Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Organometallic Chemistry 667 (2003) 112–119
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Synthesis and transition metal chemistry of 'phosphomide' ligands: a comparison of the reactivity and electronic properties of diphenyl-*P*-perfluoro-octanoyl-phosphine, *P*-acetyl-diphenylphosphine and *P*-anisoyl-diphenylphosphine. X-ray crystal structure of $[RhCp^*(Ph_2PC(O)CH_3)Cl_2]$

R. Angharad Baber, Matthew L. Clarke *, A. Guy Orpen, David A. Ratcliffe

University of Bristol, School of Chemistry, Bristol BS8 1TS, UK

Received 5 August 2002; received in revised form 27 November 2002; accepted 30 November 2002

Abstract

A convenient synthesis of several 'phosphomide' ligands (P adjacent to carbonyl group) from secondary phosphines is reported. The new anisoyl substituted phosphines are considerable more stable to hydrolysis, and are stronger σ-donor ligands than *P*-acetyl-diphenylphosphine as determined by the measurement of ν(CO) for the corresponding rhodium carbonyl complexes *trans*-$[RhL_2(CO)Cl]$. In contrast, a new phosphomide derived from perfluoro-octanoyl chloride was found to be a highly unstable, electron poor π-acceptor ligand. The crystal structure of $[RhCp^*Cl_2\{Ph_2PC(O)CH_3\}]$ showed a normal *pseudo*-octahedral piano-stool molecular geometry with a Rh–P bond length of 2.3186(5) Å. The extra stability observed for the *P*-anisoyl phosphomides has led us to apply this class of ligand in rhodium catalysed hydroformylation for the first time.

Keywords: Co-ordination chemistry; Hydroformylation; Phosphines; Rhodium complexes

1. Introduction

Phosphorus ligands play an enormously important role in catalysis and organometallic chemistry. Subtle changes in ligand structure often leads to improved catalytic processes and organometallic complexes with interesting properties. The synthesis of new types of phosphorus ligands with unusual stereo-electronic properties is therefore an important goal. In particular, there is currently great interest in π-accepting phosphorus ligands in both organometallic chemistry and catalysis. Electron withdrawing phosphite ligands are well established as ligands of choice in several catalytic reactions [1]. Phospha-benzenes and some π-accepting phosphinoamines are more recent discoveries that are finding applications in catalysis [2,3]. The chemistry of fluorocarbylphosphines has also been a subject of considerable interest in the last 10 years [4]. Phosphorus ligands that contain the phosphorus adjacent to a carbonyl group have been almost completely neglected in organometallic chemistry and catalysis. This may stem from concerns regarding the stability of the P–C bond, which has been shown to undergo degradation reactions in the presence of water or oxygen [5]. We envisaged that one of the consequences of a carbonyl group adjacent to a phosphorus atom would be an inductive electron withdrawing effect, and a tendency for the phosphorus lone pair to delocalise towards the carbonyl group (as shown below). In this paper, we report our initial efforts in

Fig. 1.

* Corresponding author. Tel.: +44-1179546341; fax: +44-1179290509.
E-mail address: matt.clarke@bristol.ac.uk (M.L. Clarke).

0022-328X/02/$ - see front matter © 2002 Elsevier Science B.V. All rights reserved.
PII: S0022-328X(02)02152-6

developing the transition metal and catalytic chemistry of phosphomide ligands.

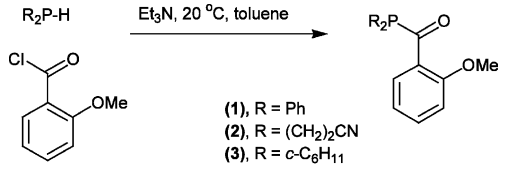
2. Results and discussion

A glance through the literature suggests that phosphomides are most effectively prepared from a trimethylsilylphosphine and acid chloride [6]. Acetyldiphenylphosphine has also been prepared by the reaction of diphenylphosphine with ketene [7], or by the reaction of various metallated phosphides with acetyl chloride [8].

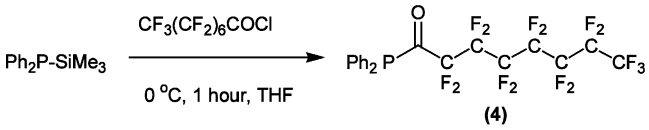
We felt that the reaction of an acid chloride with a secondary phosphine would be a very mild, efficient method to form a P–C bond, thus allowing easy access to a range of interesting phosphorus ligands. Moreover, there are now many functionalised acid chlorides and primary or secondary phosphines commercially available, and this method of synthesis should be capable of tolerating a variety of functional groups. A simple and quantitative ligand synthesis is very desirable for rapid catalytic screening. We have found that reaction of acetyl chloride with diphenylphosphine in the presence of triethylamine immediately gives a white precipitate ($Et_3N{\cdot}HCl$) and a bright yellow solution of *P*-acetyldiphenylphosphine as the only phosphorus-containing product. We have also prepared ether functionalised phosphomides, (**1**)–(**3**) as we were intrigued by a recent paper that suggested hemilabile P^O phosphine ligands may have a positive effect on both activity and selectivity in rhodium catalysed hydroformylation of olefins [9]. The reactions between *o*-anisoylchloride and a range of secondary phosphines proceeded smoothly to give the new phosphomides in essentially quantitative yield and high purity by filtration and removal of solvent Scheme 1.

Diphenyl-perfluoro-octanoylphosphine could also be prepared cleanly from readily available diphenylphosphine, perfluoro-octanoylchloride and pyridine (or by reaction of Ph_2PSiMe_3 with the acid chloride). Phosphines containing perfluorinated alkyl chains are currently attracting considerable attention as a result of their applications in catalysis in perfluorinated solvent systems and supercritical CO_2 [4] Scheme 2.

Perfluoroalkylphosphines frequently show long range P–F coupling in their NMR spectra, and (**4**) is no exception. The longest range couplings may contain a



Scheme 1.



Scheme 2.

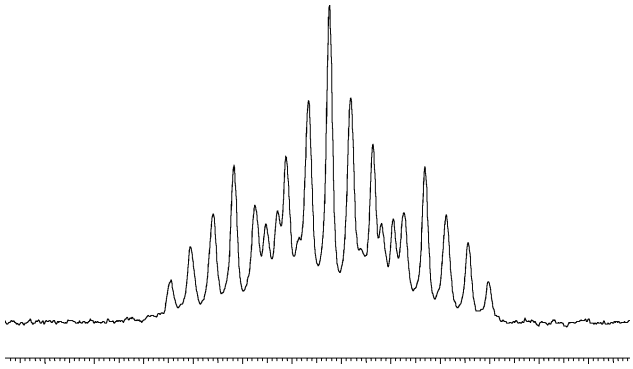


Fig. 2. $^{31}P\{^1H\}$ NMR spectrum of $Ph_2PC(O)(CF_2)_6CF_3$, (4).

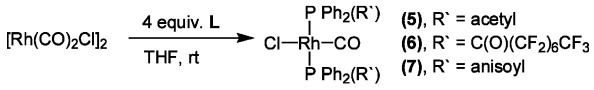
contribution from 'through space' interaction between the bending fluorinated tail. The ^{31}P-NMR spectrum is an apparent 21 line signal is derived from a 'triplet of triplet of triplets' splitting pattern (Fig. 1). Peak intensities are fully consistent with this being a simple first order spectrum in which 6 lines are hidden (Section 3).

Delocalisation of the phosphorus lone pair towards the carbonyl group (c.f. low nucleophilicity of amides) or conjugation between carbonyl group and phosphorus antibonding/3d hybrid orbitals [7] has been observed in some of the fundamental examples of phosphomides reported to date and is reflected in the C=O stretching frequency being found in the same region as amides (ν(CO) of $Ph_2PC(O)CH_3 = 1670$ cm^{-1}). However, the IR spectra of (**1**), (**2**) and (**3**) show a medium bands at 1781, 1739 and 1730 cm^{-1}, respectively which we assign as the C=O stretch. We have assigned the strong doublet band at ca. 1625 and 1595 cm^{-1} as aromatic C–C vibrations, as these are observed in this region for other derivatives of anisoic acid. This is at significantly higher wavenumber than in many amides (e.g. ν(CO) of Et_2N–anisoyl = 1640 cm^{-1}) [10], and may reflect that the phosphorus lone pair is not delocalised onto the carbonyl group to a measurable extent. The position of ν(CO) in the IR spectrum of (**4**) (1686 cm^{-1}) suggest that the phosphorus lone pair is partially delocalised into the carbonyl group.

The series of phosphomide ligands we have prepared also all differ in their sensitivity to moisture. Acetyldiphenylphosphine is instantly hydrolysed/alcoholysed on treatment with water or methanol, respectively to give the secondary phosphine (detected by ^{31}P and $^{31}P\{^1H\}$ NMR) and presumably acetic acid or methyl

acetate. Although the cyclohexyl-substituted ligand is somewhat oxygen sensitive, ligands (**1**) and (**2**) appear stable to air, moisture or methanol for several days. It is only on addition of *p*-toluenesulfonic acid to a methanolic solution of (**2**), that extensive decomposition takes place (within hours). One possible explanation for this extra stability may stem from steric shielding from the methoxy group. Indeed, this may also prevent the co-planar orientation between phosphorus lone pair and carbonyl group required for conjugation/delocalisation. Alternatively, aryl phosphomides may have increased stability w.r.t. alkyl phosphomides. The perfluorinated ligand (**4**) is particularly sensitive, and is hydrolysed within seconds of being exposed to the atmosphere, even in the solid state. Presumably, the electronegative perfluorinated chain strongly activates the carbonyl group towards nucleophillic attack by adventitious water. It remains to be seen if the P–C=O bond can be transformed to other functional groups without P–C bond breakage.

We have speculated on the electronic properties of the free phosphomide ligands but also wished to investigate the nature of M–P bonding in transition metal complexes of phosphomides. There is very little is known about the organometallic chemistry of this type of ligand [11,12], so we have studied the reactions of the diphenylphosphino-substituted ligands with organometallic Rh(I) and Rh(III) precursors. We report here the preparation of the first rhodium carbonyl complexes of phosphomides, (**5**), (**6**) and (**7**), which has allowed us to evaluate the σ-donor/π-acceptor properties of these ligands. These were prepared from $[Rh(CO)_2Cl]_2$ as described in Scheme 3. The complexes were readily isolated in high purity and yield as yellow solids. The values of $^1J_{P-Rh}$ are fairly typical for this type of complex and show the expected downfield co-ordination shift ($\Delta\delta$ +30 ppm) in going from free ligand to Rh(I) complex. The values of ν(CO) for the carbonyl ligand in *trans*-$[Rh(Ph_2Pacetyl)_2(CO)Cl]$ (1984 cm^{-1}) is consistent with the acetyl group acting as a very strongly electron withdrawing group. This is presumably due to inductive effects caused by the electronegative carbonyl functionality. The value of ν(P–CO) in the IR spectrum is increased by 30 cm^{-1} on co-ordination to the metal, which is consistent with the resonance structure containing C–O single bonds making a lesser contribution in the metal complexes of acetyl-diphenylphosphine. The position of ν(CO) of the carbon monoxide ligand in complex (**6**) is at 1990 cm^{-1}. This value suggests that the perfluoro-octanoyl group does indeed have a pronounced effect on the π-accepting properties of ligand (**4**). The position of this band shows that the perfluoro-octanoyl substituent has a similar effect to very strongly electron withdrawing pyrrolyl substituent. [ν(CO) *trans*-$[Rh(Ph_2P(pyrrolyl)(CO)Cl] = 1990$ cm^{-1} [3]; ν(CO) *trans*-$[Rh[Ph_2P(C_6F_5)]_2(CO)Cl] = 1974$ cm^{-1} [13];

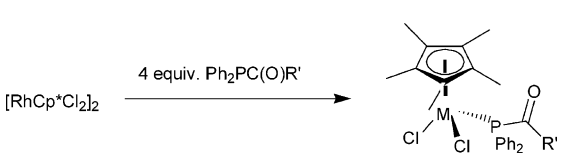


Scheme 3.

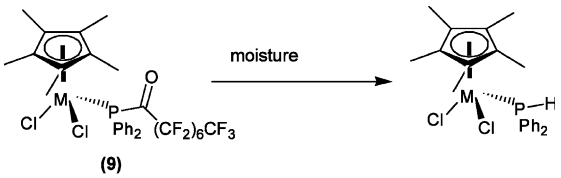
ν(CO) *trans*-$[Rh[Ph_3P]_2(CO)Cl] = 1965$ cm^{-1}]. An increase in the position of ν(CO) for the carbonyl group within the phosphomide on co-ordination to the metal is also observed. Reaction of anisoyldiphenylphosphine with $[Rh(CO)_2Cl]_2$ also gave the desired complex *trans*-$[Rh(Ph_2Panisoyl)_2Rh(CO)Cl]$, (**7**). The value of ν(CO) (1974 cm^{-1}) for the carbonyl ligand in this complex suggests that the anisoyl group is less electron withdrawing than the acetyl group, possible due to the steric requirements of the P–C=O bond as described above. The band associated with the P–C=O bond is tentatively assigned at 1725 cm^{-1}, but is of similar intensity to the C–C overtone bands that are also observed in this region.

We have also studied the reactions of the diphenylphosphino-substituted series of ligands with $[RhCp^*Cl_2]_2$. All of the ligands react in the expected way to produce complexes of type $[RhCp^*Cl_2(\eta^1\text{-L})]$. However, the reaction with the perfluorinated ligand is unusually slow requiring a couple of hours to go to completion Scheme 4.

All of the complexes show doublets in their ^{31}P-NMR spectra. The resonance's are shifted ca. 30 ppm downfield from the free ligands. The P–F couplings are not resolvable in the rhodium complexes of ligand (**4**). The magnitude of $^1J_{P-Rh}$ is somewhat larger than those observed in complexes (**5**)–(**7**) as is expected for these Rh(III) complexes. It is more difficult to assign the P–C=O bands in the IR spectra of these complexes as they are of reduced intensity. However, the possibility of delocalisation within the P–C=O bond is clearly less likely if the phosphomides are complexed to a transition metal. The rhodium complexes in this study show similar relative stabilities to those found in the free ligands: Complex (**9**) slowly and selectively decomposed to $[RhCp^*Cl_2(\eta^1\text{-}PPh_2H)]$ which was easily identified by the distinctive doublet of doublets in it's ^{31}P (^{1}H coupled) NMR spectrum [14]. In contrast,



Scheme 4.



Scheme 5.

$[Cp^*RhCl_2(\eta^1\text{-}1)]$ and $[Cp^*RhCl_2(\eta^1\text{-}Ph_2PC(O)CH_3)]$ were found to be air stable solids Scheme 5.

Crystals of complex (**8**) were grown by layering a CH_2Cl_2 solution with diethyl ether. The X-ray structure of complex (**8**) confirms the spectroscopic data that show the phosphomides co-ordinated to Rh(III) in a monodentate fashion. The complex has the expected octahedral pianostool structure with the Rh–C bonds varying in length depending on whether they are *trans* to the phosphomide or chloride ligands. From the 21 X-ray structures of transition metal that contain P–C=O bonds in the Cambridge crystallographic database, the average P–C bond length of the P–C=O substituent is 1.87 Å. The P–C bond length within the structure reported here (1.917(2) Å) is somewhat longer than in any of the structures previously reported, which may be consistent with our observations regarding the stability of this phosphomide and its metal complexes, which are readily cleaved by adventitious water. In (**8**) this P–C length is significantly longer than the two P–Ph bonds (Fig. 2). This implies little contribution of a resonance structure that involves a $P{=}C{-}O^-$ bond in phosphomide ligands. A structural comparison between free ligands and metal complexes has not proved possible due to the lack of crystallinity for the ligands prepared so far. The Rh–P and Rh–Cl bond lengths are similar to other $[RhCp^*Cl_2(PR_3)]$ complexes that we have reported [15] (Fig. 3).

The extra stability of ligands (**1**), (**2**) and (**3**) suggested to us that these ligands might be sufficiently stable for catalytic applications. Hydroformylation of olefins is one of the most important homogeneously catalysed reactions in industry and there is currently considerable interest in obtaining structure–activity/selectivity relationships for the wide array of phosphine ligands that are known. A study of this nature may, in addition to improving understanding, lead to improved ligand modified catalysts for this reaction.

Somewhat surprisingly, phosphomides are quite possibly unreported as ligands for homogeneous catalysis. Catalysts prepared in situ from the new ligands and $[Rh(acac)(CO)_2]$ were tested in hydroformylation of hex-1-ene. The two phosphomides were tested under the same conditions alongside triphenylphosphine. Rates of reaction could be estimated by following syngas uptake over time. Yield and selectivity were determined by G. C. M. S. at the end of the 3 h reaction period. Relative

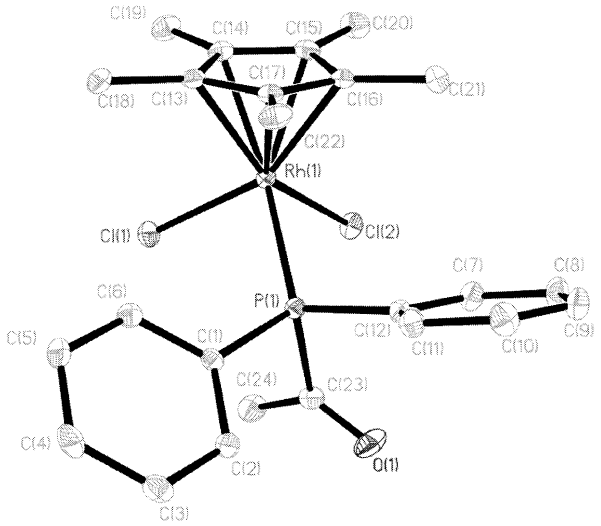
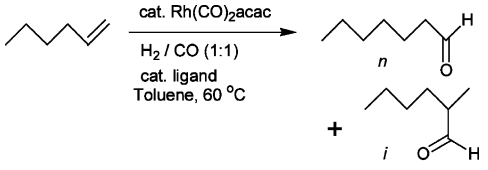


Fig. 3. Molecular structure of $[Cp^*RhCl_2\{Ph_2PC(O)CH_3\}]$. All hydrogen atoms have been omitted for clarity. Important molecular parameters: bond lengths (Å) Rh(1)-P(1) 2.3188(5), Rh(1)-Cl(1) 2.4132(6), Rh(1)-Cl(2) 2.4060(6), P(1)-C(1) 1.833(2), P(1)-C(12) 1.816(2), P(1)-C(23) 1.917(2); bond angles (°) P(1)-Rh(1)-Cl(1) 91.11(2), P(1)-Rh(1)-Cl(2) 84.68(2), Cl(1)-Rh(1)-Cl(2) 93.33(2).

rates of reaction and yield and selectivity are shown in Table 1 and Scheme 6.

The new phosphomides ligands do give active rhodium catalysts for hydroformylation of hex-1-ene. However, the reactions were catalysed more efficiently using the commercially applied catalyst $Rh(CO)_2acac/PPh_3$. Graphs of syngas uptake for the first 2 h of the



Scheme 6.

Table 1
Hydroformylation of hex-1-ene using new phosphomide ligands and $Rh(acac)(CO)_2$ as catalyst

Ligand	Conversion of hexene (%) [a,b]	*n*:*i* [a]	T.O.F. [c]
PPh_3	95	2.9	380
(1)	60	2.6	ND
(2)	77	2.0	157
(3)	85	2.1	200
(4)	0	ND	ND

Reactions were carried out under identical conditions: 60 °C, 20 bar CO/H_2 (1:1), 3 h, 0.2 mol% catalyst, L/Rh = 4.5. The values are taken from the first 50% of the reaction where gas uptake is linear (mol prod/molscatalysts/h). ND = not determined.

[a] determined by G. C. M. S. using biphenyl as an internal standard.

[b] no other products except aldehydes could be detected by G. C. M. S.

[c] calculated from a graph of syngas uptake over time.

reaction show gas consumption is still proceeding for the phosphomides, which suggests that complete conversion would be reached under more forcing conditions or longer reaction times. G. C. M. S. analysis of the reaction mixtures at the end of the reaction showed all three catalysts showed good selectivity towards aldehydes, while the two phosphomide derived catalysts show a greater proportion of branched aldehyde than triphenylphosphine catalysts. Catalysts derived from the perfluorinated ligand (**4**), do not show any catalytic activity in hydroformylation, presumably due to the intrinsic instability of the ligand.

Since (**2**) gives a greater proportion of branched products than triphenylphosphine, we have also tested this ligand in hydroformylation of 4-vinylanisole: a reaction in which the branched isomer is favoured and of more synthetic value. We have found that phosphomide (**2**) gives high conversions (80%) of vinylanisole to give the desired branched 2-aryl-propanal products with a branched to linear ratio of ca. 19:1. A triphenylphosphine based system gave 95% yield of 2-aryl-propanal with branched to linear ratio of 13:1 under similar conditions.

Although this new ligand modified catalyst offers no real advantages in hydroformylation, we have demonstrated that phosphomides can be used as ligands for this reaction. Since these ligands are so readily prepared, it should be straightforward to prepare a family of mono-, di- and hemi-labile phosphines that can be screened as ligands in homogeneous catalysis. We have also shown that the presence of the carbonyl group does not interfere with the ability of the phosphorus to act as a ligand for rhodium complexes, and that the stability of the phosphomide may be strongly influenced by the substituents that are nearby the carbonyl group. We are currently investigating the scope of the primary/secondary phosphine+acid chloride route for the synthesis of a variety of phosphorus ligands, and applying them in homogeneous catalysis.

3. Experimental

3.1. General

All manipulations were carried out under an atmosphere of nitrogen, using standard Schlenk line techniques, and at room temperature unless otherwise stated. All solvents were dried and degassed by elution through an alumina column impregnated with deoxygenating catalysts under nitrogen, and stored under nitrogen. ^{31}P-NMR spectra were recorded using an Eclipse 300 spectrometer. ^{1}H and ^{13}C-NMR spectra were recorded by the University of Bristol NMR Service using a Lambda 300 MHz spectrometer. Chemical analyses were performed by the School of Chemistry Microanalytical Laboratory. E.I. and F.A.B. mass spectra were recorded by the University of Bristol mass spectrometry service using a 'VG Analytical Autospec' mass spectrometer. IR were recorded on NaCl discs as CH_2Cl_2 solutions (rhodium complexes) or neat thin films (ligands), on a Perkin–Elmer 1600 Series FTIR (samples were prepared in air immediately prior to running spectra). All other chemicals were obtained commercially (Aldrich, Lancaster, Fluorochem).

3.2. Ph_2PCOCH_3

Acetyl chloride (0.220 g, 2.81 mmol) was added dropwise over ca. 20 min to a solution of diphenylphosphine (0.524 g, 2.81 mmol) and triethylamine (0.284 g, 2.81 mmol) in diethyl ether (20 ml) and stirred for 2 h. The reaction mixture was filtered to remove the triethylamine hydrochloride and solvent was removed in vacuo leaving a yellow oil in essentially quantitative yield. This compound has been reported previously. It was identified by comparison of NMR and MS data with those reported in Refs. [7,8]. ^{31}P-NMR (121.4 MHz, $CDCl_3$), δ 19. IR ν(CO) = 1670 cm^{-1}. EIMS: 320 (M+).

3.3. Ph_2Panisoyl, (**1**)

o-Anisoyl chloride (0.480 g, 2.813 mmol) was added dropwise over ca. 20 min to a solution of diphenylphosphine (0.524 g, 2.81 mmol) and triethylamine (0.284 g, 2.81 mmol) in diethyl ether (20 ml) and stirred for 2 h. The reaction mixture was filtered to remove the triethylamine hydrochloride and solvent was removed in vacuo leaving a yellow oil in essentially quantitative yield. This compound has been reported previously by the addition of trimethylsilyldiphenylphosphine to anisoic acid in 37% yield. It was identified by comparison of NMR and MS data with those reported in Ref. [16]. ^{31}P-NMR (121.4 MHz, $CDCl_3$), δ 25. IR ν(CO) = 1782 cm^{-1}. EIMS: 320 (M+).

3.4. $(NCCH_2CH_2)_2$Panisoyl, (**2**)

o-Anisoyl chloride (2.05 ml, 1.79 g, 10.5 mmol) was added dropwise over ca. 20 min to a solution of diethylcyanophosphine (1.47 g, 10.5 mmol) and triethylamine (0.77 ml, 1.06 g, 10.5 mmol) in toluene (30 ml) and stirred for 2 h. The reaction mixture was filtered to remove the triethylamine hydrochloride and solvent was removed in vacuo leaving a yellow oil (yield: 2.53 g, 9.2 mmol, 88%). This synthesis always gave material that was of very high purity, as determined spectroscopically. IR ν(C=O): 1730 cm^{-1} ν(CN): 2248 cm^{-1}. ^{31}P-NMR (121.4 MHz, $CDCl_3$), δ 9.6. ^{1}H-NMR (400 MHz, $CDCl_3$), δ 1.82 (2H, m, C**H**$_2$CH$_2$CN), 2.2 (2H, m, C**H**$_2$CH$_2$CN), 2.42 (2H, m, CH$_2$C**H**$_2$CN), 2.54 (2H, m,

CH_2CH_2CN), 3.9 (3H, s, OCH_3), 6.7–8.0 (4H, m, aromatic). ^{13}C-NMR (75.4 MHz, $CDCl_3$), δ 15.1, 20.7, 56.2, 112.3, 121.5 (m), 128.9, 135.1 (m), 158.5, 215.3. EIMS: Found: *m/z* 275 $(MH)^+$ requires 275.

3.5. Cy_2Panisoyl, (3)

o-Anisoyl chloride (0.74 ml, 0.85 g, 4.9 mmol) was added dropwise over ca. 20 min to a solution of dicyclohexylphosphine (1 ml, 0.98 g, 4.9 mmol) and triethylamine (0.69 ml, 4.9 mmol) in toluene (20 ml) and stirred for 2 h. The reaction mixture was filtered to remove the triethylamine hydrochloride and solvent was removed in vacuo leaving a yellow oil (yield: 1.49 g, 4.5 mmol, 91%). $C_{20}H_{29}O_2P$ requires: C, 72.26; H, 8.79. Found: C, 71.80; H, 9.35%. ν(C=O): 1739 cm^{-1}. ^{31}P-NMR (121.4 MHz, CH_2Cl_2), δ 32.1. ^{1}H-NMR (300 MHz, $CDCl_3$), δ 1.0–2.3 (12H, m, Cy), 3.8 (3H, s, OCH_3), 6.8–7.7 (4H, m, aromatic). EIMS: Found: *m/z* 332 (M^+).

3.6. Diphenyl-perfluoro-octanoylphosphine, (4)

Neat diphenyl-trimethylsilylphosphine (0.516 ml, 2.02 mmol) was added dropwise to an ice cold solution of perfluoro-octanoyl chloride (0.5 ml, 2.02 mmol) in THF. After stirring for 1 h, all volatiles were removed in vacuo to give a quantitative yield of the title compound as an air sensitive, analytically pure white powder. This ligand was also prepared in essentially quantitative yield by the reaction of Ph_2P–H with the acid chloride under similar conditions to those described for the other phosphomides above.

Anal. $C_{20}H_{10}F_{15}P_1O_1$ requires: C, 41.26; H, 1.73; Found: C, 41.07; H, 1.71. IR (ν_{max}/cm^{-1}) 1686 (CO). ^{31}P-NMR (121.4 MHz; $CDCl_3$): δ 23.3 (21 lines, app.-ttt) ($^3J_{P-F} = 23.3$, $^4J_{P-F} = 10.2$, $^5J_{P-F} = 5.6$ Hz). Intensities: septets (app.) are derived from tt

1 2 3 4 3 2 1 1 2 3 4 3 2 1
2 4 6 8 6 4 2

^{1}H-NMR (300 MHz; C_6D_6): δ 7.2–7.8 (10H, m, ArH). ^{19}F NMR (282.2 MHz, C_6D_6) δ: −82.6 tt (^3J = 10.0 Hz, $^3J = 1.9$ Hz), −115.5 qnt. App. $J = 9$ Hz), −120.2(s, br.), −120.3(s, br.), −123.4(s, br.), −124.1(s., br.), −127.7 (m, br.) MS (FAB+) 601 (M+Na+), 583 (MH+).

3.7. Trans-[Rh(Ph_2Pacetyl)$_2$(CO)Cl], (5)

Solid $[Rh(CO)_2Cl]_2$ (37 mg, 9.53×10^{-5} mol) was added in one portion to a dichloromethane solution of acetyldiphenylphosphine (87 mg, 0.382 mmol in 5 ml CH_2Cl_2). This immediately gave a solution containing the desired complex as the only product. Analytically pure material was obtained by removing solvent and washing the orange precipitate with diethyl ether (3 × 3 ml). Yield: 40 mg, 6.42×10^{-5} mol, 34%. $C_{29}H_{26}O_3P_2ClRh$ requires: C, 55.92; H, 4.21. Found: C, 55.76; H, 3.96%. ν(C=O): 1984, 1699 cm^{-1}. ^{31}P-NMR (121.4 MHz, CH_2Cl_2), δ 42.3, ($^1J_{P-Rh} = 125$ Hz). ^{1}H-NMR (300 MHz, $CDCl_3$), δ 2.96, (6H, t. app., J = 2.2 Hz, $C(O)CH_3$), 7.30 (12H, m, ArH), 8.3 (8H, m, ArH). FABMS: 588 (M–Cl)+.

3.8. Trans-[Rh(diphenyl-perfluoro-octanoylphosphine)$_2$(CO)Cl], (6)

Solid $(RhCl_2(CO)]_2$ (26 mg, 6.698×10^{-5} mol) was added in one portion to a solution of ligand (**1**) (156 mg, 2.679×10^{-6} mol) in THF. Removal of solvent and drying in vacuo gave the desired compound in quantitative yield as an air sensitive yellow powder.

Anal. $C_{41}H_{20}F_{30}P_2O_3Cl_1Rh_1$ requires: C, 37.00; H, 1.51; Found: C, 37.25; H, 1.50. IR (ν_{max}/cm^{-1}) 1990 (Rh–CO), 1724 (P–CO). ^{31}P-NMR (121.4 MHz; C_6D_6): δ 51.8 (d, $^1J_{P-Rh} = 131.9$ Hz). ^{1}H-NMR (300 MHz, $CDCl_3$), δ: 6.7–7.6 (10H, ArH). ^{19}F NMR (282.2 MHz, C_6D_6) δ: −81.1, (qnt, app., $J_{F-F} = 10.2$ Hz), −109.1 (s, br), −120.3 (s, br), −121.6 (s, br), −122.0 (s, br), −122.8 (s, br), −126.3 (s, br.).

3.9. Trans-[Rh(Ph_2Panisoyl)$_2$(CO)Cl], (7)

Solid $[Rh(CO)_2Cl]_2$ (28 mg, 7.1×10^{-5} mol) was added in one portion to a dichloromethane solution of anisoyldiphenylphosphine (91 mg, 0.284 mmol in 5 ml CH_2Cl_2). Removal of solvent gave the desired complex in high purity as determined spectroscopically. However, samples isolated in this way always gave chemical analyses that were too low for carbon (by c. 1%). Layering a CH_2Cl_2 solution with diethyl ether gave a few yellow crystals of the desired complex that analyses as the ether solvate. $C_{41}H_{34}O_5P_2Cl_1Rh \cdot Et_2O$ requires: C, 61.3; H, 5.15. Found: C, 62.1; H, 5.14%. ν(C=O): 1976 cm^{-1}. ^{31}P-NMR (121.4 MHz, CH_2Cl_2) δ 47.5, ($^1J_{P-Rh} = 130$ Hz). ^{1}H-NMR (300 MHz, $CDCl_3$), δ 3.46 (6H, s, OMe), 6.75 (2H, d, $J = 8.3$ Hz, 3-anisoylH), 6.97 (2H, t, $J = 7.5$ Hz, 4-anisoylArH), 7.44 (14H, m, ArH), 7.71 (8H, m, ArH), 7.88 (2H, dd, $J = 1.7$, 7.7 Hz, 6anisoylArH). FABMS 829 (M+Na)+, 778 (M–CO)+, 771 (M–CO–Cl)+.

3.10. [RhCp*Cl$_2$(Ph_2C(O)CH_3)], (8)

To a Schlenk tube containing $[Cp^*RhCl_2]_2$ (116 mg, 0.188 mmol) and $Ph_2PC(O)CH_3$ (86 mg, 0.377×10^{-3} mol) was added CH_2Cl_2 (3 ml). The resulting solution was stirred for 2 h prior to removal of solvent. NMR spectroscopy revealed the desired complex in essentially

quantitiative yield and purity. Recrystallisation of some of this product by layering a CH_2Cl_2 solution with diethyl ether gave good quality red crystals suitable for X-ray diffraction. $C_{24}H_{28}P_1O_1Rh_1Cl_2$ requires: C, 53.65; H, 5.25. Found: C, 53.90; H, 5.56. ν(C = O): 1654 cm^{-1}. ^{31}P-NMR (121.4 MHz, CD_2Cl_2) δ 39.3, ($^1J_{P-Rh} = 142$ Hz). ^{1}H-NMR (300 MHz, $CDCl_3$), δ: 1.4 (15H, d, $^4J_{H-P} = 3.5$ Hz), 2.45 (3H, d, $^3J_{H-P} = 4.6$ Hz), 7.4–7.7 (10H, m, ArH). FABMS: 501 (M–Cl)+.

3.11. [RhCp*Cl$_2$(Ph$_2$C(O)(CF$_2$)$_6$CF$_3$)], (9)

To a Schlenk tube containing $[Cp^*RhCl_2]_2$ (41 mg, 6.61×10^{-5} mol) and ligand (**4**) (77 mg, 1.322×10^{-4} mol) was added THF (3 ml) and CH_2Cl_2 (3 ml). After heating to reflux, the resulting solution was stirred for 2 h (Longer reaction times lead to decomposition). Removal of solvent gave the desired complex in essentially quantitiative yield and purity. $C_{30}H_{25}F_{15}P_1O_1Rh_1Cl_2$ requires: C, 40.43; H, 2.83. Found: C, 40.91; H, 3.24. ν(C=O): 1730 cm^{-1}. ^{31}P-NMR (121.4 MHz, CD_2Cl_2) δ 45.5, ($^1J_{P-Rh} = 145$ Hz). ^{1}H-NMR (300 MHz, $CDCl_3$), δ 1.3 (15H, d, $J_{H-P} = 2.7$ Hz), 7.3–7.9 (10H, m, ArH). ^{19}F NMR (282.2 MHz, C_6D_6) δ: −81.0 (t, br $^3J = 10.0$ Hz), −110.0 (s, br), −120.3 (s, br), −121.5 (s, br), −122.3 (s, br), −123.0 (s, br), −126.3 (m, br). FABMS: 855 (M–Cl)+. This red solid slowly decomposed in air to [Cp*RhCl$_2$(η^1-Ph$_2$PH); ^{31}P-NMR (121.4 MHz, CD_2Cl_2 ^{1}H coupled) δ 14.8, (dd, $^1J_{P-Rh} = 143$ Hz, $^1J_{P-H} = 388$ Hz). Lit.[14] = δ 13.5, ($^1J_{P-Rh} = 142$ Hz).

3.12. [RhCp*Cl$_2$(Ph$_2$Panisoyl)], (10)

To a Schlenk tube containing $[Cp^*RhCl_2]_2$ (42 mg, 7.02×10^{-5} mol) and Ph_2Panisoyl (45 mg, 1.405×10^{-4} mol) was added CH_2Cl_2 (3 ml). The resulting solution was stirred for 2 h prior to removal of solvent. The red ppte was washed with diethyl ether and dried in vacuo. NMR spectroscopy revealed the desired complex in essentially quantitiative yield and purity. $C_{24}H_{28}P_1O_1Rh_1Cl_2 \cdot 0.2CH_2Cl_2$ (solvent present in NMR spectrum) requires: C, 56.16; H, 5.05. Found: C, 55.33; H, 4.92. ^{31}P-NMR (121.4 MHz, CD_2Cl_2) δ: 40.1($^1J_{P-Rh} = 141$ Hz). ^{1}H-NMR (300 MHz, $CDCl_3$), δ: 1.5 (15H, d, $^4J_{P-Rh} = 3.3$ Hz), 3.4 (3H, s), 5.3 (0.4H, s, 0.2 CH_2Cl_2), 6.48 (1H, d, $J = 8.6$ Hz, 3-anisoylH), 6.8 (1H, t, $J = 7.5$ Hz, 4-anisoylH), 7.2–7.35 (7H, m, ArH), 7.6 (1H, dd, $J = 1.7$, 7.5 Hz, 6-anisoylH), 7.8 (4H, m, ArH). FABMS: 593 (M–Cl).

3.13. Hydroformylation of 1-hexene

These were conducted in a stainless steel autoclave held at constant pressure and connected to a ballast vessel from which CO (or syngas) 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, 1.9×10^{-5} mol, 0.2%), ligand (8.6×10^{-5} mol, 0.9%) biphenyl (0.468 g, 3.038 mmol) in toluene (4 ml), were added to the autoclave which was then flushed with syngas. The autoclave was then pressurised (10 bar) and stirred at 60 °C for 1 h to allow the catalyst to form. Hex-1-ene (1.2 ml) was injected and the pressure adjusted to 20 bar. The gas uptake was followed over time.

Hydroformylation of 4-vinylanisole was carried out using the same apparatus using Rh(acac)CO_2 (13.0 mg, 5.1×10^{-5} mol, 1%), ligand (1.02×10^{-4} mol, 2%) in C_6D_6 (4 ml). The reactions were carried out at 50 °C, 30 bar syngas for 16 h and analysed by ^{1}H-NMR at the end of the reaction time.

3.14. X-ray crystallography

X-ray diffraction experiments on **8** were carried out at −100 °C on a Bruker SMART diffractometer. Crystal data: red block, $0.2 \times 0.5 \times 0.5$ mm^3, $C_{24}H_{28}Cl_2OPRh$; $a = 11.9443(13)$, $b = 15.492917$, $c = 12.6695(14)$ Å, $\beta = 91.515(2)^\circ$, monoclinic, space group $P2_1/n$ (No. 14), $Z = 4$, Bruker SMART diffractometer ω scan, Mo–$K_\alpha$radiation $\lambda = 0.71073$ Å, 24550 intensity data, 5366 unique, $R_{int} = 0.0381$, 99.9% complete to $\theta = 27.5^\circ$, absorption correction based on equivalent reflections, $R_1 = 0.0232$ [for 4335 reflections with $I > 2\sigma(I)$], 374 parameters, Largest difference map peak and hole 0.462 and −0.346 e $Å^{-3}$, $wR_2 = 0.0530$ for all data refined against F_o^2 with hydrogen atoms riding in calculated positions.

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC 198449 for compound (**8**).

Acknowledgements

We would like to thank Prof. Paul Pringle (University of Bristol) for useful discussions. We also wish to thank the Leverhulme Trust and University of Bristol for financial support.

References

[1] (a) P.W.N.M. Van Leeuwen, C.F. Rooboeek, J. Organomet. Chem. 258 (1983) 343;
(b) T. Jongsma, G. Challa, P.W.N.M. Van Leeuwen, J. Organomet. Chem. 421 (1991) 121.

[2] L. Webber, Angew. Chem. I.E.E. 41 (2002) 563 (and references therein).
[3] (a) A.M. Trzeciak, T. Glowiak, R. Grzybek, J.J. Ziolkowski, J. Chem. Soc. Dalton Trans. (1997) 1831;
(b) M.P. Magee, W. Luo, W.P. Hersh, Organometallics 21 (2002) 362;
(c) K.G. Molloy, J.L. Petersen, J. Am. Chem. Soc. 117 (1995) 7696.
[4] (a) M.F. Ernst, D.M. Roddick, Inorg. Chem. 28 (1989) 1624;
(b) C.P. Casey, E.L. Pausen, E.W. Beuttenmueller, B.R. Proft, L.M. Petrovich, B.A. Matter, D.A. Powell, J. Am. Chem. Soc. 119 (1997) 11817;
(c) D.R. Palo, C. Erkey, Organometallics 19 (2000) 81;
(d) A.M. Banet Osuna, W. Chen, E.G. Hope, R.D.W. Kemmitt, D.R. Paige, A.M. Stuart, J. Xiao, L. Xu, J. Chem. Soc. Dalton Trans. (2000) 4052;
(e) D.F. Foster, D.J. Adams, D. Gudmundsen, A.M. Stuart, E.G. Hope, D.J. Cole-Hamilton, J. Chem. Soc. Chem. Commun. (2002) 722;
(f) J.D. Unruh, J.R. Christenson, J. Mol. Catal. 14 (1982) 19.
[5] (a) E. Lindner, H. Lesiecki, Chem. Ber. 112 (1979) 773;
(b) H. Lesiecki, E. Lindner, G. Voedermaier, Chem. Ber. 112 (1979) 793;
(c) A. Varchney, G.M. Gray, Inorg. Chim. Acta 148 (1988) 215.
[6] (a) A.R. Barron, S.W. Hall, A.H. Cowley, J. Chem. Soc. Chem. Commun. (1987) 1753;
(b) H. Kunzek, K. Braun, E. Nesener, K. Ruhlmann, J. Organomet. Chem. 49 (1973) 149.
[7] R.G. Kostyanovsky, V.V. Yakshin, S.L. Zimont, Tetrahedron 24 (1968) 2995.
[8] K. Issleib, E. Priebe, Chem. Ber. 85 (1952) 239.
[9] C. Roch-Neirey, N. Le Bris, P. Laurent, J. Clement, H. Des Abbayes, Tetrahedron Lett. 42 (2001) 643.
[10] H. Shargghi, F. Tamaddon, Tetrahedron 52 (1996) 13623.
[11] D.H.M.W. Thewissen, J. Organomet. Chem. 192 (1980) 115 (There is to the best of our knowledge only one rhodium complex derived from phosphomide type ligands known).
[12] We have also found that ligand (**2**) reacted readily with the well known rhodium starting materials $[(COD)RhCl]_2$, $[Cp^*RhCl_2]_2$, $[Rh(CO)_2Cl]_2$ to give the expected monodentate complexes which were characterised spectroscopically: D.A. Ratcliffe, Hons Project, University of Bristol, 2002.
[13] R.D.W. Kemmitt, D.I. Nichols, R.D. Peacock, J. Chem. Soc. Sect. A (1968) 1898.
[14] H. Werner, B. Klingert, A.L. Rheingold, Organometallics 7 (1988) 911.
[15] M.L. Clarke, A.M.Z. Slawin, M. Wheatley, J.D. Woollins, J. Chem. Soc. Dalton Trans. (2001) 3421.
[16] M. Dankowski, K. Praefcke, J. Lee, S.C. Nyburg, Phos. Sulfur Silicon 8 (1980) 359.