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Methine (CH) Transfer via a Chlorine Atom Abstraction/Benzene-Elimination Strategy: Molybdenum Methylidyne Synthesis and Elaboration to a Phosphaisocyanide Complex

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Received October 10, 2001

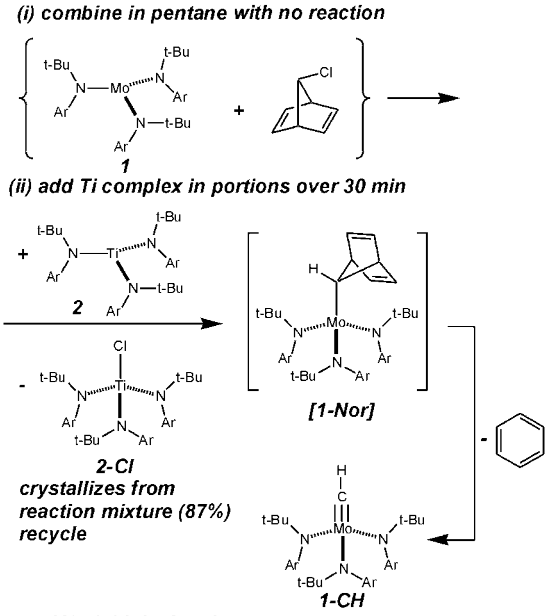
Two recent reports described the isolation and characterization of a terminal molybdenum carbide anion, an example of one-coordinate carbon bonded solely to a transition metal center.[1,2] This species was of interest with respect to both its physical properties and its reactivity. The bonding and electronic structure of the terminal carbide anion were probed by solid-state carbon NMR studies, and it was shown that carbon-element bond formation to produce functionalized alkylidyne derivatives was possible.

Problematic for expansion of the chemistry in this unique system was the multistep nature of the synthesis. It was deemed worthwhile, therefore, to develop a new reaction facilitating a more efficient synthesis of the terminal carbide anion. Targeted in this regard was the definition of a methine [CH] transfer reaction. Our previous work in the transfer of nitrogen monoanion N(1−) and in the transfer of cyanonitrene [NCN] suggested that arene-elimination might constitute a viable strategy.[3−5] Accordingly, we elected to investigate 7-chloronorbornadiene as a methine source in conjunction with chlorine atom abstraction and benzene elimination. The envisioned sequence involves chlorine atom abstraction followed by trapping of the resulting transient 7-norbornadienyl radical to give a molybdenum alkyl susceptible to benzene elimination. Our experience with titanium *tris*-anilide (**2**) as a potent halogen atom acceptor and general 1e reductant prompted its use in the present application.[6,7]

Treatment of molybdenum complex **1** with 7-chloronorbornadiene at room temperature resulted in no reaction, but the addition of titanium *tris*-anilide in portions over a period of 30 min led to precipitation of known titanium chloride **2**-Cl in 87% yield (Scheme 1).[8] Separation of pure **2**-Cl was achieved by filtration, the complex being saved for recycling to titanium *tris*-anilide **2** by reduction with sodium amalgam as reported previously.[6,9] Analysis of the crude filtrate by proton NMR spectroscopy revealed ca. 70% conversion of complex **1** to methylidyne **1**-CH as desired, while also present was a small amount of chlorotitanium complex **2**-Cl. A similar experiment carried out in toluene-d_8 revealed the formation of benzene in an approximate 1:1 ratio with respect to methylidyne **1**-CH, this being the expected result if molybdenum alkyl **1**-Nor (where Nor = 7-norbornadienyl) is an intermediate.[10] Previous reports indicate that intermediacy of the 7-norbornadienyl radical is feasible in solution chemistry.[11] For purposes of purification, potassium benzyl (KBz) was added both to deprotonate **1**-CH and to convert **2**-Cl to the highly soluble **2**-Bz; the desired dimeric tight ion-pair potassium salt ($(\mathbf{1}\text{-CK})_2$) was then crystallized and isolated in 40% yield based upon starting complex **1**.

Having in hand multigram quantities of $(\mathbf{1}\text{-CK})_2$ permitted a study on its elaboration to an unprecedented phosphorus derivative.[12] In particular, the synthesis of a complexed phosphaisocyanide ligand (CPPh) was undertaken (Scheme 2). Formation of the carbon−phosphorus bond was established by addition of dichlorophenylphosphine to $(\mathbf{1}\text{-CK})_2$ to produce the functionalized neutral alkylidyne species **1**-CP(Cl)Ph, over-reduction of which, using sodium amalgam in THF, produced the desired diamagnetic anion $[\mathbf{1}\text{-CPPh}]^-$ as a dimeric tight ion pair with sodium etherate counterions (Figure 1).[13]

Scheme 1



ca. 70% yield; isolated as potassium salt (40%, ca. 5 g)

On the basis of the molybdenum carbon bond distance of 1.762(5) Å in the anion, $[\mathbf{1}\text{-CPPh}]^-$ can be regarded as an alkylidyne derivative with the following caveat: the C(1)−P distance is shorter by ca. 0.05 Å than the P−C_{ipso} distance, an observation likely indicative of multiple bonding between phosphorus and the two-coordinate carbon to which it is adjacent. It is noted that the ^{31}P NMR signal for anion $[\mathbf{1}\text{-CPPh}]^-$ is dependent upon solvation of the sodium counterions: the chemical shift in the presence of 12-crown-4 achieves a limiting value of 126.1 ppm, while in benzene, without added ether, the shift falls to a value of 68.8 ppm.[14]

A DFT study performed on the model system $[(H_2N)_3MoCPPh]^-$ in C_s symmetry supports some of the preceding notions.[15] π-Bonding is in evidence for HOMO-3 (Figure 2) along the MoCP triatomic fragment. Furthermore, the calculated ^{31}P NMR shift (132 ppm) is in good agreement with the experimental value obtained in the presence of ethers (12-crown-4, THF), suggesting that the electronic description obtained from the DFT study is a reasonable one.

Embodied by the present work is a demonstration of methine transfer to molybdenum as a means for generating in a one-pot

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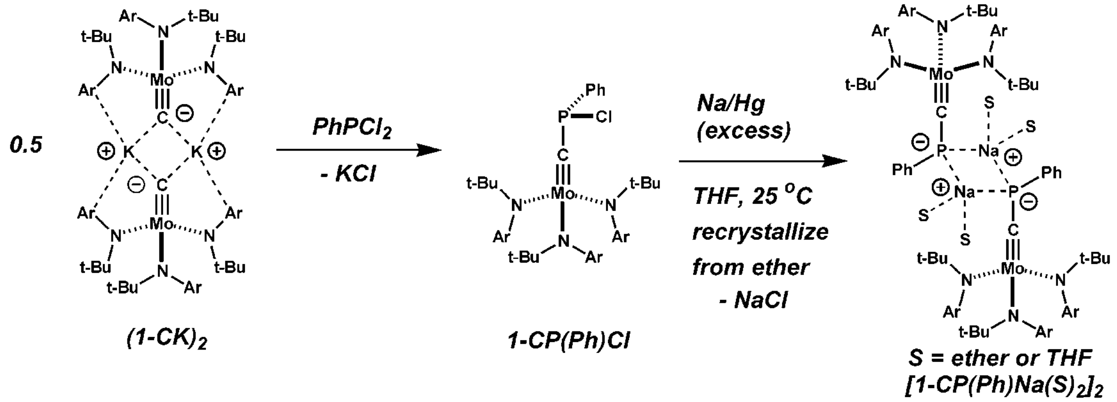
Scheme 2



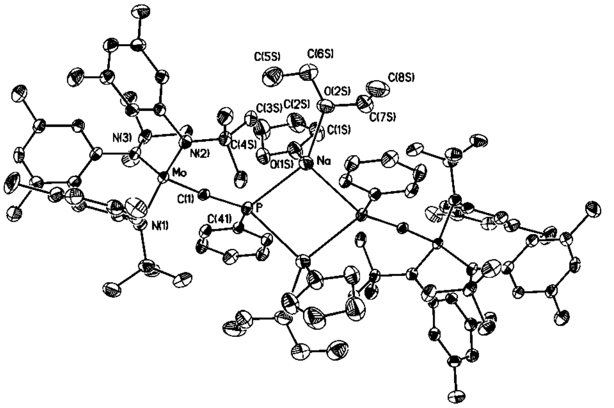


Figure 1. Structural drawing of [(**1**-CPPh)Na(Et$_2$O)(THF)]$_2$ with thermal ellipsoids at the 35% probability level. Selected interatomic distances (Å) and angles (deg): Mo−C(1), 1.762(5); P−C(1), 1.771(5); P−C(41), 1.826(5); Mo−C(1)−P, 171.0(3); C(1)−P−C(41), 106.0(2).

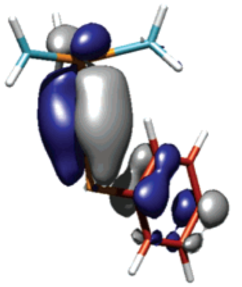


Figure 2. HOMO-3 molecular orbital displaying π bonding interaction between Mo, C, and P atoms.

synthesis the versatile and interesting methylidyne complex **1**-CH. The methine transfer reaction relies on the propensity of titanium amide **2** to effect halogen atom abstraction in concert with the selectivity of molybdenum amide **1** to serve as a trap for the 7-norbornadienyl radical.[16] This overall hypothesis remains to be validated by further detailed study, but in the present case it has permitted large-scale access to **1**-CH and the corresponding potassium salt (**1**-CK)$_2$ for elaboration to an unusual phosphorus derivative, the chemistry of which promises to be of substantial fundamental interest. With this work methine transfer assumes its rightful place alongside nitrogen, oxygen, and halogen atom transfer reactions in the context of inorganic synthesis.

Acknowledgment. For support of this work, the authors are grateful to the National Science Foundation (CHE-9988806), the Packard Foundation (Fellowship to C.C.C., 1995-2000), and the National Science Board (Alan T. Waterman award to C.C.C., 1998). T.A. thanks MIT's UROP (Undergraduate Research Opportunities Program) for funding. The authors thank a referee for drawing attention to ref 12.

Supporting Information Available: Details of the X-ray crystallography study, synthetic procedures and characterization data for the reported compounds, and ^{31}P NMR chemical shifts calculations (PDF, CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) The ^{31}P chemical shift in a THF-d_8 solution has an intermediate value of 103.5 ppm.

(15) See the Supporting Information for details and references on the DFT calculations, which were carried out using the Amsterdam Density Functional (ADF) suite of programs.

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JA017278R