

Synthesis and complexation of heptafluoroisopropylidiphenylphosphine†‡

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We report a one-step synthesis of the phosphine, $\text{PPh}_2^i\text{C}_3\text{F}_7$ from commercially available precursors. The stereoelectronic properties of the phosphine were probed by coordination to transition metals. $\text{Mo}(\text{CO})_5\text{PPh}_2^i\text{C}_3\text{F}_7$ was synthesised and the synthesis and structure of *trans*- $\text{PtCl}_2(\text{PPh}_2^i\text{C}_3\text{F}_7)_2$ are described. $\text{PPh}_2^i\text{C}_3\text{F}_7$ was found to be a bulky electron-withdrawing ligand.

Conventional phosphines with branched alkyl groups constitute an important group of bulky tertiary alkyl phosphines. Our group is interested in developing the chemistry of bulky strong π -acceptor phosphines. Ligands with this combination of properties have been highlighted as having an interesting stereoelectronic profile.¹ The coordination chemistry of such ligands is poorly developed. The heptafluoroisopropyl group is conceptually the simplest branched perfluoroalkyl substituent. Few perfluoroisopropyl-substituted phosphorus(III) compounds have been synthesised²⁻⁵ and their coordination chemistry has not been explored. A general lack of development of methodologies for the introduction of electron-poor substituents, and specifically perfluoroalkyl substituents, at phosphorus(III) has been noted.⁶ We have recently developed a convenient protocol for the general synthesis of perfluoroalkylphosphines starting from commercially available $\text{P}(\text{OAr})_3$ (or $\text{P}(\text{O}-p\text{-C}_6\text{H}_4\text{CN})_3$), R_iSiMe_3 ($\text{R}_i = n\text{-C}_n\text{F}_{2n+1}$) and CsF or other fluorides.⁷ We initially attempted to extend this strategy to secondary perfluoroalkyl groups by employing $^i\text{C}_3\text{F}_7\text{SiMe}_3$ under the same conditions. However, after treatment of $\text{P}(\text{OAr})_3$ and Ph_2POAr ($\text{Ar} = \text{Ph}$, $p\text{-C}_6\text{H}_4\text{CN}$) with $^i\text{C}_3\text{F}_7\text{SiMe}_3/\text{CsF}$ in ether, no evidence of $\text{P}-^i\text{C}_3\text{F}_7$ bond formation was found by ^{31}P or ^{19}F NMR spectroscopy.⁸

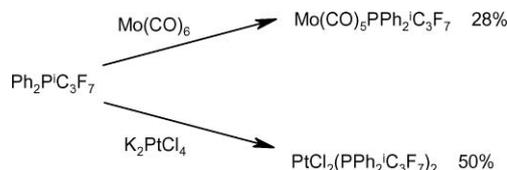
We therefore tried a different approach. Electron-rich $\text{P}(\text{NEt}_2)_3$ in combination with perfluoroalkyl bromides have been used to form perfluoroalkyl-phosphorus bonds from $\text{P}-\text{Cl}$ and $\text{P}-\text{OPh}$ linkages.⁹⁻¹¹ We now report that treatment of a mixture of perfluoroisopropyl iodide and $\text{Ph}_2\text{P}(\text{I})$ (in hexane) with $\text{P}(\text{NEt}_2)_3$

gives $\text{PPh}_2^i\text{C}_3\text{F}_7$ **1** in 53% yield (Scheme 1). Analytically pure $\text{PPh}_2^i\text{C}_3\text{F}_7$ was observed to crystallise directly after distillation.[§]



Scheme 1 Synthesis of heptafluoroisopropylidiphenylphosphine.

Thermolysis of **1** with $\text{Mo}(\text{CO})_6$ in boiling octane gave $\text{Mo}(\text{CO})_5\text{PPh}_2^i\text{C}_3\text{F}_7$ **2** in 28% yield, along with some decomposition material (Scheme 2). The ^{31}P NMR spectrum showed a doublet resonance at δ 57.5 ppm ($^2J_{\text{PF}} = 80$ Hz).[§] In the IR spectrum of **2** the $\text{A}_1^{(2)}$ $\nu(\text{CO})$ band was observed at 2081 cm^{-1} . This value is essentially identical to that obtained for the analogous complexes $\text{Mo}(\text{CO})_5\text{PPh}_2\text{CF}_3$ and $\text{Mo}(\text{CO})_5\text{PPh}_2\text{C}_2\text{F}_5$ (Table 1). Clearly, this suggests that the increase in bulk of the perfluoroalkyl group maintains the relative π -acidity of the phosphine. Furthermore, **2** may be confidently regarded as being more electron-withdrawing than PPh_3 , but significantly less electron-withdrawing than tris(perfluoroalkyl)phosphines such as $\text{P}(\text{CF}_3)_3$.



Scheme 2 Reaction of heptafluoroisopropylidiphenylphosphine with $\text{Mo}(\text{CO})_6$ and K_2PtCl_4 .

$\text{PtCl}_2(\text{PPh}_2^i\text{C}_3\text{F}_7)_2$ **3** was synthesised by treatment of aqueous K_2PtCl_4 with an acetone solution of **1**. The resulting red-orange solution was left to stand at room temperature overnight, during which time yellow crystals of **3**, were obtained in 50% yield (Scheme 2). The ^{31}P NMR of the complex showed a multiplet at δ 25 ppm with associated ^{195}Pt satellites ($I = \frac{1}{2}$, 33% abundant, $^1J_{\text{PtP}} = 3019$ Hz).[§] The magnitude of this coupling suggests a *trans* stereochemistry for the complex (see Table 2). The synthesis of $\text{PtCl}_2(\text{PPh}_2\text{CF}_3)_2$ has been reported and a *trans* geometry assigned on the basis of no observed dipole moment.¹² A *trans* geometry was

Table 1 $\text{A}_1^{(2)}$ $\nu(\text{CO})$ data for $\text{Mo}(\text{CO})_5\text{L}$ complexes

Ligand/L	$\text{A}_1^{(2)}/\text{cm}^{-1}$	Reference
$\text{PPh}_2^i\text{C}_3\text{F}_7$	2081	This work
$\text{PPh}_2\text{C}_2\text{F}_5$	2080	19
PPh_2CF_3	2081	20
$\text{PPh}_2\text{CF}=\text{CF}_2$	2077	21
PPh_3	2072	22
$\text{P}(\text{CF}_3)_3$	2104	23
PF_3	2103	24
PMe_3	2070	22

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† Electronic supplementary information (ESI) available: Experimental details and details of cone angle calculations. CCDC reference numbers 746473 (**1**) and 746474 (**3**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b918348e

‡ During preparation of this manuscript we became aware of a manuscript detailing another synthesis of $\text{PPh}_2^i\text{C}_3\text{F}_7$ (A. K. Brisdon and C. J. Herbert, *Chem. Commun.*, 2009, 6658).

§ Part of this work was presented at 19th International Symposium on Fluorine Chemistry, Abst. No. 78, August 23-28, 2009, Jackson Hole, WY, USA.

Table 2 Comparison of chemical shift and $^1J_{\text{PtP}}$ data for PtCl_2L_2

Ligand/L	δ (^1P)/ppm	$^1J_{\text{PtP}}$ /Hz	<i>cis/trans</i>	Reference
$\text{PPh}_2\text{C}_3\text{F}_7$	25	3019	<i>trans</i>	This work
$\text{PPh}_2\text{C}_2\text{F}_5$	18.5	2945	<i>trans</i>	6
PPh_3	19.8	2637	<i>trans</i>	25
PPh_3	14.3	3673	<i>cis</i>	25
PEt_3	12.3	2400	<i>trans</i>	26
PEt_3	9.6	3520	<i>cis</i>	26
$\text{PPh}_2\text{CF}=\text{CF}_2$	4.2	3698	<i>cis</i>	21

established for *trans*- $[\text{PtCl}_2(\text{PPh}_2\text{C}_2\text{F}_5)_2]$ by X-ray crystallography.⁶ Re-crystallisation of **3** from acetone yielded crystals suitable for an X-ray diffraction study. The structure obtained (Fig. 1), confirmed the formation of *trans*-**3**. **3** crystallises in the monoclinic space group $P2_1/c$. The complex has a centre of inversion. The Pt–P and Pt–Cl bond distances of 2.3174(7) and 2.3055(7) Å respectively, are in the range of those seen in similar *trans*-platinum(II) dichloride bis(phosphine) complexes.^{6,13,14} The P–Pt–Cl bond angle in **3** is 99.04(2)°; this compares with P–Pt–Cl bond angles of 97.01(5)° in *trans*- $\text{PtCl}_2(\text{PPh}_2\text{C}_2\text{F}_5)_2$ and 92.12(4)° in *trans*- $\text{PtCl}_2(\text{PPh}_3)_2$.¹³ Although the ligands in **3** are close to planar, their arrangement clearly deviates significantly from square. This suggests that the increase in branching of the perfluoroalkyl group has an impact by distorting the bond angles around the platinum metal centre.

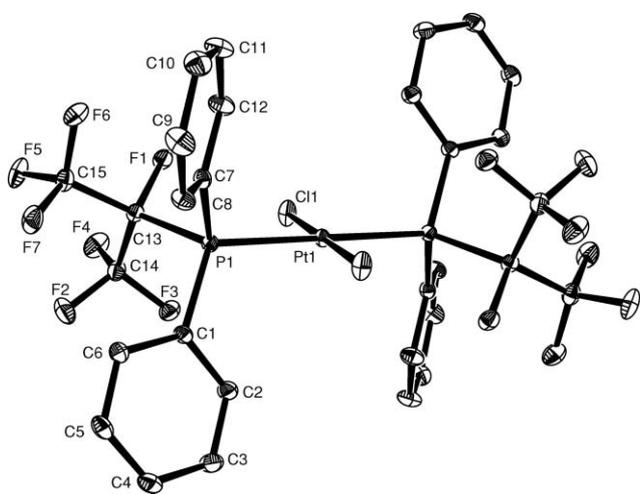


Fig. 1 An ORTEP drawing of *trans*- $\text{PtCl}_2(\text{PPh}_2\text{C}_3\text{F}_7)_2$. Thermal ellipsoids shown at the 30% probability level and hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (°): Pt(1)–P(1) 2.3174(7), Pt(1)–Cl(1) 2.3055(7), P(1)–C(1) 1.816(3), P(1)–C(7) 1.814(3), P(1)–C(13) 1.929(3); Cl(1)–Pt(1)–P(1) 99.04(2), C(1)–P(1)–Pt(1) 113.58(8), C(7)–P(1)–Pt(1) 110.28(9), C(13)–P(1)–Pt(1) 114.34(8), C(7)–P(1)–C(1) 109.87(12), C(1)–P(1)–C(13) 105.14(12), C(7)–P(1)–C(13) 103.00(12).

From the X-ray structural data for **3**, the maximum cone angle^{15,16} of $\text{PPh}_2\text{C}_3\text{F}_7$ was estimated as 156°. In order to make a comparison we also calculated the maximum cone angle of 153° for $\text{PPh}_2\text{C}_2\text{F}_5$ using Peters and co-workers data.⁶ These estimates compare with Tolman's¹⁷ original value of 142° for PPh_2CF_3 , obtained from space-filling models. (It should be noted however, that it has been suggested that this value is an overestimate.¹⁸)

In conclusion, the difference between the maximum cone angles of **1** and $\text{PPh}_2\text{C}_2\text{F}_5$ is 3°. It is evident therefore that changing from

a pentafluoroethyl group to a heptafluoroisopropyl group results in a modest increase in the steric demands of the phosphine. This modest variation in size between ligands **1**, $\text{PPh}_2\text{C}_2\text{F}_5$ and PPh_2CF_3 would allow useful comparisons of complexes of interest for catalytic screening. The increase in chain length and/or branching of the perfluoroalkyl groups on phosphorus essentially maintains the electronic characteristics of the phosphine. Therefore the use of these perfluoroalkyl groups on phosphorus is indeed useful for fine-tuning both the steric and electronic properties of phosphines.

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Notes and references

§ Synthesis of $\text{PPh}_2\text{C}_3\text{F}_7$: $\text{P}(\text{NEt}_3)_3$ (13.5 g, 55 mmol) dissolved in hexane (30 ml) was added over 30 min to a solution of Ph_2PCI (12.0 g, 55 mmol) and $^1\text{C}_3\text{F}_7\text{I}$ (19.5 g, 66 mmol) in hexane (30 ml) with vigorous stirring, at room temperature using a water bath. The mixture, which yielded a yellow precipitate, was left stirring over 2 nights, after which time ^{31}P NMR showed that the reaction gave quantitative yield. The solution was filtered *via* a cannula, the precipitate washed with 2×10 ml hexane and the filtrates were combined. Volatiles were removed *in vacuo*, yielding a solid residue. Vacuum distillation (96 °C/0.5 mmHg) of the residue yielded $\text{PPh}_2\text{C}_3\text{F}_7$ (10.4 g, 53%), which crystallised on cooling. See ESI for characterisation.†
 [Mo(CO)₂($\text{PPh}_2\text{C}_3\text{F}_7$)₂]: Anal. Calc. for $\text{C}_{20}\text{H}_{10}\text{F}_7\text{MoO}_5\text{P}$: C, 40.70; H, 1.71. Found: C, 40.75; H, 1.62%. IR (n-hexane) (cm^{-1}) (CO region): 2081 (s), 2001 (w), 1965 (vs, br), 1962 (sh), 1956 (sh). ^{31}P NMR (C_6D_6): δ 57.5 (d, $^2J_{\text{PF}} = 80$ Hz). ^{19}F NMR (C_6D_6): δ -65.5 (d, $^3J_{\text{FF}} = 9.1$ Hz); -173.6 (dsep, $^2J_{\text{FP}} = 79.4$ Hz, $^3J_{\text{FF}} = 9.3$ Hz, CF). ^1H NMR (C_6D_6): δ 7.75 (m, 2H); 6.95–7.15 (m, 3H).
 [PtCl₂($\text{PPh}_2\text{C}_3\text{F}_7$)₂]: Anal. Calc. for $\text{C}_{30}\text{H}_{20}\text{Cl}_2\text{F}_{14}\text{P}_2\text{Pt}$: C, 36.98; H, 2.07. Found: C, 36.78; H, 2.33%. ^{31}P NMR: (CDCl_3): δ 25.2 (m, $^1J_{\text{PtP}} = 3019$ Hz). ^{19}F NMR: (CDCl_3): δ -67.0 (d, $^3J_{\text{FF}} = 8.7$ Hz, CF_3); -172.5 (m, CF). ^1H NMR: (CDCl_3): δ 7.95 (dd, $^3J_{\text{HP}} = 10.0$ Hz, $^3J_{\text{HH}} = 6.0$ Hz, 2H: *ortho* C_6H_5); 7.55 (t, $^3J_{\text{HH}} = 4.0$ Hz, 1H: *para* C_6H_5); 7.45 (m, 2H: *meta* C_6H_5).

- 1 K. D. Cooney, T. R. Cundari, N. W. Hoffman, K. A. Pittard, M. D. Temple and Y. Zhao, *J. Am. Chem. Soc.*, 2003, **125**, 4318–4324.
- 2 Y. O. El Nigumi and H. J. Emeleus, *J. Inorg. Nucl. Chem.*, 1970, **32**, 3211–3212.
- 3 B. N. Ghose, *J. Indian Chem. Soc.*, 1978, **55**, 1254–1259.
- 4 R. A. Wolcott and J. L. Mills, *Inorg. Chim. Acta*, 1978, **30**, L331–333.
- 5 K. G. Sharp and I. Schwager, *Inorg. Chem.*, 1976, **15**, 1697–1701.
- 6 J. D. Palcic, P. N. Kapoor, D. M. Roddick and R. G. Peters, *Dalton Trans.*, 2004, 1644–1647.
- 7 M. B. Murphy-Jolly, L. C. Lewis and A. J. M. Caffyn, *Chem. Commun.*, 2005, 4479–4480.
- 8 E. J. Velazco, *Ph.D. Thesis*, University of the West Indies, St. Augustine, July 2009.
- 9 W. Volbach and I. Ruppert, *Tetrahedron Lett.*, 1983, **24**, 5509–5512.
- 10 L. D. Field and M. P. Wilkinson, *Tetrahedron Lett.*, 1992, **33**, 7601–7604.
- 11 M. Görg, G.-V. Rösenthaller and A. A. Kolomeitsev, *J. Fluorine Chem.*, 1996, **79**, 103–104.
- 12 M. A. A. Beg and H. C. Clark, *Can. J. Chem.*, 1962, **40**, 283–288.
- 13 M. H. Johansson and S. Otto, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 2000, **56**, e12–e15.
- 14 N. A. Barnes, A. K. Brisdon, M. J. Ellis and R. G. Pritchard, *J. Fluorine Chem.*, 2001, **112**, 35–45.
- 15 G. Ferguson, P. J. Roberts, E. C. Alyea and M. Khan, *Inorg. Chem.*, 1978, **17**, 2965–2967.
- 16 T. E. Muller and D. M. P. Mingos, *Transition Met. Chem.*, 1995, **20**, 533–539.
- 17 C. A. Tolman, *Chem. Rev.*, 1977, **77**, 313–348.
- 18 B. J. Dunne, R. B. Morris and A. G. Orpen, *J. Chem. Soc., Dalton Trans.*, 1991, 653–661.

- 19 J. D. Palcic, R. G. Baughman, M. V. Golynskiy, S. B. Frawley and R. G. Peters, *J. Organomet. Chem.*, 2005, **690**, 534–538.
- 20 M. Dhanoolal and L. C. Lewis-Alleyne, unpublished work.
- 21 K. K. Banger, R. P. Banham, A. K. Brisdon, W. I. Cross, G. Damant, S. Parsons, R. G. Pritchard and A. Sousa-Pedrares, *J. Chem. Soc., Dalton Trans.*, 1999, 427–434.
- 22 G. R. Dobson, I. W. Stolz and R. K. Sheline, *Adv. Inorg. Chem. Radiochem.*, 1966, **8**, 1–82.
- 23 Von J. Apel, R. Bacher, J. Grobe and D. Le Van, *Z. Anorg. Allg. Chem.*, 1979, **453**, 39–52.
- 24 R. L. Keiter and J. G. Verkade, *Inorg. Chem.*, 1969, **8**, 2115–2120.
- 25 L. Bemis, H. C. Clark, J. A. Davies, C. A. Fyfe and R. E. Wasylshen, *J. Am. Chem. Soc.*, 1982, **104**, 438–445.
- 26 S. O. Grim, R. L. Keiter and W. McFarlane, *Inorg. Chem.*, 1967, **6**, 1133–1137.