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Rhodium(I) complexes of robust phosphites derived from calix[4]arenes and their application in the hydroformylation of 1-hexene

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The monophosphites derived from calix[4]arene ($\mathbf{L_a}$) and *p-tert*-butylcalix[4]arene ($\mathbf{L_b}$) react with $[Rh(CO)_2(acac^*)]$ ($acac^* = Bu^tCOCHCOBu^t$) to give the mononuclear complexes $[Rh(CO)(\mathbf{L_a})(acac^*)]$ and $[Rh(CO)(\mathbf{L_b})(acac^*)]$ respectively. The crystal structure of $[Rh(CO)(\mathbf{L_b})(acac^*)]$ shows the calixarene conformation to have aryl groups in {down, out, up, up} orientations with one aryl blocking the axial site at the square planar metal. Treatment of $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ with $\mathbf{L_b}$ gives an equilibrium mixture of products which have been assigned to the *cis*/*trans* isomers of $[Rh_2(\mu\text{-}Cl)_2(CO)_2(\mathbf{L_b})_2]$. The crystal structure of *cis*-$[Rh_2(\mu\text{-}Cl)_2(CO)_2(\mathbf{L_b})_2]$ has a folded dimer geometry with both the concave and convex faces of the dimer partly blocked by the calixarene phosphite ligand. The rhodium complexes of $\mathbf{L_a}$ and $\mathbf{L_b}$ are very active and chemoselective catalysts for the hydroformylation of hexene but the regioselectivity is low.

Introduction

Rhodium(I) complexes of triphenylphosphite were first reported[1] to be hydroformylation catalysts in 1969 and variations on the $P(OPh)_3$ system continues to attract attention.[2] In the 1980s van Leeuwen *et al.*[3] and Union Carbide[4] showed that rhodium(I) complexes of bulky monodentate phosphites have hydroformylation activities two orders of magnitude greater than the commercialised rhodium–triphenylphosphine system. The rates with these catalysts are independent of alkene concentration and bulky alkenes can be used as substrates.[5] However the n : iso ratio of product aldehydes from n-alkenes are close to 1 : 1 and the catalysts are unstable with respect to ligand degradation under the hydroformylation conditions.[3] We have shown[6] that Lattman's bulky cage phosphites $\mathbf{L_a}$ and $\mathbf{L_b}$ derived from calix[4]arenes[7] are kinetically very stable with respect to other triaryl phosphites and therefore of interest as ligands for catalysis. In this paper we report rhodium(I) complexes of $\mathbf{L_a}$ and $\mathbf{L_b}$ and their hydroformylation activity which complements the work of Kamer, van Leeuwen *et al.*[8] on closely related systems.

Results and discussion

Addition of $[Rh(CO)_2(acac^*)]$ ($acac^* = Bu^tCOCHCOBu^t$) to a CH_2Cl_2 solution containing the appropriate $\mathbf{L_a}$ or $\mathbf{L_b}$ gave complexes **1a** and **1b** in over 90% yields and these have been fully characterised (see Experimental section). Attempts to displace both carbonyl groups to give a bis(phosphite) complex were unsuccessful under all conditions tried. Single crystals of **1b** as a mixed solvate were grown from CH_2Cl_2/pentane and their structure determined by X-ray crystallography (see Fig. 1, Table 1). There are two independent molecules of **1b** present in the structure, with very similar geometry. The rhodium(I) centre shows the expected square planar geometry, with relatively small deviations from ideal angles and planarity (rms deviation from plane 0.089 and 0.055 Å for the two molecules, with the phosphorus further from the RhO_2 plane than the carbonyl carbon, 0.300 and 0.120 Å respectively for molecule 1 and 0.258 and 0.025 Å for molecule 2). The calixarene ligand $\mathbf{L_b}$ has the same conformation as in the complexes $[Pt_2Cl_2(\mu\text{-}Cl)_2(\mathbf{L_b})_2]$, $[Pd_2Cl_2(\mu\text{-}Cl)_2(\mathbf{L_b})_2]$ and $[PdCl_2(CNBu^t)(\mathbf{L_b})]$, with one face of the rhodium coordination plane shielded by the "down" aryl group at O(101). As in $[PdCl_2(CNBu^t)(\mathbf{L_b})]$[6] the ligand $\mathbf{L_b}$ adopts an orientation such that the "out" aryl (at O(102)) is *cis* to the less bulky ligand at the metal (here carbonyl).

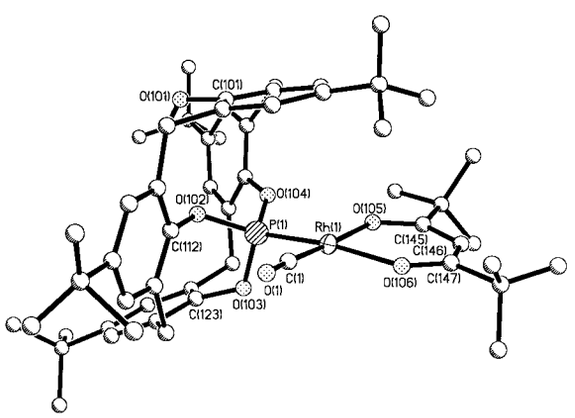
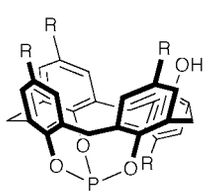
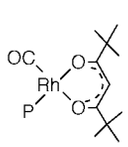


Fig. 1 Molecular structure of one of the two independent molecules of mononuclear rhodium(I) complex **1b**. Selected atoms are labelled and all hydrogens are omitted for clarity.



$\mathbf{L_a}$ R = H

$\mathbf{L_b}$ R = Bu^t



1a P = $\mathbf{L_a}$

1b P = $\mathbf{L_b}$

Addition of $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ to a CH_2Cl_2 solution containing four equivalents of $\mathbf{L_b}$ gave, according to the ^{31}P NMR spectrum, a mixture of two products in the ratio of *ca.* 1 : 4 along with free phosphite. The amount of unreacted phosphite

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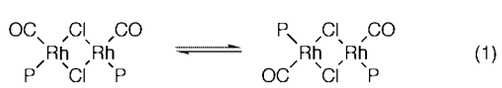
Table 1 Selected bond lengths (Å) and bond angles (°) for **1b**·1.5CH_2Cl_2·0.25C_5H_{12}

Rh(1)–P(1)	2.1842(13)
Rh(1)–C(1)	1.817(5)
Rh(1)–O(105)	2.034(3)
Rh(1)–O(106)	2.063(3)
Rh(2)–P(2)	2.1855(13)
Rh(2)–C(2)	1.814(6)
Rh(2)–O(205)	2.042(3)
Rh(2)–O(206)	2.059(3)
P(1)–O(102)	1.631(3)
P(1)–O(103)	1.611(3)
P(1)–O(104)	1.593(3)
P(2)–O(202)	1.616(3)
P(2)–O(203)	1.615(3)
P(2)–O(204)	1.596(3)
C(1)–Rh(1)–P(1)	93.1(2)
O(106)–Rh(1)–C(1)	89.4(2)
O(106)–Rh(1)–O(105)	88.70(13)
P(1)–Rh(1)–O(105)	89.36(10)
C(2)–Rh(2)–P(2)	93.6(2)
O(205)–Rh(2)–C(2)	88.4(2)
O(206)–Rh(2)–O(205)	88.60(13)
P(2)–Rh(1)–O(106)	89.25(11)
O(102)–P(1)–O(103)	101.2(2)
O(102)–P(1)–O(104)	102.7(2)
O(103)–P(1)–O(104)	104.5(2)
O(201)–P(2)–O(202)	101.2(2)
O(201)–P(2)–O(203)	103.1(2)
O(202)–P(2)–O(203)	104.6(2)

corresponded to two equivalents, suggesting that the rhodium(I) complexes that had formed had a Rh:$\mathbf{L_b}$ ratio of one. The reaction was repeated, this time using two equivalents of ligand $\mathbf{L_b}$ and the ^{31}P NMR spectrum showed the same two rhodium(I) species with no free phosphite. Single crystals were obtained from a $CDCl_3$ solution of a mixture of the two rhodium–phosphite complexes and a crystal structure determination revealed the binuclear structure *cis*-**2** (see below). Some of the crystals were redissolved in $CDCl_3$ and the ^{31}P NMR spectrum showed the presence of two rhodium complexes in a 1:4 ratio as observed in the original mixture. We suggest that *cis*-**2** in solution is in equilibrium (eqn. (1)) with



(1)

cis-**2** P = $\mathbf{L_b}$ *trans*-**2**

trans-**2** as has been observed in other dirhodium(I)–phosphite systems.[9]

The structure of *cis*-**2** is shown in Fig. 2 and some details of the rather imprecise structure are given in Table 2. As for similar Rh(I) dimers the structure has a folded $RhCl_2Rh$ bridge with the near planar coordination planes (rms deviations 0.039 and 0.054 Å for Rh(1) and Rh(2) respectively) inclined at 56.9°. The conformation of the calixarene ligands are, as in other cases, of type ***e*** (according to van Leeuwen's scheme[8]). For Rh(1) the "down" aryl covers the axial site at rhodium which is on the convex side of the folded dimer, while the concave axial site is covered for Rh(2).

As noted in the previous paper[6] the asymmetric profile of $\mathbf{L_b}$ in conformation ***e*** is not well suited to octahedral or trigonal pyramidal geometry at the metal, but is consistent with mono-$\mathbf{L_b}$ complexes with the metal in square pyramidal (with $\mathbf{L_b}$ in a basal site) or square planar or tetrahedral coordination (see Scheme 1).

Hydroformylation

Rhodium complexes of $\mathbf{L_a}$ and $\mathbf{L_b}$, were tested as catalysts for the hydroformylation of 1-hexene (Scheme 2). The branched aldehydes are products of hydroformylation of 1-, 2- and 3-hexene (*i.e.* result from isomerisation of 1-hexene); the hexane is the product of hydrogenation of the substrate and its isomers.

Table 2 Selected bond lengths (Å) and bond angles (°) for *cis*-**2**·3$CHCl_3$

Rh(1)–P(1)	2.163(5)
Rh(1)–C(1)	1.85(2)
Rh(1)–Cl(1)	2.386(5)
Rh(1)–Cl(2)	2.391(5)
Rh(2)–P(2)	2.176(5)
Rh(2)–C(2)	1.76(2)
Rh(2)–Cl(1)	2.386(5)
Rh(2)–Cl(2)	2.396(6)
Rh(1)···Rh(2)	3.147(3)
C(1)–Rh(1)–P(1)	87.5(6)
Cl(1)–Rh(1)–C(1)	93.3(6)
Cl(1)–Rh(1)–Cl(2)	84.0(2)
P(1)–Rh(1)–Cl(2)	94.8(2)
C(2)–Rh(2)–P(2)	96.0(6)
C(2)–Rh(1)–Cl(1)	90.9(6)
Cl(1)–Rh(2)–Cl(2)	83.9(2)
P(2)–Rh(1)–Cl(2)	89.3(2)

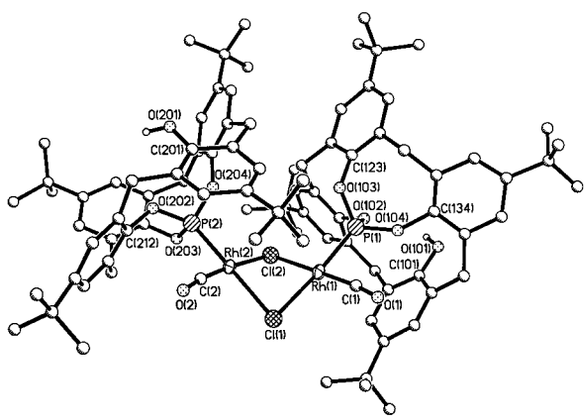
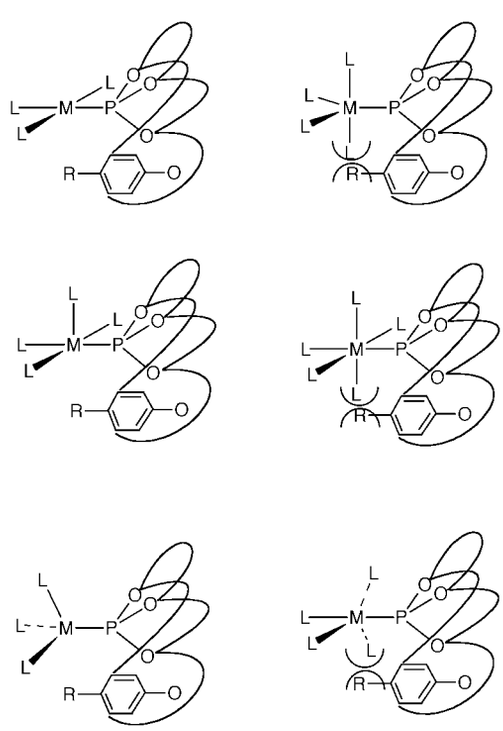


Fig. 2 Molecular structure of binuclear rhodium(I) complex *cis*-**2**. Selected atoms are labelled and all hydrogens are omitted for clarity.

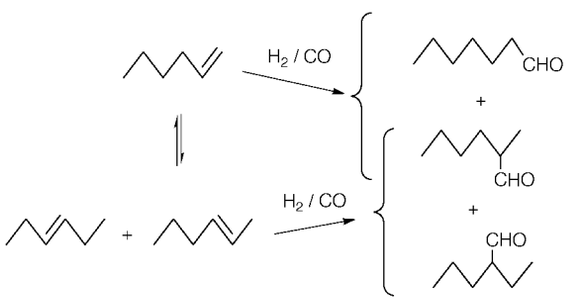


Scheme 1 Intra-coordination sphere steric interactions involving ligand $\mathbf{L_b}$.

Table 3 Hydroformylation of 1-hexene[a]

Entry	Catalyst	$L_{a,b}$: Rh	*T*/°C	Conversion (%)	Aldehydes (%)	n : iso[b]	Hexane (%)
1	$[Rh_2Cl_2(cod)_2]$	0	160	37	75	0.4	14[c]
2	$[Rh_2Cl_2(cod)_2]/L_a$	10	160	33	96	0.5	4
3	$[RhCl_2(cod)_2]/L_b$	10	160	59	85	0.9	10[c]
4	$[Rh(CO)_2(acac^*)]$	0	160	99.4	77	0.9	23
5	**1a**	1	160	99.5	84	1.2	16
6	**1a**	10	160	99.4	82	1.2	18
7	**1b**	1	160	99.5	81	1.2	19
8	**1b**	10	160	99.5	86	1.4	14
9	**1b**	1	120	99.7	90	1.0	9[c]
10	**1b**	1	80	99.4	92	0.8	7[c]

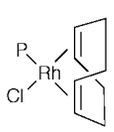
[a] See Experimental section for reaction conditions. Product yields were calculated by GC using toluene or cumene as internal standard (accuracy 1%). [b] Ratio of 1-heptanal to branched aldehydes; we were unable to obtain accurate values for the quantities of 2-ethylpentanal and 3-propylbutanal because their GC signals overlapped. [c] The mass balance is made up of a mixture of heptanols.



Scheme 2

All the products were identified by GC and the results are collected in Table 3.

In runs 2 and 3, the catalyst precursors were made *in situ* from solutions of $[Rh_2(\mu\text{-}Cl)_2(cod)_2]$ and 10 equiv. of L_a or L_b. Under these conditions but in the absence of H_2/CO, the ^{31}P NMR spectra show that only one rhodium–phosphite complex is formed in each case and assigned structures **3a** [δ 90.0, ^1J(RhP) 278 Hz] and **3b** [δ 89.3, ^1J(RhP) 275 Hz] respectively from the stoichiometry and by comparison with the corresponding structurally characterised iridium analogues.[6] These systems catalyse the hydroformylation of 1-hexene and by comparing entry 1 with entries 2 and 3, it can be seen that the ligand influences the activity and selectivity of the process. Although high aldehyde selectivites were obtained (96%, 85%), the substrate conversions were low (33%, 59%), and regioselectivities were poor. It is possible that the chloro ligand was inhibiting the hydroformylation since it is known that halide-containing rhodium complexes are often poor catalysts.[10] This prompted us to change the catalyst precursor for the remaining tests to the isolated rhodium(I)–phosphite complexes **1a** and **1b**.



3a P = L_a

3b P = L_b

Using isolated complexes **1a** and **1b** as catalyst precursors, very high substrate conversions were achieved with high aldehyde selectivities (82–92%), but poor regioselectivities (n : iso, *ca.* 1 : 1). The results for **1a** (entries 5 and 6) are essentially the same as for **1b** (entries 7 and 8).

The phosphites L_a and L_b are very bulky and will promote the formation of highly unsaturated rhodium species. This would explain the high activity of **1a** and **1b** and the low selectivity for linear aldehyde. Low n : iso ratios have previously been observed with complexes of bulky phosphites as catalysts and it has been postulated that this is due to a combination of high double-bond isomerisation rates and the runaway character of the reactions.[5,11] That is, the hydroformylation reaction proceeds so rapidly that all the CO present in solution is consumed with the result that, at low concentrations of CO, the system catalyses alkene isomerisation. The catalyst is then so active that when all terminal alkenes are converted into aldehydes, the internal alkenes are then hydroformylated. In support of this explanation for the poor regioselectivities of **1a** and **1b**, 2-ethylpentanal was observed by GC in each of runs 5 to 10.

A large excess of phosphite (Rh : P of 1 : 10) was used in runs 6 and 8 in the hope of improving the regioselectivities by suppressing any phosphite dissociation and promoting bis-(phosphite) complex formation but this had a negligible effect on the catalytic system suggesting that the active species is a rhodium–monophosphite complex.[5]

Experiments with **1b** showed that a decrease in reaction temperature resulted in an increase in aldehyde selectivity, but a decrease in linearity (entries 7, 9 and 10). This is a common feature in rhodium-catalysed hydroformylation[5,11] and has been comprehensively explained by Lazzaroni *et al.*[12]

The results obtained here for the hydroformylation of hexene are similar to those obtained by van Leeuwen, Kamer *et al.*[8] for the hydroformylation of octene with rhodium(I) complexes of calix[4]arene derived phosphites.

In conclusion, the robust, air-stable ligands, calix[4]arene phosphites L_a and L_b, form a variety of complexes with rhodium(I) which are precursors for very active catalysts for the hydroformylation of 1-hexene with high conversions and high selectivities to aldehydes but poor n : iso ratios.

Experimental

General techniques and conditions are as described in the previous paper.[6] Commercial reagents were used as supplied unless otherwise stated. $[Rh(CO)_2(acac^*)]$[13] was a gift from DuPont and $[Rh_2Cl_2(CO)_4]$,[14] $[Rh_2Cl_2(cod)_2]$[15] were prepared by literature methods. Calix[4]arene phosphites L_a and L_b were prepared as previously described.[6] Infrared spectra were recorded on either a Nicolet 5ZDX or a Perkin-Elmer 1600. NMR spectra were recorded on a JEOL GX400 at *ca.* 23 °C: ^{31}P (162 MHz, δ to high frequency of 85% H_3PO_4), ^{13}C (100 MHz, δ to high frequency of $SiMe_4$), ^{195}Pt (81 MHz, δ to high frequency Ξ(Pt) of 21.4 MHz) and ^1H (400 MHz, δ to high frequency of $SiMe_4$).

Preparation of $[Rh(CO)(acac^*)(L_b)]$ 1b

To a yellow solution of $[Rh(CO)_2(acac^*)]$ (760 mg, 2.22 mmol) in CH_2Cl_2 (100 cm^3), L_b (1.5 g, 2.22 mmol) was added. The solution was stirred for 2 h at room temperature and then all the

Table 4 Selected crystallographic details for the complexes **1b**·1.5CH_2Cl_2·0.25C_5H_{12} and *cis*-**2**·3$CHCl_3$

	1b·1.5CH_2Cl_2·0.25C_5H_{12}	*cis*-**2**·3$CHCl_3$
Empirical formula	$C_{58.75}H_{78}Cl_3O_7PRh$	$C_{93}H_{109}Cl_{11}O_{10}P_2Rh_2$
Formula weight	1136.44	2044.51
Crystal system	Triclinic	Triclinic
a/Å	15.276(2)	13.773(5)
b/Å	18.109(3)	14.778(7)
c/Å	21.303(3)	24.12(2)
α/°	94.378(10)	86.31(5)
β/°	93.617(10)	89.32(4)
γ/°	96.183(13)	77.30(5)
V/Å^3	5826.4(13)	4780(5)
T/K	173(2)	173(2)
Space group	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)
Z	4	2
μ/mm^{-1}	0.507	0.741
Total reflns	30957	17921
Independent reflns	20074	12068
R_{int}	0.0398	0.1323
R_1 [$I > 2\sigma(I)$] (data)	0.0621	0.1448

volatiles were removed *in vacuo* to yield pale yellow solid **1b** (1.70 g, 95%). Single crystals of **1b** were grown by slow diffusion of pentane into a CH_2Cl_2 solution of **1b** in an NMR tube. Elemental analysis, found (calc.): C, 68.2 (67.9); H, 7.2 (7.3); P, 2.9 (3.1)%. IR (CH_2Cl_2), 2007m (ν_{CO}). ^{31}P NMR ($CDCl_3$): δ 109.8 [d, ^1J(RhP) 309].^{1}H NMR ($CDCl_3$): δ 0.92 [s, 9H, C(CH_3)$_3$ of acac*], 1.04 [s, 9H, C(CH_3)$_3$ of acac*], 1.15 [s, 9H, C(CH_3)$_3$], 1.22 [s, 9H, C(CH_3)$_3$], 1.26 [s, 18H, C(CH_3)$_3$], 3.41 [d, 2H, Ar-CH*H*-Ar, ^2J(HH) 14.3], 3.75 [d, 2H, Ar-C*H*H-Ar, ^2J(HH) 16.3], 4.25 [d, 2H, Ar-C*H*H-Ar, ^2J(HH) 16.3], 4.44 [d, 2H, Ar-C*H*H-Ar, ^2J(HH) 14.3], 4.41 (s, 1H, OH), 5.71 [s, 1H C(O)C*H*C(O)], 7.02, 7.06, 7.07, 7.09 (s, 8H, Ar). ^{13}C NMR ($CDCl_3$): δ 28.8–41.3 (many overlapping signals, Ar-*C*H_2-Ar, t-butyls from calixarene and acac*), 91.5 [s, C(O)*C*HC(O)], 124.0 (m, Ar), 143.8–144.5 (m, Ar), 148.8–150.0 (m, Ar), 188.3 (br,*C*O), 194.7 [s, C*C*(O)CH], 196.2 [s, C*C*(O)CH]. Using a similar procedure [Rh(CO)(acac*)(**L**$_a$)] **1a** was prepared from **L**$_a$ in 93% yield. Elemental analysis, found (calc.); C, 63.0 (62.3); H, 5.4 (5.3); P, 3.5 (4.0)%. IR (CH_2Cl_2), 1999m (ν_{CO}). ^{31}P NMR ($CDCl_3$] δ 110.5 [d, ^1J(RhP) 311]. ^{1}H NMR ($CDCl_3$): δ 0.98 [s, 9H, C(CH_3)$_3$ of acac*], 1.11 [s, 9H, C(CH_3)$_3$ of acac*], 3.48 [d, 2H, Ar-CH*H*-Ar, ^2J(HH) 14.0], 3.75 [d, 2H, Ar-C*H*H-Ar, ^2J(HH) 16.5], 4.25 [d, 2H, Ar-C*H*H-Ar, ^2J(HH) 16.5], 4.44 [d, 2H, Ar-C*H*H-Ar, ^2J(HH) 14.0], 4.45 (s, 1H, OH), 5.74 [s, 1H C(O)C*H*C(O)], 6.70–7.18 (m, 12H, Ar). ^{13}C NMR ($CDCl_3$): δ 27.5–40.3 (m, Ar-*C*H_2-Ar, *tert*-butyls from acac*), 90.8 [s, C(O)*C*HC(O)], 122.2–133.4 (m, Ar), 148.3–152.2 (m, Ar), 185.4 (br, *C*O), 195.7 (s, C*C*OCH), 197.1 (s, C*C*OCH).

Reaction of [Rh_2(μ-Cl)$_2$(CO)$_4$] with L_b

To a yellow solution of [Rh_2(μ-Cl)$_2$(CO)$_4$] (21.6 mg, 0.055 mmol) in CH_2Cl_2 (10 cm^3) was added **L**$_b$ (150 mg, 0.22 mmol). The solution was stirred for 2 h at room temperature and then all volatiles were removed *in vacuo* to yield a red solid. ^{31}P NMR spectroscopy showed this to be a mixture of two Rh-containing species assigned (see Results and discussion) the structures *cis*-**2** [δ 102.4, ^1J(RhP) 317 Hz] and *trans*-**2** [δ 103.0, ^1J(RhP) 317 Hz]. Single crystals of *cis*-**2** were grown from a $CDCl_3$ solution of the mixture by slow evaporation of the solvent from an NMR tube.

Hydroformylation catalysis

In a typical reaction, a CH_2Cl_2 solution of **1a** or **1b** (0.063 mmol) and 1-hexene (1.575 g, 18.8 mmol) were placed in a 50 cm^3 glass vessel and inserted into a steel autoclave. The autoclave was then evacuated and refilled three times with a 1:1 mixture of H_2 and CO. The pressure was then increased to 30 atm with H_2/CO and heated to 160 °C. Once the temperature had been reached, the pressure was increased to 60 atm and the reaction left for 3 h with agitation. The autoclave was allowed to cool to room temperature and then the pressure was slowly released and a sample removed for GC analysis.

X-Ray crystal structure determinations

Details of the structure determinations of compounds **1b**·1.5CH_2Cl_2·0.25C_5H_{12} and *cis*-**2**·3$CHCl_3$ are given in Table 4. All non-hydrogen atoms were assigned anisotropic displacement parameters and refined without positional constraints, except for some disordered atoms. In **1b**·1.5CH_2Cl_2·0.25C_5H_{12}, two *tert*-butyl groups [at C(118), and C(229)] and two dichloromethane solvate molecules were disordered across two sites. The pentane solvent molecule was disordered over a centre of inversion.

CCDC reference number 186/1837.

See http://www.rsc.org/suppdata/dt/a9/a908961f/ for crystallographic files in .cif format.

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