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The electron-poor phosphines $P\{C_6H_3(CF_3)_2\text{-}3,5\}_3$ and $P(C_6F_5)_3$ do not mimic phosphites as ligands for hydroformylation. A comparison of the coordination chemistry of $P\{C_6H_3(CF_3)_2\text{-}3,5\}_3$ and $P(C_6F_5)_3$ and the unexpectedly low hydroformylation activity of their rhodium complexes

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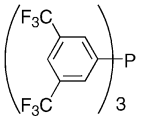
The fluoroaryl phosphines $P\{C_6H_3(CF_3)_2\text{-}3,5\}_3$ ($\mathbf{L_a}$) and $P(C_6F_5)_3$ ($\mathbf{L_b}$) form the complexes *trans*-$[MCl_2(\mathbf{L_a})_2]$ and *trans*-$[MCl_2(\mathbf{L_b})_2]$ (M = Pd or Pt) which have been isolated and fully characterised. ^{31}P NMR studies of competition experiments show that the stability of *trans*-$[PdCl_2L_2]$ is in the order $L = \mathbf{L_b} < \mathbf{L_a} < PPh_3$. The crystal structure of *trans*-$[PtCl_2(\mathbf{L_a})_2]$ is reported and reveals that the Pt–P bond lengths in *trans*-$[PtCl_2L_2]$ are in the order $L = \mathbf{L_b} < \mathbf{L_a} < PPh_3$. The equilibria established when $[Pt(norbornene)_3]$ is treated with $\mathbf{L_a}$ or $\mathbf{L_b}$ are investigated by ^{31}P and ^{195}Pt NMR spectroscopy and the species $[PtL_n(norbornene)_{3-n}]$ (n = 1–3) identified. Ligands $\mathbf{L_a}$ and $\mathbf{L_b}$ appear to have similar affinities for platinum(0). The complexes *trans*-$[MCl(CO)(\mathbf{L_a})_2]$ and *trans*-$[MCl(CO)(\mathbf{L_b})_2]$ (M = Rh or Ir) have been synthesised and fully characterised; the values of ν_{CO} are comparable with those for analogous phosphite complexes. The ligands $\mathbf{L_a}$, $\mathbf{L_b}$, $P(C_6H_2F_3\text{-}3,4,5)_3$ ($\mathbf{L_c}$), $P\{C_6H_4(CF_3)\text{-}2\}_3$ ($\mathbf{L_d}$), PPh_3 and $P(OPh)_3$ have been tested in rhodium-catalysed hydroformylation of 1-hexene and $\mathbf{L_a}$, $\mathbf{L_b}$, and PPh_3 have been tested in rhodium-catalysed hydroformylation of 4-methoxystyrene. Ligands $\mathbf{L_a}$, and $\mathbf{L_b}$, have been shown to be stable under the hydroformylation catalysis conditions. For the 1-hexene reaction, the activity and selectivity for $\mathbf{L_a}$ and $\mathbf{L_c}$ are very similar to the PPh_3 catalyst (TOF *ca.* 400 h^{-1}; *n* : *iso* 2.5–3.0) but for the sterically demanding $\mathbf{L_b}$ and $\mathbf{L_d}$ the activity and selectivity was much lower than with PPh_3 (TOF *ca.* 15, *n* : *iso* ratio 0.6). Thus, the yield of heptanals obtained with the catalyst derived from $\mathbf{L_a}$ is 94% while under the same conditions with $\mathbf{L_b}$ only 6%. The TOF for the $\mathbf{L_a}$/Rh catalyst was 5 times lower than for the $P(OPh)_3$/Rh catalyst despite the superficially similar ligand electronic characteristics for $\mathbf{L_a}$ and $P(OPh)_3$.

Introduction

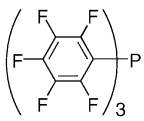
The applications of Wilkinson's $[RhH(CO)(PPh_3)_3]$ hydroformylation catalyst[1] in synthesis has been one of the most impressive successes of homogeneous catalysis over the last 30 years.[2] Rhodium-phosphite hydroformylation catalysts are generally more active[3–6] than their phosphine analogues and very bulky phosphites have found industrial application.[2] However, one limitation of the applications of phosphite ligands is the kinetic lability of the P–O bonds which make them susceptible to hydrolysis[7] and therefore robust ligands that may mimic phosphites would be useful.[8] Fluoroarylphosphines are attractive in this regard because they are ostensibly similar donors to phosphites[9] and contain relatively inert P–C bonds.

It is well established that electron-withdrawing groups on arylphosphines increase the activity of the derived rhodium hydroformylation catalysts.[10–13] For example a fluoroaryl derivative of bisbi has been shown[13] to give a hydroformylation catalyst that is five times more active and even more selective (*n* : *iso* up to 123 : 1) than the parent bisbi system. Hope and co-workers have reported[14] very active rhodium catalysts from *para*-substituted fluoroarylphosphines that can be used in fluorous biphasic systems or supercritical CO_2 though recently, Erkey and Palo[15] were unable to detect coordination of $P(C_6F_5)_3$ to rhodium in supercritical CO_2.

According to their Tolman electronic parameters, the electron-poor phosphines $P\{C_6H_4(CF_3)_2\text{-}3,5\}_3$, ($\mathbf{L_a}$) and $P(C_6F_5)_3$, ($\mathbf{L_b}$) would be expected to have donor properties similar to phosphites.[16] Moreover $\mathbf{L_b}$ has a cone angle comparable with the bulkiest phosphites[16] and therefore it was of interest to investigate the potential of these commercially available ligands in hydroformylation catalysis. In this paper we report that rhodium complexes of $\mathbf{L_a}$ and $\mathbf{L_b}$ have modest hydroformylation catalytic activity and relate this to their coordination chemistry.



$\mathbf{L_a}$



$\mathbf{L_b}$

Results and discussion

Co-ordination chemistry of $P\{C_6H_4(CF_3)_2\text{-}3,5\}_3$ and $P(C_6F_5)_3$

Complexes of $\mathbf{L_b}$ with late transition metals were first reported by Kemmitt *et al.*[17] but the analogues with $\mathbf{L_a}$ have not been previously described.

Platinum and palladium. Treatment of $[PtCl_2(SMe_2)_2]$ or $[PtCl_2(cod)]$ (cod = 1,5-cyclooctadiene) with $\mathbf{L_a}$ gave *trans*-$[PtCl_2(\mathbf{L_a})_2]$ (**1a**) which has been fully characterised (see Experimental) and its crystal structure has been determined (see below). The formation of the *trans* isomer **1a** reflects the steric bulk of $\mathbf{L_a}$ ($\theta = 160°$) since the reaction of $[PtCl_2(cod)]$ with PPh_3

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(θ = 145°) under similar conditions yields *cis*-[$PtCl_2(PPh_3)_2$] exclusively.

Under the mild conditions used to make **1a** above, [$PtCl_2(SMe_2)_2$] did not react with L_b; however, when a mixture of [$PtCl_2(SMe_2)_2$] and L_b was refluxed in toluene for 6 days, two platinum-containing species in a 1 : 1 ratio along with free L_b were detected by ^{31}P NMR spectroscopy. One of the products was identified as the known[18] complex *trans*-[$PtCl_2(L_b)_2$] (**1b**) from its ^{31}P NMR data and the triplet in the ^{195}Pt NMR spectrum. The doublet ^{195}Pt NMR signal observed for the second product shows that it has one coordinated phosphine and therefore could be [$Pt_2(\mu\text{-}Cl)_2Cl_2(L_b)_2$] or [$PtCl_2(SMe_2)(L_b)$] but was not further characterised (see Experimental for the data).

1a $PAr_3 = L_a$ **2a** $PAr_3 = L_a$

1b $PAr_3 = L_b$ **2b** $PAr_3 = L_b$

The palladium analogues **2a** and **2b** were prepared from [$PdCl_2(NCPh)_2$] and have been fully characterised; complex **2a** has been previously reported.[17] In order to probe the relative affinities of L_a, L_b and PPh_3 for palladium(II), the reactions shown in Scheme 1 were monitored by ^{31}P NMR spectroscopy. Complex **2b** was treated with 2 equivalents of L_a in $CDCl_3$ and initially, the intermediate mixed ligand complex **2ab** was observed, identified from the characteristic AX pattern with chemical shifts close to the symmetrical analogues **2a** and **2b** (see Experimental for data) and a very large ^2J(PP) of 641 Hz consistent with inequivalent *trans*-PR_3 ligands. After 1 h, no further changes in the spectra were observed and the only species detected were **2a** and L_b. Treatment of the mixture of **2a** and L_b with 2 equivalents of PPh_3 gave, within 10 min, exclusively [$PdCl_2(PPh_3)_2$] (as the *trans* isomer predominantly) with free L_a and L_b.

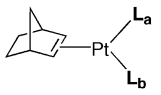
Thus, under these conditions, the order of affinity for palladium(II) is unambiguously established as $L_b < L_a < PPh_3$ which is the order of increasing ligand σ-donor strength. It is also the order of decreasing ligand bulk though it seems reasonable to assume that steric considerations would be less important in these *trans* complexes.

A mixture of platinum(0) species are formed upon addition of L_a or L_b to [Pt(norbornene)$_3$] which have been unambiguously identified in solution by ^{31}P and ^{195}Pt NMR spectroscopy (see Experimental for data). Thus when 1–3 equivalents of L_a was added to a CH_2Cl_2 solution of [Pt(norbornene)$_3$], mixtures containing **3a, 4a, 5a** and L_a were formed in varying proportions indicating that the equilibria shown in Scheme 2 were present.

The structures of **3a, 4a** and **5a** were assigned on the basis of the doublet, triplet or quartet observed in the ^{195}Pt NMR spectra. Addition of a large excess of L_a did not give any new platinum-containing species such as [$Pt(L_a)_4$], consistent with the large steric bulk of L_a.[19] Under similar conditions using L_b, complexes **3b** and **4b** were identified by ^{195}Pt NMR spectroscopy but no evidence was found for **5b** even in the presence of a large excess of ligand L_b. None of these platinum(0) species were isolated in pure form but solids containing predominantly **3b** or **4b** were obtained, as shown by ^{31}P and ^{195}Pt NMR spectroscopy.

The values of ^1J(PtP) for the platinum complexes **3–5a,b** and their PPh_3 analogues are in the order $PPh_3 < L_a < L_b$ which is in agreement with the relationship between ^1J(PtP) and the electron richness of phosphorus(III) ligands on platinum(0).[20]

From the fact that **5a** readily formed while **5b** was not observed, it might be concluded that L_a has a greater affinity for platinum(0) than L_b. However, when 2 equivalents of L_a were added to a toluene solution containing a mixture of **3b** and **4b**, the main species present in the complicated mixture produced was identified as the mixed species **4ab** from the ^{31}P NMR data: $\delta(P_a)$ 37.2 {$^1J(PtP_a)$ 3928 Hz, $^2J(P_aP_b)$ 82 Hz} and $\delta(P_b)$ 20.8 {$^1J(PtP_b)$ not resolved, $^2J(P_aP_b)$ 82}. This suggests that any difference in affinity between L_a and L_b for platinum(0) is small which contrasts with the clear distinction for palladium(II) noted above. The lack of evidence for the formation of **5b** is likely a consequence of the large bulk of L_b (θ = 184°).



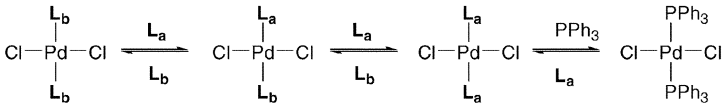
4ab

X-Ray crystal structure of *trans*-[$PtCl_2(L_a)_2$] (1a). The crystal structure of *trans*-[$PtCl_2\{P(C_6H_3(CF_3)_2\text{-}3,5)_2\}_2$] (**1a**) was determined (Fig. 1). Complex **1a** crystallises in space group $P\bar{1}$ with the platinum atom on a centre of inversion consistent with the *trans* configuration of the complex. Selected bond lengths and angles are given in Table 1. The mean P–C bond lengths (1.823(4) Å in **1a**) are close to those reported[21] in *trans*-[$PtCl_2(PPh_3)_2$] (1.820(2) Å). The C–P–C angles range from 103.49(11)° to

Table 1 Selected bond lengths (Å) and angles (°) for (**1a**)[a]

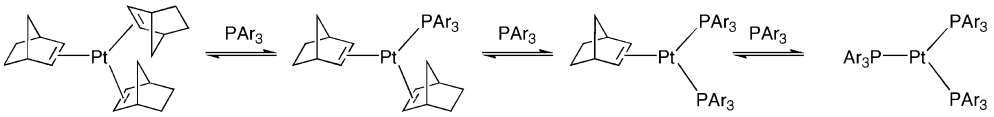
Pt(1)–P(1)	2.3017(8)
Pt(1)–Cl(1)	2.3079(7)
Cl(1)–Pt(1)–P(1)	88.49(3)
Cl(1A)–Pt(1)–P(1)	91.51(3)
P(1A)–Pt(1)–Cl(1)	180.0(2)

[a] Symmetry transformation for 1A atoms $-x, -y, -z$.



2b **2ab** **2a**

Scheme 1



3a $PAr_3 = L_a$ **4a** $PAr_3 = L_a$ **5a** $PAr_3 = L_a$

3b $PAr_3 = L_b$ **4b** $PAr_3 = L_b$ **5b** $PAr_3 = L_b$

Scheme 2

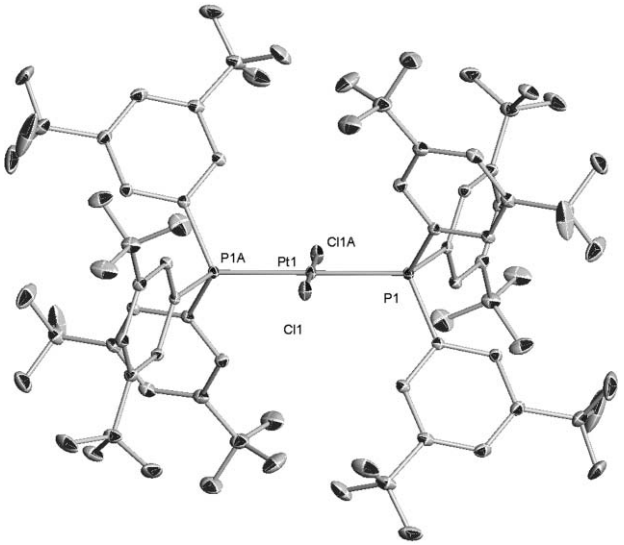
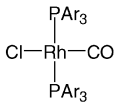


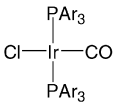
Fig. 1 Structure of *trans*-[$PtCl_2(\mathbf{L}_a)_2$] (**1a**). Hydrogen atoms have been omitted for clarity.

105.79(11)°. The arrangement of the aryl groups with respect to the PtP_2Cl_2 plane can be represented in terms of the three Cl–Pt–P–C*ipso* torsion angles [71.3°, −168.4° and −49.5°] which shows that one of the aryl groups is almost eclipsed with respect to the chlorine atoms.

The Pt–P bond length in **1a** of 2.3017(8) is longer than in **1b** (2.280(1) Å)[22] and shorter than in *trans*-[$PtCl_2(PPh_3)_2$] (2.319(3), 2.316(3) Å).[21] The decrease in Pt–P bond lengths in *trans*-[$PtCl_2(L)_2$] correlates well with increasing ^1J(PtP): L = $\mathbf{L}_b$ (3145 Hz) < $\mathbf{L}_a$ (2798 Hz) < PPh_3 (2638 Hz). Short Pt–PR_3 bond lengths and large ^1J(PtP) values are normally associated with strong Pt–P σ–bonding[23] but the electronegative substituents in $\mathbf{L}_a$ and $\mathbf{L}_b$ would surely make these poorer σ–donors than PPh_3. The shorter Pt–P bond lengths are most likely a result of the smaller covalent P radius in the electron-poor phosphines.

Iridium and rhodium chemistry. The sparingly soluble complexes **6a,b** and **7a,b** were made from [$Rh_2Cl_2(CO)_4$] and [IrCl(CO)$_2$(*p*-toluidine)], respectively, and fully characterised (see Experimental); complexes **6b** and **7b** have been previously reported.[17,24] The value of ν(CO) for *trans*-[MCl(CO)L_2] is a measure of the σ/π-bonding characteristics of L. The values are given in Table 2 for **6a,b** and **7a,b** together with the values for the PPh_3 and $P(OR)_3$ analogues for comparison. From these data it can be concluded that the order of decreasing σ–donor and/or increasing π-acceptor ability is PPh_3 < $\mathbf{L}_a$ < $\mathbf{L}_b$ < $P(OR)_3$.





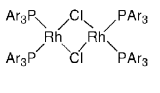
6a $PAr_3 = \mathbf{L}_a$ **7a** $PAr_3 = \mathbf{L}_a$

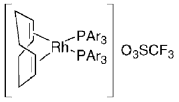
6b $PAr_3 = \mathbf{L}_b$ **7b** $PAr_3 = \mathbf{L}_b$

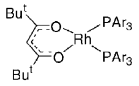
Table 2 ν(CO) for *trans*-[MCl(CO)L_2]

L	M	ν(CO)/cm^{-1}
$P(OPh)_3$	Rh	2016
$\mathbf{L}_b$	Rh	2004
$\mathbf{L}_a$	Rh	2000
PPh_3	Rh	1965
$P(OBu^n)_3$	Ir	1993
$\mathbf{L}_b$	Ir	1992
$\mathbf{L}_a$	Ir	1987
PPh_3	Ir	1950

The complexes [Rh_2Cl_2(cyclooctene)$_4$], [Rh(cod)$_2$]SO_3CF_3 and [Rh(CO)$_2$(acac*)] (acac* = $Bu^tC(O)CHC(O)Bu^t$) react smoothly with $\mathbf{L}_a$ to give the expected products **8a, 9a** and **10a**, respectively, which have all been characterised fully (see Experimental). However under similar conditions, $\mathbf{L}_b$ reacts with [Rh_2Cl_2(cyclooctene)$_4$] or [Rh(CO)$_2$(acac*)] to give mixtures of products with complexes **8b** and **10b** identified in solution on the basis of the ^{31}P NMR data; no reaction was observed between $\mathbf{L}_b$ and [Rh(cod)$_2$]CF_3SO_3.







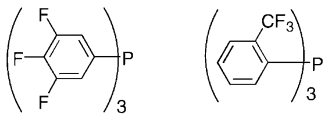
8a $PAr_3 = \mathbf{L}_a$ **9a** $PAr_3 = \mathbf{L}_a$ **10a** $PAr_3 = \mathbf{L}_a$

8b $PAr_3 = \mathbf{L}_b$ **10b** $PAr_3 = \mathbf{L}_b$

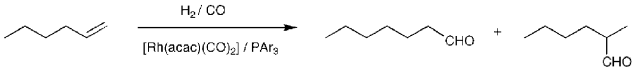
By modifying the literature procedures for [RhH(CO)-(PPh_3)$_3$][25] and [IrH(CO)(PPh_3)$_3$][26] the syntheses of analogues with $\mathbf{L}_a$ and $\mathbf{L}_b$ were attempted. However, treatment of rhodium complexes **6a** or **6b** or iridium complexes **7a** or **7b** with $NaBH_4$ in ethanol in the presence of $\mathbf{L}_a$ or $\mathbf{L}_b$ or by treatment of **6a** with H_2 in the presence of $\mathbf{L}_a$ and NEt_3 were unsuccessful; in each case, only starting materials were detected with no evidence for hydride formation from ^{1}H NMR spectroscopy.

Hydroformylation catalysis

The phosphines $\mathbf{L}_a$ and $\mathbf{L}_b$ have been tested as ligands for rhodium catalysed hydroformylation of 1-hexene (eqn. (1)) under standard[2] conditions (see Experimental) and the results compared with those for PPh_3, $P(OPh)_3$ and ligands $\mathbf{L}_c$ and $\mathbf{L}_d$. The catalysts were generated *in situ*, the product distributions were determined by GC and the rates were determined by measuring gas uptakes as a function of time at constant pressure. Under the conditions used, in the absence of added phosphorus ligand, only traces of aldehyde were detected.



$\mathbf{L}_c$ $\mathbf{L}_d$



(1)

The results are given in Table 3 (Entries 1–6). The PPh_3 derived catalyst efficiently converts 1-hexene to C-7 aldehydes with no by-products and selectivity to the linear aldehydes is modest (Entry 1). The $P(OPh)_3$ derived catalyst shows over 5 times the activity of the PPh_3 catalyst under these conditions (Entry 2).

The catalysts derived from the electron-poor phosphines $\mathbf{L}_a$ (Entry 3) and $\mathbf{L}_c$ (Entry 5) show similar activity to PPh_3. These catalysts also gave similarly modest selectivity (*n* : *i* of 2–3) with 2-methylhexanal (and traces of 2-ethylpentanal) accounting for the majority of the branched product. The bulky, electron-poor phosphins $\mathbf{L}_b$ (Entry 4) and $\mathbf{L}_d$ (Entry 6) gave low activity catalysts and a greater proportion of *iso*-products. Of the branched aldehyde product (formed in 4% yield), about one third is 2-ethylpentanal which is derived from 2-hexene and indicates that isomerisation of 1-hexene to 2-hexene is a competing reaction when using the bulky phosphine catalysts. After the hydroformylation catalysis runs with $\mathbf{L}_a$ (Entry 3) and $\mathbf{L}_b$ (Entry 4) the product solutions were investigated by ^{31}P NMR spectroscopy which revealed strong signals for free ligands (which were used in excess) showing that the ligands were stable under the hydroformylation conditions; in addition a weak doublet was observed in the solution with ligand $\mathbf{L}_b$

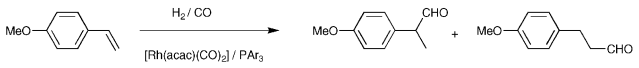
Table 3 Hydroformylation catalysis

Entry	Substrate	Conditions[a]	Ligand	θ^b/°	Conversion[c]	*n* : *iso*[c]	TOF[d]
1	1-hexene	i	PPh_3	145	95	2.9	380
2	1-hexene	i	$P(OPh)_3$	128	92	2.6	2000
3	1-hexene	i	$\mathbf{L}_a$	160	94	3.0	400
4	1-hexene	ii	$\mathbf{L}_b$[b]	184	6	0.6	~15
5	1-hexene	i	$\mathbf{L}_c$	145	94	2.5	400
6	1-hexene	ii	$\mathbf{L}_d$[b]	>200	6	0.6	~15
7	4-methoxystyrene	iii	PPh_3	145	100	0.13	n.d.
8	4-methoxystyrene	iii	$\mathbf{L}_a$	160	100	0.20	n.d.
9	4-methoxystyrene	iii	$\mathbf{L}_b$	184	25	0.29	n.d.

[a] Reaction conditions (see Experimental for more details): (i) at 60 °C, 20 bar, 0.2 mol% catalyst, L/Rh = 4.5, 3 h; (ii) at 100 °C, 5 mol% catalyst, L/Rh = 4.5, 4 h; (iii) at 55 °C, 7 bar, 5 mol% catalyst, L/Rh = 5, 4 h. [b] Values from ref. 16 [c] In % as determined by GC. For 1-hexene reactions, the conversions are based on 1-hexene consumed against biphenyl as an internal standard and selectivity to aldehydes is essentially 100%. For the 4-vinylanisole hydroformylation in Entry 9, the by-product was polyvinylanisole. [d] Determined by monitoring gas uptake with time over the first 2 h, except in the case of entries 4 and 6 which were determined by conversion h^{-1}; n.d. = not determined

consistent with the presence of a rhodium(I) complex (δ 28.4, ^1J(RhP) 131 Hz).

Rhodium-catalysed hydroformylation of 4-vinylanisole (eqn. (2)) with PPh_3, $\mathbf{L}_a$ and $\mathbf{L}_b$ was investigated and the results are presented in Table 3 (Entries 7–9).



(2)

Similar trends in activity to the 1-hexene reaction are apparent: $\mathbf{L}_a$ and PPh_3 give catalysts of similar activity while $\mathbf{L}_b$ gives low activity. Of the aldehyde product obtained, the selectivity for the more valuable (in terms of potential applications[27]) branched aldehyde decreases in the order $PPh_3 > \mathbf{L}_a > \mathbf{L}_b$.

Several features of the catalytic results are worthy of further discussion. There is no doubt that phosphites generally give more active rhodium catalysts for hydroformylation than phosphines and our measurements of the rates obtained with PPh_3 and $P(OPh)_3$ above concur with this. The explanation given is that the σ/π-bonding characteristics of the electron-poor phosphites leads to weaker Rh–CO bonding which in turn facilitates the rate-determining CO displacement by the alkene substrate.[2] For the same reasons, electron-withdrawing substituents on phosphines would be expected to lead to higher activity hydroformylation catalysts. Such activity enhancements have been observed although many of these have been with diphosphines[2] for which other factors may complicate the interpretation.[28] For monophosphines Moser *et al.*[10] showed, using $P(C_6H_4Z\text{-}4)_3$ (Z = H, Cl, F, CF_3) as ligands in 1-hexene hydroformylation, that electron-withdrawing substituents led to increased catalytic activity; the most rapid (with $P(C_6H_4CF_3\text{-}4)_3$) was a factor of 1.4 times faster than with PPh_3. In the light of this, the negligible difference in rate between PPh_3 and $\mathbf{L}_a$ is unexpected. The greater bulk of $\mathbf{L}_a$ ($\theta = 160°$) than PPh_3 ($\theta = 145°$) may be a factor although we also detected very little difference in the rate with $\mathbf{L}_c$. We conclude that for our PAr_3 catalyst systems, electronic effects are apparently not very significant.

The very bulky phosphines $\mathbf{L}_b$ and $\mathbf{L}_d$ gave low activity hydroformylation catalysts. The coordination chemistry described above revealed that $\mathbf{L}_b$ is generally a poorer ligand than $\mathbf{L}_a$ for late transition elements and thus it may be incomplete coordination of $\mathbf{L}_b$ to rhodium under the catalytic conditions that is responsible for the low observed rate. The ligand $\mathbf{L}_d$ is apparently an even poorer ligand than $\mathbf{L}_b$ since we have been unable to make complexes of $\mathbf{L}_d$ with Pt, Pd or Rh using the conditions described above for the synthesis of complexes of $\mathbf{L}_a$ and $\mathbf{L}_b$.

The ν_{CO} values for $[RhCl(CO)(\mathbf{L}_b)_2]$ given above and the reported Tolman electronic parameter[16] for $\mathbf{L}_b$ suggest that the ligand properties of $\mathbf{L}_b$ are more similar to $P(OAr)_3$ than PPh_3. Furthermore the Tolman cone angle for $\mathbf{L}_b$ ($\theta = 184°$) is comparable to that of the bulky monophosphite $P(OC_6H_4Bu^t\text{-}2)_3$ (θ = 175°). Thus the low activity of the catalyst derived from $\mathbf{L}_b$ contrasts sharply with the exceptionally high activity of the catalyst derived from the bulky monophosphite $P(OC_6H_4Bu^t\text{-}2)_3$.[4,29]

The conclusion to be drawn is that despite superficial stereoelectronic similarities, monodentate fluoroarylphosphines do not mimic monophosphites in terms of delivering high-activity hydroformylation catalysts. Further theoretical work is in progress to understand why this is so.

Experimental

All preparations were carried out in a dry nitrogen atmosphere using Schlenk techniques. Unless otherwise stated, the metal complexes were found to be air stable in the solid state, so once prepared were stored in air. All reaction solvents were dried by refluxing over appropriate drying reagents (calcium hydride for dichloromethane and acetonitrile, sodium/benzophenone for diethylether, tetrahydrofuran, toluene, benzene, pentane, and hexane, and anhydrous magnesium sulfate for acetone) and distilled under nitrogen prior to use. Commercial reagents were used as supplied and other reagents were prepared by literature methods: $[PtCl_2(cod)]$ and $[PtCl_2(SMe_2)_2]$;[30] $[IrCl(CO)_2(p\text{-toluidine})]$;[31] $[Pt(norbornene)_3]$;[32] elemental analyses were carried out in the Microanalytical Laboratory of the School of Chemistry, Bristol University. ^{1}H, ^{31}P and ^{195}Pt NMR spectra were recorded on Jeol FX90Q, Jeol GX400, and Jeol ecp 300 NMR spectrometers with chemical shifts to high frequency of TMS, 85% H_3PO_4, and Ξ(Pt) 21.4 MHz respectively. $P\{C_6H_3(CF_3)_2\text{-}3,5\}_3$ ($\mathbf{L}_a$, δ(P) −2.0 in d_8-thf) was purchased from Fluorochem, $P(C_6F_5)_3$ ($\mathbf{L}_b$, δ(P) −74.0, hpt, ^3J(PF) 36 Hz in d_8-thf) was purchased from Aldrich and $P\{C_6H_4(CF_3)\text{-}2\}_3$ ($\mathbf{L}_d$) was made by the literature method.[33]

Tris(3,4,5-trifluorophenyl)phosphine ($\mathbf{L}_c$)

The Grignard reagent 3,4,5-$C_6H_2F_3MgBr$ was prepared by gradually adding a solution of 1-bromo-3,4,5-trifluorobenzene (7.07 g, 33.5 mmol) in Et_2O (20 cm^3) into a cooled suspension of magnesium (0.81 g, 33.5 mmol) in Et_2O (20 cm^3). The mixture was warmed to room temperature before the addition of a solution of PCl_3 (1.53 g, 11.2 mmol). After stirring overnight, the solvents were removed *in vacuo* and the residue dissolved in toluene and filtered through a sinterstick. The toluene solution was washed with brine solution, dried with sodium sulfate and the solvent was removed *in vacuo* to give $\mathbf{L}_c$ in high purity (3.1 g, 7.31 mmol, 65%) (This is an unoptimised yield as some product was lost during the filtration stage). Elemental analysis (calc.): C, 50.96 (50.96); H, 1.24 (1.43); MS (EI) *m*/*z*: 424 (M^+); $^{31}P\{^1H\}$ NMR (C_6D_6): $\delta = -1.0$; ^{19}F NMR (C_6D_6): $\delta = -132.4$ (6F, dd, ^3J(FF) = 20.8 Hz; ^3J(FH) = 7.0 Hz), −156.0 (3F, tt, ^3J(FF) = 20.8 Hz, ^4J(FH) = 6.2 Hz); ^{1}H NMR (C_6D_6): δ = 6.5 (6H, q. app., J = 6.8 Hz).

trans-[$PtCl_2(L_a)_2$] (1a)

Ligand $\mathbf{L_a}$ (69 mg, 0.103 mmol) was added to a solution of [$PtCl_2(SMe_2)_2$] (20 mg, 0.052 mmol) in pentafluorobenzene (5 cm^3). This gave a yellow solution which was stirred at room temperature for 24 h. The solvent was then removed *in vacuo* and toluene (10 cm^3) was added to form a yellow suspension which was stirred for 30 min. The product was then filtered off under nitrogen and washed with toluene (2 × 2 cm^3) to give **1a** as a pale yellow solid (59 mg, 0.037 mmol, 72%). Elemental analysis (calc.): C, 35.85 (35.90); H, 1.05 (1.15); MS (FAB) *m/z*: 1571 ($M^+ - Cl$), 1535 ($M^+ - 2Cl$); $^{31}P\{^1H\}$ NMR (C_6F_5H/C_6D_6): $\delta = 22.9$ ($^1J(PPt) = 2798$ Hz); ^{195}Pt NMR (C_6F_5H/C_6D_6): $\delta = 393.4$ (t); ^{19}F NMR ($CDCl_3$): $\delta = -64.2$ (s);^1H NMR ($CDCl_3$): $\delta = 8.11$ (6H, s); 8.06 (12H, t, $J(PH) = 5.5$ Hz).

Reaction of [$PtCl_2(SMe_2)_2$] with $\mathbf{L_b}$

Ligand $\mathbf{L_b}$ (100 mg, 0.19 mmol) was added to a solution of [$PtCl_2(SMe_2)_2$] (37 mg, 0.094 mmol) in toluene (20 cm^3) to give a yellow solution which was stirred and heated to reflux for 6 days. ^{31}P NMR spectroscopy revealed the formation of two platinum-containing products (see Results and discussion) one of which is *trans*-[$PtCl_2(\mathbf{L_b})_2$] (**1b**).[18] $^{31}P\{^1H\}$ NMR ($C_6H_5CH_3/C_6D_6$): $\delta = -25.8$ ($^1J(PPt) = 3145$ Hz); ^{195}Pt NMR ($C_6H_5CH_3/C_6D_6$): $\delta = 487.1$ (t). The other species had parameters: $\delta(P) = -30.7$ ($^1J(PPt) = 3694$ Hz); $\delta(Pt) = 705.7$ (d).

trans-[$PdCl_2(L_a)$] (2a)

Ligand $\mathbf{L_a}$ (262 mg, 0.20 mmol) was added to a solution of [$PdCl_2(NCPh)_2$] (75 mg, 0.20 mmol) in CH_2Cl_2 (15 cm^3). This gave a brown/orange solution which was stirred at room temperature for 6 h. The solvent was then removed *in vacuo* and toluene (10 cm^3) was added to form a brown suspension. The suspension was stirred for 30 min, filtered off under nitrogen and washed with toluene (2 × 2 cm^3) to give **2a**[17] as a light brown solid (183 mg, 0.121 mmol, 62%). Elemental analysis (calc.): C, 37.55 (37.95); H, 1.20 (1.20); MS (FAB) *m/z*: 1446 ($M^+ - 2Cl$); $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 24.8$;^{19}F NMR ($CDCl_3$): $\delta = -64.2$ (s); ^1H NMR ($CDCl_3$): $\delta = 8.12$ (6H, s); 8.05 (12H, t, $^3J(PH) = 5.1$ Hz).

trans-[$PdCl_2(L_b)_2$] (2b)

Ligand $\mathbf{L_b}$ (140 mg, 0.26 mmol) was added to a solution of [$PdCl_2(NCPh)_2$] (50 mg, 0.13 mmol) in CH_2Cl_2 (10 cm^3). This gave an orange/brown solution which was stirred at room temperature for 2 h. The solvent was then removed *in vacuo* and toluene (4 cm^3) was added followed by pentane (10 cm^3). The reaction mixture was left in the fridge for 24 h after which time a yellow suspension was formed. The product was then filtered off under nitrogen and washed with pentane (2 × 4 cm^3) to give **2b** as a yellow solid (85 mg, 0.068 mmol, 52%). Elemental analysis (calc.): C, 34.70 (34.85); MS (FAB) *m/z*: 1170 ($M^+ - 2Cl$); $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = -27.0$ (br, s); ^{19}F NMR ($CDCl_3$): $\delta = -126.2$ (12F, *o*-F), −143.8 (6F, *p*-F), −158.8 (12F, *m*-F).

Reaction of *trans*-[$PdCl_2(L_b)_2$] (2b) with L_a and then PPh_3

Complex **2b** (21.6 mg, 0.017 mmol) was dissolved in $CDCl_3$ (0.7 cm^3) in an NMR tube. $\mathbf{L_a}$ (23.3 mg, 0.035 mmol) was added and the tube was shaken to give a yellow solution. The reaction was monitored by ^{31}P NMR spectroscopy which after 1 h showed a mixture of predominantly complex **2a** and ligand $\mathbf{L_b}$. $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 25.6$ (s, **2a**), −73.7 (hpt, $^3J(PF) = 36$ Hz, $\mathbf{L_b}$) (initially the mixed ligand complex **2ab** was detected with $\delta = 30.4$ and -25.5 ($^2J(PP) = 641$ Hz)). Triphenylphosphine (9.2 mg, 0.035 mmol) was then added to the mixture and the tube was shaken to give a yellow solution. $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 24.0$ (s, *trans*-[$PdCl_2(PPh_3)_2$]), 22.4 (s, *cis*-[$PdCl_2(PPh_3)_2$]) (ratio ~ 4 : 1), −3.6 (s, $\mathbf{L_a}$) − 73.7 (hpt, $^3J(PF) = 36$ Hz, $\mathbf{L_b}$).

Reaction of [Pt(norbornene)$_3$] with $\mathbf{L_b}$

One equivalent (56 mg, 0.105 mmol), two equivalents (112 mg, 0.210 mmol), three equivalents (167 mg, 0.314 mmol) or four equivalents (224 mg, 0.421 mmol) of $\mathbf{L_b}$ were added to a solution of [Pt(norbornene)$_3$] (50 mg, 0.105 mmol) in α,α,α-trifluorotoluene (4 cm^3). This gave a light brown solution which was stirred at room temperature for 1 h. The solvent was then removed *in vacuo* to give a light brown solid. In each reaction $^{31}P\{^1H\}$ and ^{195}Pt NMR spectroscopy showed a mixture of uncoordinated $\mathbf{L_b}$ and complexes **3b** and **4b** in varying proportions. Spectroscopic data for **3b**: $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = -27.1$ (s, $^1J(PPt) = 3577$ Hz); ^{195}Pt NMR ($CDCl_3$): $\delta = -958$ (d);^{19}F NMR ($CDCl_3$): $\delta = -128.1$ (6F, *o*-F), −146.0 (3F, *p*-F), −157.8 (6F, *m*-F). Spectroscopic data for **4b**: $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = -23.3$ (s, $^1J(PPt) = 4006$ Hz); ^{195}Pt NMR ($CDCl_3$): $\delta = -318$ (t); ^{19}F NMR ($CDCl_3$): $\delta = -130.3$ (12F, *o*-F), −148.2 (6F, *p*-F), −159.7 (12F, *m*-F).

Reaction of [Pt(norbornene)$_3$] with L_a

This was carried out as above to give mixtures of **3a, 4a** and **5a**. Spectroscopic data for **3a**: $^{31}P\{^1H\}$ NMR ($C_6H_5CF_3/C_6D_6$): $\delta = 32.8$ (br, s, $^1J(PPt) = 3523$ Hz); ^{195}Pt NMR ($C_6H_5CF_3/C_6D_6$): $\delta = -1117.5$ (d). Spectroscopic data for **4a**: $^{31}P\{^1H\}$ NMR ($C_6H_5CF_3/C_6D_6$): $\delta = 38.6$ (s, $^1J(PPt) = 3706$ Hz); ^{195}Pt NMR ($C_6H_5CF_3/C_6D_6$): $\delta = -510.0$ (t). Spectroscopic data for **5a**: $^{31}P\{^1H\}$ NMR (C_6F_5H/C_6D_6): $\delta = 53.2$ (s, $^1J(PPt) = 4551$ Hz); ^{195}Pt NMR (C_6F_5H/C_6D_6): $\delta = 166$ (q).

Reaction of [Pt(norbornene)$_3$] with L_b and L_a successively

Three equivalents of $\mathbf{L_b}$ (39.4 mg, 0.074 mmol) were added to a solution of [Pt(norbornene)$_3$] (12 mg, 0.025 mmol) in toluene (0.7 cm^3) in an NMR tube. The tube was shaken to give a pale yellow solution. $^{31}P\{^1H\}$ NMR ($C_6H_5CH_3$): $\delta = -22.4$ (s, $^1J(PPt) = 4003$ Hz, **4b**), −26.4 (s, $^1J(PPt) = 3577$ Hz, **3b**) (ratio ~ 1 : 4), −73.9 (hpt, $^3J(PF) = 36$ Hz, $\mathbf{L_b}$). Three equivalents of $\mathbf{L_a}$ (50 mg, 0.074 mmol) were added to this mixture and the contents were shaken to give a cloudy solution. $^{31}P\{^1H\}$ NMR spectroscopy showed a complex mixture with the major species being **4ab**. $^{31}P\{^1H\}$ NMR ($C_6H_5CH_3$): $\delta = 37.2$ (d, $^2J(PP) = 82$ Hz, $^1J(PPt) = 3928$ Hz, P_a), 20.8 (d, $^2J(PP) = 82$ Hz, $^1J(PPt)$ not resolved, P_b).

trans-[$RhCl(CO)(L_a)_2$] (6a)

Ligand $\mathbf{L_a}$ (1.05 g, 1.54 mmol) was added to a solution of [$Rh_2Cl_2(CO)_4$] (150 mg, 0.39 mmol) in C_6H_6 (15 cm^3). CO was evolved and the yellow solution was stirred for 36 h. The solvent was then removed under vacuum and CH_2Cl_2 (5 cm^3) was added to give a yellow suspension which was then stirred for 1 h before filtering off the product under nitrogen. The solid was washed with CH_2Cl_2 (2 × 5 cm^3) to give **6a** as a pale yellow solid (256 mg, 0.170 mmol, 87%). Elemental analysis (calc., **6a**·H_2O): C, 38.35 (38.60); H, 1.15 (1.30); MS (FAB) *m/z*: 1524 ($M^+ + H_2O$), 1506 (M^+), 1478 ($M^+ - CO$), 1443 ($M^+ - CO - Cl$); IR: ν(CO) 2000 cm^{-1}; $^{31}P\{^1H\}$ NMR ($C_6H_5CF_3/C_6D_6$): $\delta = 33.0$ (d, $^1J(PRh) = 134.7$ Hz); ^{19}F NMR (C_6D_6): $\delta = -62.8$ (s); ^1H NMR (C_6D_6): $\delta = 8.12$ (m). The analogous complex **6b** was made by the literature method.[17]

trans-[$IrCl(CO)(L_a)_2$] (7a)

Ligand $\mathbf{L_a}$ (100 mg, 0.15 mmol) was added to a solution of [$IrCl(CO)_2$(*p*-toluidine)] (29 mg, 0.075 mmol) in toluene (10 cm^3). CO was evolved and a yellow solution was formed which was stirred at room temperature for 24 h. After this time a yellow suspension was formed and this was filtered off under nitrogen and washed with toluene (2 × 4 cm^3) to give **7a** as a yellow solid (69 mg, 0.043 mmol, 58%). Elemental analysis (calc.): C, 36.55 (36.90); H, 0.95 (1.15); MS (FAB) *m/z*:

1596 (M^+), 1568 ($M^+ - CO$); IR: ν(CO) 1987 cm^{-1}; $^{31}P\{^1H\}$ NMR (C_6F_5H/C_6D_6): $\delta = 27.8$ (s); ^{19}F NMR (THF/C_6D_6): $\delta = -61.6$ (s).

trans-[IrCl(CO)(L_b)$_2$] (7b)

Ligand L_b (150 mg, 0.282 mmol) was added to a solution of [IrCl(CO)$_2$(*p*-toluidine)] (55 mg, 0.141 mmol) in C_6H_6 (15 cm^3). This gave a dark green solution which was stirred at room temperature for 48 h. The solvent was then removed *in vacuo* and CH_2Cl_2 (10 cm^3) was added to form a yellow suspension in the dark green solution. The product was filtered off under nitrogen and washed with CH_2Cl_2 (2 × 4 cm^3) to give **7b**[17] as a yellow solid (56 mg, 0.042 mmol, 31%). Elemental analysis (calc.): C, 33.10 (33.70); MS (FAB) *m*/*z*: 788 ($M^+ - L_b$), 768 ($M^+ - L_b - CO$), 725 ($M^+ - L_b - CO - Cl$); IR: ν(CO) 1992 cm^{-1}; $^{31}P\{^1H\}$ NMR ($C_6F_5CF_3/C_6D_6$): $\delta = -31.7$ (s).

[Rh$_2$(μ-Cl)$_2$(L_a)$_4$] (8a)

A solution of L_a (280 mg, 0.42 mmol) in CH_2Cl_2 (5 cm^3) was added dropwise over 2 min to a solution of [Rh$_2$Cl$_2$(cyclooctene)$_4$)] (75 mg, 0.11 mmol) in CH_2Cl_2 (5 cm^3) and the resulting bright red solution was stirred at room temperature for 24 h to give a red suspension. The solid was filtered off under nitrogen and washed with toluene (2 × 5 cm^3) to give the product **8a** (268 mg, 0.091 mmol, 86%). Elemental analysis (calc): C, 38.75 (39.00); H, 1.35 (1.25); $^{31}P\{^1H\}$ NMR (C_4D_8O), $\delta = 57.3$ (d, ^1J(PRh) = 195.8 Hz); ^{19}F NMR (CD_2Cl_2): $\delta = -63.4$ (s); ^1H NMR (CD_2Cl_2): $\delta = 8.20$ (12H, s), 8.13 (24H, d, $J = 12.5$).

Reaction of [Rh$_2$(μ-Cl)$_2$(cyclooctene)$_4$] with L_b

A solution of L_b (100 mg, 0.19 mmol) in CH_2Cl_2 (5 cm^3) was added dropwise over 2 min to a solution of [Rh$_2$Cl$_2$(cyclooctene)$_2$)] (34 mg, 0.047 mmol) in CH_2Cl_2 (5 cm^3) and the resulting bright red solution was stirred at room temperature for 24 h. A mixture of products was obtained and one signal at δ(P) = 2.4 (d, ^1J(PRh) = 261 Hz) was tentatively assigned to **8b**.

[Rh(cod)(L_a)$_2$]O$_3$SCF$_3$ (9a)

Ligand L_a (100 mg, 0.15 mmol) was added to a solution of [Rh(cod)$_2$]O$_3$SCF$_3$ (34 mg, 0.075 mmol) in CH_2Cl_2 (10 cm^3). This gave a yellow solution which was stirred at room temperature for 24 h. The solvent was then removed *in vacuo* and pentane (10 cm^3) was added to form a yellow suspension. The suspension was stirred for 24 h, filtered off under nitrogen and washed with pentane (2 × 5 cm^3) to give **9a** as a yellow solid (64 mg, 0.038 mmol, 51%). Elemental analysis (calc., **9a**.CH_2Cl_2): C, 38.80 (39.00); H, 2.05 (1.80); MS (FAB) *m*/*z*: 1443 (M^+ − cod − CF_3SO_3), 881 ($M^+ - L_a$ − cod − CF_3SO_3); $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 25.1$ (d, ^1J(PRh) = 160.4 Hz); ^{19}F NMR (CD_2Cl_2): $\delta = -63.5$ (36F, s), −79.2 (3F, s); ^1H NMR (CD_2Cl_2): $\delta = 2.5$ (8H, br, s, cod CH_2), 5.5 (4H, br, s, cod CH), 8.0 (12H, d, ^3J(HP) = 10.1, ArH), 8.1 (6H, s, ArH).

[Rh(acac*)(L_a)$_2$] (10a)

Ligand L_a (150 mg, 0.22 mmol) was added to a solution of [Rh(CO)$_2$(acac*)] (39 mg, 0.11 mmol) in CH_2Cl_2 (15 cm^3). This gave a yellow solution and CO was evolved. The reaction mixture was stirred at room temperature for 5 h and then all volatiles were removed *in vacuo* to give **10a** as a bright yellow solid (142 mg, 0.087 mmol, 78%). Elemental analysis (calc., **10a**·CH_2Cl_2): C, 42.10 (42.10); H, 2.20 (2.30); MS (FAB) *m*/*z*: 1626 (M^+); $^{31}P\{^1H\}$ NMR (C_6D_6/CH_2Cl_2): $\delta = 59.2$ (d, ^1J(PRh) = 194.2 Hz); ^{19}F NMR ($CDCl_3$): $\delta = 63.0$ (s); ^1H NMR ($CDCl_3$): $\delta = 7.55$ (6H, s), 7.48 (12H, d, $J = 12.2$), 6.61 (1H, s), −0.07 (18 H).

Reaction of [Rh(CO)$_2$(acac*)] with L_b

Ligand L_b (100 mg, 0.188 mmol) was added to a solution of [Rh(CO)$_2$(acac*)] (32 mg, 0.094 mmol) in CH_2Cl_2 (10 cm^3). CO was evolved and a yellow solution was formed which was stirred at room temperature for 4 h. $^{31}P\{^1H\}$ NMR spectroscopy and FAB mass spectrometry showed the product to be a mixture of [Rh(acac*)(L_b)$_2$] (**10b**) and unreacted L_b which we were unable to separate. $^{31}P\{^1H\}$ NMR (C_6D_6/CH_2Cl_2): $\delta = -7.0$ (d, ^1J(PRh) = 200.0 Hz).

Hydroformylation of 1-hexene

These experiments were conducted in a stainless steel autoclave held at constant pressure and connected to a ballast vessel from which 1 : 1 CO/H_2 was fed. Reaction rates were determined by measuring gas uptake over time up to 50% conversion, and further confirmed by GC/MS analysis of the reaction products. The identities of the reaction products were established by comparison of retention times and mass spectra with authentic samples. [Rh(acac)(CO)$_2$] (5.0 mg, 0.019 mmol) and ligand (0.90 mmol) in toluene (4 cm^3) were added to the autoclave which was then flushed with 1 : 1 CO/H_2. The autoclave was then pressurised (10 bar) and stirred at 60 °C for 1 h to allow the catalyst to form. 1-Hexene (1.2 cm^3) was injected and the pressure adjusted to 20 bar. The gas uptake was monitored as a function of time.

Hydroformylation of 4-vinylanisole

In a glove box under nitrogen, a solution of 4-vinylanisole (39 mg, 0.291 mmol), polydimethylsiloxane (21 mg, 0.290 mmol), [Rh(acac*)(CO)$_2$] (5.0 mg, 0.015 mmol) and ligand (5 equivalents with respect to Rh, 0.073 mmol) in C_6D_6 (3 cm^3) was prepared in a 10 cm^3 vial. The mixture was then shaken, pressurised to 7 bar with 1 : 1 CO/H_2 and heated to 55 °C for 4 h. The solution was analysed by ^1H NMR spectroscopy with polydimethylsiloxane peak used as the standard to calculate the yields of each product given in Table 3.

X-Ray crystal structure of 1a

X ray diffraction experiments on *trans*-[PtCl$_2${P(C$_6$H$_3$(CF$_3$)$_2$-3,5)$_2$}$_2$] (**1a**) were performed at −100 °C on a Bruker SMART diffractometer using Mo K_α X-radiation, α = 0.71073 Å. Crystal data: *trans*-[PtCl$_2${P(C$_6$H$_3$(CF$_3$)$_2$-3,5)$_2$}$_2$] (**1a**), $C_{48}H_{18}Cl_2F_{36}P_2Pt$, $M = 1606.55$, triclinic, space group, *P*$\bar{1}$ (No. 2), $a = 10.372(2)$, $b = 11.649(2)$, $c = 12.263(3)$ Å, $\alpha = 69.43(2)$, $\beta = 86.03(2)$, $\gamma = 85.14(2)°$, $V = 1381.0(5)$ Å^3, $Z = 1$, $\mu = 2.853$ mm^{-1}, reflections measured, 6660, independent reflections, 4735, R_{int} 0.0177, $R1 = 0.019$. Absorption corrections were based on equivalent reflections and structures refined against all F_o^2 data with hydrogen atoms riding in calculated positions. The fluorine atoms on carbons C(8) {F(4), F(5), F(6)}, C(18) {F(10), F(11), F(12)} and C(27) {F(13), F(14), F(15)} were disordered with occupancies 0.696(5) and assigned constrained anisotropic displacement parameters.

CCDC reference number 257444.

See http://www.rsc.org/suppdata/dt/b4/b418193j/ for crystallographic data in CIF or other electronic format.

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