SUPPORTING INFORMATION

for

Synthesis, Structure, and Reactivity of Fluorous Phosphorus/Carbon/Phosphorus Pincer Ligands and Metal Complexes

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Additional experiments and details relevant to Scheme 3 are as follows.

In preliminary experiments, **5**-R_{f8} and *n*-BuLi were combined at 0 or –40 °C in THF to generate the phosphorus anion $LiP(CH_2CH_2R_{f8})_2$. However, when **2** was added to the resulting deep purple suspensions, a multitude of products were obtained. Note that the initially formed phosphine can react with further **2**, providing a route to **7**-R_{f8}. In another experiment based upon close literature precedent,[s1] **5**-R_{f8}, CsOH, and powdered molecular sieves were combined in DMF. Then **2** was added. However, no reaction was observed over the course of 2 d.

A reaction sequence involving the fluorous phosphine borane **9**-R_{f8}, *t*-BuOK, THF, and **2** was conducted with similar conditions to that using KOH and ethanol (see experimental below). However, a multitude of products formed. Finally, **9**-R_{f8} and *n*-BuLi were combined in THF at –78 °C in an NMR tube. A ^{31}P NMR spectrum of the resulting brown suspension showed the apparent consumption of **9**-R_{f8}. No new signals appeared as the sample was warmed to –40 °C. Then **2** was added. However, no substitution products formed over an extended period. Only the starting **9**-R_{f8} and some **5**-R_{f8} could be detected.

1,3-$C_6H_4(CH_2P(CH_2CH_2R_{f8})_2)_2$ (**3**-R_{f8}). **D**. A Schlenk flask was charged with $(H_3B)PH(CH_2CH_2R_{f8})_2$ (**9**-R_{f8}; 0.1660 g, 0.1766 mmol)[21b] and ethanol (3 mL). Then a solution of KOH (0.0085 g, 0.15 mmol) in ethanol (0.2 mL) was added with stirring. The colorless solution turned light yellow. After 15 min, **2** (0.0187 g, 0.0708 mmol) was added. After 3 d, the solvent was removed by oil pump vacuum. The residue was dissolved in THF/$HNEt_2$ (8 mL, 1:1 v/v). The mixture was immersed in a 50 °C oil bath. After 1 h, the solvents were removed by oil pump vacuum. The residue was dissolved in THF. Integration of a ^{31}P NMR spectrum (internal $[D_6]$DMSO capillary) showed the major species to be **5**-R_{f8}, and less than 5% of **3**-R_{f8}.

(s1) M. T. Honaker, B. J. Sandefur, J. L. Hargett, A. L. McDaniel, R. N. Salvatore, *Tetrahedron Lett.* **2003**, *44*, 8373.