Supplementary Information for

Synthesis and complexation of heptafluoroisopropyldiphenylphosphine

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Experimental

General Procedures

Manipulations were carried out under Argon using standard Schlenk techniques. Solvents were distilled from the appropriate drying agents and stored over 4 Å molecular sieves before use. Infrared spectra were acquired using a Perkin-Elmer Spectrum RXI FTIR spectrometer. ^{31}P, ^{19}F, ^{13}C and ^{1}H NMR were recorded at room temperature on a Bruker Avance 400 MHz spectrometer with 85% H_3PO_4, CCl_3F and $SiMe_4$ as external references respectively. Elemental Analyses were performed by Medac Ltd.

Synthesis of $Ph_2P^iC_3F_7$ in hexane: $P(NEt_2)_3$ (13.5 g, 55 mmol) dissolved in hexane (30ml) was added over 30 minutes to a solution of Ph_2PCl (12.0 g, 55 mmol) and $^iC_3F_7I$ (19.5 g, 66 mmol) in hexane (30ml) 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 cannula, the precipitate washed with 2 x 10ml hexane and the filtrates were combined. Volatiles were removed *in vacuo*, yielding a solid residue. Vacuum distillation (96°C/ 0.5mmHg) of the residue yielded $Ph_2P^iC_3F_7$ (10.4g, 53%), which crystallised on cooling. m.p. = 47.4 – 48.0°C. Anal. Calc. for $C_{15}H_{10}F_7P$: C, 50.86; H, 2.85. Found: C, 50.56; H, 2.64 %. ^{31}P NMR (C_6D_6): δ 0.65 (dm $^2J_{PF}$ = 83.3 Hz, $^3J_{PF}$ = 9.1 Hz). ^{19}F NMR (C_6D_6): δ -69.8 (dd, $^3J_{FP}$ = 16.8 Hz, $^3J_{FF}$ = 12.0 Hz, CF_3); -185.0 (dsep $^2J_{FP}$ = 74.0 Hz, $^3J_{FF}$ = 11.4 Hz, CF). ^1H NMR (C_6D_6): δ 7.85 (m 2H); 7.0-7.15 ppm (m 3H).

Synthesis of $[Mo(CO)_5PPh_2{}^iC_3F_7]$: N-octane (18 ml) was added, with stirring, to a flask containing $[Mo(CO)_6]$ (0.286 g, 1.08 mmol) and $Ph_2P^iC_3F_7$ (0.498 g, 1.41 mmol) under argon. The mixture was heated to reflux during which time it became a yellow solution, with significant dark-coloured residue deposited. After refluxing for three hours, then cooling the reaction mixture to room temperature, the volatile materials were removed *in vacuo,* and the residue was extracted with *n*-hexane (4 x 1ml). Re-crystallisation from *n*-hexane at -78°C yielded a yellow-green powder with some grey discolouration. A second re-crystallisation from *n*-hexane at -10°C yielded beige coloured crystals of $[Mo(CO)_5PPh_2{}^iC_3F_7]$,.(0.179g, 28 %).

Synthesis of $[PtCl_2(PPh_2{}^iC_3F_7)_2]$: $Ph_2P^iC_3F_7$ (0.219 g, 0.618 mmol) dissolved in acetone (2.5 ml) was added to an aqueous solution (2.5 ml) of K_2PtCl_4 (0.105 g, 0.253 mmol), and the mixture swirled to give a uniform red solution. The mixture was left to stand overnight, and

yellow crystals were yielded from solution. The supernatant was removed via syringe and the solid, $[PtCl_2(PPh_2{}^{i}C_3F_7)_2]$ (0.085 g, 50%), was re-crystallised from acetone under argon.

Cone angle estimate.

The maximum cone angle of **1** was estimated from the X-ray structural data for **3** as follows: Phosphorus to fluorine non-bonding distances and phosphorus-platinum-fluorine angles were measured using the PLATON and MERCURY software packages.[1,2] The van der Waals radius of fluorine was taken as 1.35 Å. The individual half angles ($\theta_i/2$) for the Ph and $CF(CF_3)_2$ substituents on P were $\theta_i/2$ = 84.4°, 73.2° and 76.2°. Using the formula: Cone angle, $\Theta = 2/3\ \Sigma_i\ \theta_i/2$, this gives a value for the maximum cone angle of **1** of 156°. Likewise the maximum cone angle of $PPh_2C_2F_5$ was estimated from the X-ray structural data of $PtCl_2(PPh_2C_2F_5)_2$.[3] The individual half angles ($\theta_i/2$) for the Ph and C_2F_5 substituents on P were $\theta_i/2$ = 81.35°, 76.7° and 71.4°. This gives a value for the maximum cone angle of $PPh_2C_2F_5$ of 153°.

References

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