

New Avenues in Phosphorus-Carbonyl Chemistry

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Targeting phosphorus carbonyl species, we describe several synthetic approaches. In an initial approach, reactions of Ph_3GePCO with phosphides were probed. This was shown to provide a modular synthetic route to dissymmetric diphospha-ureas. Further study showed this could be modified via reaction with borohydride to unveil a synthetic strategy to monomethyl and dimethylformyl phosphines, $\text{Ph}_3\text{GeP}(\text{Me})\text{C}(\text{H})\text{O}$ and $\text{Me}_2\text{PC}(\text{H})\text{O}$, respectively. The latter species is the phosphorus analog of DMF. A second approach has exploited the concept of frustrated Lewis pair (FLP) chemistry. While we had demonstrated that alkali metal species behave as FLP, for the current purpose we have examined the reactions of potassium phosphides with CO. These reactions generate transient carbene-like species and undergo t-Bu group migration or dimerization to give an acyl-phosphide anion and dianion, respectively. Further reaction of the acyl-phosphide anion with CO affords a bis-acyl phosphorus anionic chelate. The utility of these synthetic approaches is discussed and the implication beyond phosphorus-carbonyl species is considered.