

SYNTHESIS AND REACTIVITY OF METALLOPHOSPHANES

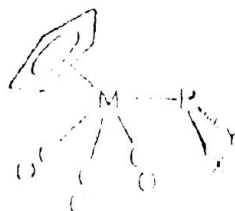
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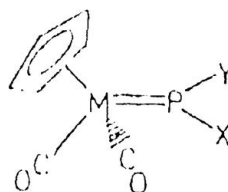
Abstract Aspects of the reactivity of metallophosphanes are presented along with the synthesis and structure determinations for new aluminophosphanes.

INTRODUCTION

Nucleophilic metal carbonylates $\text{NaCpM}(\text{CO})_3$ and $\text{NaCpM}(\text{CO})_2$ when allowed to react with several classes of monochlorophosphanes, $\text{P}(\text{X})(\text{Y})\text{Cl}$, usually form metallophosphanes (A) $\text{CpM}(\text{CO})_3[\text{P}(\text{X})(\text{Y})]$ [$\text{M}=\text{Cr}, \text{Mo}, \text{W}$] and $\text{CpM}(\text{CO})_2[\text{P}(\text{X})(\text{Y})]$ [$\text{M}=\text{Fe}$] which possess a pyramidal phosphorus atom and an active lone pair^{1,2} or metallophosphonium complexes (B) $\text{CpM}(\text{CO})_2[\text{P}(\text{X})(\text{Y})]$ [$\text{M}=\text{Cr}, \text{Mo}, \text{W}$], which contain a formal $\text{M}=\text{P}$ multiple bond, planar phosphorus atom geometry and coordinated phosphorus lone pair^{3,4}. The subtle factors which control the formation of A and B and the subsequent reactivity



A

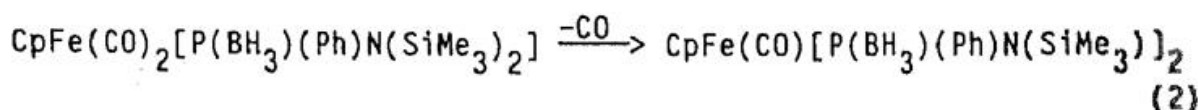
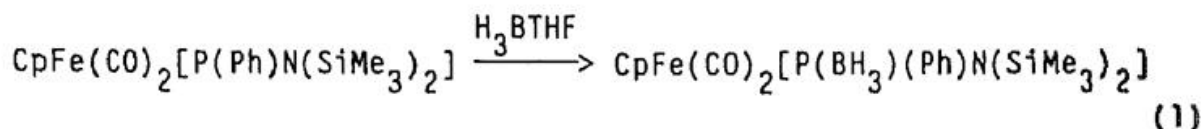


B

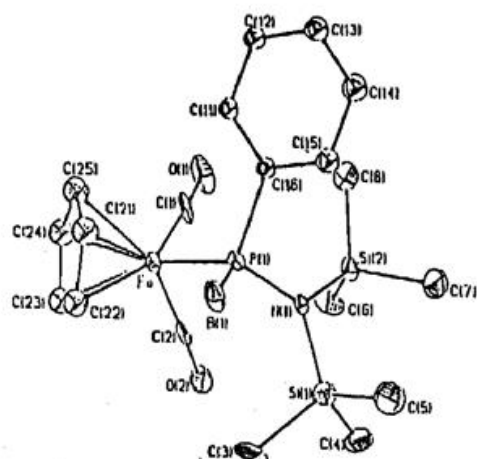
of the compounds have been a topic of study in our group.

RESULTS

Simple MO theory would predict that B_2 complexes should not be susceptible to Lewis acid addition reactions at the phosphorus atom. However, we have recently reported⁵ that combination of B_2H_6 with $CpMo(CO)_2[P(Ph)N(SiMe_3)_2]$ results in attack of BH_3 at phosphorus although the resulting complex is not a simple addition complex. Instead, an unprecedented $\overline{Mo-P-B(H_2)(\mu-H)}$ ring is generated and MO analyses reveal fully the unanticipated reactivity mode. Borane(3) would be expected to add smoothly to the pyramidal phosphorus in the A type complex $CpFe(CO)_2[P(Ph)N(SiMe_3)_2]$. We report here that chemistry summarized by equations 1 and 2.



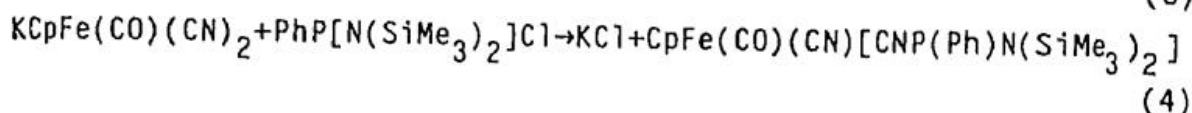
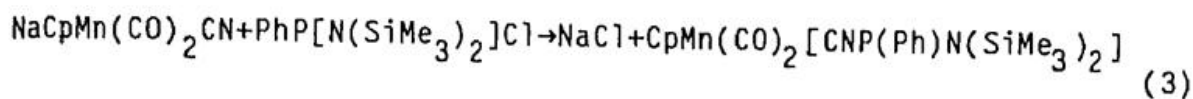
The initial complex is a simple metallophosphane borane(3) complex similar to a complex reported by Malisch⁶. This compound, however, is unstable toward thermal activated loss of CO, and the structure of the final compound is not yet determined.



Fe-P(1)	= 2.289(5) Å
P(1)-B(1)	= 2.006(22) Å
P(1)-N(1)	= 1.681(11) Å

Figure 1. Molecular structure of $CpFe(CO)_2[P(BH_3)(Ph)N(SiMe_3)_2]$

We have examined reactions of metal carbonyl cyanates with $\text{PhP}[\text{N}(\text{SiMe}_3)_2](\text{Cl})$ and some of that chemistry is summarized by the following equations. The initial complexes are similar to Mn complexes reported by Höfler using other phosphane reagents⁷.



However, the compounds obtained here undergo self-condensation/elimination chemistry. The molecular structure of the bimetallic manganese complex is shown in Figure 2.

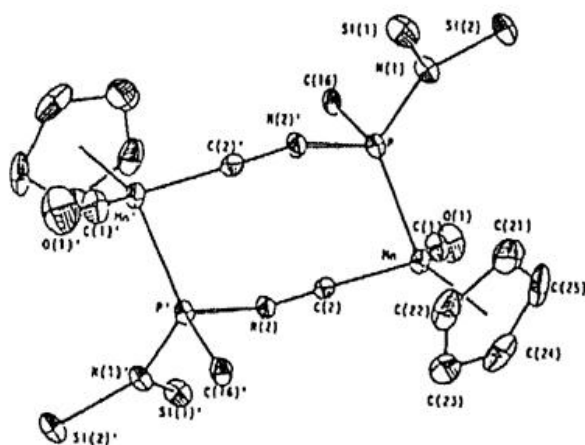


Figure 2. Molecular structure of $\{\text{CpMn}(\text{CO})[\text{CNP}(\text{Ph})\text{N}(\text{SiMe}_3)_2]\}_2$

The reactions of organoaluminum reagents with phosphanes are of interest since, if properly designed, the products can serve as useful precursors to new electronic materials. We have observed that the reactions of $\text{Al}(\text{SiMe}_2)_3$ with Ph_2PH , PhPH_2 , (c-hexyl) PH_2 , $\text{Ph}(\text{Me}_3\text{Si})\text{PH}$ and PH_3 result in the formation of $[(\text{Me}_3\text{Si})_2\text{Al-PX}_2]_2$ or 3 complexes. The molecular structures of $[(\text{Me}_3\text{Si})_2\text{Al-PPh}_2]$ and $[(\text{Me}_3\text{Si})_2\text{Al-P}(\text{c-hexyl})\text{H}]_3$ are shown in Figures 3 and 4.

$(\text{Me}_3\text{Si})_3\text{Al}$ and PH_3 form a preceramic polymer which on thermolysis gives crystalline AlP.

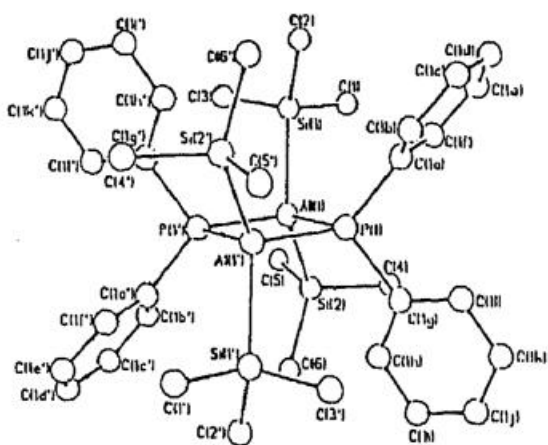


Figure 3. Molecular structure of $[(\text{Me}_3\text{Si})_2\text{AlPPh}_2]_2$

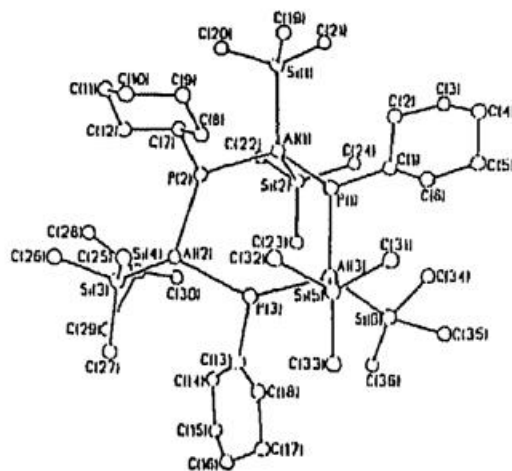


Figure 4. Molecular structure of $[(\text{Me}_3\text{Si})_2\text{Al}(\text{c-hexyl})\text{H}]_3$

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