Filling a niche in “ligand space” with bulky, electron-poor phosphorus (III) alkoxides

Sharifa Hussein,[a] Denis Priester,[a] Paul Beet,[a] Jonathon Cottom,[a] Sam J. Hart,[a] Tim James,[a] Robert J. Thatcher,[a] Adrian C. Whitwood[a] and John M. Slattery,*[a]

Abstract: The chemistry of phosphorus(III) ligands, which are of key importance in coordination chemistry, organometallic chemistry and catalysis, is dominated by relatively electron-rich species. Many of the electron-poor P(III) ligands that are readily available have relatively small steric profiles. As such, there is a significant gap in “ligand space” where more sterically bulky, electron-poor P(III) ligands are needed. This contribution discusses the coordination chemistry, steric and electronic properties of P(III) ligands bearing highly fluorinated alkoxide groups of the general form $PR_n(OR^F)_{3-n}$, where R = Ph, R^F = $C(H)(CF_3)_2$ and $C(CF_3)_3$; n = 1-3. These ligands are simple to synthesize and a range of experimental and theoretical methods suggest that their steric and electronic properties can be “tuned” by modification of their substituents, making them excellent candidates for large, electron-poor ligands.

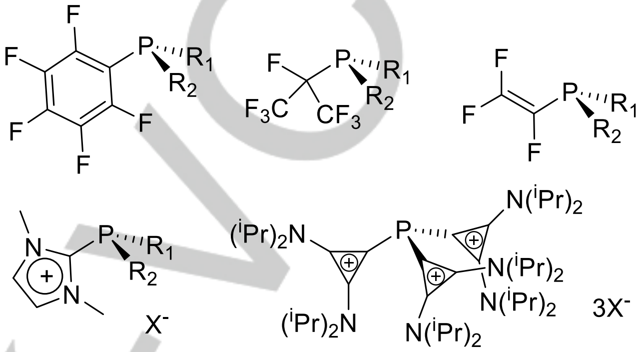


Figure 1. Selected examples of electron-poor P(III) ligand systems that have been explored. R_1 and R_2 are a range of alkyl, aryl or heteroatom-based functional groups and X^- is a suitable anion.

Introduction

Phosphorus(III)-centered Lewis bases are amongst the most commonly encountered ligands in organometallic chemistry and catalysis. The ability to “tune” the steric and electronic properties of these ligands by modification of the ligand substituents allows the properties of a metal complex to be tailored to suit a particular application. In order to facilitate the application of P(III)-ligands a number of parameters may be used to describe their steric and electronic properties. Ligand “cone angles”, S4′ and He_8 parameters, amongst others, are frequently used to describe steric properties.[1] The CO stretching vibrations of metal-carbonyl complexes e.g. $[Ni(L)(CO)_3]$, $[W(L)(CO)_5]$, $[Rh(L)(CO)_2Cl]$ and $[CpIr(L)(CO)]$, where L = the ligand of interest, or other spectroscopic features such as metal-phosphorus coupling constants are commonly used as indicators of electronic properties.[1f, 1i, 2] When combined, these data can provide a stereo-electronic map of phosphine “ligand space” that can be used to link structure to function and aid in the design of ligands and complexes for particular applications. Such design principles are exemplified in concepts such as Ligand Knowledge Bases (LKBs).[1h, 1i, 3]

It has been noted, when considering a map of ligand space, derived from computed steric and electronic parameters, that a large proportion of available P(III)-ligands are species that are relatively electron rich.[1f] The electron-poor P(III) ligands available are often relatively small, e.g. $P(CF_3)_3$ (cone angle = 137 °). Therefore, there exists a significant gap in ligand space corresponding to electron-poor, sterically bulky P(III) ligands. Several groups have attempted to fill this gap in ligand space, e.g. with ligands such as those in Figure 1. One approach has been to prepare P(III) ligands bearing perfluorinated *tert*-butyl, *iso*-propyl and *cyclo*-hexyl substituents.[1f, 4] However, studies involving these ligands are still relatively rare and their syntheses are often not trivial. Brisdon *et al.* and others have worked extensively on perfluorovinyl-containing phosphines ($PR_{3-n}(vinyl^F)_n$ {where R = Ph, NMe_2, NEt_2, EtO, ^iPr, Cy, BuO; n =1,2; $vinyl^F$ = $CF{=}CF_2$, $CCl{=}CF_2$, $CF{=}CFH$, $CCCF_3$} and the P-stereogenic phosphine $^nBuPhP(CF{=}CF_2)$.[4d, 5] These perfluorovinyl groups are quite electron withdrawing, similar electronically to alkoxy groups, but sterically smaller than that of a perfluorinated phenyl group.

An alternative approach to the use of fluorinated, electron-withdrawing groups in the preparation of electron-poor phosphines has been to include cationic groups at phosphorus. The area of α-cationic phosphines has seen tremendous growth in recent years and has uncovered some exciting ligands whose strongly electron-withdrawing properties have unlocked novel catalytic processes.[6] While these are undoubtedly exciting ligands, they also have some disadvantages, which mean they will not be appropriate for all situations. These include changes in solubility compared to neutral species, weaker M-L bonding and the potential for unwanted reactions at the cationic component. In addition, the more highly charged ligands, which

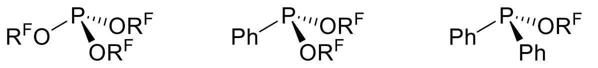
---

[a] Dr S. Hussein, Mr D. Priester, Dr J. Cottom, Mr S. J. Hart, Mr T. James, Dr R. J. Thatcher, Dr. A. C. Whitwood and Dr. J. M. Slattery.
Department of Chemistry
University of York, Heslington, York YO10 5DD (UK)
Fax: (+44) 01904 322516
E-mail: john.slattery@york.ac.uk

Supporting information for this article is given via a link at the end of the document.

are the most electron poor, have so far displayed only limited coordination chemistry. As such, there is still significant scope for the development of simple to synthesize, bulky P(III) ligands that are electron poor, to complement existing species and help to fill the gap in ligand space.

This paper discusses the coordination chemistry, steric and electronic properties of a series of phosphite, phosphonite and phosphinite ligands with the general formula $PR_{3-n}(OR^F)_n$ {R = Ph, OR^F = $C(CF_3)_3$, $C(H)(CF_3)_2$; n = 1-3} (Figure 2) using a combination of experimental and theoretical approaches. These species are simple to synthesize and the fluorinated alkoxide groups impart both steric bulk, and significant π-acceptor character to the ligands. The steric and electronic properties of these species can be tuned by varying R and R^F to give a variety of ligands with different electronic and steric combinations.



1: $R^F = C(H)(CF_3)_2$ **2**: $R^F = C(H)(CF_3)_2$ **3**: $R^F = C(H)(CF_3)_2$
4: $R^F = C(CF_3)_3$ **5**: $R^F = C(CF_3)_3$ **6**: $R^F = C(CF_3)_3$

Figure 2. Phosphorus ligands investigated in this work.

The chemistry of fluorinated phosphorus alkoxides has a long history and compounds **1**, **2**, **3** and **4** have previously been described.[7] However, their ligand chemistry and catalytic applications are not well developed. To the best of our knowledge **5** and **6** have not previously been reported. Of all the ligands that are known, the catalytic applications of $P\{OCH(CF_3)_2\}_3$ **1** have been investigated in the most detail. In early work, van Leeuwen investigated the use of **1** as a ligand in the Ni-catalysed cyclodimerisation of isoprene.[8] However, the observed yields were quite low. The same group later found that **1**, along with other sterically bulky, electron-poor ligands, formed highly active hydroformylation catalysts with Rh.[9] Ligand **1** has also been used successfully in catalytic systems for [4+2] cycloaddition reactions, for example those involving substrates that are electronically not well differentiated.[10] Recent work has shown that **1** can play an important role in the development of active catalysts for C-H functionalization reactions, primarily with Rh-based systems, but also with Pd.[10f, 10g, 11] As part of this work, Yanagisawa *et al.* demonstrated that the use of very bulky, electron-poor ligands appears to be essential for successful catalysis when $[RhCl(CO)L_2]$, where L = **1**, **2** and **3**, complexes are used as catalysts for the direct C-H coupling of heteroarenes with haloarenes.[11a] When L = **1**, 94 % conversions can be achieved, but when the number of fluorinated alkoxy groups at P are reduced (i.e. when L = **2**) conversions drop to 31 % and no conversion is seen for PPh_3 for the same substrates. It has also been possible to utilize **1** for the Ir-catalysed hydrosilylation of amides.[12]

Results and Discussion

Synthetic routes to compounds **1-3** have previously been reported by reaction of $PPh_{3-n}Cl_n$ (n = 1-3) with either $LiOC(H)(CF_3)_2$ or $HOC(H)(CF_3)_2$ and NEt_3. However, in our hands, reaction of the relevant P-chlorophosphine with $NaOC(H)(CF_3)_2$ in dry, degassed CH_2Cl_2 under ultrasonic activation has proved the most convenient source of these ligands. Compound **4** has previously only been synthesized by reaction of PCl_3 with $ClOC(CF_3)_3$.[13] The preparation of this hypochlorite, from ClF and $HOC(CF_3)_3$ with the elimination of HF, makes this route less accessible for standard synthetic labs and we were pleased to find that reaction of 3 equivalents of $NaOC(CF_3)_3$ with PCl_3 also gives **2**. Compounds **5** and **6** have, to the best of our knowledge, not been reported previously and can be synthesized in a similar manner to the above. Although all compounds reported here can be purified by distillation (sublimation in the case of **4**) for complexation reactions (see below) it is often possible to use the ligands as prepared in CH_2Cl_2 solution, after filtration to remove NaCl, without further purification. The $^{31}P\{^1H\}$, ^{19}F and ^1H NMR spectroscopic data for each compound can be found in Table 1.

Table 1. Spectroscopic data and isolated yields for ligands **1-6**.

Ligand	Isolated Yield (%)	δ $^{31}P\{^1H\}$ (ppm)	δ ^{19}F (ppm)	δ ^1H (ppm)[a]
1	39[b]	140	-74.7	4.80
2	61	190	-74.3 and -74.1[c]	4.64
3	70	143	-73.8	4.71
4	53	149	-72.3	NA
5	69	190	-71.4	NA
6	69	132	-71.7	NA

[a] Selected ^1H NMR chemical shifts, for $OC(H)(CF_3)_2$ groups only, are reported. [b] Although ^{31}P and ^{19}F NMR spectroscopy suggests that the formation of **1** is quantitative, the volatility of **1** means that loss of some product under vacuum is difficult to avoid during isolation.[c] Two environments are observed for each $C(H)(CF_3)_2$ group in the ^{19}F NMR of **2**, due to atropisomerism because of hindered rotation around either the P-O or O-C bond.

While **1**, **2**, **3**, **5** and **6** are liquids under standard conditions, **4** is a solid that crystallizes readily from CH_2Cl_2 solution. Although significant disorder (even at low temperature) appears to be present in all crystals of **4** grown under a variety of conditions, it was possible to obtain a single-crystal X-ray structure of this compound of suitable quality to establish structural connectivity (Figure 3). While a full discussion of the structural parameters of **4** is not appropriate given the quality of the model, the geometry around phosphorus appears to be similar to related aryl phosphites (e.g. $P(OPh)_3$, av. P-O 1.604 Å)[14] A space-fill representation of the structure of **4** (superimposed on Figure 3) suggests that **4** is a very sterically bulky ligand. In addition, the perfluoro-*t*-butoxide substituents appear to have little room for conformational flexibility, which suggests that this phosphite should have a relatively rigid steric profile compared to many phosphites, where conformational flexibility typically allows the alkoxide groups at phosphorus to adjust to the steric requirements of a metal complex.

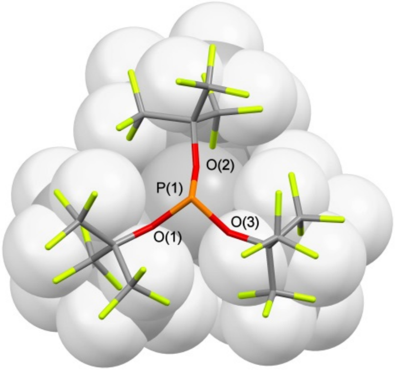


Figure 3. Single-crystal X-ray structure of $P\{OC(CF_3)_3\}_3$ (**4**). Monoclinic, C2/c, 110 K, R_1 = 0.1565, wR_2 = 0.4462. Whole-molecule disorder (modelled over two positions) in addition to CF_3 rotational disorder is present in the structure. Only one position is shown (and bond lengths and angles given for this) for clarity. Selected bond lengths (Å) and angles (°): P(1)-O(1) 1.609(11), P(1)-O(2) 1.615(11), P(1)-O(3) 1.610(12), O(1)-P(1)-O(2) 92.8(6), O(1)-P(1)-O(3) 93.0(6), O(2)-P(1)-O(3) 94.1(6).

The free ligands **1**-**6** are susceptible to hydrolysis, but unlike many electron-rich P(III) ligands do not appear susceptible to oxidation in air. In the case of **4**, it was possible to identify a product of partial hydrolysis, the pyrophosphite $(R^FO)_2P$-*μ*O-$P(OR^F)_2$ $\{R^F = C(CF_3)_3\}$ (**7**) in NMR spectroscopic ($^{31}P\{^1H\}$ NMR δ = 135 ppm; ^{19}F NMR δ = -71.4 ppm) studies and crystals of this species were fortuitously obtained from a reaction involving **4** where small amounts of water were inadvertently introduced. This species gives some insight into the mechanism of hydrolysis, but also suggests the possibility that bidentate analogues of **4** may be accessible *via* a suitable synthetic route. **7** has a characteristic multiplet at 135 ppm in the $^{31}P\{^1H\}$ NMR spectrum and crystals suitable for X-ray structural analysis were grown from CH_2Cl_2 solution (Figure 4).

As with the single-crystal X-ray structure of **4**, all crystals of **7** are heavily disordered, even at 110 K. In the case of **7**, this was modelled with the entire phosphorus-oxygen core being disordered over two positions (each with 50 % occupancy). As the model is still relatively poor, an extensive structural description is not appropriate. However, the data serve to confirm structural connectivity and suggest that the phosphorus centers exhibit distorted pyramidal geometries (with smaller O-P-O angles than in an ideal tetrahedral geometry). In addition, the phosphorus lone pairs point in opposite directions to each other, presumably as a consequence of the steric bulk of the two large $-OC(CF_3)_3$ groups at each phosphorus center. Structurally characterized examples of free, uncoordinated pyrophosphites are very rare. To the best of our knowledge only one previous example is present in the Cambridge Structural Database, the sterically congested pyrophosphite 6-[(2,4,8,10-tetrakis(1,1-dimethylethyl)-dibenzo[*d,f*][1,3,2]dioxaphosphepin-6-yl)oxy]-2,4,8,10-tetrakis(1,1-dimethylethyl)-dibenzo[*d,f*][1,3,2]dioxaphosphepin reported by DeBellis *et al.*[15] This displays a similar phosphorus-oxygen core conformation to that shown by **7**, with P-lone pairs pointing away from each other. Although any comparison of structural parameters is tentative, given the quality of the data for **7**, it appears that the P-O distances and O-P-O angles in **7** are comparable to those reported by DeBellis (although any subtle effects due to the inclusion of fluorinated alkoxides would not be identifiable in these data).

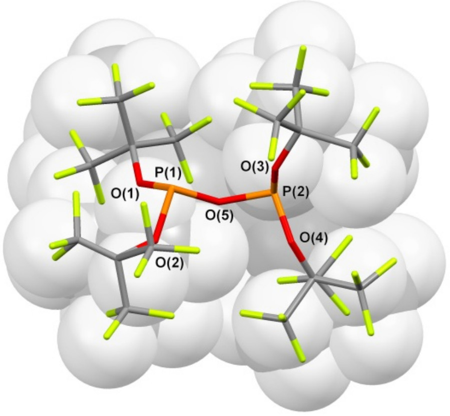


Figure 4. Single-crystal X-ray structure of $(R^FO)_2P$-*μ*O-$P(OR^F)_2$ $\{R^F = C(CF_3)_3\}$ (**7**). Orthorhombic, Pbca, 110 K, R_1 = 0.1170, wR_2 = 0.3379. Extensive disorder (modelled over two positions) is present in the structure. Only one position is shown (and bond lengths and angles given for this) for clarity. Selected bond lengths (Å) and angles (°): P(1)-O(1) 1.589(9), P(1)-O(2) 1.637(9), P(1)-O(5) 1.63(5), P(2)-O(3) 1.611(8), P(2)-O(4) 1.643(9), P(2)-O(5) 1.62(4), P(1)-O(5)-P(2) 136(3), O(1)-P(1)-O(2) 93.6(4), O(1)-P(1)-O(5) 96(2), O(2)-P(1)-O(5) 96.2(9), O(3)-P(2)-O(4) 93.4(5), O(3)-P(2)-O(5) 101(2), O(4)-P(2)-O(5) 100.2(8).

Steric properties

The steric properties of P(III) ligands are very important in coordination chemistry and catalysis and establishing the steric parameters of ligands **1**-**6** is important for understanding their relationship to more commonly encountered ligands. Tolman's cone angles (θ) have been chosen here to describe steric properties,[1a] as cone angles are widely available for other ligand systems and so wider comparison can be made, but also because some alternative steric parameters (i.e. S4′) are known to fail for phosphites. A ligand's cone angle can vary quite considerably depending on the metal fragment that it is attached to. As conformational flexibility in many ligands allows their steric profile to respond to the steric requirements of other ligands at the metal center, we have calculated θ for **1**-**6** using structural data for a range of complexes (from both experimental and DFT studies). The results are shown in Table 2, alongside data for some commonly encountered ligands for comparison. The magnitude of θ relates to size of the ligand, with larger θ values associated with more sterically bulky ligands. The range of θ values observed for a particular ligand can be interpreted as a rough measure of its conformational flexibility.

Table 2. Ligand cone angles (θ in °) for **1**-**6**. Where two ligands are present at the metal center, θ for both ligands are reported. X-ray diffraction data were not available for all complexes.

Ligand	$[Ni(CO)_3L]$[a]	$[W(CO)_5L]$[a]	[Ru 1] [b]	[Ru 2][c]	[Rh-complex][d]
1	178	155	160, 157	-	167, 160
2	173	162	146	147, 140	-
3	170	152	147	142, 142, 147, 158	-
4	195	180	180, 173	-	-
5	163	165	178	-	-
6	170	163	164	144, 144, 143, 142	193, 163
PMe_3	118[f]				
$P(CF_3)_3$	137[f]				
PPh_3	145[f]				
$P(OBu^t)_3$	175[f]				
PBu^t_3	182[f]				
$P(C_6F_5)_3$	184[f]				
$PMes_3$[e]	212[f]				

[a] From optimised structures at the (RI-)BP86/SV(P) level. [b] From single-crystal X-ray diffraction studies of $[(\eta^5C_5H_5)Ru(NCMe)_2L][PF_6]$. [c] From single-crystal X-ray diffraction studies of $[(\eta^5C_5H_5)Ru(NCMe)L_2][PF_6]$. In the case of ligand **3** two independent complexes are present in the asymmetric unit, so cone angles for both complexes are reported. [d] From single-crystal X-ray diffraction studies of $ClRh(CO)L_2$, including structure published in ref. [16]. [e] Mes = 2, 4, 6 trimethylphenyl. [f] Taken from references [17].

The cone angles for $[Ni(CO)_3L]$ complexes of ligands **1**-**6** allow a comparison of their steric properties with a range of examples from the literature. A selection of relevant cone angles from previously published data are included in Table 2. These data suggest that ligands **1**-**6** are somewhat larger than $P(CF_3)_3$ and PPh_3 and have similar steric properties to the bulky ligands $P(Bu^t)_3$, $P(C_6F_5)_3$ and $P(OBu^t)_3$. However, the conformational flexibility of the $–C_6F_5$ and $–OBu^t$ groups in the latter may allow these ligands to change their steric profile quite dramatically depending on the requirements of a particular metal fragment, whereas significantly reduced conformational flexibility is expected with ligands such as **4**. As expected, $P\{OC(CF_3)_3\}_3$ (**4**) shows a very large cone angle of 195 ° at $Ni(CO)_3$, which is considerably larger than $P(Bu^t)_3$ and even approaches the size of *ortho*-substituted aryl phosphines such as $PMes_3$ (θ = 212 °). When cone angles for **1**-**6** from all available crystal structures/calculations are considered it is clear that **4** is consistently larger than the other ligands across a range of complexes. This suggests that the bulky $–OC(CF_3)_3$ groups are locked into one conformation in **4**, rather than exhibiting the multiple conformations often observed for phosphites, giving this ligand a relatively stable steric profile across a range of coordination environments. However, trends for the other ligands are less clear. As with **4**, the phosphite **1** has a large cone angle for many complexes, but in the case of $[W(CO)_5L]$ θ is similar for **1** to other ligands with the $–OC(H)(CF_3)_2$ group. This may be an indication of some conformational flexibility that allows **1** to rearrange in response to the crowded environment around tungsten in these complexes. Those ligands with $–OC(CF_3)_3$ groups appear to be a little less flexible than those with $–OC(H)(CF_3)_2$ groups (on the basis of their generally smaller changes in θ on moving from $[Ni(CO)_3L]$ to the more crowded $[W(CO)_5L]$). Ligands **2, 3**, **5** and **6** have relatively similar θ values when all complexes are considered, due to conformational flexibility induced by the Ph substituents in these species. However, the reduced flexibility of the $–OC(CF_3)_3$ groups in **5** and **6** may mean that these ligands are able to have a greater steric influence at a metal center than **2** and **3**. All ligands occupy the desired “bulky” region of ligand space and are comparable, or larger than recently reported α-cationic phosphines.[6a]

Electronic properties

The electronic properties of ligands can be assessed using a variety of methods, but a convenient approach, which we have used previously to assess the donor properties of very electron-rich ligands, has been proposed by Gusev *et al*.[2d, 18] This involves geometry optimizations and vibrational frequency analyses of $[(\eta^5\text{-}C_5H_5)Ir(CO)L]$ complexes (where L is the desired ligand), using DFT methods, to obtain CO stretching frequencies and C-O bond lengths that vary as a function of the donor/acceptor properties of L. Gusev has shown that the use of this complex as opposed to other commonly used gauges of electronic properties {e.g. $[Ni(L)(CO)_3]$}, allows the comparison of a large range of different ligand classes using the same scale. A plot of ν(CO) against CO bond length for a range of ligands including **1**-**6** is shown in Figure 5.

Strongly donating ligands, e.g. PMe_3 appear at the top left of Figure 5, as these increase the extent of back bonding from Ir to the CO ligand. Electron-poor ligands, e.g. PF_3, appear at the bottom right of Figure 4, as they are more π-acidic and reduce the amount back bonding from the metal to CO. PH_3 has electronic properties in-between these two extremes. Ligands **1** and **4** are found to have similar electronic properties to PF_3. Substituting fluorinated alkoxide groups for phenyl groups brings the ligands’ electronic properties closer to PH_3. An interesting feature of these data is that although one would expect the perfluoro-*t*-butyl phosphite **4** to have greater π-acidity than **1,** due to the extra CF_3 groups, the data suggest that in fact the electronic properties of the two ligands are similar. This may be a consequence of the steric bulk of **2**, which prevents a close approach of the ligand to the metal center. This would reduce metal-phosphorus orbital overlap and prevent metal-ligand back donation. There is a slight elongation of the Ir-P bond in the optimized structure of $[(\eta^5\text{-}C_5H_5)Ir(CO)(\mathbf{4})]$ (2.198 Å) compared to $[(\eta^5\text{-}C_5H_5)Ir(CO)(\mathbf{1})]$ (2.194 Å) that may be related to this.

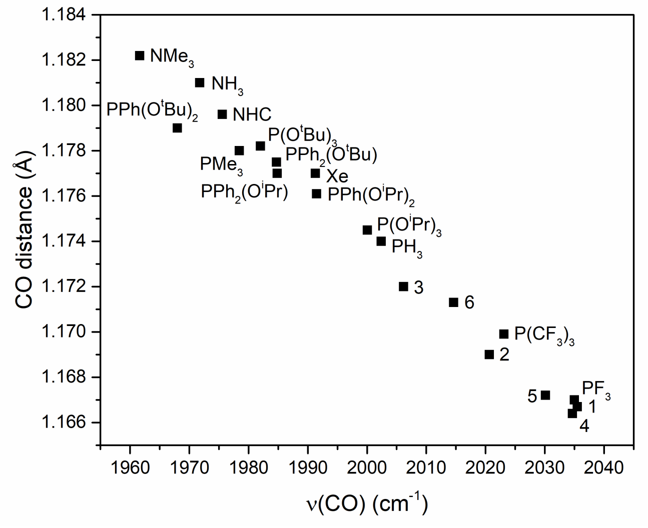


Figure 5. A plot of ν(CO)/cm^{-1} against CO bond length/Å for a range of ligands including **1**-**6**. NHC = 1,3-Dimethylimidazol-2-ylidene. Geometry optimisations and vibrational frequency calculations performed at the (RI-)BP86/SV(P) level.

In order to assess the electronic properties of these ligands via experimental measurements, tungsten and rhodium carbonyl complexes of **1**-**6** were prepared. Tungsten carbonyl complexes of the form [W(CO)$_5$L], where L = **1**-**6** were prepared by reaction of [W(CO)$_5$(THF)] with the relevant ligand in tetrahydrofuran (THF) solution.[19] The ^{31}P{^{1}H} NMR spectroscopic data for these complexes in THF, along with the carbonyl IR stretching frequencies (solution phase in THF/hexane) are summarized in Table 3. Four of these complexes were amenable to purification by sublimation (to remove excess [W(CO)$_6$] present in the crude products). However, complexes involving ligands **4** and **5** consistently decomposed under these conditions. It appears that ligand loss/exchange resulting in the formation of [W(CO)$_6$] and unidentified tungsten containing species is facile for these ligands. EI-MS confirmed the presence of the tungsten pentacarbonyl-ligand complexes ([M]$^+$ observed) in all cases and there is no evidence for the formation of [W(CO)$_4$L$_2$].

Both the IR stretching frequencies and $^1J_{WP}$ coupling constants in these complexes can be used as indicators of the electronic properties of the ligands. The $^1J_{WP}$ coupling constants appear to follow a trend where increasingly large values are seen for more electron-poor, π-acidic ligands. The $^1J_{WP}$ values for **1**-**3** (452, 357 and 291 Hz respectively) follow a trend that fits with the expectation that increasing the number of fluorinated alkoxide groups at P increases the π-acceptor character of the ligand. Steric effects appear to have an influence on the $^1J_{WP}$ coupling constants for ligands involving the bulky perfluorinated *t*-butoxy groups, as a simple relationship between $^1J_{WP}$ and the number of alkoxy groups at P is not found for **4**-**6** ($^1J_{WP}$ = 292, 374 and 304 Hz respectively). As observed with the [(η^5-C$_5$H$_5$)Ir(CO)L] stretching frequencies, the perfluorinated *t*-butyl phosphite **4** appears less π-acidic than would be expected given the number of fluorinated substituents. Presumably this is because of its large size, which prevents a close approach to the metal. The effect appears to be more pronounced for [W(CO)$_5$L] complexes, due to the larger steric requirements of the W(CO)$_5$ fragment compared to (η^5-C$_5$H$_5$)Ir(CO). When the $^1J_{WP}$ data for [W(CO)$_5$L] complexes involving **1**-**6** are compared to some common ligands in the literature the similarity in electronic properties between PF$_3$ and **1** are again evident (496 vs. 452 Hz respectively). The other ligands span a range of $^1J_{WP}$ values that place their electronic properties between those of P(CF$_3$)$_3$ and non-fluorinated phosphites at this metal fragment, consistent with their occupation of the electron-poor region of ligand space.

Table 3. Selected spectroscopic data for [W(CO)$_5$L] complexes, where L = **1**-**6**.

Ligand	δ **^{31}P{^{1}H} ($^1J_{PW}$)[a]**	**(*A$_1$*)$_1$ νCO[b]**	**(*A$_1$*)$_2$ νCO[b]**	**(*E*) νCO[b]**	**(*B$_1$*) νCO[b]**
1	147 (452)	2097	2002	1975	2017
2	183 (357)	2088	1970	1962	2002
3	150 (291)	2080	1968	1953	1992
4	150 (292)	2097 [c]	1989 [c]	1976 [c]	2007 [c]
5	174 (374)	2089 [c]	1980 [c]	1967 [c]	1999 [c]
6	149 (304)	2081	1964	1954	1996
PF$_3$ [20]	121 (496)	2101	2005	1975	-
P(CF$_3$)$_3$ [21]	55 (300)	2101	2001	1989	-
P(OMe)$_3$ [22]	138 (386)	2081	1952	1952	1980
P(OPr^i)$_3$ [22a, 23]	130 (381)	2075	1952	1937	-
PPh$_3$ [22b]	21 (243)	2075	1942	1942	1980
PMe$_3$ [21]	-40 (230)	2071	1949	1941	-

[a] Chemical shifts in ppm and coupling constants in Hz. [b] Stretching frequencies in cm^{-1}. Note that the antisymmetric {*E* and (*A$_1$*)$_2$} stretches are greater in peak intensity, therefore are more easily identified in the IR spectrum. As such, the reported vibrational frequencies for these stretches may be more reliable. *B$_1$* symmetric stretches are observed for **1**-**6** as the ligands result in complexes without perfect C$_4$v symmetry. [c] IR data extrapolated from (RI-)BP86/SV(P) calculations (see ESI for details).

The CO stretching frequencies for these tungsten complexes also show a trend of increasing π-acidity when more fluorinated alkoxy groups are substituted on the P(III) ligands. For example, the antisymmetric *E* stretch moves to lower wavenumbers from **1**-**3** (1975, 1962, 1953 cm^{-1} respectively) and from **4**-**6** (1976, 1967, 1954 cm^{-1} respectively). Interestingly these data are similar for related –OC(H)(CF$_3$)$_2$ and –OC(CF$_3$)$_3$ substituted ligands, suggesting similar electronic effects from both substituents, despite the higher degree of fluorination in the perfluoro-*t*-butyl case. Again, this may be due to steric effects. When compared to ligands in the literature, the CO stretching frequencies agree with the trends seen in the tungsten-phosphorus ($^1J_{WP}$) coupling constants in most cases, but there are some subtle differences. For example, the similarity between **1** and PF_3 is still evident {e.g. (E) νCO = 1975 cm^{-1} for both}. However, the relative ordering of ligands **1**-**6** compared to $P(CF_3)_3$ and the non-fluorinated phosphites is different to that suggested by the $^1J_{WP}$ data {with $P(CF_3)_3$ appearing to be the best acceptor ligand and ligands **1**-**6** showing better π-acceptor properties (i.e. νCO at higher wavenumbers) than the non-fluorinated phosphites}. This highlights the complexities involved in determining the relative electronic properties of different ligands and is a reminder that an electronic scale based on a single-property may not give a complete picture. In fact, a ligand's steric and electronic properties are probably best assessed in a range of different situations using several descriptors.

Coordination chemistry

Unfortunately it was not possible to grow crystals of $[W(CO)_5L]$ (L = **1**-**6**) complexes that were suitable for X-ray structural analysis. This is hampered in part by the slow decomposition of all complexes, even at -20 °C under an inert atmosphere. However, Itami *et al.* have recently reported Rh complexes of the form [*trans*-RhCl(CO)$(L)_2$] where L = **1** and **2** and explored their application in catalytic C-C bond forming reactions.[16] In order to make some comparisons across a range of ligand types we have synthesized analogous complexes where L = **4**, **5** and **6** by reaction of $[RhCl(CO)_2]_2$ with two equivalents of the free ligands in CD_2Cl_2. In the case of [*trans*-RhCl(CO)$(\mathbf{5})_2$] (**8**), crystals suitable for single-crystal X-ray diffraction studies were obtained by slow evaporation of the solvent from a solution of **8** in CH_2Cl_2 and the structure of this complex is shown in Figure 6. The complex shows a slightly distorted square planar geometry around Rh, where the P-Rh-Cl angle for P(1) is slightly larger than ideal (92.3 °) and the P-Rh-C distance for P(1) slightly smaller than ideal (88.7 °), with the opposite trend being seen for P(2). Of particular note in this structure are the relatively short Rh-P distances (2.287 and 2.302, av. 2.295 Å), which are significantly shorter than the average Rh-P distance (2.328 Å) for [*trans*-RhCl(CO)$(PR_3)_2$] complexes (with R_1 < 10 %) in the Cambridge Structural Database (CSD).[24] This may be a structural indication of increased π-back donation from Rh to this relatively electron poor ligand. The observation of even shorter Rh-P distances (2.2597(8) and 2.2550(7), av. 2.257 Å) in the *trans*-RhCl(CO)$(L)_2$ complex of the more electron-poor ligand **1**, support this suggestion. The [*trans*-RhCl(CO)$(L)_2$] complexes of **1**, **2**, **4**, **5** and **6** from this work and that of Itami *et al.* also allow a comparison of donor properties across the series using ν(CO) and $^1J_{RhP}$ data in a similar way to the Ir and W complexes described above. As this shows similar features to the data discussed for the Ir and W species a summary of key data is included in the ESI rather than here.

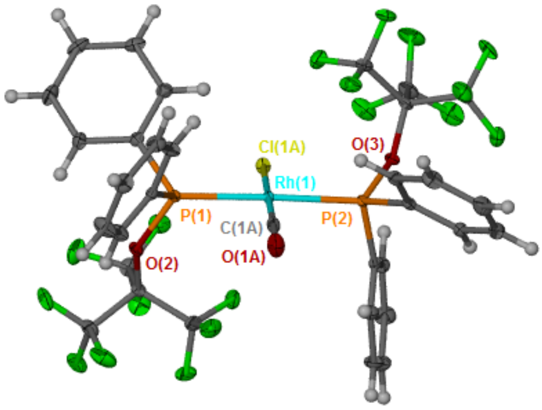


Figure 6. Single-crystal X-ray structure of RhCl(CO)(PPh_2OR^F) (**8**), where R^F = $C(CF_3)_3$. Tetragonal, $P4_2/n$, 110 K, R_1 = 0.0306, wR_2 = 0.0645. Cl and CO positions are disordered, disordered parts omitted for clarity. Thermal ellipsoids are drawn at the 50 % probability level. Selected bond lengths (Å) and angles (°): Rh(1)-P(1) = 2.2866(4), Rh(1)-P(2) = 2.3017(4), Rh(1)-Cl(1A) = 2.381(1), Rh(1)-C(1A) = 1.779(8), C(1A)-O(1A) = 1.15(1), P(1)-Rh-P(2) = 177.96(2), C(1A)-Rh-Cl(1A) = 169.68(5), P(1)-Rh(1)-Cl(1A) = 92.34(3), P(2)-Rh(1)-Cl(1A) = 87.22(3), C(1A)-Rh(1)-P(1) = 88.7(1), C(1A)-Rh(1)-P(2) = 91.62(14).

In addition to the W and Rh complexes described above, Ru complexes of the form $[(\eta^5\text{-}C_5H_5)Ru(NCMe)_{3-n}(L)_n][PF_6]$, where L = **1**-**6** and n = 1 or 2, have been synthesized by reaction of the free ligand in the relevant stoichiometry with $[(\eta^5\text{-}C_5H_5)Ru(NCMe)_3][PF_6]$ in CH_2Cl_2. Ru complexes of this type are of relevance in a range of catalytic transformations including alkyne dimerisation, alkyne hydration etc.[25] The spectroscopic data for these complexes are presented in Table 5. In all cases it was possible to obtain crystals suitable for analysis by single-crystal X-ray diffraction studies by slow diffusion of hexane into a solution of the complex in CH_2Cl_2 at room temperature. Representative structures of n = 1 and n = 2 complexes are shown in Figure 7 and 8 respectively and a .cif file containing all structures is included as supporting information.

In all structurally characterized $[(\eta^5\text{-}C_5H_5)Ru(NCMe)_{3-n}(L)_n][PF_6]$ (L = **1**-**6**, n = 1, 2) complexes Ru is found to adopt a distorted tetrahedral geometry (if the centroid of the C_5H_5 ring is taken as one vertex). The phosphite, phosphonite and phosphinite ligands in these complexes show a variety of conformations, due to rotation around the P-O bond, in the different structures. In the majority of cases the oxygen lone pairs on the OR^F group(s) point either towards the metal or broadly perpendicular to the M-P bond, which has the effect of moving the R^F group(s) away from the metal. This presumably reduces steric repulsion between the R^F groups and other ligands. Interestingly, in all ruthenium complexes of ligands containing the $–C(H)(CF_3)_2$ group the ^{19}F NMR spectra show two signals relating to inequivalent CF_3 environments. This suggests that coordination restricts rotation around the P-O or C-O bonds at room temperature on the NMR timescale, resulting in atropisiomerism (atropisiomers are only observed in the free ligands for ligand **2**, *vide supra*).

Table 5. Spectroscopic and structural data for [(η^5-C_5H_5)Ru(NCMe)$_{3-n}$(L)$_n$][PF_6] complexes, where L = **1-6** and n = 1 or 2.

Ligand (L)	δ ^{31}P	δ ^{19}F [a]	Ru-P(1)	Ru-P(2)	Ru-N(1)	Ru-N(2)
1, n = 1 (**9**)[b]	162	-73.8, -74.0	2.206	-	2.05	2.05
1, n = 2 [c]			-	-	-	-
2, n = 1 (**10**)	199	-73.4, -73.6	2.224	-	2.061	2.065
2, n = 2 (**11**)	199	-73.2, -73.4	2.262	2.265	2.059	-
3, n = 1 (**12**)	172	-72.6, -72.8	2.264	-	2.059	2.054
3, n = 2 (**13**)	168	-72.4, -72.7	2.278	2.277	2.046	-
4, n = 1 (**14**)	117	-71.0	2.233	-	2.015	2.071
4, n = 2 [c]	-	-	-	-	-	-
5, n = 1 (**15**)	192	-70.5	2.254	-	2.047	2.061
5, n = 2 [c]	-	-	-	-	-	-
6, n = 1 (**16**)	167	-70.4	2.263	-	2.069	2.065
6, n = 2 (**17**)	185	-69.1	2.289	2.299	2.048	-

[a] Two environments are observed for each C(H)(CF_3)$_2$ group in the ^{19}F NMR of complexes containing this functional group, due to atropisomerism. [b] There is significant disorder present in this structure (for C_5H_5, [PF_6]$^-$), which resulted in a relatively poor data set compared to other Ru complexes. [c] We found no evidence of the formation of these species in solution NMR spectroscopic studies.

The Ru-P distances in these complexes appear to follow a trend based on the π-acidity of the P-ligand(s) and the number of P-ligands at Ru. In general the Ru-P distances are shortest for the most π-acidic ligands for each type of alkoxide substituent {O(H)(CF_3)$_2$ and OC(CF_3)$_3$}. This can be interpreted as being due to an increase in π-backdonation from Ru to the more electron-poor ligands, which strengthens the Ru-P bond. For example, where R^F = O(H)(CF_3)$_2$ and n = 1 a very short Ru-P bond is seen for the phosphite **1** (2.206 Å) whereas a significantly longer Ru-P bond is seen for the phosphinite **3** (2.264 Å). A similar trend of increasing Ru-P bond length with decreasing π-acidity of the P-ligand is also seen where R^F = OC(CF_3)$_3$ and n = 1. However, it is interesting to note that the Ru-P bond in the Ru-complex of phosphite **4** (2.233 Å) is significantly longer than that seen in the hexafluoroisopropyl-substituted analogue (complex **9**, Ru-P = 2.206 Å), presumably due to the much larger steric profile of **4**. When comparing complexes of the same ligand with n = 1 and n = 2 (only complexes **12** and **13** allow this from the available data) it appears that increasing the number of P-ligands at Ru leads to an increase in the R-P bond lengths (from 2.264 to 2.278 Å in the case of **12** and **13**). This may be a result of competition between the P-ligands for π-backdonation from Ru or simply due to steric repulsion between these relatively large ligands.

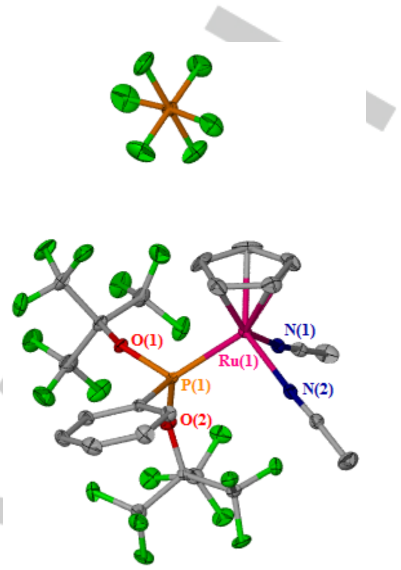


Figure 7. Single-crystal X-ray structure of [(η^5-C_5H_5)Ru(NCMe)$_2${PPh(OC{CF_3}$_3$)$_2$}][PF_6], **17**. Monoclinic, $P2_1/c$, R_1 = 0.0401, wR_2 = 0.0833. Hydrogen atoms and disordered parts (of [PF_6]$^-$ anion) omitted for clarity. Thermal ellipsoids are drawn at the 50 % probability level. Selected distances (Å) and angles (˚): Ru(1)-P(1) = 2.2541(6), Ru(1)-N(1) = 2.047(2), Ru(1)-N(2) = 2.061(2), N(1)-Ru(1)-P(1) = 94.77(6), N(2)-Ru(1)-P(1) = 97.49(6), N(1)-Ru(1)-N(2) = 86.63(8), O(1)-P(1)-O(2) = 94.10(9).

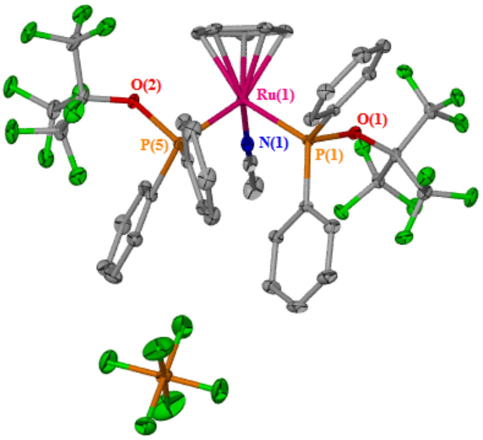


Figure 8. Single-crystal X-ray structure of [(η^5-C_5H_5)Ru(NCMe){PPh_2(OC{CF_3}$_3$)}][PF_6].0.5CH_2Cl_2, **16**. Monoclinic, $P2_1$, R_1 = 0.0332, wR_2 = 0.0745. The asymmetric unit contains two ion pairs, only one of which is shown for clarity. Hydrogen atoms and solvent of crystallisaion omitted for clarity. Thermal ellipsoids are drawn at the 50 % probability level. Selected distances (Å) and angles (˚): Ru(1)-P(1) = 2.2881(9), Ru(1)-P(2) = 2.2988(7) Ru(1)-N(1) = 2.048(2), N(1)-Ru(1)-P(1) = 89.96(7), N(1)-Ru(1)-P(2) = 96.01(6), P(1)-Ru(1)-P(2) = 99.07(3).

When compared to structural data in the literature, it was found that complexes **9-18** have Ru-P bond lengths that are significantly shorter than the average Ru-P distances for [(η^5-C_5H_5)Ru(NCMe)(L)$_2$]$^+$ (where L = any P(III) ligand) salts reported in the CSD (av. Ru-P = 2.33 Å for > 180 structures with $R_1 < 0.1$). Indeed, complex **9** shows the shortest Ru-P distance for any analogous complex with n = 1 or 2. The shortest Ru-P distance previously reported was 2.231(2) Å.[26] The Ru-N distances are, in most cases, relatively insensitive to the other ligands at Ru.

The solution chemistry in this system for the very bulky phosphite **4** is more complex than for the other ligands. Some evidence for the formation of $[(\eta^5\text{-}C_5H_5)Ru(NCMe)_2(P\{OC(CF_3)_3\}_3)][PF_6]$ (**14**) was found in the ^{31}P and ^{19}F NMR spectra with the appearance of signals at 117 and -71.1 ppm respectively after addition of a CH_2Cl_2 solution of **4** to $[(\eta^5\text{-}C_5H_5)Ru(NCMe)_3][PF_6]$ at room temperature. These were accompanied by the observation of free MeCN (at δ = 2.10 ppm) in the ^1H NMR spectrum. However, even after 4 days of stirring at room temperature ligand exchange is incomplete, with free **4** being seen in the ^{31}P NMR spectrum and a significant quantity of colorless crystalline material (undissolved **4**, which is relatively poorly soluble) seen in the reaction vessel. Heating the reaction mixture at 43 ºC for 24 hours in an attempt to solubilize ligand **4** and facilitate ligand exchange resulted in a decrease in the intensity of signals for **14** in the NMR spectra and a new species with $\delta(^{31}P)$ = 120.7 (doublet of multiplets, $^1J_{PF}$ = 1252 Hz). This was assigned as the complex $[(\eta^5\text{-}C_5H_5)Ru(NCMe)_2(PF\{OC(CF_3)_3\}_2)][PF_5\{OC(CF_3)_3\}]$ (**19**), which is supported by ESI-MS data which showed a strong signal at 768.9 m/z (for $[M]^+$) in the positive mode and 576.9 m/z (for $[PF_5\{OC(CF_3)_3\}]^-$) in the negative mode. ^{19}F NMR data also suggest the presence of this anion $\delta(^{19}F)$ = -62.3 ($F_{equatorial}$, doublet of doublet of multiplets, $^1J_{PF}$ = 746 Hz, $^2J_{FF}$ = 50 Hz) -73.86 (F_{axial}, doublet of quintets, $^1J_{PF}$ = 700 Hz, $^2J_{FF}$ = 50 Hz) and the P-F group on the substituted ligand $\delta(^{19}F)$ = 1.25 (doublet of multiplets, $^1J_{PF}$ = 1252 Hz, $^4J_{FF}$ = 4 Hz) ppm. The mechanism for this fluoride-alkoxide group exchange between ligand **4** and the $[PF_6]^-$ anion is unclear, but the driving force is likely to be reduction of the steric bulk of the ligand and so formation of a less sterically congested complex.

Although the reaction of **4** with $[(\eta^5\text{-}C_5H_5)Ru(NCMe)_3][PF_6]$ does not proceed to completion at room temperature, it was possible to identify crystals containing the desired cation (**14**), after decanting to remove unreacted **4** and crystallisation from a mixture of CH_2Cl_2 and Et_2O. The molecular structure of **14** is shown in Figure 9. While this contains the desired cation $[(\eta^5\text{-}C_5H_5)Ru(NCMe)_2\{P(OC\{CF_3\}_3)_3\}]^+$, in **14** it crystallises as a salt with the unusual counterion $[Na_4\{OC(CF_3)_3\}_4PF_6.MeCN]^-$. This anion results from the coordination of a $[PF_6]^-$ anion and a molecule of MeCN to a neutral sodium alkoxide cluster $[Na_4\{OC(CF_3)_3\}_4]$, which was present as a low concentration impurity in the sample of **4** used in this reaction. Cubic clusters are common structural forms in alkoxides of this type.[27] To the best of our knowledge compound **14** is the first structurally characterized example of a metal complex of **4**. The basic structure of **14** is similar to the other complexes described above. However, given the size of this ligand, the remarkably short Ru-P bond length (2.233 Å) is particularly noteworthy and may be an indication of relatively strong π-backdonation from Ru to P. Another interesting feature is the marked asymmetry in the Ru-N bond lengths (2.015 and 2.071 Å), which appear in other complexes described here to be relatively insensitive to the nature of the ligand. Although the ligand is heavily disordered (by rotation of CF_3 groups in the $–C(CF_3)_3$ groups) it appears that there is a closer approach of one C-F bond from **4** to the C≡N bond of the coordinated MeCN that displays a particularly short Ru-N distance (2.015 Å). It is possible that this asymmetry in the weak intramolecular interactions in the solid-state structure of **14** results in the asymmetry observed in the Ru-N bond distances, rather than this being related to the nature of the metal to P-ligand interaction.

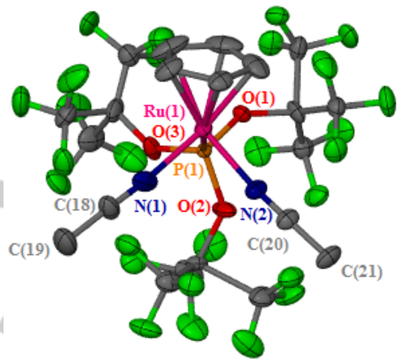


Figure 9. Single-crystal X-ray structure of $[(\eta^5\text{-}C_5H_5)Ru(NCMe)_2\{P(OC\{CF_3\}_3)_3\}][Na_4(OR^F)_4PF_6.MeCN]$, **14**. Monoclinic, $P2_1/n$, R_1 = 0.0623, wR_2 = 0.1677. Hydrogen atoms, anion and disordered parts (the C_4F_9 groups of both the anion and cation are heavily disordered by CF_3 group rotation) omitted for clarity. Thermal ellipsoids are drawn at the 50 % probability level. Selected distances (Å) and angles (˚): Ru(1)-P(1) = 2.233(1), Ru(1)-N(1) = 2.015(5), Ru(1)-N(2) = 2.071(4), N(1)-Ru(1)-P(1) = 94.00(13), N(2)-Ru(1)-P(1) = 93.18 (10), N(1)-Ru(1)-N(2) = 86.70 (17), O(1)-P(1)-O(2) = 98.4(3), O(1)-P(1)-O(3) = 97.8(3), O(2)-P(1)-O(3) = 96.2(4).

Conclusions

The steric profiles, electronic properties and coordination chemistry of a range of phosphorus(III) ligands bearing highly fluorinated alkoxide substituents has been investigated using a range of experimental and computational approaches. These ligands are relatively easy to synthesize and their steric and electronic properties are tunable depending on the substituents present at the phosphorus center. All ligands occupy the bulky, electron-poor region of ligand space where there are currently relatively few ligands available. Coordination of these ligands to a range of metal centers of relevance in homogeneous catalysis is possible and suggests that there are a range of potential applications of this class of ligand.

Experimental Section

All air-sensitive experimental procedures were performed under an inert atmosphere of nitrogen, using standard Schlenk line and glovebox techniques. Dichloromethane and hexane were purified with the aid of an Innovative Technologies anhydrous solvent engineering system. Et_2O and tetrahydrofuran were dried over sodium and distilled and stored under N_2 prior to use. CD_2Cl_2 used for NMR experiments was dried over

CaH_2 and degassed with three freeze-pump-thaw cycles. $CDCl_3$ was dried over 4 Å molecular sieves, distilled and stored under N_2 prior to use. All reagents were purchased from commercial sources, unless their preparation is described in the ESI. Solid reagents were used in the glove box without further purification. Fluoroinated alcohols were dried using 4 Å molecular sieves, distilled and stored under N_2 before use.

NMR spectra were acquired on a Jeol ECX-400 (Operating frequencies ^{1}H 399.78 MHz, ^{31}P 161.83 MHz, ^{19}F 376.17 MHz, ^{13}C 100.53 MHz) or a Bruker AVANCE 500 (Operating frequencies ^{1}H 500.13 MHz, ^{31}P 202.47 MHz, ^{13}C 125.77 MHz). ^{31}P and ^{13}C spectra were recorded with proton decoupling. Mass spectra were recorded on a Bruker micrOTOF or Esquire 6000 using electrospray ionisation. Infrared (IR) spectra were recorded on a Thermo-Nicolet Avator 370 FTIR spectrometer using CsCl solution cells for sample insertion at *ca.* 200 mg/mL concentration. A Unicam RS 10000E FTIR instrument, averaging 16 scans at resolution 1 cm^{-1} , was used with a SensIR ATR-IR accessory for solid samples.

Geometry optimisations and vibrational frequency analyses were performed at the (RI-)BP86/SV(P) level with the full ligand substituents used in the experimental study using TURBOMOLE.[28]

Full details of all synthetic, spectroscopic and computational procedures are given in the ESI.

Acknowledgements

We gratefully acknowledge the University of York and the EPSRC (DTA award to SH) for funding. We would also like to thank Professor Robin Perutz and Dr Jason Lynam for valuable discussions.

Keywords: Phosphorus ligands • coordination chemistry • ligand design • catalysis • DFT

[1] a) C. A. Tolman, *Chem. Rev.* **1977**, *77*, 313-348; b) B. J. Dunne, R. B. Morris, A. G. Orpen, *J. Chem. Soc., Dalton Trans.* **1991**, 653-661; c) T. L. Brown, K. J. Lee, *Coord. Chem. Rev.* **1993**, *128*, 89-116; d) D. White, N. J. Coville, *Adv. Organomet. Chem.* **1994**, *36*, 95-158; e) K. A. Bunten, L. Z. Chen, A. L. Fernandez, A. J. Poe, *Coord. Chem. Rev.* **2002**, *233*, 41-51; f) K. D. Cooney, T. R. Cundari, N. W. Hoffman, K. A. Pittard, M. D. Temple, Y. Zhao, *J. Am. Chem. Soc.* **2003**, *125*, 4318-4324; g) I. A. Guzei, M. Wendt, *Dalton Trans.* **2006**, 3991-3999; h) N. Fey, A. C. Tsipis, S. E. Harris, J. N. Harvey, A. G. Orpen, R. A. Mansson, *Chem. Eur. J.* **2006**, *12*, 291-302; i) N. Fey, A. G. Orpen, J. N. Harvey, *Coord. Chem. Rev.* **2009**, *253*, 704-722.

[2] a) L. Perrin, E. Clot, O. Eisenstein, J. Loch, R. H. Crabtree, *Inorg. Chem.* **2001**, *40*, 5806-5811; b) C. H. Suresh, N. Koga, *Inorg. Chem.* **2002**, *41*, 1573-1578; c) O. Kuhl, *Coord. Chem. Rev.* **2005**, *249*, 693-704; d) D. G. Gusev, *Organometallics* **2009**, *28*, 763-770; e) D. Cremer, E. Kraka, *Dalton Trans.* **2017**, *46*, 8323-8338; f) Q. Shi, R. J. Thatcher, J. Slattery, P. S. Sauari, A. C. Whitwood, P. C. McGowan, R. E. Douthwaite, *Chem. Eur. J.* **2009**, *15*, 11346-11360; g) J. Slattery, R. J. Thatcher, Q. Shi, R. E. Douthwaite, *Pure Appl. Chem.* **2010**, *82*, 1663-1671; h) R. J. Thatcher, D. G. Johnson, J. M. Slattery, R. E. Douthwaite, *Chem. Eur. J.* **2012**, *18*, 4329-4336.

[3] a) R. A. Mansson, A. H. Welsh, N. Fey, A. G. Orpen, *J. Chem. Inf. Model.* **2006**, *46*, 2591-2600; b) N. Fey, J. N. Harvey, G. C. Lloyd-Jones, P. Murray, A. G. Orpen, R. Osborne, M. Purdie, *Organometallics* **2008**, *27*, 1372-1383; c) N. Fey, M. F. Haddow, J. N. Harvey, C. L. McMullin, A. G. Orpen, *Dalton Trans.* **2009**, 8183-8196; d) 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; e) 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* **2012**, *31*, 5302-5306; f) N. Fey, S. Papadouli, P. G. Pringle, A. Ficks, J. T. Fleming, L. J. Higham, J. F. Wallis, D. Carmichael, N. Mezailles, C. Muller, *Phosphorus Sulfur Silicon Relat. Elem.* **2015**, *190*, 706-714.

[4] a) N. S. Imyanitov, G. I. Shmelev, *Zh. Obshch. Khim.* **1987**, *57*, 2161-2167; b) H. G. Ang, G. Manoussakis, Y. O. El-Nigumi, *J. Inorg. Nucl. Chem.* **1968**, *30*, 1715-1717; c) K. K. Banger, A. K. Brisdon, C. J. Herbert, H. A. Ghaba, I. S. Tidmarsh, *J. Fluorine Chem.* **2009**, *130*, 1117-1129; d) N. A. Barnes, A. K. Brisdon, F. R. William Brown, W. I. Cross, I. R. Crossley, C. Fish, C. J. Herbert, R. G. Pritchard, J. E. Warren, *Dalton Trans.* **2011**, *40*, 1743-1750; e) A. K. Brisdon, C. J. Herbert, *Chem. Commun. (Cambridge, U. K.)* **2009**, 6658-6660; f) Y. O. El Nigumi, H. J. Emeleus, *J. Inorg. Nucl. Chem.* **1970**, *32*, 3211-3212; g) B. N. Ghose, *J. Indian Chem. Soc.* **1978**, *55*, 1254-1259; h) J. Grobe, V. D. Le, *Chem. Ber.* **1990**, *123*, 1047-1049; i) M. Kato, K. Akiyama, M. Yamabe, *Asahi Garasu Kenkyu Hokoku* **1982**, *32*, 117-128; j) M. Kato, M. Yamabe, *J. Chem. Soc., Chem. Commun.* **1981**, 1173-1174; k) S.-i. Kawaguchi, Y. Minamida, T. Ohe, A. Nomoto, M. Sonoda, A. Ogawa, *Angew. Chem., Int. Ed.* **2013**, *52*, 1748-1752; l) L. C. Lewis-Alleyne, M. B. Murphy-Jolly, X. F. Le Goff, A. J. M. Caffyn, *Dalton Trans.* **2010**, *39*, 1198-1200; m) K. G. Sharp, I. Schwager, *Inorg. Chem.* **1976**, *15*, 1697-1701; n) Y. Sato, S.-i. Kawaguchi, A. Ogawa, *Chem. Commun. (Cambridge, U. K.)* **2015**, *51*, 10385-10388.

[5] a) E. A. Allan, L. W. Reeves, *J. Phys. Chem.* **1963**, *67*, 591-594; b) K. K. Banger, R. P. Banham, A. K. Brisdon, W. I. Cross, G. Damant, S. Parsons, R. G. Pritchard, A. Sousa-Pedrares, *J. Chem. Soc., Dalton Trans.* **1999**, 427-434; c) N. A. Barnes, A. K. Brisdon, F. R. W. Brown, W. I. Cross, I. R. Crossley, C. Fish, J. V. Morey, R. G. Pritchard, L. Sekhri, *New J. Chem.* **2004**, *28*, 828-837; d) N. A. Barnes, A. K. Brisdon, F. R. W. Brown, W. I. Cross, C. J. Herbert, R. G. Pritchard, G. Sadiq, *Dalton Trans.* **2008**, 101-114; e) N. A. Barnes, A. K. Brisdon, M. J. Ellis, R. G. Pritchard, *J. Fluorine Chem.* **2001**, *112*, 35-45; f) N. A. Barnes, A. K. Brisdon, J. G. Fay, R. G. Pritchard, J. E. Warren, *Inorg. Chim. Acta* **2005**, *358*, 2543-2548; g) N. A. Barnes, A. K. Brisdon, C. Fish, J. V. Morey, R. G. Pritchard, J. E. Warren, *J. Fluorine Chem.* **2010**, *131*, 1156-1164; h) N. A. Barnes, A. K. Brisdon, M. Nieuwenhuyzen, R. G. Pritchard, G. C. Saunders, *J. Fluorine Chem.* **2007**, *128*, 943-951; i) A. H. Cowley, M. W. Taylor, *J. Amer. Chem. Soc.* **1969**, *91*, 1922-1933; j) S. S. Dubov, F. N. Chelobov, R. N. Sterlin, *Zh. Vses. Khim. O-va. im. D. I. Mendeleeva* **1962**, *7*, 585; k) S. S. Dubov, B. I. Tetel'baum, R. N. Sterlin, *Zh. Vses. Khim. O-va. im. D. I. Mendeleeva* **1962**, *7*, 691-692; l) H. G. Horn, R. Koentges, F. Kolkmann, H. C. Marsmann, *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1978**, *33B*, 1422-1426; m) H. G. Horn, F. Kolkmann, *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1978**, *33B*, 1427-1429; n) Y. Y. Kharitonov, C. Ni, A. V. Babaeva, *Zh. Neorg. Khim.* **1962**, *7*, 21-33; o) R. G. Peters, J. D. Palcic, R. G. Baughman, *Acta Crystallogr., Sect. E: Struct. Rep. Online* **2003**, *59*, m1198-m1200; p) R. N. Sterlin, S. S. Dubov, *Zh. Vses. Khim. O-va. im. D. I. Mendeleeva* **1962**, *7*, 117-118; q) R. N. Sterlin, S. S. Dubov, W.-K. Li, L. P. Vakhomchik, I. L. Knunyants, *Zh. Vses. Khim. O-va. im. D. I. Mendeleeva* **1961**, *6*, 110-111; r) R. N. Sterlin, R. D. Yatsenko, L. N. Pinkina, I. L. Khunyants, *Khim. Nauka Prom-st.* **1959**, *4*, 810-811; s) R. N. Sterlin, R. D. Yatsenko, L. N. Pinkina, I. L. Knunyants, *Izv. Akad. Nauk SSSR, Ser. Khim.* **1960**, 1991-1997.

[6] a) M. Alcarazo, *Acc. Chem. Res.* **2016**, *49*, 1797-1805; b) K. Schwedtmann, G. Zanoni, J. J. Weigand, *Chem. Asian J.* **2018**, *13*, 1388-1405; c) A. G. Barrado, J. M. Bayne, T. C. Johnstone, C. W. Lehmann, D. W. Stephan, M. Alcarazo, *Dalton Trans.* **2017**, *46*, 16216-16227; d) Y. Garcia-Rodeja, I. Fernandez, *Organometallics* **2017**, *36*, 460-466; e) E. Gonzalez-Fernandez, L. D. M. Nicholls, L. D. Schaaf, C. Fares, C. W. Lehmann, M. Alcarazo, *J. Am. Chem. Soc.* **2017**, *139*, 1428-1431; f) L. H. Gu, L. M. Wolf, A. Zielinski, W. Thiel, M. Alcarazo, *J. Am. Chem. Soc.* **2017**, *139*, 4948-4953; g) M. Mehta, T. C. Johnstone, J. Lam, B. Bagh, A. Hermannsdorfer, M. Driess, D. W. Stephan, *Dalton Trans.* **2017**, *46*, 14149-14157; h) L. C. Wilkins, R. L. Melen, J. A. Platts, P. D. Newman, *Dalton Trans.* **2017**, *46*, 14234-14243; i) K. Abe, M. Kitamura, H. Fujita, M. Kunishima, *Molecular Catalysis* **2018**, *445*, 87-93; j) J. F. Binder, S. C. Kosnik, C. L. B. Macdonald, *Chem. Eur. J.* **2018**, *24*, 3556-3565; k) L. H. Gu, L. M. Wolf, W. Thiel, C. W. Lehmann, M. Alcarazo, *Organometallics* **2018**, *37*, 665-672; l) L. D. M. Nicholls, M. Marx, T. Hartung, E. Gonzalez-Fernandez, C. Golz, M. Alcarazo, *Acs Catal.* **2018**, *8*, 6079-6085; m) N. Kuhn, J. Fahl, D. Blaser, R. Boese, *Z Anorg Allg Chem* **1999**, *625*, 729-734; n) D. J. Brauer, K. W. Kottsieper, C. Liek, O. Stelzer, H. Waffenschmidt, P. Wasserscheid, *J. Organomet. Chem.* **2001**, *630*, 177-184; o) J. Y. Li, J. J. Peng, Y. Bai, G. D. Zhang, G. Q. Lai, X. N. Li, *J. Organomet. Chem.* **2010**, *695*, 431-436; p) J. Petuskova, H. Bruns, M. Alcarazo, *Angew. Chem. Int. Ed.* **2011**, *50*, 3799-3802; q) J. Petuskova, M. Patil, S. Holle, C. W. Lehmann, W. Thiel, M. Alcarazo, *J. Am. Chem. Soc.* **2011**, *133*, 20758-20760; r) C. Maaliki, C. Lepetit, Y. Canac, C. Bijani, C. Duhayon, R. Chauvin, *Chem. Eur. J.* **2012**, *18*, 7705-7714; s) M. Alcarazo, *Chem. Eur. J.* **2014**, *20*, 7868-7877; t) A. Kozma, T. Deden, J. Carreras, C. Wille, J. Petuskova,

J. Rust, M. Alcarazo, *Chem. Eur. J.* **2014**, *20*, 2208-2214; u) H. Tinnermann, C. Wille, M. Alcarazo, *Angew. Chem. Int. Ed.* **2014**, *53*, 8732-8736; v) I. Abdellah, Y. Canac, C. D. Mboyi, C. Duhayon, R. Chauvin, *J. Organomet. Chem.* **2015**, *776*, 149-152; w) C. D. Mboyi, C. Maaliki, A. M. Makaya, Y. Canac, C. Duhayon, R. Chauvin, *Inorg. Chem.* **2016**, *55*, 11018-11027.

[7] a) R. K. Oram, S. Trippett, *J. Chem. Soc., Perkin Trans. 1* **1973**, 1300-1310; b) E. Evangelidou-Tsolis, F. Ramirez, *Phosphorus* **1974**, *4*, 121-127; c) D. Dakternieks, G. V. Roeschenthaler, R. Schmutzler, *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1978**, *33B*, 507-510; d) D. Dakternieks, G. V. Roeschenthaler, R. Schmutzler, Inst. Mond. Phosphate, **1978**, pp. 591-597; e) G. V. Roeschenthaler, *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1978**, *33B*, 131-135; f) Q.-C. Mir, R. W. Shreeve, J. n. M. Shreeve, *Phosphorus Sulfur Silicon Relat. Elem.* **1980**, *8*, 331-334.

[8] P. W. N. M. Van Leeuwen, C. F. Roobeek, *Tetrahedron* **1981**, *37*, 1973-1983.

[9] P. W. N. M. Van Leeuwen, C. F. Roobeek, *J. Organomet. Chem.* **1983**, *258*, 343-350.

[10] a) R. S. Jolly, G. Luedtke, D. Sheehan, T. Livinghouse, *J. Am. Chem. Soc.* **1990**, *112*, 4965-4966; b) P. A. Wender, T. E. Jenkins, S. Suzuki, *J. Am. Chem. Soc.* **1995**, *117*, 1843-1844; c) P. A. Wender, T. E. Smith, *J. Org. Chem.* **1996**, *61*, 824-825; d) M. Murakami, M. Ubukata, K. Itami, Y. Ito, *Angew. Chem., Int. Ed.* **1998**, *37*, 2248-2250; e) D. J. R. O'Mahony, D. B. Belanger, T. Livinghouse, *Org. Biomol. Chem.* **2003**, *1*, 2038-2040; f) K. Shen, T. Livinghouse, *Synlett* **2010**, 247-249; g) S. Huang, X. Li, C. L. Lin, I. A. Guzei, W. Tang, *Chem. Commun. (Cambridge, U. K.)* **2012**, *48*, 2204-2206.

[11] a) S. Yanagisawa, T. Sudo, R. Noyori, K. Itami, *J. Am. Chem. Soc.* **2006**, *128*, 11748-11749; b) S. Yanagisawa, T. Sudo, R. Noyori, K. Itami, *Tetrahedron* **2008**, *64*, 6073-6081; c) S. Yanagisawa, K. Ueda, H. Sekizawa, K. Itami, *J. Am. Chem. Soc.* **2009**, *131*, 14622-14623; d) K. Ueda, S. Yanagisawa, J. Yamaguchi, K. Itami, *Angew. Chem., Int. Ed.* **2010**, *49*, 8946-8949, S8946/8941-S8946/8968; e) C. Meyer, D. Schepmann, S. Yanagisawa, J. Yamaguchi, K. Itami, B. Wuensch, *Eur. J. Org. Chem.* **2012**, *2012*, 5972-5979; f) R. Liu, G. N. Winston-McPherson, Z.-Y. Yang, X. Zhou, W. Song, I. A. Guzei, X. Xu, W. Tang, *J. Am. Chem. Soc.* **2013**, *135*, 8201-8204; g) K. Ueda, K. Amaike, R. M. Maceiczyk, K. Itami, J. Yamaguchi, *J. Am. Chem. Soc.* **2014**, *136*, 13226-13232.

[12] A. Tahara, Y. Miyamoto, R. Aoto, K. Shigeta, Y. Une, Y. Sunada, Y. Motoyama, H. Nagashima, *Organometallics* **2015**, *34*, 4895-4907.

[13] Q. C. Mir, R. W. Shreeve, J. M. Shreeve, *Phosphorus Sulfur and Silicon and the Related Elements* **1980**, *8*, 331-333.

[14] J. Senker, J. Ludecke, *Z. Naturforsch. B* **2001**, *56*, 1089-1099.

[15] A. D. DeBellis, S. D. Pastor, G. Rihs, R. K. Rodebaugh, A. R. Smith, *Inorg. Chem.* **2001**, *40*, 2156-2160.

[16] a) S. Yanagisawa, T. Sudo, R. Noyori, K. Itami, *J. Am. Chem. Soc.* **2006**, *128*, 11748-11749; b) S. Yanagisawa, T. Sudo, R. Noyori, K. Itami, *Tetrahedron* **2008**, *64*, 6073-6081.

[17] C. A. Tolman, *Chem. Rev.* **1977**, *77*, 313.

[18] a) R. J. Thatcher, D. G. Johnson, J. M. Slattery, R. E. Douthwaite, *Chem. Eur. J.* **2012**, *18*, 4329-4336; b) J. Slattery, R. J. Thatcher, Q. Shi, R. E. Douthwaite, *Pure Appl. Chem.* **2010**, *82*, 1663–1671; c) Q. Shi, R. J. Thatcher, J. Slattery, P. S. Sauari, A. C. Whitwood, P. C. McGowan, R. E. Douthwaite, *Chem. Eur. J.* **2009**, *15*, 11346-11360.

[19]

[20] a) G. Frenking, K. Wichmann, N. Fröhlich, J. Grobe, W. Golla, D. L. Van, B. Krebs, M. Läge, *Organometallics* **2002**, *21*, 2921-2930; b) S. H. Strauss, K. D. Abney, *Inorg. Chem.* **1984**, *23*, 515-516.

[21] J. Apel, R. Bacher, J. Grobe, D. Le Van, *Z. Anorg. Allg. Chem.* **1979**, *453*, 39-52.

[22] a) G. T. Andrews, I. J. Colquhoun, W. McFarlane, S. O. Grim, *J. Chem. Soc., Dalton Trans.* **1982**, 2353-2358; b) M. S. A. A. El-Mottaleb, *J. Mol. Struct.* **1976**, *32*, 203-205.

[23] G. R. Dobson, P. M. Hodges, M. A. Healy, M. Poliakoff, J. J. Turner, S. Firth, K. J. Asali, *J. Am. Chem. Soc.* **1987**, *109*, 4218-4224.

[24] F. H. Allen, *Acta Crystallogr. B* **2002**, *58*, 380.

[25] a) M. Tokunaga, T. Suzuki, N. Koga, T. Fukushima, A. Horiuchi, Y. Wakatsuki, *J. Am. Chem. Soc.* **2001**, *123*, 11917-11924; b) M. Tokunaga, Y. Wakatsuki, *Angew. Chem. Int. Ed.* **1998**, *37*, 2867-2869; c) L. M. Milner, L. M. Hall, N. E. Pridmore, M. K. Skeats, A. C. Whitwood, J. M. Lynam, J. M. Slattery, *Dalton Trans.* **2016**, *45*, 1717-1726; d) L. M. Milner, N. E. Pridmore, A. C. Whitwood, J. M. Lynam, J. M. Slattery, *J. Am. Chem. Soc.* **2015**, *137*, 10753-10759; e) J. M. Lynam, L. M. Milner, N. S. Mistry, J. M. Slattery, S. R. Warrington, A. C. Whitwood, *Dalton Trans.* **2014**, *43*, 4565-4572; f) B. Breit, U. Gellrich, T. Li, J. M. Lynam, L. M. Milner, N. E. Pridmore, J. M. Slattery, A. C. Whitwood, *Dalton Trans.* **2014**, *43*, 11277-11285; g) D. G. Johnson, J. M. Lynam, N. S. Mistry, J. M. Slattery, R. J. Thatcher, A. C. Whitwood, *J. Am. Chem. Soc.* **2013**, *135*, 2222-2234; h) T. Naota, H. Takaya, S. I. Murahashi, *Chem. Rev.* **1998**, *98*, 2599-2660.

[26] K. Onitsuka, N. Dodo, Y. Matsushima, S. Takahashi, *Chem. Commun.* **2001**, 521-522.

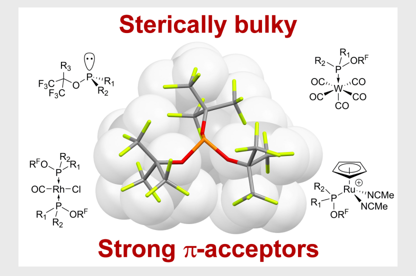
[27] J. A. Samuels, K. Folting, J. C. Huffman, K. G. Caulton, *Chem. Mater.* **1995**, *7*, 929-935.

[28] a) R. Ahlrichs, M. Baer, M. Haeser, H. Horn, C. Koelmel, *Chem. Phys. Lett.* **1989**, *162*, 165; b) M. v. Arnim, A. R., *J. Chem. Phys.* **1999**, *111*, 9183-9190; c) P. Császár, P. Pulay, *J. Mol. Str.* **1984**, *114*, 31-34; d) P. Deglmann, F. Furche, *J. Chem. Phys.* **2002**, *117*, 9535; e) P. Deglmann, F. Furche, R. Ahlrichs, *Chem. Phys. Lett.* **2002**, *362*, 511; f) K. Eichkorn, O. Treutler, H. Oehm, M. Haeser, R. Ahlrichs, *Chem. Phys. Lett.* **1995**, *240*, 283; g) K. Eichkorn, F. Weigend, O. Treutler, R. Ahlrichs, *Theo. Chem. Acc.* **1997**, *97*, 119; h) T. Koga, H. Kobayashi, *J. Chem. Phys.* **1985**, *82*, 1437-1439; i) P. Pulay, *Chem. Phys. Lett.* **1980**, *23*, 393-398; j) O. Treutler, R. Ahlrichs, *J. chem. Phys.* **1995**, *102*, 346; k) F. Weigend, *Phys. Chem. Chem. Phys.* **2006**, *8*, 1057.

Entry for the Table of Contents

FULL PAPER

A comprehensive overview of the synthesis, stereoelectronic properties and coordination chemistry of large, electron-poor P(III) ligands bearing highly fluorinated alkoxides is described.



*Sharifa Hussein, Denis Priester, Paul Beet, Jonathon Cottom, Sam J. Hart, Tim James, Robert J. Thatcher, Adrian C. Whitwood and John M. Slattery**

Page No. – Page No.

Filling a niche in “ligand space” with bulky, electron-poor phosphorus (III) alkoxides