

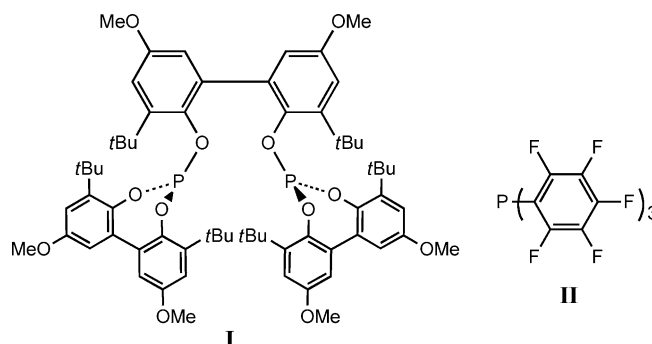
Stable Fluorophosphines: Predicted and Realized Ligands for Catalysis**

Natalie Fey,* Michael Garland, Jonathan P. Hopewell, Claire L. McMullin, Sergio Mastroianni, A. Guy Orpen, and Paul G. Pringle*

Phosphorus(III) compounds are the ancillary ligands of choice in many areas of modern homogeneous catalysis,^[1,2] from bulk chemical processes (e.g. hydroformylation, hydrocyanation, carbonylation) to fine-chemicals production (e.g. asymmetric hydrogenation, C–C coupling, C–N coupling). The field is dominated by ligands containing P–C and P–O bonds with a few examples featuring P–N bonds. This fact is not surprising, because these P–X bonds are generally thermally robust and inert to cleavage by transition metals under the catalysis conditions; these ligand properties are essential for the maintenance of catalyst integrity.

Triaryl phosphites are used as ligands in the commodity chemical processes hydroformylation and hydrocyanation.^[1] However, the susceptibility of P(OAr)₃ ligands to hydrolysis has necessitated the installation of large hydrophobic groups in diphosphites such as **I** to provide sufficient protection of the P–O functionality to make their commercial deployment feasible.^[3] Furthermore, the lability of phosphites makes their application as ligands problematic for catalytic processes in aqueous or alcoholic media^[4] and with substrates containing protic functional groups. Therefore, there is a need for robust, π -acceptor ligands as alternatives to phosphites.^[5] Fluoroaryl phosphines such as **II** were considered candidates, since they feature non-labile P–C bonds and their Tolman electronic and steric parameters^[6] are similar to those for bulky phosphites. Disappointingly, we found that ligand **II** gives catalysts with essentially zero activity in hydroformylation and hydrocyanation.^[7] Thus the fact that ligands have similar Tolman parameters is not a reliable predictor of catalyst activity.

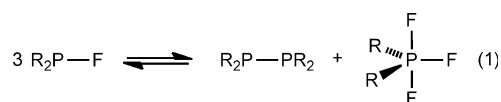
Recently we reported a map (Figure 1)^[8] derived from a broader range of calculated ligand parameters collected in the ligand knowledge base. On this ligand map, fluoroaryl



phosphines (green triangles) are clearly distinguished from aryl phosphites (blue triangles) and therefore, on this measure, would not be expected to resemble each other as ligands for catalysis. It was of interest to explore whether this map could be used to discover non-labile ligands with activities similar to bulky aryl phosphites.

With the limited experimental data available for predictive modeling (see Ref. [8] for a discussion of multivariate regression models), proximity in ligand space was used as a first indicator of catalytic potential. It is evident in Figure 1 that fluorophosphines of the type R₂PF (red squares) lie in the vicinity of triaryl phosphites.

Fluorophosphines R₂PF are readily made from the corresponding compound R₂PCl and have been known for over 50 years.^[9] The P^{III}–F bond is very strong at 545 kJ mol^{–1},^[10] and metal complexes have been reported for some R₂PF ligands.^[11] However, no applications of fluorophosphines in catalysis have been described,^[12] perhaps because of the instability of R₂PF with respect to the disproportionation reaction shown in Equation (1).^[13]



Schmutzler, Riesel, and others^[13–17] have thoroughly investigated this disproportionation and found that 1) fluorophosphines such as Ph₂PF, Me₂PF, and *n*Bu₂PF disproportionate readily,^[13,14] which essentially precludes their application in catalytic processes that involve ligand dissociation; 2) fluorophosphines with bulky or electron-withdrawing substituents such as (C₆F₅)₂PF,^[15] (CF₃)₂PF,^[9,16] and *t*Bu₂PF^[17] are thermally stable. Whether the source of the stability is thermodynamic or kinetic has not been determined (see below).

[*] Dr. N. Fey, M. Garland, Dr. J. P. Hopewell, C. L. McMullin, Prof. A. G. Orpen, Prof. P. G. Pringle
School of Chemistry, University of Bristol
Cantock's Close, Bristol BS8 1TS (UK)
E-mail: natalie.fey@bristol.ac.uk
paul.pringle@bristol.ac.uk

Homepage:
http://www.inchm.bris.ac.uk/people/fey/group_top.html
<http://www.inchm.bris.ac.uk/people/pringle/welcome.html>

Dr. S. Mastroianni
Rhodia Centre de Recherches et Technologies de Lyon
85 Rue des Frères Perretts, 69192 Saint-Fons Cedex (France)

[**] We would like to thank the EPSRC (Grant No. EP/E059376/1 to N.F.), COST Network CM0802, and Rhodia for support and Johnson–Matthey for the loan of precious metals.

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/anie.201105954>.

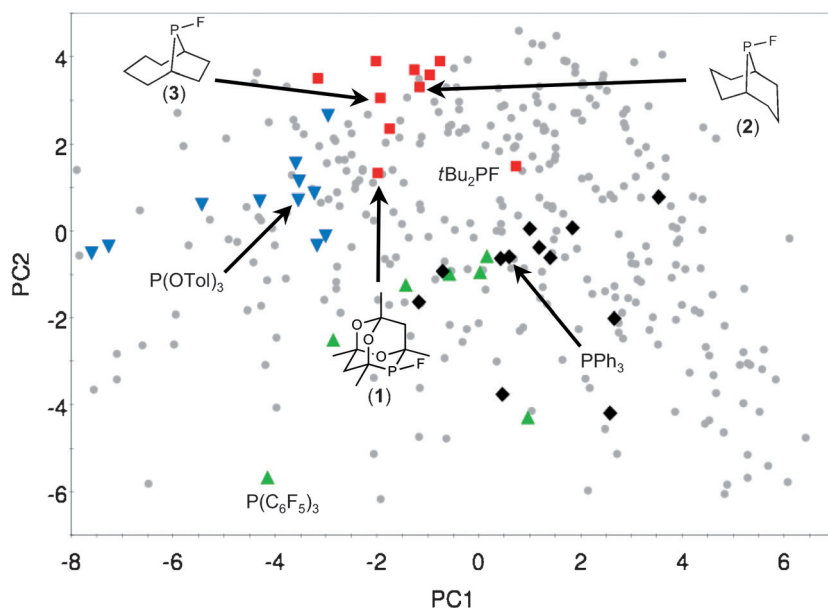
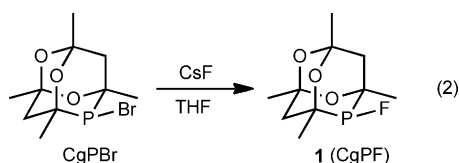


Figure 1. Map of ligand space, showing PAr_3 (black diamonds), $\text{P}(\text{Ar}^{\text{F}})_3$ (green triangles), $\text{P}(\text{OAr})_3$ (blue triangles), and R_2PF (red squares). Other ligand classes are represented as gray dots. Ar^{F} = fluoroaryl, Tol = toluene, PC = Principal Component.

The phosphatrioxa-adamantane cage moiety [denoted CgP in Eq. (2)] behaves like a bulky and electron-withdraw-



ing R_2P group,^[18] and therefore we reasoned that the compound CgPF (**1**) may be a particularly stable fluorophosphine. Indeed, treatment of CgPBr with CsF in THF gave **1** quantitatively as an air-stable, white solid, which has been fully characterized. Single crystals of **1** were grown from CHCl_3 , and its structure is shown in Figure 2. This is the first reported crystal structure of a fluorophosphine. The small C-P-C angle of 94.5° is a result of the constraints of the cage.^[18]

Compound **1** is remarkably thermally and hydrolytically stable. As a solid it can be stored in air indefinitely, and

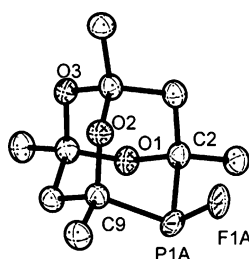
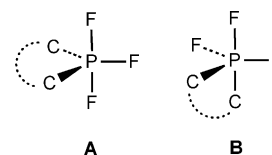


Figure 2. Molecular structure of **1**. Thermal ellipsoids are set at the 50% probability level. Selected bond lengths [Å] and angles [°]: P1A–F1A 1.574(7), P1A–C2 1.887(6), P1A–C9 1.873(8); F1A–P1A–C2 99.0(4), F1A–P1A–C9 100.9(4), C2–P1A–C9 92.7(3).

solutions of **1** in aqueous MeCN (1%) remained unchanged after 60 days. The stability of CgPF is consistent with the bulk and electronegativity of the CgP moiety. For the following reasons, we suggest that a third component of the stability of CgPF is the constraint that the cage puts on the C-P-C angle. The higher apicophilicity of F than of alkyl ligands explains the observation that the isomer formed by R_2PF_3 has the R groups diequatorial.^[19] If CgPF were to disproportionate according to Equation (1), the same apicophilicity arguments would lead to the prediction that the favored isomer of CgPF₃ would have the cage occupying diequatorial sites (isomer **A**). However, the cage imposes a C-P-C angle close to 90° that would destabilize isomer **A** and relatively favor the apical-equatorial isomer **B**.^[20] Either way, the energy of CgPF₃ will be raised, and this increase would contribute to the stability of CgPF to disproportionation.



These ideas led us to consider whether the thermodynamic stability of R_2PF to disproportionation could be predicted from computational studies. Some very simple density functional theory (DFT) calculations were carried out on R_2PF compounds to assess their stability with respect to disproportionation [Eq. (1)] (see the Supporting Information for details). It is observed experimentally that **1** and $t\text{Bu}_2\text{PF}$ are stable with respect to disproportionation,^[17] while Ph_2PF and Me_2PF are unstable.^[13,14] Consistent with this finding, the calculated DFT energies (Table 1) for the disproportionation were calculated to be greater than zero for **1** and $t\text{Bu}_2\text{PF}$ and less than zero for Ph_2PF and Me_2PF . Calculations also

Table 1: DFT calculated relative energy differences (ΔE) for the disproportionation shown in Equation (1) and relative isomer stabilities for **A** and **B**.

Ligand	Disproportionation ΔE [kcal mol ⁻¹]	Relative energy [kcal mol ⁻¹]	
		A	B
Me_2PF	–15.8	0.0	12.7 ^[a]
$t\text{Bu}_2\text{PF}$	5.4	0.0	37.1 ^[a]
Ph_2PF	–15.9	0.0	18.6 ^[a]
1	3.2	1.3	0.0
2	4.2	0.8	0.0
3	–2.5	not found ^[b]	0.0

[a] Optimized with frozen C-P-C angle. [b] Optimized to axial-equatorial isomer **B**.

suggested that the new bicyclic fluorophosphines **2** and **3** (see Figure 1) should be tenable, and so these then became synthetic targets (see below). In agreement with our ideas on the relative destabilization of the diequatorial isomer **A** for ligands with constrained C-P-C angles, ligands **1–3** no longer favor diequatorial isomer **A** for R_2PF_3 , whereas the others showed a substantial preference for **A**. The source of the stability of tBu_2PF with respect to disproportionation lies in the high energy of the very hindered $tBu_2P-PtBu_2$ product. (Similarly, the congestion in $CgP-PCg$ destabilizes this product.^[21]) The energies of all trigonal-bipyramidal R_2PF_3 isomers and key structural parameters have been included in the Supporting Information. In cognizance of the ligand-map information (Figure 1) and the stability predictions, we decided to focus the catalyst testing on ligands **1–3** and tBu_2PF .

The synthesis of *sym*-PhobPF (**2**) and *asym*-PhobPF (**3**) was straightforward from the corresponding chlorophobanes and CsF in MeCN, and both compounds showed no tendency towards disproportionation. In aqueous MeCN (1 %) 50 % of **2** or **3** was hydrolyzed in approximately ten hours, which makes them less hydrolytically stable than **1** but much more stable than tBu_2PF (100 % hydrolyzed under the same conditions in less than four minutes).

Treatment of $[Rh_2Cl_2(CO)_4]$ with **1** gave *trans*- $[RhCl(CO)(CgPF)_2]$ as a mixture of *rac* and *meso* isomers (associated with the C_1 symmetry of the $CgPF$);^[18] the two well-resolved AA'MM'X patterns in the ^{31}P NMR spectrum of the product are evident in Figure 3. Fluorophosphines **2**, **3**, and tBu_2PF also gave complexes of the type

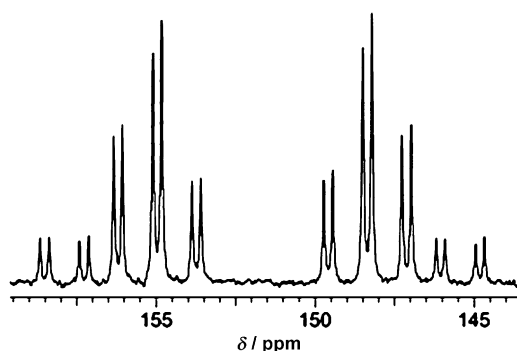


Figure 3. ^{31}P NMR spectrum of *trans*- $[RhCl(CO)(CgPF)_2]$.

trans- $[RhCl(CO)(R_2PF)_2]$, and the ν_{CO} values for these complexes (see Table 2) reflect the stronger σ -donor properties of ligands **2**, **3**, and tBu_2PF compared to **1**. Treatment of $[Ni(cod)_2]$ ($cod = 1,5$ -cyclooctadiene) with one to four equivalents of **1** in toluene gave solutions that, according to the ^{31}P NMR spectrum, contained mixtures of Ni^0 complexes. In the presence of two equivalents of **1** (as in the catalysis described below) the product consists predominantly of two species in a 3:1 ratio. The ^{31}P NMR spectrum at ambient temperature showed broad signals which at higher temperatures resolved into two characteristic AA'XX' patterns. These signals have been assigned to the *rac* and *meso* isomers of $[Ni(cod)(CgPF)_2]$; the fluxionality is tentatively assigned to

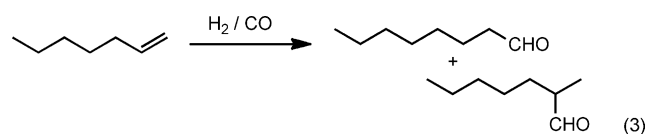
Table 2: Catalytic hydroformylation of 1-heptene.^[a]

	Ligand	ν_{CO} [cm^{-1}]	Conversion [%]	Aldehyde ^[b] [%]	<i>n</i> / <i>iso</i>
1	1	2011	95	89	3.9
2	2	1991	73	95	2.9
3	3	1995	98	95	2.4
4	tBu_2PF	1992	84	85	1.9
5	PPh_3	1965 ^[18]	99	90	2.2

[a] Reactions carried out in toluene except for entry 4, which was carried out in MeCN. At the end of a catalytic run, the autoclave was cooled rapidly and the catalyst quenched by addition of an excess of $P(OMe)_3$.^[25] See experimental details in the Supporting Information for catalysis conditions. IR spectra measured in CH_2Cl_2 . [b] The remaining product is a mixture of 2- and 3-heptene.

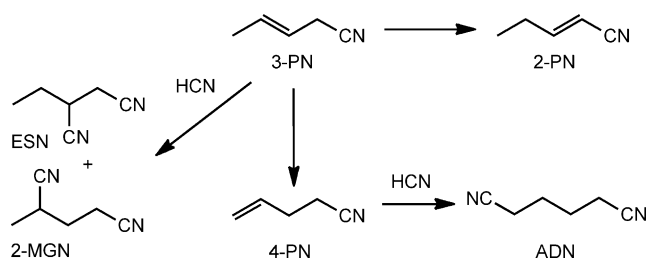
the presence of rotamers, as has been observed in complexes featuring $\{M(CgPH)_2\}$ moieties.^[22]

The hydroformylation of 1-heptene [Eq. (3)] is the first step in the Sasol process for its homologation to 1-octene.^[23] The hydroformylation was carried out under conditions that



allowed comparison to be made between the performance of the fluorophosphines and the commercial PPh_3 analogue (see experimental details in the Supporting Information). The results given in Table 2 show that the catalysts derived from **1–3** and tBu_2PF have comparable activities to the PPh_3 analogue. The *n*/*iso* ratio for **1** is a considerable improvement on the PPh_3 analogue. The ^{31}P NMR spectra of the reaction mixtures after the catalytic runs with **1** showed the presence of a rhodium-fluorophosphine complex, and thus it is clear that the P–F bond has remained intact during the catalysis.^[24]

The hydrocyanation of 3-pentenitrile (3-PN) to give adiponitrile (ADN, Scheme 1) is the most challenging step in the nickel(0)-catalyzed hydrocyanation of butadiene.^[26] It requires isomerization of 3-PN to the terminal isomer 4-PN and subsequent regioselective hydrocyanation. The results given in Table 3 show that **1** is an excellent ligand for the isomerization–hydrocyanation catalysis, comparing favorably with the commercial tritolyl phosphite nickel catalyst (Table 3, entry 7)^[27] in terms of activity (with $ZnCl_2$ cocata-



Scheme 1. Hydrocyanation of 3-PN. ESN = ethylsuccinonitrile, 2-MGN = 2-methylglutaronitrile.

Table 3: Catalytic hydrocyanation of 3-pentenitrile.^[a]

Entry	Ligand	Lewis acid	Yield [%]	Linearity [%]
1	1	ZnCl ₂	83	66
2	1	Ph ₂ BOBPh ₂	21	85
3	2	ZnCl ₂	13	76
4	2	Ph ₂ BOBPh ₂	28	52
5	<i>t</i> Bu ₂ PF	ZnCl ₂	4	50
6	<i>t</i> Bu ₂ PF	Ph ₂ BOBPh ₂	10	52
7 ^[b]	P(O- <i>o</i> -Tol) ₃	ZnCl ₂	60	82

[a] See experimental details in the Supporting Information for conditions. Linearity denotes the amount (%) of ADN formed relative to the total dinitrile (ADN/ESN/2-MGN) product. The results with ligand **3** showed that only traces (less than 1%) of hydrocyanation products were formed. [b] Data from Ref. [29].

lyst, Table 3, entry 1) and selectivity (with Ph₂BOBPh₂ cocatalyst, Table 3, entry 2). The fluorine substituent is decisive for the success of ligand CgPF (**1**) in this catalysis since, under the same conditions, the catalyst derived from CgPBr or CgPPH gave negligible (lower than 3%) yields of dinitriles.^[28]

The more electron-rich fluorophosphines **2** (Table 3, entries 3 and 4) and *t*Bu₂PF (Table 3, entries 5 and 6) also give active hydrocyanation catalysts. To our knowledge, these are the first ligands that are not based on P-OR groups to be reported which produce hydrocyanation catalysts for 3-PN (Scheme 1).

Guided by a ligand knowledge base map, we have investigated the viability of fluorophosphines as ligands for catalysis. Fluorophosphines based on a phosphadamantane cage or a phosphabicyclic are remarkably thermally stable, and this stability has been partly traced to the constrained C-P-C angles in these molecules, which inhibit disproportionation reactions. These new ligands are the first fluorophosphines to be used in catalysis and have been shown to perform as well as, or better than, commercial rhodium-based catalysts for heptene hydroformylation and nickel-based catalysts for 3-pentenitrile hydrocyanation. Further applications of this new class of ligands are under investigation, and exploitation of the stabilization of exocyclic P-X bonds in the design of new ligands for catalysis is being pursued.

Received: August 23, 2011

Published online: November 11, 2011

Keywords: homogeneous catalysis · hydrocyanation · hydroformylation · phosphacycles · phosphane ligands

- [1] a) *Applied Homogeneous Catalysis with Organometallic Compounds*, 2nd ed. (Ed.: B. Cornils), Wiley-VCH, Weinheim, **2002**; b) P. W. N. M. van Leeuwen, *Homogeneous Catalysis: Understanding the Art*, Springer, New York, **2004**; c) *Rhodium Catalyzed Hydroformylation*, 2nd ed. (Eds.: P. W. N. M. van Leeuwen, C. Claver), Kluwer, Dordrecht, **2000**.
- [2] a) *The Handbook of Homogeneous Hydrogenation* (Eds.: J. G. de Vries, C. J. Elsevier), Wiley-VCH, Weinheim, **2007**; b) A. Börner, *Phosphorus Ligands in Asymmetric Catalysis*, Wiley-VCH, Weinheim, **2008**; c) *Handbook of Metathesis* (Ed.: R. H.

Grubbs), Wiley-VCH, Weinheim, **2003**; d) *Metal-Catalyzed Cross-Coupling Reactions* (Eds.: A. de Meijere, F. Diederich), Wiley-VCH, Weinheim, **2004**.

- [3] a) E. Billig, A. G. Abatjoglou, D. R. Bryant (Union Carbide), U.S. Patent 4 599 206, **1986**; b) G. J. H. Buisman, L. A. van der Veen, P. C. J. Kamer, P. van Leeuwen, *Organometallics* **1997**, *16*, 5681–5687; c) G. J. H. Buisman, E. J. Vos, P. C. J. Kamer, P. W. N. M. van Leeuwen, *J. Chem. Soc. Dalton Trans.* **1995**, 409–417; d) G. D. Cuny, S. L. Buchwald, *J. Am. Chem. Soc.* **1993**, *115*, 2066–2068; e) G. Erre, S. Enthaler, K. Junge, S. Gladiali, M. Beller, *J. Mol. Catal. A* **2008**, *280*, 148–155, and references therein; f) R. Paciello, L. Siggel, H.-J. Kneuper, N. Walker, M. Röper, *J. Mol. Catal. A* **1999**, *143*, 85–97; g) A. van Rooy, P. C. J. Kamer, P. W. N. M. van Leeuwen, K. Goubitz, J. Fraanje, N. Veldman, A. L. Spek, *Organometallics* **1996**, *15*, 835–847; h) P. W. N. M. van Leeuwen, *Appl. Catal. A* **2001**, *212*, 61–81.
- [4] C. J. Cobley, P. G. Pringle, *Catal. Sci. Technol.* **2011**, *1*, 239–242.
- [5] a) M. N. Birkholz née Gensow, Z. Freixa, P. van Leeuwen, *Chem. Soc. Rev.* **2009**, *38*, 1099–1118; b) J. A. Gillespie, D. L. Dodds, P. C. J. Kamer, *Dalton Trans.* **2010**, *39*, 2751–2764, and references therein.
- [6] a) N. Fey, A. G. Orpen, J. N. Harvey, *Coord. Chem. Rev.* **2009**, *253*, 704–722; b) C. A. Tolman, *Chem. Rev.* **1977**, *77*, 313–348.
- [7] M. L. Clarke, D. Ellis, K. L. Mason, A. G. Orpen, P. G. Pringle, R. L. Wingad, D. A. Zaher, R. T. Baker, *Dalton Trans.* **2005**, 1294–1300.
- [8] a) N. Fey, A. C. Tsipis, S. E. Harris, J. N. Harvey, A. G. Orpen, R. A. Mansson, *Chem. Eur. J.* **2006**, *12*, 291–302; b) J. Jover, N. Fey, J. N. Harvey, G. C. Lloyd-Jones, A. G. Orpen, G. J. J. Owen-Smith, P. Murray, D. R. J. Hose, R. Osborne, M. Purdie, *Organometallics* **2010**, *29*, 6245–6258.
- [9] A. B. Burg, G. Brendel, *J. Am. Chem. Soc.* **1958**, *80*, 3198–3202.
- [10] D. J. Grant, M. H. Matus, J. R. Switzer, D. A. Dixon, J. S. Francisco, K. O. Christe, *J. Phys. Chem. A* **2008**, *112*, 3145–3156.
- [11] a) R. Bartsch, M. Hausard, O. Stelzer, *Chem. Ber.* **1978**, *111*, 1420–1433; b) L. Heuer, D. Schomburg, *J. Organomet. Chem.* **1995**, *495*, 53–59; c) T. G. Meyer, P. G. Jones, R. Schmutzler, *Z. Naturforsch. B* **1993**, *48*, 875–885; d) W. S. Sheldrick, O. Stelzer, *J. Chem. Soc. Dalton Trans.* **1973**, 926–929; e) O. Stelzer, R. Schmutzler, *J. Chem. Soc. A* **1971**, 2867–2873; f) O. Stelzer, R. Schmutzler, *Inorg. Synth.* **1978**, *18*, 173–179; g) O. Stelzer, E. Unger, *J. Chem. Soc. Dalton Trans.* **1973**, 1783–1788; h) O. Stelzer, E. Unger, *Chem. Ber.* **1975**, *108*, 1246–1258; i) A. R. Al-Ohaly, J. F. Nixon, *Inorg. Chim. Acta* **1981**, *47*, 105–109; j) C. G. Barlow, J. F. Nixon, J. R. Swain, *J. Chem. Soc. A* **1969**, 1082–1087; k) C. G. Barlow, J. F. Nixon, M. Webster, *J. Chem. Soc. A* **1968**, 2216–2223; l) A. B. Burg, G. B. Street, *Inorg. Chem.* **1966**, *5*, 1532–1537; m) F. T. Delbeke, E. G. Claeys, G. P. van der Kelen, *J. Organomet. Chem.* **1970**, *25*, 219–222; n) R. C. Dobbie, S. Morton, *J. Chem. Soc. Dalton Trans.* **1976**, 1421–1423; o) J. Grobe, D. Levan, W. Meyring, *Z. Anorg. Allg. Chem.* **1990**, *586*, 149–158; p) R. M. Lynden-Bell, J. F. Nixon, R. Schmutzler, *J. Chem. Soc. A* **1970**, 565–567; q) J. F. Nixon, *J. Chem. Soc. A* **1967**, 1136–1139.
- [12] Fluorophosphites have been reported as ligands for hydroformylation. See a) T. A. Puckette (Eastman), U. S. Patent US7301054, **2007**; b) T. A. Puckette, G. E. Struck (Eastman), U. S. Patent US5840647, **1998**; c) Y.-S. Liu, J. L. Rodgers (Eastman), U. S. Patent US2009071121, **2009**.
- [13] a) F. Seel, K. Rudolph, W. Gombler, *Angew. Chem.* **1967**, *79*, 686–687; *Angew. Chem. Int. Ed.* **1967**, *6*, 708–708; b) F. Seel, K. Rudolph, *Z. Anorg. Allg. Chem.* **1968**, *363*, 233–244; c) C. Brown, M. Murray, R. Schmutzler, *J. Chem. Soc. C* **1970**, 878–881; d) M. Pabel, A. C. Willis, S. B. Wild, *Inorg. Chem.* **1996**, *35*, 1244–1249.

- [14] a) J. Haenel, G. Ohms, L. Riesel, *Z. Anorg. Allg. Chem.* **1992**, 607, 161–163; b) L. Riesel, J. Haenel, *J. Fluorine Chem.* **1988**, 38, 335–340.
- [15] M. Fild, R. Schmutzler, *J. Chem. Soc. A* **1969**, 840–843.
- [16] H. G. Ang, R. Schmutzler, *J. Chem. Soc. A* **1969**, 702–703.
- [17] a) M. Fild, R. Schmutzler, *J. Chem. Soc. A* **1970**, 2359–2364; b) L. Riesel, J. Haenel, *Z. Anorg. Allg. Chem.* **1991**, 603, 145–150.
- [18] a) R. A. Baber, M. L. Clarke, K. M. Heslop, A. C. Marr, A. G. Orpen, P. G. Pringle, A. Ward, D. E. Zambrano-Williams, *Dalton Trans.* **2005**, 1079–1085; b) J. H. Downing, J. Floure, K. Heslop, M. F. Haddow, J. Hopewell, M. Lusi, H. Phetmung, A. G. Orpen, P. G. Pringle, R. I. Pugh, D. Zambrano-Williams, *Organometallics* **2008**, 27, 3216–3224.
- [19] a) E. L. Muettert, R. Schmutzler, W. Mahler, *Inorg. Chem.* **1963**, 2, 613–618; b) L. S. Bartell, K. W. Hansen, *Inorg. Chem.* **1965**, 4, 1777–1782; c) A. J. Downs, R. Schmutzler, *Spectrochim. Acta Part A* **1967**, 23, 681–701.
- [20] a) S. A. Bone, S. Trippett, P. J. Whittle, *J. Chem. Soc. Perkin Trans. 1* **1977**, 80–84; b) R. R. Holmes, *J. Am. Chem. Soc.* **1978**, 100, 433–446.
- [21] D. L. Dodds, J. Floure, M. Garland, M. F. Haddow, T. R. Leonard, C. L. McMullin, A. G. Orpen, P. G. Pringle, *Dalton Trans.* **2011**, 40, 7137–7146.
- [22] a) J. Hopewell, P. Jankowski, C. L. McMullin, A. G. Orpen, P. G. Pringle, *Chem. Commun.* **2010**, 46, 100–102; b) P. Jankowski, C. L. McMullin, I. D. Gridnev, A. G. Orpen, P. G. Pringle, *Tetrahedron: Asymmetry* **2010**, 21, 1206–1209.
- [23] P. W. N. M. van Leeuwen, N. D. Clément, M. J. L. Tschan, *Coord. Chem. Rev.* **2011**, 255, 1499–1517.
- [24] The ^{31}P NMR spectrum of the reaction mixture after the catalysis with **1** showed the presence of a Rh-CgPF complex along with ligand oxide, which is presumably due to reaction of the ligand with the aldehyde product. NMR spectroscopy data: complex $\delta = 171$ ppm, ($J_{\text{RhP}} = 172$, $J_{\text{PF}} = 849$ Hz); CgP(O)F $\delta = 41.7$ ppm, ($J_{\text{PF}} = 1144$ Hz).
- [25] M. Kranenburg, Y. E. M. van der Burgt, P. C. J. Kamer, P. W. N. M. van Leeuwen, K. Goubitz, J. Fraanje, *Organometallics* **1995**, 14, 3081–3089.
- [26] a) I. S. Mikhel, M. Garland, J. Hopewell, S. Mastroianni, C. L. McMullin, A. G. Orpen, P. G. Pringle, *Organometallics* **2011**, 30, 974–985; b) L. Bini, C. Müller, D. Vogt, *Chem. Commun.* **2010**, 46, 8325–8334; c) L. Bini, C. Müller, D. Vogt, *ChemCatChem* **2010**, 2, 590–608.
- [27] a) Y. Chia, W. C. Drinkard, E. N. Squire (DuPont), U. S. Patent 3766237, **1973** b) C. A. Tolman, *J. Chem. Educ.* **1986**, 63, 199–201; c) C. A. Tolman, R. J. McKinney, W. C. Seidel, J. D. Druline, W. R. Stevens, *Adv. Catal.* **1985**, 33, 1–46, and references therein.
- [28] S. Mastroianni, P. G. Pringle, M. Garland, J. Hopewell (Rhodia), World Patent WO 2010/145960, **2010**.
- [29] S. Mastroianni (Rhodia), World Patent WO 2009/153171, **2009**.