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Phenylphosphatrioxa-adamantanes: bulky, robust, electron-poor ligands that give very efficient rhodium(I) hydroformylation catalysts

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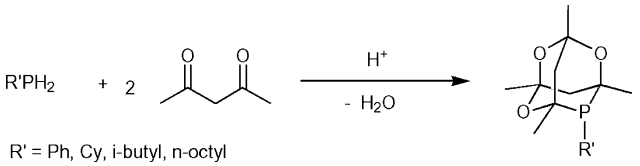
The cage phosphines 1,3,5,7-tetramethyl-6-phenyl-2,4,8-trioxa-6-phosphaadamantane (**1a**) and 1,3,5,7-tetraethyl-6-phenyl-2,4,8,trioxa-6-phosphaadamantane (**1b**) have been made by the acid catalysed addition of $PhPH_2$ to the appropriate β-diketones; the acid used (HCl, H_3PO_4 or H_2SO_4) and its concentration affect the rate and selectivity of these condensation reactions. Phosphines **1a** and **1b** react with $[PdCl_2(NCPh)_2]$ to form complexes *trans*-$[PdCl_2(\mathbf{1a})_2]$ (**2a**) and *trans*-$[PdCl_2(\mathbf{1b})_2]$ (**2b**) as mixtures of *rac* and *meso* diastereoisomers. The platinum(II) chemistry is more complicated and when **1a** or **1b** is added to $[PtCl_2(cod)]$, equilibrium mixtures of *trans*-$[PtCl_2L_2]$ and $[Pt_2Cl_4L_2]$ (L = **1a** or **1b**) are formed in CH_2Cl_2 solution. *Meso*/*rac* mixtures of *trans*-$[MCl(CO)(\mathbf{1a})_2]$ M = Ir (**6a**) or Rh (**7a**) are formed upon treatment of $MCl_3{\cdot}nH_2O$ with an excess of **1a** and the anionic cobalt complex $[NHEt_3][CoCl_3(\mathbf{1a})]$ (**9**) was isolated from the product formed by $CoCl_2{\cdot}6H_2O$ and **1a**. The ν_{CO} values from the IR spectra of **6a** and **7a** suggest that **1a** resembles a phosphonite in its bonding to Rh and Ir. Crystal structures of *meso*-**2a**, *meso*-**2b**, *rac*-**6a** and **9** are reported and in each case a small intracage C–P–C angle of *ca.* 94° is observed and this may partly explain the bonding characteristics of ligands **1a** and **1b**. The cone angles for **1a** and **1b** are similar and large (*ca.* 200°). Rhodium complexes of ligands **1a** and **1b** are hydroformylation catalysts with similarly high activity to catalysts derived from phosphites. The catalysts derived from **1a** and **1b** gave unusually low linear selectivity in the hydroformylation of hexenes. This feature has been further exploited in quaternary-selective hydroformylations of unsaturated esters; catalysts derived from **1a** give better yields and regioselectivities than any previously reported catalyst.

Introduction

The reaction of primary phosphines with acetylacetone to give phosphatrioxa-adamantanes (eqn. (1)) was first reported by Epstein and Buckler[1] in 1961.



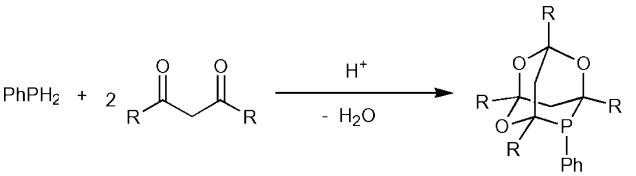
(1)

The coordination chemistry and potential catalytic applications of these unusual cage-phosphines have only recently been explored.[2–4] Here we report an improved synthesis of **1a** and the new cage phosphine **1b**, their coordination chemistry with palladium(II), platinum(II), cobalt(II), rhodium(I) and iridium(I), and the remarkably high turnovers in hydroformylation catalysis achieved with the rhodium complexes of **1a** and **1b**.

Results and discussion

Ligand synthesis

The ligands **1a** and **1b** were made by the route shown in eqn. (2) and the products were fully characterised (see Experimental). Under similar conditions, the reaction of $PhPH_2$ with 3,5-heptadione to give the new phosphine **1b** was much slower than the analogous reaction with 2,4-pentadione to give **1a**. This can be rationalised by considering the greater steric hindrance to nucleophilic attack by phenylphosphine offered by the ethyl groups in the 3,5-heptadione reaction compared with the methyls in the 2,4-pentadione reaction. The lower solubility of the more lipophilic 3,5-heptadione in the aqueous reaction medium may also contribute to its slower reaction with $PhPH_2$.

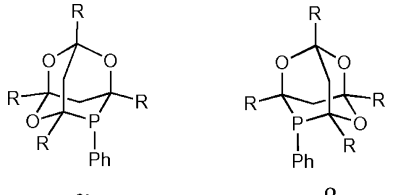


1a R = Me

1b R = Et

(2)

Phosphines **1a** and **1b** are racemic mixtures of enantiomers (labelled α and β) associated with the C_1 symmetry of the cages.



α β

It was found that the yields and purity of the products **1a** and **1b** were critically dependent on the nature and concentration of the acid catalyst. Thus for **1a**, the literature yield[1] of 49% was increased to 86% by increasing the molarity of the HCl used in the synthesis from 6 M to 12 M HCl (see Experimental); many by-products were observed if H_2SO_4 or H_3PO_4 were used. For the synthesis of **1b**, as expected, increasing the acid catalyst

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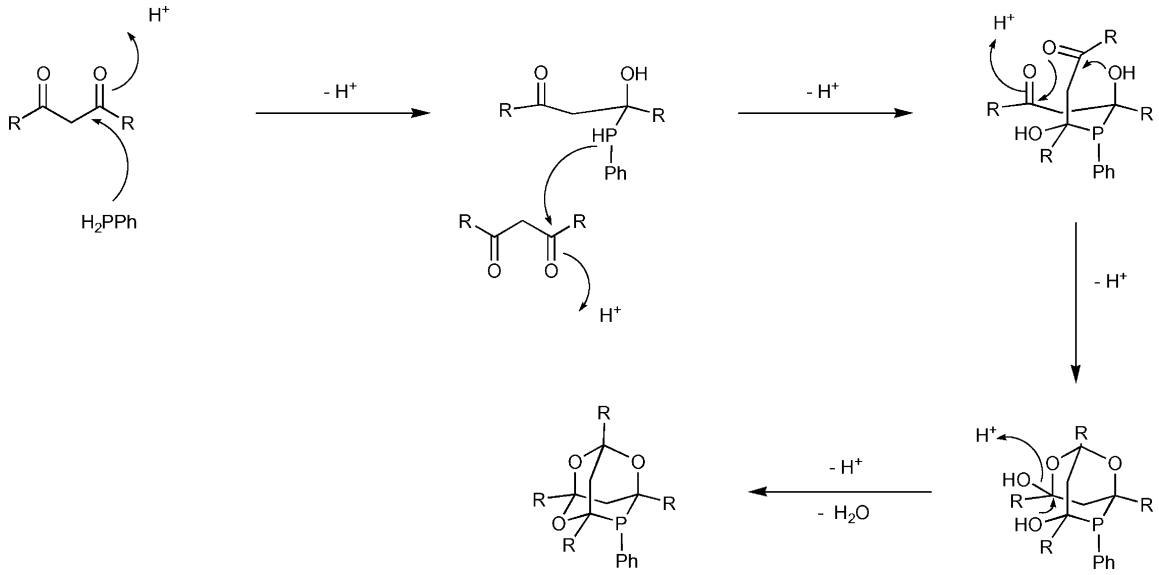


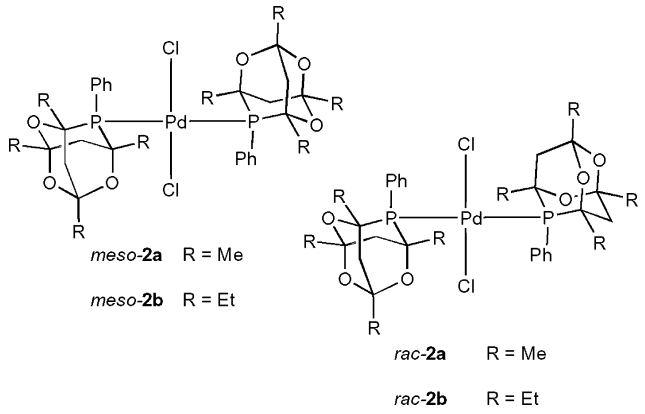
Scheme 1 Proposed mechanism for cage phosphine formation.

concentration increased the rate of consumption of $PhPH_2$ but surprisingly, the selectivity to the product **1b**, depended on the acid: HCl (44%) < H_3PO_4 (62%) < H_2SO_4 (90%). It is not obvious why the counterion has this effect on selectivity since ostensibly it has no role in the suggested mechanism[5] (Scheme 1). Perhaps ion-pairing is important in one or more of the intermediates. In the light of these results, the conditions for the synthesis of **1b** were optimised to give **1b** rapidly and in high yield (see Experimental).

Both phosphines **1a** and **1b** are very stable to air. For example, solid **1a** has been stored in air for 2 years without any sign of oxidation. Furthermore, a toluene solution of **1a** was refluxed in air for 4 h and no change was detected by ^{31}P NMR.

Palladium(II) and platinum(II) complexes

The reaction of 2 equiv. of **1a** or **1b** with $[PdCl_2(NCPh)_2]$ gave mononuclear complexes of the form $[PdCl_2(phosphine)_2]$ which have been fully characterised (see Experimental for the data). The ^{31}P NMR spectra of the products showed, in each case, two closely spaced singlets (*ca.* 1 : 1 ratio) which were assigned to the expected *meso* (αβ) and *rac* (αα/ββ) diastereoisomers of **2a** and **2b** shown below (only the αα enantiomer of the racemate is depicted).



meso-**2a** R = Me

meso-**2b** R = Et

rac-**2a** R = Me

rac-**2b** R = Et

Crystals of *meso*-**2a** (as its dichloromethane solvate) and *meso*-**2b** suitable for X-ray crystallography were obtained by slow diffusion of hexane into their CH_2Cl_2 solutions. The structures of *meso*-**2a** and *meso*-**2b** are shown in Figs. 1 and 2. The cage phosphines are in *trans* postions in both cases and the complexes both have exact C_i symmetry. The Pd–Cl and Pd–P distances in the two complexes are essentially the same (Pd–Cl

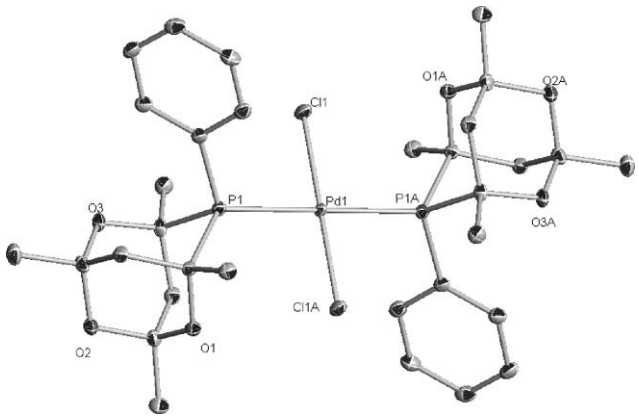


Fig. 1 Crystal structure of *meso*-**2a**. All hydrogen atoms are omitted for clarity. Atoms suffixed A are related by symmetry operation (−*x*, −*y*, −*z*) to those without suffix. Ellipsoids enclose 50% probability density.

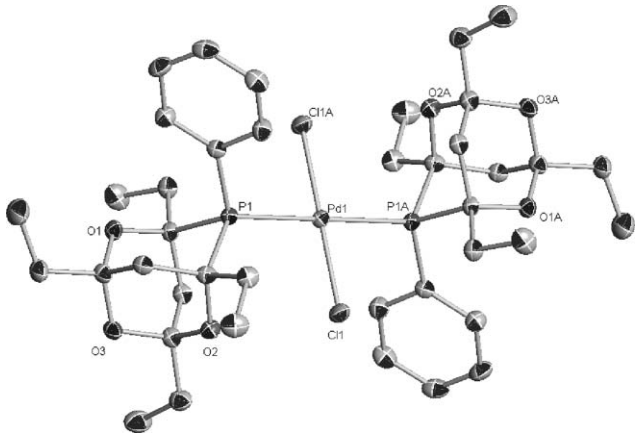
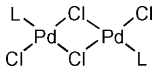


Fig. 2 Crystal structure of *meso*-**2b**. All hydrogen atoms are omitted for clarity. Atoms suffixed A are related by symmetry operation (−*x*, 2−*y*, 2−*z*) to those without suffix. Ellipsoids enclose 50% probability density.

2.293(1) and 2.297(1) Å; Pd–P 2.340(1) and 2.338(1) Å). As is usual in these cage phosphines[2,6] the intra-cage C–P–C angles (94.0(1) and 94.6(1)°) are small compared with C–P–C angles in unconstrained tertiary phosphines. The cone angles for the phosphine ligands **1a** and **1b** are essentially the same in **2a** and **2b** at 202 and 199° respectively, indicating that, at least in the

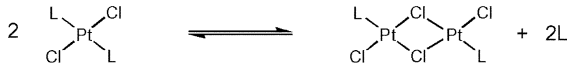
conformation present in the crystals of **2b**, the ethyls have no more steric influence than the methyls of **2a**.

The reaction of $[PdCl_2(NCPh)_2]$ with 1 equiv. of **1a** gave an orange solid, the main component of which was tentatively assigned the binuclear structure **3a** on the basis of the IR spectrum which showed bands for terminal and bridging Pd–Cl (see Experimental) and the ^{31}P NMR spectrum which showed two singlets for the predominant species (80%) assigned to *meso*/*rac*-**3a** (δ_P 26.9, 26.8). Two ^{31}P resonances would be predicted for the C_1-symmetric *meso*-**3a** (and the other *meso*-binuclear complexes described below) but only one was observed presumably because of accidental equivalence. Under similar conditions **1b** gave a similar mixture in solution, tentatively assigned to the analogues *meso*/*rac*-**3b** on the basis of the δ_P values (30.2, 30.3).



3a L = **1a**
3b L = **1b**

The reaction of **1a** with $[PtCl_2(cod)]$ was monitored by ^{31}P NMR spectroscopy. Addition of 2 equiv. of **1a** to $[PtCl_2(cod)]$ gave a mixture of species and the following were tentatively identified from their ^{31}P NMR parameters: *trans*-mononuclear **4a** as a *meso*/*rac* mixture (δ 0.8, $^1J_{PtP}$ 2692 Hz and δ 0.9, $^1J_{PtP}$ 2716 Hz) and binuclear **5a** (δ 11.5 $^1J_{PtP}$ 4550 Hz and δ 11.9 $^1J_{PtP}$ 4524) along with free ligand at δ −24.3, a broad signal, presumably because of ligand exchange. Addition of more **1a** to the **4a**/**5a** mixture produced more of the mononuclear **4a** and therefore the species are in equilibrium (eqn. (3)). A similar equilibrium mixture was detected by ^{31}P NMR spectroscopy upon addition of 2 equiv. of **1b** to $[PtCl_2(cod)]$: **4b** (δ 4.2, $^1J_{PtP}$ 2682 Hz and δ 3.9, $^1J_{PtP}$ 2674 Hz) and **5b** (δ 15.3, $^1J_{PtP}$ 4570 Hz and δ 14.7, $^1J_{PtP}$ 4531 Hz).



4a L = **1a** **5a** L = **1a**
4b L = **1b** **5b** L = **1b** (3)

These equilibria reflect the binding properties of the cage phosphines **1a** and **1b**. The formation of binuclear species $[Pt_2Cl_2(PR_3)_2]$ is typical of bulky phosphines. The similarity in the equilibrium constants for eqn. (3) (the ratio of the intensities of the ^{31}P NMR signals for **4a**/**5a** and **4b**/**5b** was *ca.* 1 in each case) and the similarity of the $^1J_{PtP}$ values is consistent with **1a** and **1b** having very similar stereoelectronic properties.

The chemistry of the more readily available ligand **1a** was studied in further detail.

Iridium(I), rhodium(I) and cobalt(II) complexes

The complexes *trans*-$[MCl(CO)(\mathbf{1a})_2]$ M = Ir (**6a**) or Rh (**7a**) as *meso*/*rac* mixtures were made by methods similar to those for their PPh_3 analogues[7] (see Experimental for details).

The crystal structure of *rac*-**6a** has been determined and is shown in Fig. 3. The cage phosphines are in *trans* positions and the complex has C_1 symmetry in the solid state. The Ir–C, Ir–Cl and Ir–P distances are of normal dimensions for a Vaska's compound analogue (Ir–C 1.817(4) Å, Ir–Cl 2.362(1) Å, Ir–P 2.328 and 2.318(1) Å). The intra-cage C–P–C angles are small (94.1(1) and 93.7(1)°). Cone angles for the phosphine ligands are again close to 200° (at 200 and 198°).

The ν_{CO} for **6a**, **7a** and analogues with other phosphorus(III) donors are given in Table 1 and it can be seen that the values for the cage phosphine **1a** most closely resembles the $PPh(OEt)_2$ analogue indicating that it is relatively electron-poor and the σ/π-bonding of **1a** to rhodium(I) or iridium(I) is similar to a phosphonite.

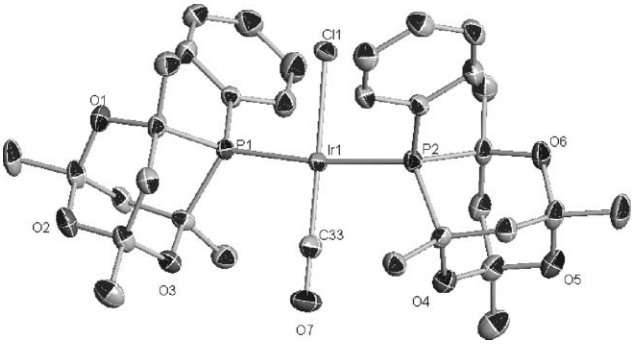


Fig. 3 Crystal structure of *rac*-**6a**. All hydrogen atoms are omitted for clarity. Ellipsoids enclose 50% probability density.

Table 1 ν_{CO} for $[MCl(CO)(PR_3)_2]$

M	L	ν_{CO}	Reference
Ir	PPh_3	1950	10
Ir	$PPh_2(OEt)$	1962	10
Ir	$PPh(OEt)_2$	1968	10
Ir	**1a**	1970	[a]
Ir	$P(OBu^n)_3$	1993	10
Rh	PPh_3	1965	11
Rh	**1a**	1986	[a]
Rh	$P(OPh)_3$	2016	12

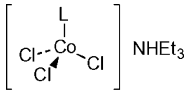
[a] IR spectra from this work, recorded as Nujol mulls.

The electron withdrawing effect of the cage can be traced to a combination of the electronegative O groups on the carbons α to the P and the small C–P–C angle[8] of *ca.* 90° detected in the solid state structures discussed here.

The hydroformylation catalysts described below were generated by mixing $[Rh(acac)(CO)_2]$ with an excess of ligands **1a** or **1b**. The reaction of $[Rh(acac)(CO)_2]$ with one equivalent of **1a** produced $[Rh(acac)(CO)(\mathbf{1a})]$ (**8a**) which was fully characterised (see Experimental). The position of ν_{CO} in this complex (1984 cm^{-1}) is higher than in the PPh_3 analogue (ν_{CO} = 1975 cm^{-1}),[9] consistent with the discussion above. The reaction of an excess of **1a** with complex **8a** in CH_2Cl_2 was monitored by ^{31}P NMR spectroscopy. Broad peaks were observed for **1a** and **8a** but there was no evidence for the formation of $[Rh(acac)(\mathbf{1a})_2]$.

Attempts to prepare the analogue of the well known hydroformylation precursors $[RhH(CO)(PR_3)_3]$ by hydride reduction of **7a** failed. Similarly treatment of a mixture of **8a** and two equivalents of ligand **1a** with syngas at room temperature produces many (>8) Rh–P containing species with complete consumption of **8a**.

$CoCl_2{\cdot}6H_2O$ was treated with an excess of **1a** in ethanol in the expectation of making a bis(phosphine) complex.[13] However the blue solid product which formed upon addition of NEt_3 was shown by X-ray crystallography to be the anionic cobalt(II) complex **9**.



9

The crystal structure of **9** was determined and is shown in Fig. 4. The metal anion has tetrahedral geometry at the Co(II) centre (P–Co–Cl angles in the range 102–108°; Cl–Co–Cl angles in the range 107–114°). The Co–Cl and Co–P distances are of normal dimensions for such a species (Co–Cl 2.24–2.28 Å; Co–P 2.408(1) Å). The intra-cage C–P–C angle is again small (94.4(1)°) and the cone angle for the phosphine ligand close to earlier values (at 196°). One chlorine ligand is hydrogen bonded to the cation (Cl···HN 2.37 Å, Co–Cl···H 97°).

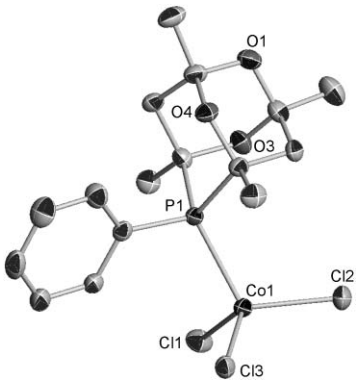


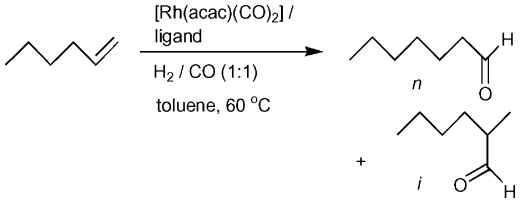
Fig. 4 Crystal structure of the anion in **9**. All hydrogen atoms are omitted for clarity. Ellipsoids enclose 50% probability density.

The formation of the monophosphine complex anion in **9** rather than a $[CoCl_2(PR_3)_2]$ species is perhaps due to the first row metal being unable to accommodate two bulky **1a** ligands in its coordination sphere.

Hydroformylation catalysis

Triphenylphosphine is an excellent ligand for hydroformylation catalysis as shown by the megaton industrial plants that use Rh–PPh_3 catalysts.[14] Bulky triarylphosphites have been shown to be even better ligands in terms of activity and selectivity.[15] However phosphites are prone to hydrolysis and reaction with the aldehydes produced by the hydroformylation.[14] There is considerable interest in combining the high activity of the phosphite based catalysts with the robust properties of the triphenylphosphine derived catalysts.[16] The cage phosphines **1a** and **2a** are attractive candidates as ligands for hydroformylation catalysis because they are inert to decomposition and stereoelectronically similar to a bulky phosphonites *vide supra*. Phosphonites have also been shown to provide highly active rhodium catalysts for hydroformylation.[17]

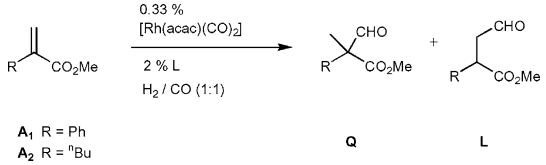
Initially rhodium catalysed hydroformylation of 1-hexene (eqn. (4)) under constant pressure conditions was investigated. The syngas uptake was monitored with time to allow comparison of the rates of hydroformylation using PPh_3, $P(OPh)_3$ and the cage phosphines **1a** and **1b**. The results given in Table 2 show that the cage phosphines give very much more active Rh catalysts for hydroformylation of 1-hexene than PPh_3. The turnover frequencies, which are not optimised, resemble those observed for a phosphite-based catalyst. ^{1}H NMR and GC analysis of the products obtained revealed that the reactions all gave high chemoselectivity to aldehydes. The n : i ratio of the aldehydes produced is unusually low. Van Leeuwen and co-workers reported similar findings using bulky phosphite derived Rh catalysts, and rationalised the high activity and low regioselectivity in terms of a mono-phosphite Rh complex, $[RhH(CO)_2(L)]$ being the active species.[12,13]



(4)

The main industrial interest in hydroformylation is in the selective synthesis of linear aldehydes which are important bulk chemicals. However, hydroformylation reactions that deliver branched products regioselectively are attracting increasing interest due to their potential applications in organic synthesis and fine chemical production.[18–20] We therefore screened 1-hexene and 3-hexene at higher temperatures. The normal preference for Rh phosphine catalysts to give predominantly linear products from terminal alkenes is reversed at high temperatures; the major products are the branched aldehydes, 2-methylhexanal and 2-ethylpentanal. 3-Hexene was chemoselectively hydroformylated to predominantly 2-methylhexanal and 2-ethylpentanal.

Clarke[19] has recently described the Rh/phosphite catalysed hydroformylation of acrylate esters which, under certain conditions, defies Keulemans' rule that states 'aldehydes are not produced at quaternary carbon centres'.[21] By variation of the temperature and pressure, linear and branched quaternary aldehydes were made. However, these acrylate esters were extremely unreactive substrates requiring the use of a phosphite based catalyst. From Table 3 the results for hydroformylation of acrylate esters (eqn. (5)) with catalyst derived from **1a** can be compared with the bulky phosphite used in the original study.



(5)

Ligand **1a** formed the most selective catalyst examined so far for this reaction, enabling extremely high regioselectiviy and good yields in the hydroformylation of methyl atropate. The hydroformylation of acrylate ester $\mathbf{A}_2$ was found to be problematic in the original study and some improvements in yield and selectivity were found using the Rh catalysts derived from **1a**.

Conclusion

The phospha-adamantanes **1a** and **1b** have been shown to be readily made and are very stable to air and water. From a study

Table 2 Influence of ligands on rate and selectivity of rhodium catalysed hydroformylation of hexenes[a]

Entry	Ligand	1-Hexene	2-Hexene	3-Hexene	Heptanal (n : i)	2-Methyl hexanal	2-Ethyl pentanal	Rate / (mol prod/mol cat) h^{-1}
1[b]	PPh_3	<1	<1	<1	74 (3.1)	24	<1	380
2	$P(OPh)_3$	<1	8	<1	66 (2.6)	25	<1	2 000
3	**1a**	<1	<1	<1	61 (1.6)	38	<1	1 700
4	**1b**		<1	<1	49 (1.0)	49	<1	2 200
5[c]	**1a**	1.4	1.6	<1	46 (0.9)	37	14	n.d.
6[c,d]	**1a**	<1	<1	<1	7 (0.1)	27	63	n.d.

[a] Reactions were carried out in a 100 mL stainless steel autoclave at constant pressure (20 bar) of syngas ($CO/H_2 = 1 : 1$) and constant temperature (60 °C). 0.2 mol% of pre-catalyst $[Rh(acac)(CO)_2]$ and 0.9% of ligand were dissolved in 5 mL of toluene to form catalyst solution in each case. Reactions were stopped after 3 h and products analysed. Rates were calculated at 50% conversion from the slope of syngas uptake *versus* time plots. These plots show that the reactions are essentially complete within ≈20 minutes. Conversion (given as %), GC yield and selectivity were measured using a GC equipped with a FID detector and are measured against biphenyl (20 mol%) added as an internal standard. Product identities and distributions were further confirmed by ^{1}H NMR integration and GCMS; n.d. = not determined. [b] Taken from ref. 16*d*. [c] These reactions were carried out at 110 °C and 10 bar syngas pressure. [d] Hex-3-ene was used as substrate.

Table 3 Hydroformylation of acrylate esters $\mathbf{A}_1$ and $\mathbf{A}_2$[a]

Entry	Alkene	Ligand[b]	Pressure/bar	Temp/°C	Time/h	% Conv.	% Hydrogenation	Q/L
1	$\mathbf{A}_1$	tbpp	35	45[c]	70	>98	13	13/1
2	$\mathbf{A}_1$	tbpp	12	100[c]	40	>98	13	1/12
3	$\mathbf{A}_1$	**1a**	10	100	40	90	30	1/28
4	$\mathbf{A}_1$	**1a**	50	45	70	>98	15	49/1
5	$\mathbf{A}_2$	$P(OPh)_3$	8	100[c]	20	49	<5	1/11
6	$\mathbf{A}_2$	$P(OPh)_3$	32	40[c]	40	15	n.d.	4/1
7	$\mathbf{A}_2$	tbpp	32	50	70	33	n.d.	2/1
8	$\mathbf{A}_2$	**1a**	50	50	66	61	0	7/1
9	$\mathbf{A}_2$	**1a**	32	40	40	25	n.d.	4/1
10	$\mathbf{A}_2$	**1a**	10	100	20	62	0	1/10

[a] Reactions were carried out in a 100 mL stainless steel autoclave under the conditions described in this table. Conversion, GC yield and selectivity were measured using a GC equipped with a FID detector and are measured against biphenyl (20 mol%) added as an internal standard; n.d. = not determined. Product identities and distributions were further confirmed by ^{1}H NMR integration and EI or CI mass spectrometry. [b] tbpp = tris(2,4-di-*t*-butylphenyl)phosphite. [c] Results taken from ref. 19.

of their coordination chemistry, it is concluded that they have the stereoelectronic properties of a bulky phosphonite. This is further supported by the very high hydroformylation catalytic activity of their rhodium complexes. This high activity coupled with their robustness makes phospha-adamantanes potentially useful ligands for hydroformylation catalysis.

Experimental

General

Unless otherwise stated, all work was carried out under a dry nitrogen atmosphere, using standard Schlenk line techniques. Dry N_2-saturated solvents were collected from a Grubbs system[22] in flame and vacuum dried glassware. NMR spectra were measured on a Jeol Eclipse 300, Jeol Eclipse 400 or Jeol GX 400. Unless otherwise stated ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded at 300, 100, and 121 MHz, respectively, at +23 °C. Mass spectra were recorded on a MD800. Infrared spectra were recorded on Perkin-Elmer Spectrum 1 Spectrometer as Nujol mulls between polythene plates. Elemental analyses were carried out by the Microanalytical Laboratory of the School of Chemistry, University of Bristol.

Preparation of 1,3,5,7-tetramethyl-6-phenyl-2,4,8-trioxa-6-phosphaadamantane (1a)

A solution of 2,4-pentanedione (2.6 cm^3, 25.1 mmol) in N_2-saturated aqueous HCl (10 cm^3, 12 M) was stirred for *ca.* 1 h. To this solution, phenylphosphine (**CAUTION**: highly flammable) (1.0 cm^3, 9.1 mmol) was added dropwise over 5 min. After 4 d water (10 cm^3) was added to the solution and a white precipitate formed. The solid was filtered off under reduced pressure and washed with water (2 × 10 cm^3) to give ^{Me}CgPPh (2.314 g, 86%). Elemental analysis, found (calc.): C 65.7 (65.7), H 7.6 (7.2). ^{1}H NMR ($CDCl_3$) δ_H 7.78–7.86 (m, 2 H, ArH), 7.26–7.39 (m, 3 H, ArH), 1.74–2.11 (m, 4 H, CH_2), 1.42 and 1.43 (s, 3 H, CH_3), 1.25 and 1.51 (d, 3 H, CH_3, J_{PH} 13 Hz). ^{31}P NMR ($CDCl_3$): δ_P −23.6 (s). ^{13}C NMR ($CDCl_3$): δ_C 133.7–135.2 (m, PC_6H_5), 128.2–129.4 (m, PC_6H_5), 96.8 (s, $OCCH_3$), 96.1 (s, $OCCH_3$), 73.5 (s, $PCCH_3$), 73.3 (s, $PCCH_3$), 73.1 (s, $PCCH_3$), 73.0 (s, $PCCH_3$), 45.4 (d, $^2J_{PC}$ = 18 Hz, $PCCH_2$), 36.3 (s, $PCCH_2$), 27.9 (d, $^2J_{PC}$ = 21 Hz, $PCCH_2$), 27.5 (s, $PCCH_3$), 27.3 (s, $PCCH_3$), 26.9 (s, $OCCH_3$), 26.7 (s, $OCCH_3$). EI mass spectrum: *m*/*z* 292 (M^+).

Synthesis of 1,3,5,7-tetraethyl-6-phenyl-2,4,8,trioxa-6-phosphaadamantane (1b)

A solution of 3,5-heptanedione (2.6 cm^3, 1.5 g, 11.4 mmol) in N_2-saturated aqueous H_2SO_4 (10 cm^3, 12 M) was stirred for *ca.* 2 h. To this solution, phenylphosphine (**CAUTION**: highly flammable) (0.5 cm^3, 460 mg, 4.6 mmol) was added dropwise over 5 min. The reaction mixture was stirred for 5 h, after which time yellow oil drops had formed. The solution was neutralized with N_2-saturated NaOH (80 cm^3, 2.5 M) until pH = 7 and then $CHCl_3$ (30 cm^3) was added to give two layers. The lower organic layer was separated and the aqueous phase was washed with $CHCl_3$ (3 × 20 cm^3), the extracts combined and the solvent was removed *in vacuo*. The crude product was passed through a (30 cm × 2 cm) silica column under N_2 using CH_2Cl_2 as eluent (250 cm^3), and the solvent was removed *in vacuo*. The product was collected to afford ^{Et}CgPPh (1.5 g, 92%) as a viscous white oil. ^{1}H NMR ($CDCl_3$): δ_H 7.73–7.81 (m, 2 H, ArH), 7.20–7.29 (m, 3 H, ArH), 1.65–1.96 (m, 12 H, CH_2), 0.8–1.05 (m, 12 H, CH_2). ^{13}C NMR ($CDCl_3$): δ_C 134.5–135.7 (m, PC_6H_5), 128.1–129.4 (m, PC_6H_5), 97.9 (s, $OCCH_2$), 97.0 (m, $OCCH_2$), 77.0 (s, $PCCH_2$), 76.7 (s, $PCCH_2$), 75.7 (s, $PCCH_2$), 75.6 (s, $PCCH_2$), 31.9–34.3 (m, CH_2CH_3), 6.4–7.2 (m, CH_2CH_3). ^{31}P NMR ($CDCl_3$): δ_P −30.7 (s). EI mass spectrum: *m*/*z* 349 ($M^+ + H$).

Synthesis of *trans*-[$PdCl_2$(1a)$_2$] (2a)

To a solution of [$PdCl_2(NCPh)_2$] (39.5 mg, 0.103 mmol) in CH_2Cl_2 (2 cm^3) was added **1a** (60 mg, 0.205 mmol) in CH_2Cl_2 (2 cm^3) and left overnight. A yellow solid formed (45 mg, 0.059 mmol, 57%) which was filtered off in air and dried *in vacuo*. Elemental analysis, found (calc.): C 50.5 (50.4), H 5.8 (5.6). IR *ν*(Pd–Cl): 357 cm^{-1}. ^{31}P NMR ($CDCl_3$): δ_P 7.5 (s). This compound was also characterised by X-ray crystallography.

Synthesis of *trans*-[$PdCl_2$(1b)$_2$] (2b)

To a solution of [$PdCl_2(NCPh)_2$] (41.0 mg, 0.11 mmol) in CH_2Cl_2 (2 cm^3) was added **1b** (75 mg, 0.216 mmol) in CH_2Cl_2 (2 cm^3). The pale yellow solution was stirred for 2 d, after which time a yellow precipitate was formed. The solvent was removed *in vacuo* leaving a yellow solid (65 mg, 70%). Elemental analysis, found (calc.): C 55.9 (55.0), H 7.5 (6.7). IR *ν*(Pd–Cl): 359 cm^{-1}. ^{31}P NMR ($CDCl_3$): δ_P 9.7 (s). *m*/*z* (FAB) 837 ($M - Cl^+$), 802 ($M - 2Cl^+$). This compound was also characterised by X-ray crystallography.

Reactions of [$PdCl_2(NCPh)_2$] with one equivalent of 1a or 1b

To a solution of [$PdCl_2(NCPh)_2$] (79 mg, 0.206 mmol) in CH_2Cl_2 (2 cm^3) was added **1a** (60 mg, 0.205 mmol) in CH_2Cl_2 (2 cm^3) and left overnight. An orange solid formed (38 mg) which was filtered off in air and dried *in vacuo*. Elemental analysis, found (calc. for {$PdCl_2$(**1a**)}$_n$): C 40.1 (40.9), H 4.4 (4.5). IR *ν*(Pd–Cl): 357, 302, 290, 269 cm^{-1}. ^{31}P NMR ($CDCl_3$): δ_P 26.9 (s), 26.8 (s), 25.6 (s), 25.2 (s). The reaction between [$PdCl_2(NCPh)_2$] and **1b** was carried out similarly but the product remained in solution

Table 4 Crystal and refinement data for *meso*-**2a**·CH_2Cl_2, *meso*-**2b**, *rac*-**6a** and **9**

Compound	*meso*-**2a**·CH_2Cl_2	*meso*-**2b**	*rac*-**6a**	**9**
Formula	$C_{34}H_{46}Cl_6O_6P_2Pd$	$C_{40}H_{58}Cl_2O_6P_2Pd$	$C_{33}H_{42}ClIrO_7P_2$	$C_{22}H_{37}Cl_3CoNO_3P$
Formula weight	931.75	874.10	840.26	559.78
Crystal system	Triclinic	Triclinic	Triclinic	Monoclinic
Space group (no.)	$P\bar{1}$ (2)	$P\bar{1}$ (2)	$P\bar{1}$ (2)	$P2_1/c$(14)
a/Å	7.6097(15)	8.6852(13)	8.4760(11)	17.914(3)
b/Å	10.758(2)	9.8884(14)	13.0531(14)	11.206(2)
c/Å	12.984(3)	11.9403(17)	16.115(2)	13.4602(19)
α/°	90.03(3)	96.531(2)	93.375(11)	90.00
β/°	103.56(3)	98.137(2)	102.595(12)	98.157(11)
γ/°	108.26(3)	94.415(2)	100.232(11)	90.00
V/Å^3	978.1(4)	1004.0(3)	1703.5(4)	2674.8(7)
Z	1	1	2	4
μ/mm^{-1}	1.008	0.720	4.136	1.024
Unique data	4471	4576	7703	6104
R_{int}	0.0308	0.0353	0.0346	0.0398
Final R_1 [$I > 2\sigma(I)$]	0.0334	0.0362	0.0281	0.0297

and was characterised by ^{31}P NMR (CH_2Cl_2) δ_P 30.2 (s), 30.3 (s) 35.3 (br).

Reactions of [$PtCl_2$(cod)] with 1a or 1b

The phosphine **1a** (30 mg, 0.102 mmol) was added to a solution of [$PtCl_2$(cod)] (19 mg, 0.051) in CH_2Cl_2 (2 cm^3) and the mixture stirred. The reaction was monitored over 24 h by ^{31}P NMR spectroscopy (see Results and discussion for the data). The same procedure was carried out for the reaction of **1b** with [$PtCl_2$(cod)].

Preparation of *trans*-[$IrCl(CO)(1a)_2$] (6a)

To a solution of $IrCl_3 \cdot nH_2O$ (0.072g, assay 53.1% Ir) in dmf (10 cm^3) was added **1a** (0.29 g, moles). The solution was heated at reflux temperature for 20 h and then reduced to 3 cm^3 under vacuum. The solution was cooled in ice to initiate the precipitation of a yellow solid. The solid was collected and dried under vacuum. Elemental analysis, found (calc.): C 47.5 (47.2), H 5.0 (5.0). IR (CH_2Cl_2): ν_{CO} 1973 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ_H 1.37–2.04 (m, 32 H,Cg), 7.29–7.43 (m, 6 H, Ph), 7.97–8.17 (m, 4 H, Ph). ^{31}P NMR ($CDCl_3$): δ_P 23.32 (s), 23.15 (s). IR (CH_2Cl_2) ν_{CO}: 1973 cm^{-1}.

Preparation of *trans*-[$RhCl(CO)(1a)_2$] (7a)

Method A. The rhodium analogue of Vaska's compound can be prepared by warming $RhCl_3 \cdot 3H_2O$ and an excess of phosphine in ethanol and formaldehyde. The solution was cooled in ice to initiate the precipitation of a yellow solid. The solid was collected and dried under vacuum. Elemental analysis, found (calc.): C 53.0 (52.8), H 5.6 (5.6). ^{1}H NMR ($CDCl_3$): δ_H 1.36–1.92 (m, 32 H, Cg), 7.29–7.41 (m, 6 H, *m*,*p*-Ph), 7.94–8.05 (m, 4 H, *o*-Ph). ^{31}P NMR ($CDCl_3$): δ_P 26.7 (d, $J_{Rh-P} = 133$ Hz), 26.8 (d, $J_{Rh-P} = 134$ Hz). IR ν_{CO}: 1986 cm^{-1}. MS (FAB) m/z 750 (M); 722 (M − CO); 715 (M − Cl).

Method B. [$Rh_2Cl_2(CO)_4$] (40 mg, 0.102 mmol) dissolved in CH_2Cl_2 (2 cm^3) was treated with a solution of **1a** (60 mg, 0.205 mmol) in CH_2Cl_2. A ^{31}P NMR spectrum recorded at this stage showed the formation of what is assigned as the chloride bridged dimer formed by replacement of two CO ligands from [$Rh_2Cl_2(CO)_4$] ($\delta_P = 46.6$, $^1J_{Rh-P} = 184$ Hz). Further addition of **1a** (71 mg, 0.243 mmol) in CH_2Cl_2 (2 cm^3) generates compound **7a**. This compound can be isolated by concentration of the solution and collecting the pale yellow precipitate (0.106 g, 69%). It shows identical spectroscopic data as that described above.

Preparation of [Rh(acac)(CO)(1a)] (8a)

To a Schlenk tube containing [Rh(acac)$(CO)_2$] (50 mg, 0.194 mmol) and **1a** (56 mg, 0.194 mmol) was added CH_2Cl_2. After stirring the mixture for 1 h, the solution was filtered through a pipette containing cotton wool and alumina (0.3 cm × 0.6 cm). The solvent was removed *in vacuo* to give analytically pure **8a** in quantitative yield. Elemental analysis, found (calc.): C 50.4 (50.6), H 5.4 (5.2). ^{1}H NMR ($CDCl_3$): δ_H 7.80–7.95 (m, 2 H, ArH), 7.10–7.25 (m, 3 H, ArH), 1.55–1.9 (m, 12 H, CH_2), 1.05–1.25 (m, 12 H, CH_2). ^{31}P NMR ($CDCl_3$): $\delta_P = 46.3$ ($^1J_{RhP} = 184$ Hz). IR (Nujol) ν_{CO}: 1983 cm^{-1}. MS (FAB) m/z 522 (M); 494 (M − CO).

Formation of [$NHEt_3$][$CoCl_3$(1a)] (9)

$CoCl_2 \cdot 6H_2O$ (34 mg, 0.14 mmol) and **1a** (86 mg, 0.30 mmol) were dissolved in ethanol (10 cm^3) and the mixture heated for 4 d at 60 °C under N_2. The volume of the resulting blue solution was reduced to 2 cm^3 at reduced pressure and then cooled in ice. The precipitated unreacted **1a** was filtered off and the filtrate reduced to dryness to give a blue solid which analysed for H[$CoCl_3$(**1a**)]·HCl (40 mg, 50%); found (calc.): C 38.4 (38.8), H 4.7 (4.7). The product was dissolved in Et_2O and a few drops of Et_3N were added. Dark blue crystals of **9** slowly formed.

Typical procedure for hydroformylation of 1-hexene

[Rh(acac)$(CO)_2$] (5 mg, 0.019 mmol), and biphenyl (0.468 g, 3.038 mmol) were added to a solution of **1b** (30 mg, 0.086 mmol) in dry toluene (5 cm^3) and loaded into the autoclave, which was then flushed with syngas and pressurised to 10 bar. After 1 h at 60 °C, the 1-hexene (1.2 cm^3, 0.80 g, 9.5 mmol) was injected and the autoclave brought up to 20 bar syngas pressure. The reaction was monitored for 2.5 h by following the syngas uptake from the ballast vessel. After 3 h, the autoclave was allowed to cool and the reaction solution analysed by ^{1}H NMR and GC. ^{1}H NMR ($CDCl_3$): δ_H 9.7 (n, 62%), 9.6 (i, 38%). The reactions were diluted with toluene (note that the starting materials elute from the GC before toluene) and analysed by GC equipped with a FID. The yields and selectivities were calculated using biphenyl as internal standard. Authentic samples of all possible products were calibrated against biphenyl in separate experiments. Some reactions were also analysed by GC-MS to further authenticate all the possible products.

Typical procedure for hydroformylation of acrylate esters

These were conducted in a stainless steel autoclave sealed at the pressures given in Table 3. The identities of the products were established by comparison of retention times and mass spectra with authentic samples that were prepared in the previous

work.[19] A solution of [Rh(acac)(CO)$_2$] (5.0 mg, 0.019 mmol), ligand (0.011 mmol) biphenyl (0.174 g, 1.126 mmol) and alkene (5.63 mmol) in toluene (5 cm^3), were added to the autoclave which was then flushed with syngas. The autoclave was then pressurised, sealed and stirred at the desired temperature for the appropriate time (see Table 3). The reaction solutions were then analysed by GC. The quaternary products all had shorter retention times than the linear compounds. Conversions to each product were calculated by comparing peak integrations using the response ratios between biphenyl (internal standard) and authentic samples of each constituent. The products were then further characterised by ^{1}H NMR and mass spectrometry.

X-Ray crystal structure analyses of *meso*-2a·CH_2Cl_2, *meso*-2b, *rac*-6a and 9

X-Ray diffraction experiments on *meso*-**2a**·CH_2Cl_2, *meso*-**2b**, *rac*-**6a** and **9** were carried out at 173 K on Bruker CCD diffractometers using Mo-Kα X-radiation (λ = 0.71073 Å). Crystal and refinement data are given in Table 4 below. Absorption corrections were based on equivalent reflections and structures refined against all F_0^2 data with hydrogen atoms riding in calculated positions. Final difference maps showed no features of chemical significance.

CCDC reference numbers 257575–257578 for *rac*-**6a**, *meso*-**2a**·CH_2Cl_2, *meso*-**2b**, and **9**, respectively.

See http://www.rsc.org/suppdata/dt/b4/b418259f/ for crystallographic data in CIF or other electronic format.

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