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Synthesis and crystal structure of a dinuclear rhodium complex. Catalytic activity of mono- and di-nuclear rhodium phosphite complexes in hydroformylation †

Esther K. van den Beuken,[a] Wim G. J. de Lange,[b] Piet W. N. M. van Leeuwen,[b] Nora Veldman,[c] Anthony L. Spek[c] and Ben L. Feringa*[,a]

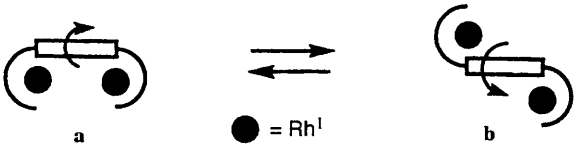
[a] *Department of Organic and Molecular Inorganic Chemistry, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands*
[b] *Department of Inorganic Chemistry, University of Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands*
[c] *Bijvoet Center for Biomolecular Research, Department of Crystal and Structural Chemistry, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands*

A new bidentate phosphite, {bis[2-(diphenoxyphosphinoxy)-1-naphthyl]methyl}benzene L^1 and a tetradentate phosphite, 1,4-bis{bis[2-(diphenoxyphosphinoxy)-1-naphthyl]methyl}benzene L^2 were prepared in a facile two-step procedure involving condensation of 2-naphthol with respectively benzaldehyde or terephthalaldehyde, followed by treatment with chlorodiphenoxyphosphine. The corresponding monuclear rhodium(I) complex $[RhL^1(acac)]$ **1** (acac = acetylacetonate) and dinuclear complexes $[Rh_2L^2(acac)_2]$ **2** and $[Rh_2L^2Cl_2(CO)_2]$ **3** have been isolated. The fluxial behaviour of the ligand in the mono- and di-nuclear rhodium complexes in solution was studied by dynamic ^1H and ^{31}P NMR spectroscopy, showing hindered rotation in the biarylmethane units. The crystal structure of complex **2**, obtained by X-ray analysis, reveals its dinuclear nature and an 'unfolded' geometry. Complexes **1** and **2** catalyse the hydroformylation of cyclohexene with average turnover frequencies of 428 and 344 mm^{-1} h^{-1}, respectively, over 4 h. A notable increase was observed in turnover frequency during the course of reaction. High-pressure (20 bar H_2–CO) IR and ^1H and ^{31}P NMR studies with complex **1** revealed a single rhodium hydride species in solution.

The use of dinucleating ligands in the synthesis of homo- and hetero-dinuclear transition-metal complexes, and in particular the study of the catalytic activity of bimetallic complexes, has attracted considerable interest in recent years.[1] When two metals are in close proximity the formation of metal–metal bonds,[2] insertion of small molecules into a metal–metal bond,[3] ligand mobility from terminal to bridging site[4] and the transfer of ligands from one metal centre to the other[5] can all be observed. Co-operative effects of two distinct metal centres in numerous metalloenzymes[6] are well established, and several complexes have been designed as structural and functional mimics.[7] A number of dinuclear complexes have been synthesized recently in attempts to effect bimetallic catalysis, albeit with limited success so far.[8]

Following our interest in bimetallic catalysis[9] we have focused on structurally well defined dinuclear rhodium phosphite complexes, and the study of their catalytic activity in olefin hydroformylation, using a unique dinucleating ligand. In our approach (Scheme 1) two binding sites are connected by a rigid spacer, which simultaneously allows sufficient flexibility for the rhodium centres to act (co-operatively) as a dinuclear catalyst ('folded'; geometry **a**) or as mononuclear catalyst sites ('unfolded'; geometry **b**). Extensive mechanistic studies on the hydroformylation reaction point to two possible pathways: (*i*) *via* a mononuclear metal catalyst and (*ii*) *via* a dinuclear catalyst.[10] Mechanistic studies employing the bulky tri(*o*-*tert*-butylphenyl) phosphite as ligand showed that the pathway *via* a dimeric rhodium complex could be excluded.[11] Fyhr and Garland[12] also found evidence for a catalytic route involving a monometallic rhodium complex starting with $[Rh_4(CO)_{12}]$ as precursor.

† *Non-SI unit employed:* bar = 10^5 Pa.



Scheme 1 'Unfolded' and 'folded' conformations of a dinuclear rhodium complex

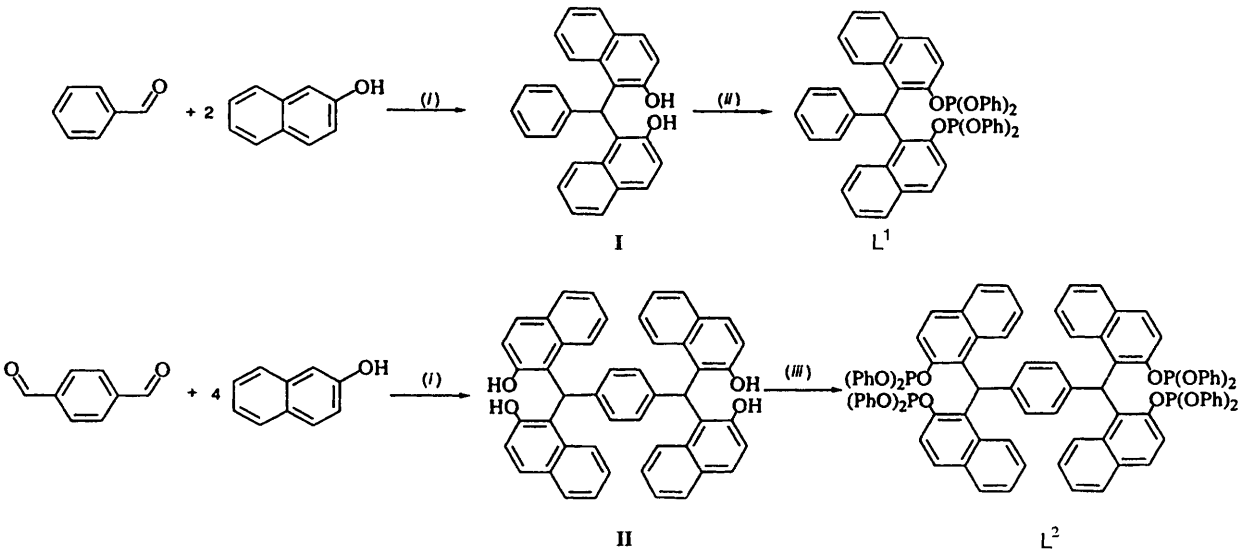
Recently an important example of a dinuclear mechanism has been reported with a bimetallic rhodium phosphine complex as catalyst.[13] The key step in the hydroformylation reaction is proposed to be the transfer of the hydride ligand from one rhodium centre to the other in the bimetallic catalyst.

We describe here a relatively simple synthetic route to a bidentate compound L^1 with two phosphite groups and a tetradentate one with four phosphite groups L^2. The preparation of novel mononuclear $[RhL^1(acac)]$ and dinuclear complexes $[Rh_2L^2(acac)_2]$ (acac = acetylacetonate) and $[Rh_2L^2Cl_2(CO)_2]$ is also described. Further, the crystal structure determination of $[Rh_2L^2(acac)_2]$ is reported as well as the results of hydroformylation reactions of cyclohexene.

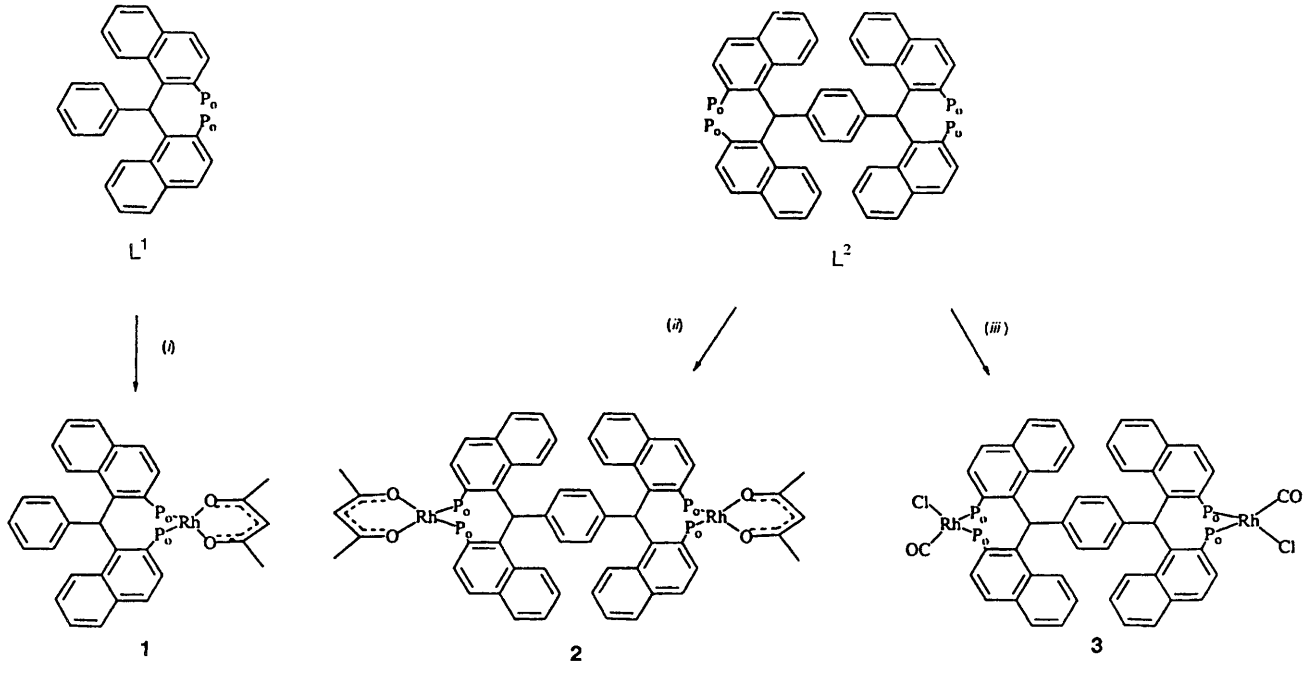
Results and Discussion

Synthesis of the pro-ligands

The bidentate phosphite {bis[2-(diphenoxyphosphinoxy)-1-naphthyl]methyl}benzene L^1 was prepared in a two-step synthesis (Scheme 2). [Bis(2-hydroxy-1-naphthyl)methyl]benzene **I** was obtained by acid-mediated condensation of benzaldehyde and 2 equivalents of 2-naphthol.[14] Treatment of **I** with 2.5 equivalents of chlorodiphenoxyphosphine[15] in



Scheme 2 (*i*) HCl in $MeCO_2H$; (*ii*) 2.5 equivalents $(PhO)_2PCl$, NEt_3 in CH_2Cl_2; (*iii*) 5 equivalents $(PhO)_2PCl$, NEt_3 in CH_2Cl_2



Scheme 3 $P_o = OP(OPh)_2$. (*i*) [Rh(acac)(cod)] in CH_2Cl_2; (*ii*) [Rh(acac)$(CO)_2$] in CH_2Cl_2; (*iii*) $[Rh_2Cl_2(CO)_4]$ in CH_2Cl_2

dichloromethane in the presence of triethylamine gave L^1 in 67% yield after purification by column chromatography. The tetradentate phosphite ligand 1,4-bis{bis[2-(diphenoxyphosphinoxy)-1-naphthyl]methyl}benzene L^2 was synthesized *via* a new and highly effective tetracondensation reaction of terephthalaldehyde and 4 equivalents of 2-naphthol in acetic acid under ambient conditions. Pure 1,4-bis[bis(2-hydroxy-1-naphthyl)methyl]benzene **II** was obtained in 65% yield. Treatment of **II** with 5 equivalents of chlorodiphenoxyphosphine [15] in the presence of triethylamine gave tetraphosphite L^2 in 73% yield after crystallisation from dichloromethane–hexane. When less than 5 equivalents of chlorodiphenoxyphosphine were used not all the phenolic groups were converted and minor products were obtained with only two or three phosphite groups according to ^{31}P NMR analysis.

Synthesis of the complexes

The mononuclear complex [RhL^1(acac)] **1** was prepared by ligand exchange [16] of L^1 with [Rh(acac)(cod)] [cod = cycloocta-1,5-diene] in dichloromethane (Scheme 3). The dinuclear complex $[Rh_2L^2(acac)_2]$ was obtained in 71% yield by the reaction of tetradentate compound L^2 and 2 equivalents of [Rh(acac)$(CO)_2$] in dichloromethane. Mass spectroscopy and elemental analysis of this product indicated a formula $C_{106}H_{84}O_{16}P_4Rh_2{\cdot}CH_2Cl_2$ suggesting that indeed two rhodium atoms were bound to the ligand in accordance with the results of the NMR study of complexes **1** and **2** (see below).

The dinuclear complex $[Rh_2L^2Cl_2(CO)_2]$ **3** was prepared by the reaction of L^2 and $[Rh_2Cl_2(CO)_4]$ in dichloromethane and the proposed structure was supported by NMR and FAB mass spectrometry. [17] This product is very unstable and crystals suitable for X-ray analysis could not be obtained. An analogous reaction of L^1 with $[Rh_2Cl_2(CO)_4]$ gave a mixture of products and unfortunately a pure mononuclear rhodium complex could not be isolated.

NMR spectroscopy

Both the diphosphite L^1 and the tetraphosphite L^2 showed one absorption at δ 126 in the ^{31}P NMR spectrum. When L^1 is coordinated to Rh^I by reaction with [Rh(acac)(cod)], the ^{31}P

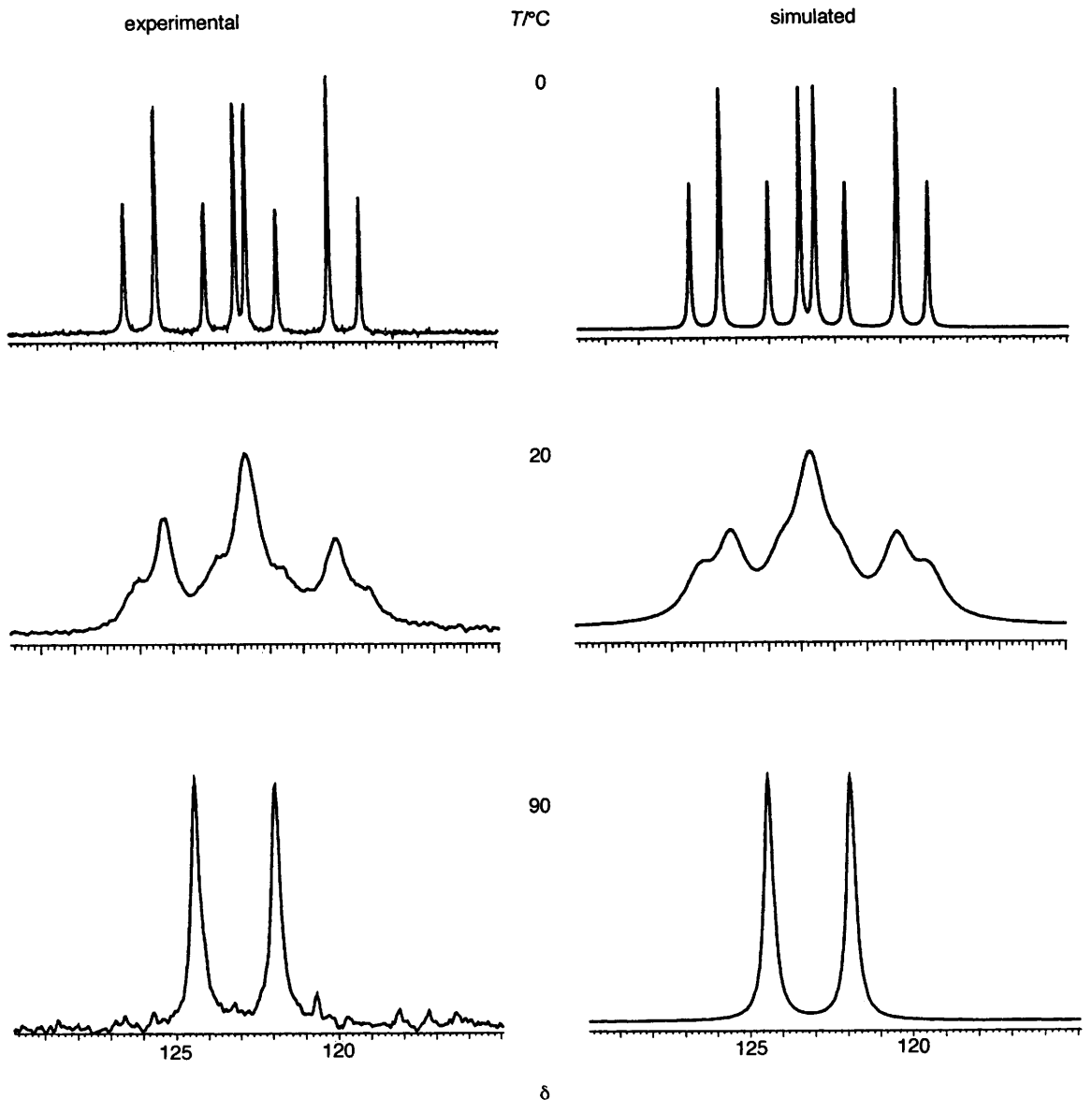
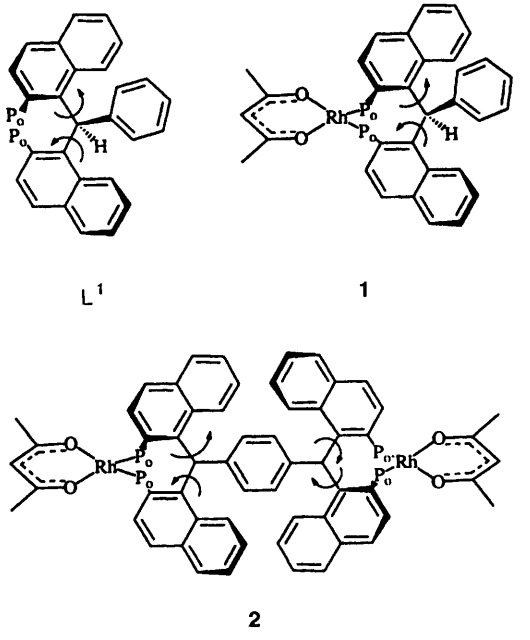


Fig. 1 The ^{31}P NMR spectra of complex **1**

NMR spectrum of the resulting complex **1** showed a broad signal between δ 127 and 118 at 20 °C. Upon lowering the temperature to 0 °C two double doublets were observed (Fig. 1). This spectrum has been successfully simulated and analysed as an [ABX] spin system. At higher temperature (90 °C) only one doublet at δ 123 was found.

The dynamic NMR results can be explained as follows: at lower temperature the steric bulk of the two naphthalene units in complex **1** makes the two phosphorus atoms diastereotopic as a consequence of hindered rotation around the C_{101}-naphthyl bonds (Scheme 4). This would lead to an AB system in the ^{31}P NMR spectrum. Owing to the fact that ^{103}Rh has a spin of a $\frac{1}{2}$ an ABX system is observed.[18] At higher temperatures the ligand becomes more flexible, the naphthalene units are able to move with respect to each other and the two phosphorus atoms become magnetically equivalent. As a result only one doublet (AX system, J_{Rh-P} = 305 Hz) is observed by ^{31}P NMR spectroscopy at 90 °C. In the ^1H NMR spectrum at 0 °C two signals were found at δ 2.2 and 1.5 for the methyl protons of the acetylacetonate moiety. Since the two phosphorus atoms are diastereotopic, the two methyl groups are positioned in different environments and are magnetically inequivalent. In accordance with the enhanced conformational flexibility at 90 °C, when the two phosphorus atoms are equivalent, only one singlet at δ 1.8 was obtained for the methyl protons.



Scheme 4 Hindered rotation in compounds L^1, **1** and **2** around the C(101)- and C(201)-aryl bonds

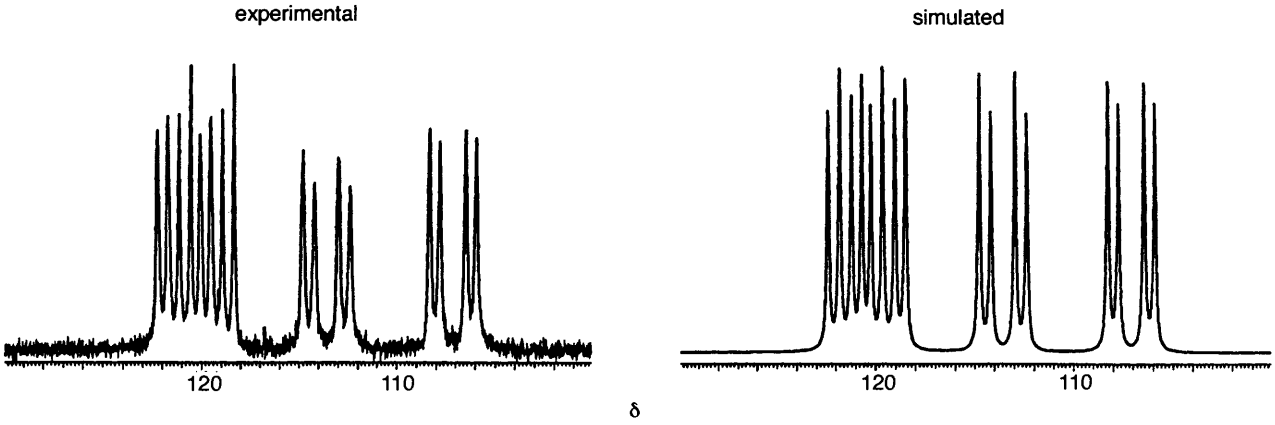


Fig. 2 The ^{31}P NMR spectra of $[Rh_2L^2Cl_2(CO)_2]$ **3** at 25 °C ($CDCl_3$)

Table 1 Phosphorus NMR data for $[RhL^1(acac)]$ **1** and $[Rh_2L^2(acac)_2]$ **2**

Complex	T/°C	Solvent	δ_{P_a}	δ_{P_b}	J_{P-P}/Hz	J_{Rh-P_a}/Hz	J_{Rh-P_b}/Hz
1	0	$CDCl_3$	123.1	119.4	116	297	306
	20	$CDCl_3$	122.7	119.4	120	305	329
	90	$C_6D_5CD_3$	123.0	—	—	305	—
2	20	$CDCl_3$	124.8	120.8	117	296	307
	120	$C_6D_5CD_3$	127.2	—	—	308	—

At 20 °C the ^{31}P and ^1H NMR spectra of the dinuclear complex $[Rh_2L^2(acac)_2]$ **2** showed similar patterns to those found for the mononuclear complex $[RhL^1(acac)]$ **1** at 0 °C. Since rotation around the C(101)- and C(201)-aryl bonds (Scheme 4) in **2** is already severely hindered at 20 °C, the two phosphorus atoms are inequivalent at room temperature. Heating to 120 °C was necessary to achieve coalescence of the absorptions of the phosphorus nuclei to a doublet at δ 127.2. The calculated spin-coupling constants of **1** and **2** are listed in Table 1.

The ^{31}P NMR spectrum of $[Rh_2L^2Cl_2(CO)_2]$ **3** was complex and is shown in Fig. 2. At room temperature four double doublets are observed and spin simulation is consistent with two ABX systems.[18] The spectrum can be explained in the following way. One of the phosphorus atom (P^1) is orientated *trans* to carbonyl and the second (P^2) *trans* to chlorine. For each phosphorus atom a double doublet is obtained. Furthermore, the two phosphorus atoms are diastereotopic due to the steric bulk of the naphthalene moieties leading to inherently dissymmetric binaphthylmethane units (see above). This results in another set of two double doublets in the ^{31}P NMR spectrum (isomers **3a** and **3b**). Since carbon monoxide is a good π acceptor (back donation from rhodium)[19] the two upfield signals with δ 107.2 (J_{Rh-P} = 226, J_{P-P} = 64) and 114 (J_{Rh-P} = 221, J_{P-P} = 72 Hz) are due to the phosphorus atoms *trans* to the carbon monoxide and the two downfield signals with δ 120 (J_{Rh-P} = 268, J_{P-P} = 72) and 121 (J_{Rh-P} = 264, J_{P-P} = 64 Hz) to the phosphorus atoms *trans* to chlorine.

When the temperature is lowered to −10 °C each absorption in the ^{31}P NMR spectrum of complex **3** is split into two signals leading to 32 lines as shown in Fig. 3. This additional splitting of the phosphorus signals might be attributed to the possible *cis* and *trans* orientations of the CO ligands (and Cl) on the distinct rhodium centres leading to four stereoisomers **3a**–**3d**.* This means that the geometrical different dinuclear rhodium complexes with *cis* or *trans* binding of the two CO (*e.g.* **3a** and **3c**) are not distinguished at ambient temperatures, but at −10 °C conformational flexibility is sufficiently lowered to allow the subtle steric and electronic differences between the two possible complexes to be observed.

Crystal structure of $[Rh_2L^2(acac)_2]$ 2

The crystal structure together with the adopted numbering scheme is shown in Fig. 4 and selected bond distances and angles are collected in Table 2. A non-symmetrical structure is apparent, containing disordered solvent presumably CH_2Cl_2 of crystallisation whereas for one of the phenyl rings C(30)–C(34) two orientations were found. Only one orientation is shown.

The very bulky complex **2** consists of two rhodium atoms which are linked by ligand L^2. Two phosphorus atoms P(11) and P(12) co-ordinate *cis* to one rhodium centre Rh(1) and the other two P(21) and P(22) co-ordinate in a *cis* mode to Rh(2). The remaining sites are occupied by two oxygen atoms from acetylacetonate; O(17) and O(18) for Rh(1) and O(27) and O(28) for Rh(2). The most notable stereochemical features are the dissymmetry in the binaphthylmethane units in both halves of the complex and the 'unfolded' conformation (see Scheme 1). The bond angles P(11)–Rh(1)–P(12) and P(21)–Rh(2)–P(22), 91.51(13)° and 91.76(13)°, are relatively small compared to those of 94.8(2)° for $[Rh(acac)\{P(OPh)_3\}_2]$[21] and 99.87(3)° for (acetylacetonato)bis[(3,3′,5,5′-tetra-*tert*-butylbiphenyl-2,2′-dioxy)phenoxyphosphine]rhodium.[22] The O(17)–Rh(1)–O(18) bond angle [89.4(3)°] is slightly larger than the corresponding angle in $[Rh(acac)\{P(OPh)_3\}_2]$ [88.8(2)°], whereas the O(27)–Rh(2)–O(28) bond angle [88.1(3)°] is slightly lower. The Rh–P bond lengths [2.134(3), 2.148(3), 2.145(3) and 2.145(4) Å] are comparable with those found in $[Rh(acac)\{P(OPh)_3\}_2]$ [2.147(2) and 2.156(2)°]. The Rh–O distances [2.037(7), 2.044(7), 2.063(8) and 2.063(7) Å] are in the range found for $[Rh(acac)\{P(OPh)_3\}_2]$ [2.067(5) and 2.061(5) Å]. A remarkable structural feature is the Rh···Rh distance 12.2610(19) Å, which is very large in the 'unfolded' conformer found in the crystal. It should be emphasised, however, that examination of molecular models indicates free rotation around the C(1)–C(101) and C(4)–C(201) bonds. As a consequence, the rhodium centres can come in close proximity (conversion of an 'unfolded' into a 'folded' conformation) and a mutual effect of

* An alternative explanation might be that the splitting is the effect of *cis* and *trans* isomers as a result of the asymmetric CH centres in complex **3** connecting the two chiral binaphthylmethane units. This can be excluded, however, because lowering the temperature of complex **2** gave no additional splitting in ^{31}P NMR spectrum.

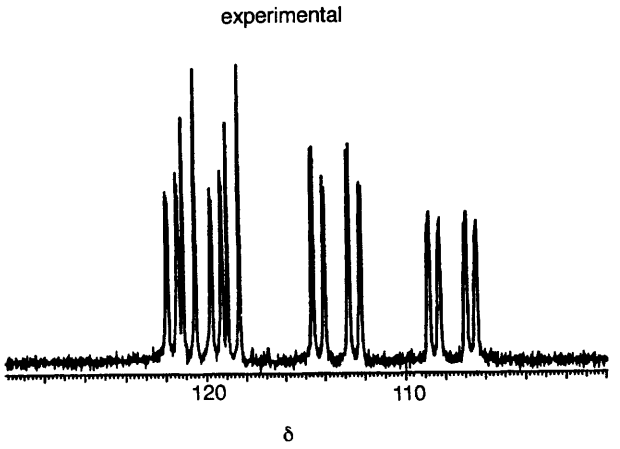
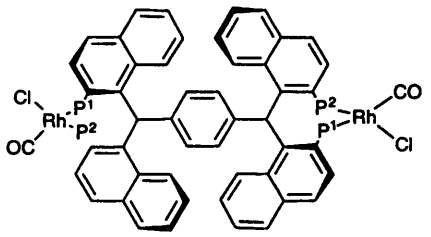
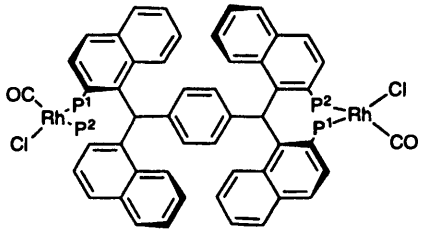


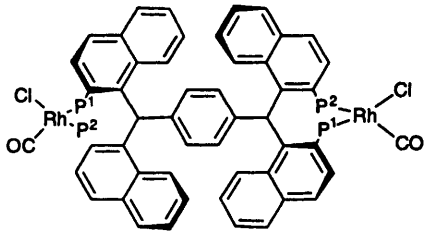
Fig. 3 The ^{31}P NMR spectrum of $[Rh_2(L^2)Cl_2(CO)_2]$ **3** at −10 °C ($CDCl_3$)



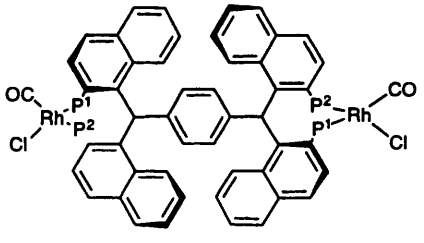
3a



3b



3c



3d

the two rhodium centres in catalysis is not excluded. This situation is comparable with the dinuclear rhodium phosphine complex reported by Stanley and co-workers[13] for which it is proposed that in the catalytic cycle two types of rhodium complex are present: one in which the two rhodium atoms are far apart from each other and one in which they are close to another, allowing a hydride to bridge the metals.

Table 2 Selected bond lengths (Å) and angles (°) for complex **2** with estimated standard deviations in parentheses

Rh(1)–P(11)	2.134(3)	Rh(2)–P(21)	2.145(3)
Rh(1)–P(12)	2.148(3)	Rh(2)–P(22)	2.145(4)
Rh(1)–O(17)	2.037(7)	Rh(2)–O(27)	2.063(8)
Rh(1)–O(18)	2.044(7)	Rh(2)–O(28)	2.063(7)
P(11)–Rh(1)–P(12)	91.51(13)	P(21)–Rh(2)–P(22)	91.76(13)
P(11)–Rh(1)–O(17)	87.5(2)	P(21)–Rh(2)–O(27)	88.5(3)
P(12)–Rh(1)–O(18)	91.6(2)	P(22)–Rh(2)–O(28)	91.5(2)
O(17)–Rh(1)–O(18)	89.4(3)	O(27)–Rh(2)–O(28)	88.1(3)

Table 3 Hydroformylation of cyclohexene by L^2

t/h	Conversion (%)	Turnover (overall) mol cyclohexene per mol Rh	t.o.f.(average)/ $mmol^{-1}$ h^{-1}
1	1.5	75	75
2	9.0	450	225
3	19.4	970	323
4	27.5	1375	344
5	34.6	1730	326
23	80	4000	174

Hydroformylation of cyclohexene

The bidentate compound L^1 and the tetradentate L^2 were used in the rhodium-catalysed hydroformylation reaction of cyclohexene in toluene. First, the active catalysts were prepared overnight from L^1 and L^2 and $[Rh(acac)(CO)_2]$ under 20 bar H_2–CO at 60 °C. The hydroformylation was carried out at 80 °C and was monitored over a period of 23 h. Cyclohexanecarbaldehyde was the only product formed. The experimental data are collected in Tables 3 and 4.

Average turnover frequencies (t.o.f.s) of 344 (for L^2) and 428 mm^{-1} h^{-1} (for L^1) were reached after 4 h. The initial rates using L^2 are slightly lower than those with L^1, but after 23 h equal t.o.f.s were reached. Remarkably, the t.o.f. increased in the first few hours, although it was demonstrated by high-pressure ^{31}P and ^1H NMR spectroscopy that for both complexes **1** and **2** a rhodium hydride species, which is supposed to be the active catalyst, had been formed overnight.* Compared to other phosphites, L^1 and L^2 give moderate rates in the hydroformylation reaction of cyclohexene.[23] Similar rates were obtained for the mono- and di-nuclear rhodium complexes obtained from L^1 and L^2, respectively. Probably, in the preferred conformation of the active catalyst the two rhodium atoms are turned away from each other in an 'unfolded' geometry (see Scheme 1).

In order to get more information on the nature of the rhodium complexes under hydroformylation conditions, high-pressure IR, ^{31}P and ^1H NMR measurements were performed with the RhL^1 system where the spectra were expected to be less complicated than for RhL^2. The starting material $[Rh(acac)(CO)_2]$, dissolved in cyclohexane, showed IR absorptions at 2083, 2013 (CO vibrations) and 1582, 1526 cm^{-1} (acac vibrations) which rapidly disappeared upon addition of L^1. Subsequently a pressure of 20 bar H_2–CO was applied to the solution and the conversion of the rhodium complex was monitered by high-pressure IR spectroscopy during 20 h at 30 °C. A gradual increase in various IR bands was observed together with the appearance of absorptions at 2071, 2038, 2019

* The ^1H NMR spectrum showed for the RhL^2 system a RhH signal at δ −10.6 and the ^{31}P NMR spectrum showed a shift of the phosphorus signal to δ 148. The RhL^1 system is discussed later.

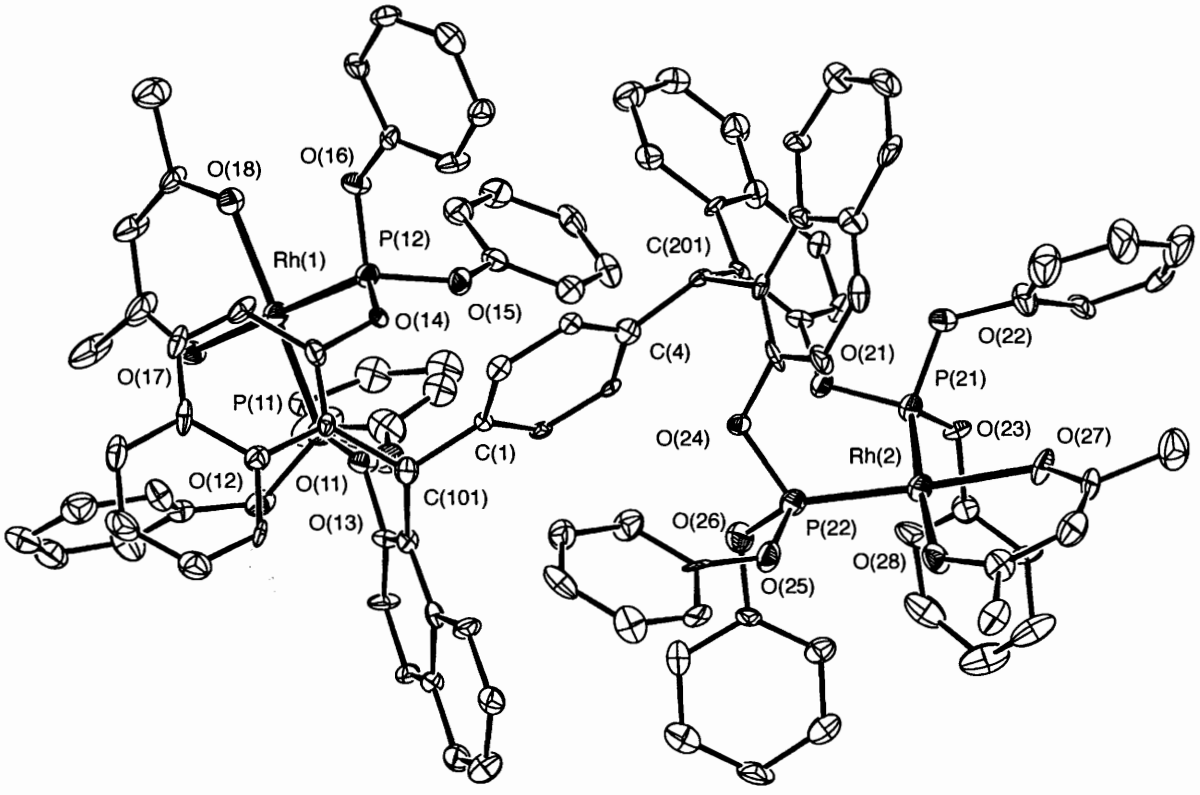


Fig. 4 An ORTEP[20] plot of complex **2** at 30% probability level (hydrogen atoms and the minor disordered part have been left out for clarity)

Table 4 Hydroformylation of cyclohexene by L^1

t/h	Conversion (%)	Turnover (overall) mol cyclohexene per mol Rh	t.o.f.(average)/ $mmol^{-1}$ h^{-1}
1	3.2	160	160
2	17.6	880	440
3	26.0	1100	367
4	34.2	1710	428
5	39.9	1995	399
22.5	78	3900	173

and 2000 cm^{-1}, which were assigned to $[RhL^1(H)(CO)_2]$* and confirmed by NMR spectroscopy (see below). No change is seen when the pressurised solution is heated to 60 °C during 24 h or 80 °C during 72 h indicating very stable rhodium species under these conditions. Proton and ^{31}P NMR measurements were performed both in the absence and in the presence of aldehyde. The latter experiment was executed to examine the possible influence of aldehyde on catalyst activity. In a typical experiment $[Rh(acac)(CO)_2]$, L^1 and nonanal (1:1:1 ratio) dissolved in C_6D_6 was pressurised with 20 bar H_2–CO and the conversion was monitored by ^1H NMR spectroscopy at 40 °C. After 3 h the formation of the rhodium hydride species (double triplet at δ −10.34, J_{P-H} = 69.3, J_{Rh-H} = 6.4 Hz) was complete and the complex remained stable for 64 h. Further the hydride was perfectly stable over 24 h when the temperature was raised to 60 °C. When the formation of the hydride species was monitored by ^{31}P NMR spectroscopy a decrease in the broad absorptions of $[RhL^1(acac)]$ at δ 120 and 128 with a simultaneous increase in the sharp absorptions at δ 146 and 151 (J_{Rh-P} = 213, J_{H-P} = 70 Hz) of $[RhL^1(H)(CO)_2]$ was seen. Infrared measurements at atmospheric pressure on the solution obtained in the high-pressure NMR experiment showed similar results to those found previously in the high-pressure IR measurement. From these experiments it is clear that the rhodium hydride species is perfectly stable under the high-pressure syngas conditions and that the product aldehyde has no effect on the nature of the catalyst.

Besides the hydroformylation experiments in toluene, the solvent dependency was briefly examined. In cyclohexanone, employing the same conditions, a similar time dependency of reaction rate was observed to that in toluene although only 50% conversion was reached after 16 h. It is remarkable that only one rather stable, rhodium hydride complex is observed using L^1 in solution. Since hydroformylation showed an initial increase in t.o.f., we must assume that the hydride is actually the precursor to the, as yet unseen, active species. Further confirmation of an increase in turnover frequency during the reaction was obtained from high-pressure experiments. The rhodium hydride complex was formed in toluene and after 16 h cyclohexene was added. The hydroformylation reaction was monitored at 80 °C under 20 bar syngas. The H_2–CO pressure decrease and increase in aldehyde concentration (as measured by high-pressure IR) showed an S-shaped time dependency similar to the trend observed in the autoclave experiments. Fig. 5 illustrates this effect; it should be noted that the aldehyde absorption can only be monitored by IR spectroscopy under the actual high-pressure conditions of the hydroformylation in the early stages of the reaction due to the large absorption coefficient of the aldehyde carbonyl group. Our experiments performed so far indicate that extensive mechanistic studies will be required to elucidate the origin of this effect.

Conclusion

A facile two-step procedure for the synthesis of new bi- and tetra-dentate phosphites has been found. The molecular structure of the intriguing dinuclear rhodium complex of L^2 shows an 'unfolded' conformation whereas in solution fluxional behaviour of the ligand is observed. Proton and ^{31}P NMR studies indicate inherent dissymmetry in the bis(naphthyl)methane units due to hindered rotation. No major differences in the

* Only three of the vibrations can be assigned to $[RhL^1(H)(CO)_2]$. One extra vibration cannot be explained.

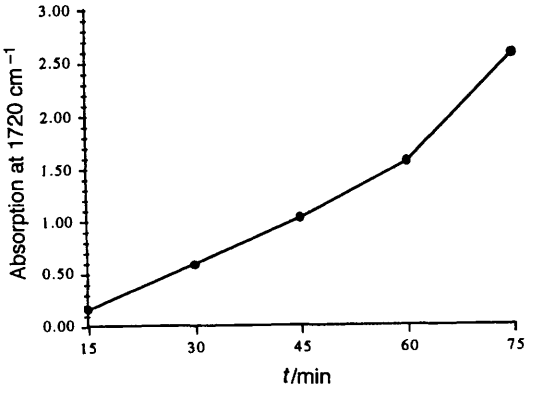


Fig. 5 Increase in the aldehyde carbonyl absorption at 1720 cm^{-1} with time

hydroformylation activities of the mono- and di-nuclear rhodium complexes of the ligands described here were observed.

Experimental

All operations were performed under an atmosphere of argon. Dichloromethane, hexane and pentane were distilled under a nitrogen atmosphere from phosphorus pentaoxide. Bis(2-hydroxy-1-naphthyl)methylbenzene[14] and chlorodiphenoxyphosphine[15] were prepared by literature procedures. The complexes $[Rh(acac)(CO)_2]$, [Rh(acac)(cod)] and $[Rh_2Cl_2(CO)_4]$ were obtained from Aldrich and used without further purification. Infrared spectra were measured by using a Perkin-Elmer 841, high-pressure-IR spectra using an *in-situ* IR-autoclave[24] and recorded on a Nicolet 510 FTIR spectrophotometer with a resolution of 2 cm^{-1}. Proton and ^{31}P NMR spectra were recorded with Varian Gemini 200 and Gemini 300 Fourier-transform NMR spectrometers; ^1H chemical shifts are denoted in ppm relative to the solvent and converted into the $SiMe_4$ scale, for ^{31}P relative to $(NPCl_2)_3$ at δ 19.91. Spectrum simulations were done on Varian VXR 300 spectrometer with the program LACOON.[25] High-pressure NMR measurements were performed on a Bruker AMX 300 spectrometer. Gas–liquid chromatography analyses were run on a Fisons Instruments HRGC Mega 2-8533 chromatograph (split/splitless injector, J & W Scientific; DB-1 30 m column, film thickness 3.0 μm, carrier gas 70 kPa He, flame ionisation detector). Electron-ionisation (EI) mass spectra were recorded on a AEI-MS-902 spectrometer, electrospray (ES) mass spectra using a Nermag-R-30-10 and fast atom bombardment (FAB) mass spectra on a JEOL HX 110 magnetic sector instrument. Elemental analyses were determined in the Microanalytical department of the University of Groningen and the rhodium analysis was obtained in the Microanalytical department of H. Kolbe in Mülheim an der Ruhr.

Syntheses

1,4-Bis[bis(2-hydroxy-1-naphthyl)methyl]benzene II. Concentrated hydrochloric acid (1 cm^3) was added to 2-naphthol (13.2 g, 0.09 mol) and terephthalaldehyde (3 g, 0.02 mol) in acetic acid (50 cm^3) at room temperature and the mixture was stirred for 50 h. It was filtered and the resulting white solid was heated for 15 min with boiling dichloromethane (CH_2Cl_2) and filtered again to afford **II** as a white powder (8.6 g, 65%), m.p. 220 °C (Found: C, 85.4; H, 5.15%; *m/z* 674. $C_{48}H_{34}O_4$ requires C, 85.4; H, 5.10%; *M* 674). $\delta_H[(CD_3)_2SO]$ 9.52 (4 H, br, OH), 8.11 (4 H, d, J = 8 Hz, arylH), 7.67 (8 H, m, arylH), 7.15 (12 H, m, arylH), 7.02 (2 H, s, CH) and 6.87 (4 H, s, arylH).

{Bis[2-(diphenoxyphosphinoxy)-1-naphthyl]methyl}benzene L¹. To a solution of [bis(2-hydroxy-1-naphthyl)methyl]benzene (1.0 g, 2.7 mmol) in CH_2Cl_2 (30 cm^3) were added chlorodiphenoxyphosphine (1.1 cm^3, 6.8 mmol) and triethylamine (1 cm^3). The mixture was stirred for 1 h at room temperature, then washed twice with 5% $NaHCO_3$, dried over Na_2SO_4 and the solvent removed under vacuum. The crude diphosphite was purified by column chromatography (silica gel; hexane–ethyl acetate, 85:15) to yield compound L^1 as a colourless oil (1.5 g, 67%) (Found: C, 75.6; H, 4.85; P, 7.50%; *m/z* 808. $C_{51}H_{38}O_6P_2$ requires C, 75.7; H, 4.75; P, 7.65%; *M* 808). $\delta_P(CDCl_3)$ 126 (s); $\delta_H(CDCl_3)$ 9.77 (2 H, d, J = 9, arylH), 7.7 (5 H, m, arylH), 7.4–7.0 (23 H, m, arylH), 6.81 (8 H, dd, J = 23 and 8 Hz, arylH); *m/z* (EI) 808 (M^+), 715 (M − PhO) and 498 [M − $P(OPh)_3$].

1,4-Bis{bis[2-(diphenoxyphosphinoxy)-1-naphthyl]methyl}benzene L². To a solution of tetranaphthol compound **II** (1 g, 1.5 mmol) in CH_2Cl_2 (30 cm^3) were added chlorodiphenoxyphosphine (1.2 cm^3, 7.4 mmol) and triethylamine (1 cm^3). The mixture was stirred for 1 h at room temperature, then washed twice with 5% $NaHCO_3$, dried over Na_2SO_4 and the solvent removed under vacuum. The solid residue was crystallised from CH_2Cl_2–hexane yielding compound L^2 as a white powder (1.7 g, 73%) (Found: C, 74.5; H, 4.65; P, 7.90%; *m/z* 1539. $C_{104}H_{70}O_{12}P_4$ requires C, 74.9; H, 4.60; P, 8.05%; *M* 1539). $\delta_P(CDCl_3)$ 126 (s); $\delta_H(CDCl_3)$ 8.0–7.6 (16 H, m, arylH) and 7.5–6.5 (54 H, m, arylH); *m/z* (ES) 1539 (M^+).

({[2-(Diphenoxyphosphinoxy)-1-naphthyl]methyl}benzene)(pentane-2,4-dionato)rhodium 1. To a solution of diphosphite L^1 (65 mg, 80 μmol) in CH_2Cl_2 (2 cm^3) was added [Rh(acac)(cod)] (25 mg, 80 μmol). The mixture was stirred for 1 h. The yellow solution was evaporated to dryness and the resulting solid crystallised from CH_2Cl_2–pentane yielding analytically pure complex **1** as yellow crystals (52 mg, 64%) (Found: C, 66.2; H, 4.50; Rh, 10.25. $C_{56}H_{45}O_8P_2Rh$ requires C, 66.5; H, 4.50; Rh, 10.12%). $\delta_P(CDCl_3$, 273 K) 123.1 ($1P^1$, J_{Rh-P} = 297, J_{P-P} = 116) and 119.4 ($1P^2$, J_{Rh-P} = 306, J_{P-P} = 116 Hz); $\delta_H(CDCl_3$, 273 K) 8.1–6.0 (23 H, m), 2.2 (3 H, s, CH_3) and 1.5 (3 H, s, CH_3); *m/z* (ES) 993 (M − acac + $2CH_3CN$), 952 (M − acac + CH_3CN) and 911 (M − acac).

(1,4-Bis{bis[2-(diphenoxyphosphinoxy)-1-naphthyl]methyl}benzene)bis(pentane-2,4-dionato)dirhodium 2. To a solution of tetraphosphite L^2 (100 mg, 65 μmol) in CH_2Cl_2 (2 cm^3) was added $[Rh(acac)(CO)_2]$ (33 mg, 130 μmol). The mixture was stirred for 1 h. The yellow solution was evaporated to dryness and the solid residue was crystallised from CH_2Cl_2–hexane yielding yellow crystals of complex **2** which were suitable for X-ray analysis (90 mg, 71%) (Found: C, 63.8; H, 4.55; Rh, 9.45%; *m/z* 1943. $C_{106}H_{84}O_{16}P_4Rh_2{\cdot}CH_2Cl_2$ requires C, 63.3; H, 4.25; Rh, 10.1%; *M* 1943). $\delta_P(CDCl_3)$ 124.8 ($2P^1$, dd, J_{Rh-P} = 296, J_{P-P} = 117) and 120.8 ($2P^2$, dd, J_{Rh-P} = 307, J_{P-P} = 117 Hz); $\delta_H(CDCl_3)$ 8.1–6.0 (94 H, m, arylH), 2.0 (3 H, s, CH_3) and 1.4 (3 H, s, CH_3); *m/z* (ES) 1943 (M^+), 1846 (M − acac) and 1744 (M − 2acac).

(1,4-Bis{bis[(2-diphenoxyphosphinoxy)-1-naphthyl]methyl}benzene)dicarbonyldichlorodirhodium 3. To a solution of tetraphosphite L^2 (100 mg, 65 μmol) in CH_2Cl_2 (2 cm^3) was added $[Rh_2Cl_2(CO)_4]$ (25 mg, 65 μmol). The mixture was stirred for 1 h. The yellow solution was evaporated to dryness to afford a yellow oil (> 95%). $\nu_{max}/cm^{-1}(CDCl_3)$ 2083s and 2019s (CO); $\delta_P(CDCl_3)$ 121.0 [$2P^1$, dd, J_{Rh-P} = 264, $J(P^1–P^2)$ = 64], 107.2 [$2P^2$, dd, J_{Rh-P} = 226, $J(P^2–P^1)$ = 64], 119.9 [$2P^3$, dd, J_{Rh-P} = 268, $J(P^3–P^4)$ = 72] and 113.7 [$2P^4$, dd, J_{Rh-P} = 221, $J(P^3–P^4)$ = 72 Hz); *m/z* (FAB) 1744 (M − 2Cl − 2CO).

Crystallography

A yellowish transparent crystal (0.25 × 0.25 × 0.45 mm) of complex **2** was mounted on a Lindemann-glass capillary and

Table 5 Crystallographic data for complex **2**

Formula	$C_{106}H_{84}O_{16}P_4Rh_2 \cdot 2CH_2Cl_2$
M	2113.39
Crystal system	Monoclinic
Space group	$P2_1/c$ (no. 14)
a/Å	23.519(2)
b/Å	17.593(2)
c/Å	23.985(2)
β/°	109.335(8)
U/Å^3	9364.5(16)
D_c/g cm^{-3}	1.499
Z	4
$F(000)$	4328
μ/cm^{-1}	6.0
Crystal size/mm	0.25 × 0.25 × 0.45
T/K	150
θ_{min}, θ_{max}/°	1.9, 22.5
(Mo-Kα)/Å	0.710 73 (graphite monochromated)
Scan type	ω–2θ
Δω/°	0.80 + 0.35 tan θ
Horizontal, vertical aperture/mm	3.00, 4.00
X-Ray exposure time/h	46
Reference reflections	−4 −7 −8, 3 0 −12
hkl Data set	−23 to 25, −18 to 0, −25 to 0
Total data	12 544
Total unique data	12 187
No. refined parameters	1154
Final $R1$ [a]	0.0808 [5420 $F_o > 4\sigma(F_o)$]
Final $wR2$ [b]	0.1692 (12186 data)
Goodness of fit	0.899

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = \{[\Sigma w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{\frac{1}{2}}$. $w = 1/[\sigma^2(F_o^2) + (0.0603P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$.

transferred to the cold nitrogen stream on an Enraf-Nonius rotating-anode CAD4-T diffractometer. It reflected poorly. Accurate unit-cell parameters and an orientation matrix were determined from the setting angles of 25 reflections (SET 4)[26] in the range $10.1 < \theta < 13.8°$. Reduced-cell calculations did not indicate higher lattice symmetry.[27] Crystal data and details on data collection and refinement are shown in Table 5. Data were corrected for Lorentz-polarisation effects, and for linear decay of 18% of the three periodically measured reference reflections. The structure was solved by automated Patterson methods and subsequent Fourier-difference techniques using DIRDIF 92.[28] Refinement on F^2 was carried out by full-matrix least-squares techniques (SHELXL 93);[29] no observance criterion was applied during refinement (one beamstop-truncated reflection omitted). All non-hydrogen atoms were refined with anisotropic thermal parameters, except those of the disordered phenyl ring which were refined isotropically. The hydrogen atoms were refined with a fixed isotropic thermal parameter amounting to 1.5 or 1.2 times the value of the equivalent isotropic thermal parameter of their carrier atoms, for the methyl and all other hydrogen atoms, respectively. One of the phenyl rings [C(128), C(129), C(30A/B), C(31A/B), C(32A/B) and C(33A/B)] is orientationally disordered over two positions. Both major and minor components (0.58 : 0.42) of the disorder model were included in the refinement with an isotropic thermal parameter. After anisotropic refinement of the Rh, P and O atoms and introduction of the hydrogen atoms at expected positions, an R value of 0.100 was obtained. A solvent-accessible area contained some density, however no discrete solvent model could be refined. In a region of 234 Å an electron count of approximately 64 electrons was encountered (PLATON/SQUEEZE),[30] probably representing two dichloromethane molecules. After application of SQUEEZE the refinement became more stable. Weights were optimised in the final refinement cycles. Neutral atom scattering factors and anomalous dispersion corrections were taken from ref. 31.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/168.

Hydroformylation reaction, general procedure

An autoclave (200 cm^3) was charged with toluene (20 cm^3), L^1 (4 μmol) or L^2 (2 μmol) and [Rh(acac)(CO)$_2$] (4 μmol) and pressurised to the appropriate initial pressure with syngas ($CO:H_2 = 1:1$). It was heated at 60 °C for 16 h, then to 80 °C and cyclohexene (20 mmol) and internal standard (decane, 5 mmol) were added. During the reaction a number of samples were taken. After 23 h the autoclave was cooled, depressurised and the contents analysed by gas chromatography.

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