SUPPORTING INFORMATION

for

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

Róbert Tuba, Verona Tessevic, Long V. Dinh, Frank Hampel, and J. A. Gladysz*
Institut für Organische Chemie, Friedrich-Alexander Universität Erlangen-Nürnberg, Henkestrasse 42, 91054 Erlangen, Germany

submitted to: Dalton Transactions
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 $-40 \, ^\circ\text{C}$ in THF to generate the phosphorus anion $\text{LiP(CH}_2\text{CH}_2R_{f8})_2$. 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,$^1$ $5$-$R_{f8}$, 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 $-78 \, ^\circ\text{C}$ 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 $-40 \, ^\circ\text{C}$. 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$_6$H$_4$(CH$_2$P(CH$_2$CH$_2$R$_{f8}$)$_2$)$_2$ (3-$R_{f8}$). D. A Schlenk flask was charged with (H$_3$B)PH-(CH$_2$CH$_2$R$_{f8}$)$_2$ ($9$-$R_{f8}$; 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 $^\circ\text{C}$ 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 $3$-$R_{f8}$.