (J(CRh) 66, J(CP) 43, J(CP) 15 Hz) confirming a trigonal bipyramidal orientation with P(1) and P(4) mutually *trans*. Carbonylation could not be reversed by multiple evacuation at room temperature, and this behaviour stands in contrast to the corresponding bis-diphenylphosphinoethane complex [10] which displayed no reactivity towards carbon monoxide.

Thus all adducts of the *dl*-rhodium tetraphosphine cation are based on configuration **2B**, predicted to be the more stable. The *meso*-rhodium tetraphosphine cation is less reactive but forms a dioxygen adduct based on structure **2C**. It illustrates the fact that small changes in ligand geometry can have profound effects on its coordination chemistry.

The homologous ligand **12** [11] was briefly investigated. Rather than follow the literature synthesis involving diphenylvinylphosphine, an alternative approach via 1-(diphenylphosphino)-2-phenylphosphinoethane [12] was adopted. The phosphine was deprotonated with butyllithium in diethyl ether and then reacted with 1,3-dibromopropane at reflux, giving after work-up a yellow oil whose ^{31}P NMR indicated

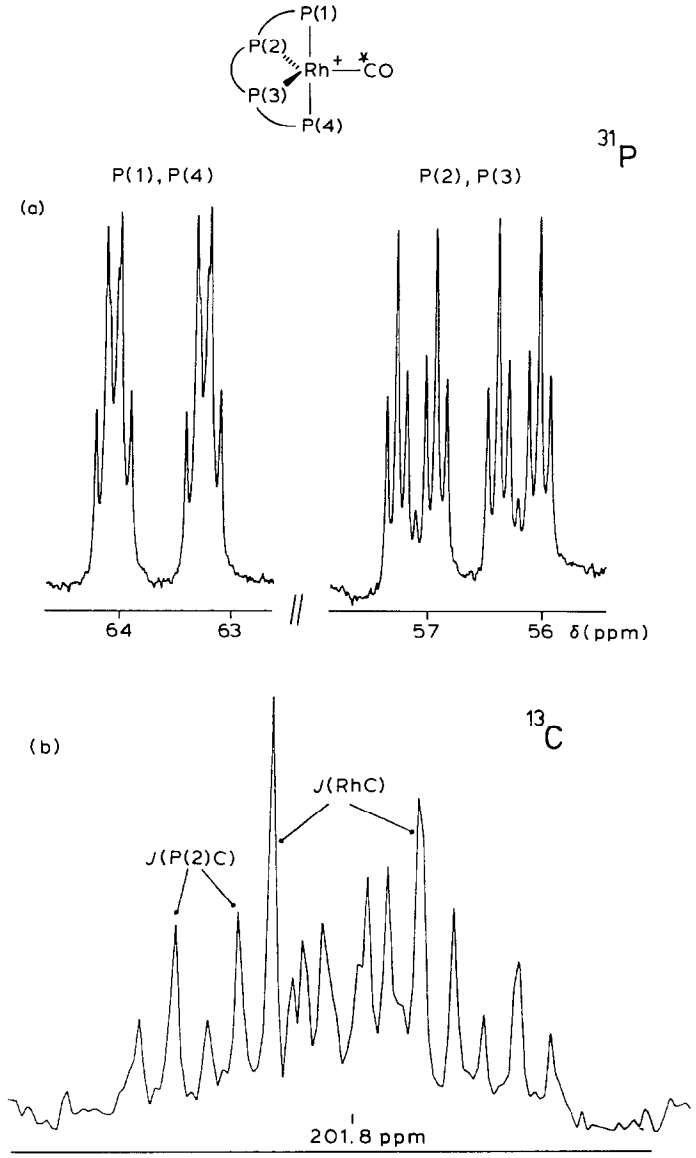
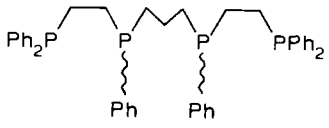


Fig. 3. ^{31}P and ^{13}C NMR spectra of carbonyl complex **11** prepared from ^{13}C-enriched CO (CO*) in dichloromethane-d_2.

formation of a diastereomeric mixture. This was purified by fractional crystallisation from acetone/methanol giving a single diastereomer of **10** with unknown configuration. On reaction with 1,5-cyclooctadienepentanedionatorhodium and fluoroboric acid this gave rise to the stable orange complex **13**, whose ^{13}P NMR spectrum exhibited clean first-order double doublets. Its solution in methanol reacted with hydrogen to give a mixture of solvates [13] tentatively assigned structures **14a** and **14b**, there being precedent for bridging methanol moieties in solvate complexes [6].

The integrity of the dinuclear framework was proved by the quantitative reformation of **13** on addition of excess 1,5-cyclooctadiene.



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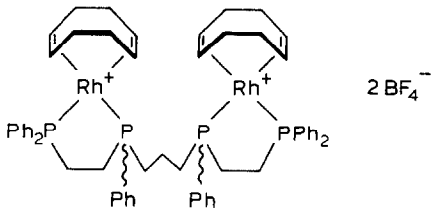

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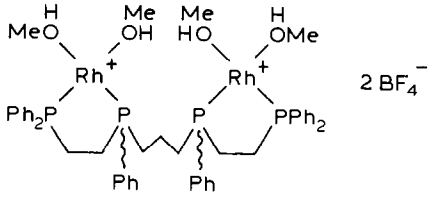
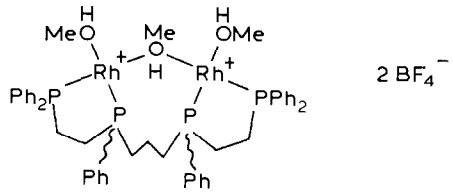


(14a)



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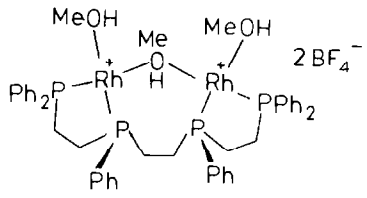

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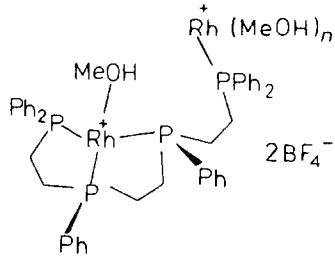

(16)

The difference in behaviour of Tetraphos complexes **3** and **4** on hydrogenation compared to their homologue **13** presumably reflects a kinetic effect since ligand **12** would be expected to form mononuclear tetracoordinated complexes readily. Consider the hydrogenation of **3** to a hypothetical solvate (**15**) in which methanol dissociation and recombination [14] is rapid. Dissociation of P(2) from Rh(1) would be followed by its attack at Rh(2) to form **16** in competition with its return, and this may be the crucial step in degradation of the dinuclear complex. It is well-known that the formation of five-membered chelate rings is faster than the formation of six-membered rings. This being the case, solvate **15** will be much less stable than its counterpart **13**.

Experimental

Melting points were taken on a Reichert Köfler block and are uncorrected. Microanalyses were carried out by Dr. F.B. Strauss, Oxford. All manipulations involving air-sensitive species were carried out in Schlenk apparatus under an

atmosphere of dry argon, and pre-purified solvents were degassed before use. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker WH 300 spectrometer equipped with a wide-bore probe.

1. Separation of the stereoisomers of 1,1,4,7,10,10-hexaphenyl-1,4,7,10-tetraphosphadecane

A sample of the commercial phosphine (0.98 g) was maintained at 200°C for 5 min under argon and then rapidly cooled to −80°C. The pale glassy gum thus obtained was recrystallised repeatedly from dichloromethane/ethanol to give high-melting isomer, m.p. 189–191°C. The combined residues from recrystallisation were evaporated to dryness giving a thick gum which was further purified by recrystallisation from methanol until a constant melting point of 118–118.5°C was obtained, this being a pure sample of the low-melting isomer.

2. Chemistry of the high-melting isomer (meso)

Bis-cyclooctadiene meso-1,1,4,7,10,10-hexaphenyl-1,4,7,10-tetraphosphadecanedirhodium

1,5-Cyclooctadiene-2,4-pentanedionatorhodium(I) (80 mg, 0.25 mmol) was dissolved in THF (2 cm^3) under argon. Three drops of 40% aqueous fluoroboric acid were added, the system cooled to −80°C and degassed. 1,1,4,7,10,10-Hexaphenyl-1,4,7,10-tetraphosphadecane (88 mg, 0.26 mmol) was added in one portion. The mixture was maintained below −20°C and agitated until the phosphine had completely dissolved. Removal of solvent in vacuo gave a yellow powder. This was redissolved in dichloromethane (ca. 3 cm^3) and diluted with an equal volume of methanol. The red solution was concentrated gently in vacuo until turbidity was evident and the Schlenk tube set aside. Orange crystals of the product formed which were collected, washed with a little methanol and dried in vacuo (100 mg, 72%), m.p. > 190°C (with darkening). Analysis Found: C, 54.29; H, 5.42; P, 9.12; F, 11.44; $C_{58}H_{66}Rh_2P_4B_2F_8$ calcd.: C, 54.98; H, 5.25; P, 9.78; F, 11.9%. Mass spectrum (*m/z*, field desorption) 1179. NMR (^{1}H, 300 MHz, $CDCl_3$): δ 7.5 (30H, m, Ar), 5.55, 5.05, 4.8, 4.65 (each 1H, s, vinyl), 1.55 (28 H, br, CH_2) ppm. (^{31}P, 121.5 MHz, CH_2Cl_2) δ 55.5 (dd, *J*(RhP) 148, *J*(PP) 24 Hz), 54.3 (dm, *J*(RhP) 153 Hz).

meso-1,1,4,7,10,10-Hexaphenyl-1,4,7,10-tetraphosphadecanerhodium(I) tetrafluoroborate

Di-μ-chlorobis(bicyclo[2.2.1]hepta-2,5-diene)dirhodium (40 mg, 0.087 mmol) was dissolved in dichloromethane (3 cm^3) and the solution degassed under argon. Solid tetraphosphine (high-melting isomer) (116 mg, 0.17 mmol) was added to the stirred solution under a vigorous stream of argon and stirring continued for 45 min. Sodium tetrafluoroborate (87 mg, 0.79 mmol) in distilled water (2 cm^3) was added and the mixture was stirred for a further 4 h. The two layers were allowed to settle and the orange organic phase was passed into excess ether (20 cm^3). The resulting yellow precipitate was filtered, washed with more ether (3 × 5 cm^3) and dried in vacuo giving a yellow-orange, air-sensitive powder (131 mg, 88%). NMR (^{1}H, 300 MHz, $CDCl_3$): δ 8.3–6.7 (30H, m, Ar), 3.5–1.2 (12 H, br m, CH_2) ppm. (^{31}P, 121.5 MHz, CH_2Cl_2) δ 94.5 (ddm, *J*(RhP) 128, *J*(PP(*trans*)) 242 Hz), 52.0 (ddm, *J*(RhP) 139 Hz) ppm.

Dioxygen meso-1,1,4,7,10,10-hexaphenyl-1,4,7,10-tetraphosphadecanerhodium(I) tetrafluoroborate

The above cationic complex (51 mg, 0.059 mmol) was dissolved in dichloromethane (3 ml). Oxygen was passed through the solution for 1 min and stirring continued for 15 min under an oxygen atmosphere. The resulting green-yellow solution was filtered into excess diethyl ether (50 ml) and the resulting precipitate separated, washed with diethyl ether and dried in vacuo giving the dioxygen complex as a pale yellow powder (0.045 g, 85%). Mass spectrum (field desorption, m/z) 805 ($M - BF_4^-$) NMR (^1H, 300 MHz, $CDCl_3$): δ 8.35–6.75 (30H, m, Ar), 3.35–2.0 (12H, m, CH_2) ppm. (^{31}P, 121.5 MHz, CH_2Cl_2): δ +111.0 (ddt, J(RhP) 120.6, J(P(2)P(3)) ~ J(P(2)P(4)) 10.5 Hz, J(P(1)P(2)) 2.2 Hz; P(2)), +67.3 (ddt, J(RhP) 95.7, J(P(2)P(3)) ~ J(P(3)P(4)) 10.5 Hz, J(P(1)P(3)) 415.7 Hz; P(3)), +58.1 (ddt, J(RhP) 122.1 Hz, J(P(2)P(4)) ~ J(P(3)P(4)) 10.5 Hz, J(P(1)P(4)) 22.4 Hz; P(4)), +42.1 (dddd, J(RhP) 91.6 Hz, J(P(1)P(2)) 2.2 Hz, J(P(1)P(3)) 415.7 Hz, J(P(1)P(4)) 22.4 Hz; P(1)) ppm.

3. Chemistry of the low-melting isomer (dl)

Bis-cyclooctadiene-dl-1,1,4,7,10,10-hexaphenyl-1,4,7-10-tetraphosphadecanedirhodium

This was prepared in similar manner to the *meso*-isomer and purified by recrystallisation from methanol/water, m.p. 185°C(dec); mass spectrum (field desorption) m/z 1179. NMR (^1H, 300 MHz, $CDCl_3$), δ 7.6 (30H, m, Ar), 5.65, 5.15, 4.95 and 4.55 (1H each, br s, vinyl), 1.55 (28H, br, CH_2) ppm. (^{31}P, 121.5 MHz, CH_2Cl_2), δ 55.2 (dd, J(RhP) 148, J(PP) 24 Hz), 50.6 (dm, J(RhP) 152 Hz) ppm.

dl-1,1,4,7,10,10-Hexaphenyl-1,4,7,10-tetraphosphadecanerhodium(I) tetrafluoroborate

The complex was generated in situ in an 8 mm NMR tube, in a two-stage reaction. A degassed solution of *dl*-1,1,4,7,10,10-hexaphenyl-1,4,7,10-tetraphosphadecane (0.022 g, 0.033 mmol) in dichloromethane (1.7 ml) was added to solid bis(bicyclo[2.2.1]hepta-2,5-diene)rhodium(I) tetrafluoroborate (0.010 g, 0.027 mmol) in an 8 mm NMR tube at −80°C. The sample was thoroughly degassed, agitated vigorously and then allowed to reach room temperature, giving a clear yellow solution, ascribed to *dl-1-(2-diphenylphosphinoethyl)1,4,7,7-tetraphenyl-1,4,7-triphosphaheptane (bicyclo[2.2.1]heptadiene)rhodium(I) tetrafluoroborate*. NMR (^{31}P, 36.43 MHz, CH_2Cl_2) δ 95.6 (dt, P2, J(RhP) 121, J(P1P2) = J(P2P3) = 23 Hz), 60.8 (dt, P1, J(RhP)127, J(P1P3) = 23 Hz) 51.1 (dq, P3, J(RhP) 122, J(P2P3) = J(P3P4) = 23 Hz) −11.8 (d, P4) ppm. On standing for 24 h at room temperature this species had reacted completely to give product with a very similar ^{31}P NMR spectrum to the *meso*-isomer: δ 104.9 (ddm, J(RhP) 128, $J(PP_{trans})$ 255 Hz) 47.6 (ddm, $J(PP_{cis})$ 138 Hz) ppm.

Dioxygen-dl-1,1,4,7,10,10-hexaphenyl-1,4,7,10-tetraphosphadecanerhodium(I) tetrafluoroborate

A solution of the *dl*-tetraphosphinerodium complex prepared in dichloromethane (0.058 g to 3 ml) was stirred under an oxygen atmosphere for 30 min. The solution was then filtered into excess diethyl ether (20 ml). The resulting pale yellow

precipitate was filtered, washed with diethyl ether (3 × 5 cc) and dried in vacuo giving product (0.052 g, 87%). Mass spectrum (field desorption) *m/z* 805 ($M^+ - BF_4^-$). NMR (^{1}H, $CDCl_3$, 300 MHz) δ 7.8–7.0 (30H, m, Ar), 3.3–2.0 (12H, br m, CH_2) ppm. (^{31}P, 121.5 MHz, CH_2Cl_2): δ 74.2 (dt, P(2), *J*(RhP) 119, *J*(PP) 15 Hz), 52.0 (dt, P(1), *J*(RhP) 92 Hz) ppm.

In situ preparation of dihydride and carbonyl adducts

(i) The *dl*-tetraphosphinerhodium complex was prepared as described above and then dichloromethane and bicyclo[2.2.1]heptadiene removed in vacuo. The residue was dissolved in methanol-d_4 (1.6 ml), the yellow solution degassed three times under argon and three times under hydrogen. No colour change was observed, but distinct changes had taken place in the NMR spectra: (^{1}H, 300 MHz, $CDCl_3$) δ 8.2–6.65 (30H, m, Ar), 3.5–1.8 (12H, brm, CH_2), −7.75 (2H, d quintet, $J(PH_{trans})$ 150, $J(PH_{cis})$ 13 Hz ppm, (^{31}P, 121.5 MHz, CD_3OD) δ 83.2 (br m with Rh coupling, P(2)) 72.5 (dt, P(1), dt, *J*(RhP) 101, *J*(PP) 13 Hz) ppm.

(ii) Preparation of the tetraphosphinerhodium complex was carried out as above. The reaction vessel was attached to a ^{13}CO gas line, thoroughly degassed and then filled with ^{13}CO. The sample was allowed to reach room temperature and equilibrated by agitation. There was thus obtained *[^{13}C-]carbonyl-dl-1,1,4,7,10,10-hexaphenyl-1,4,7,10-tetraphosphadecanerhodium(I) tetrafluoroborate,* NMR (^{13}C, 75.5 MHz, CD_2Cl_2) δ 201.8 (ddt, *J*(RhC) 65.6, *J*(PC) 43.0, 14.7 Hz) ppm (^{31}P, 121.5 MHz, CD_2Cl_2) δ 67.7 (dq, P(1), *J*(RhP) 98, *J*(PC) 15, *J*(PP) = 11 Hz), 59.8 (ddt, *J*(RhP) 111, *J*(PC) 43 Hz) ppm.

4. 1,1,4,8,11,11-Hexaphenyl-1,4,8,11-tetraphosphaundecane and its dirhodium complexes

[2-(Phenylphosphino)ethyl]diphenylphosphine (2.06 g, 6.4 mmol) was slurried in dry degassed diethyl ether (50 ml). n-Butyllithium in hexane (4.15 ml, 6.4 mmol) was added in one portion and the mixture stirred for 40 min. 1,3-Dibromopropane (freshly distilled, 0.325 ml, 3.20 mmol) was added by syringe and the solution refluxed under argon for 4 h. The yellow colour of the solution slowly faded and a yellow precipitate formed. After cooling to room temperature methanol (2 ml) and water (40 ml) were added sequentially. The layers were separated and the aqueous layer extracted with more diethyl ether (2 × 30 ml). Removal of solvent from the combined organic extracts in vacuo gave a white solid. This was recrystallised repeatedly from acetone/methanol to give product in several crops as a single diastereomer (0.195 g, 9%) m.p. 110–112°C. Analysis Found: C, 75.43, H, 6.48, P, 18.10. $C_{43}H_{44}P_4$ calcd.: C, 75.43; H, 6.48; P, 18.10%. NMR (^{31}P, 36.43 MHz, CH_2Cl_2): δ −8.1 (d, *J*(PP) 28.6 Hz, P(1) −16.4 (d, P(4)) ppm.

1,5-Cyclooctadiene-2,4-pentanedionatorhodium (0.0515 mg, 0.166 mmol) was dissolved in THF (2 ml) and aqueous HBF_4 (40 μl, 40%) was added and the solutions agitated, then cooled to −80°C under argon. The phosphine (0.052 g, 0.082 mmol) was added and the mixture allowed to reach ambient temperature. The resulting orange solution was filtered into excess degassed diethyl ether (20 ml) and the yellow precipitate washed with further diethyl ether (3 × 5 ml) and dried in vacuo giving *bis(1,5-cyclooctadiene)(1,1,4,8,11,11-hexaphenyl-1,4,8,11-tetraphosphaundecane)dirhodium(I)bis(tetrafluoroborate)* as a yellow powder (0.089 g, 85%) m.p. > 120°C (dec). NMR (^{1}H, 300 MHz, $CDCl_3$): δ 8.1–7.0 (30H, m, Ar), 5.75, 4.68 (2 × 2H, br

s, CH=CH), 3.0–1.5 (30H, br m, CH_2) ppm; (^{31}P, 121.4 MHz, CH_2Cl_2) δ 58.7 (dd, J(RhP) 150, J(PP) 25 Hz, PPh_2), 50.7 (dd, J(RhP) 148 Hz, PPh) ppm.

Hydrogenation of this complex (ca. 0.020 g) in methanol solution gave a new ^{31}P NMR spectrum in which two species were apparent: **A**: δ 81.8 (dd, P(1), J(RhP) 217, J(PP) 45 Hz), 76.8 (dd, P(2), J(RhP) 192 Hz) ppm; **B**: δ 78.1 (dd, P(1), J(RhP) 205, J(PP) 31 Hz), 73.3 (J(RhP) 200 Hz) ppm. On addition of excess cyclooctadiene to the solution the starting complex was re-formed quantitatively.

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