Isolation and Characterization of the Molybdenum Alkylidyne Complex $[(F_3C)Me_2CO]_2Mo(C\text{-}t\text{-}Bu)[N(Ar)P{=}C(H)(CMe_2Ph)]$ and Its Conversion to a Phosphamolybdacyclobutene

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*Summary: Novel molybdenum alkylidyne $[(F_3C)Me_2CO]_2Mo(C\text{-}t\text{-}Bu)[N(Ar)P{=}C(H)(CMe_2Ph)]$ (Ar = 2,6-(i-Pr)$_2C_6H_3$; **3b**) is formed in the reaction of tert-butylphosphaalkyne **2** with molybdenum alkylidene **1b**. Alkylidyne **3b**, which contains a formal (phosphaalkenyl)amido ligand, rearranges quantitatively at elevated temperature to form the alkoxide-shifted phosphamolybdacyclobutene **4b**. Complexes **3b** and **4b** have been fully characterized by spectroscopic and X-ray crystallographic analysis; cleavage of the P≡C-t-Bu triple bond in complex **3b** is confirmed.*

Recent attention has turned to the reactivity of phosphaalkynes[1,2] with mononuclear organotransition-metal complexes, including low-valent metal alkylidenes and vinylidenes.[3] We recently reported the synthesis and characterization of the first 1-phospha-3-metallacyclobut-2-ene, **4a**, as the isolated product in the reaction of P≡C-*t*-Bu (**2**) with the d^0 alkylidene **1a**.[4] A distinguishing feature of the unique complex **4a** is an unusual metal-to-phosphorus alkoxide ligand shift accompanying the apparent head-to-tail [2+2] alkylidene−phosphaacetylene cycloadduct formation (an initial step in the metathesis polymerization of acetylenes).[5,6] We felt that one potential route to intercepting this intermediate was to change the migratory aptitude of the alkoxide ligands. The increased basicity of the alkoxide ligands, however, provides a new and entirely unexpected result. Instead of isolation of the phosphametallacycle prior to alkoxide migration, the unique molybdenum alkylidyne intermediate $[(F_3C)Me_2CO]_2Mo(C\text{-}t\text{-}Bu)[N(Ar)P{=}C(H)(CMe_2Ph)]$ (**3b**) is formed in the reaction of alkylidene **1b** with P≡C-*t*-Bu. Of particular note is the *cleavage of the phosphaacetylene triple bond*, leaving the *t*-Bu-C≡ group of **2** as a molybdenum neopentylidyne, and the phosphorus terminus is incorporated into the amido ligand. Furthermore, we observe that **3b** undergoes a thermal rearrangement in solution to generate phosphamolybdacyclobutene **4b**.

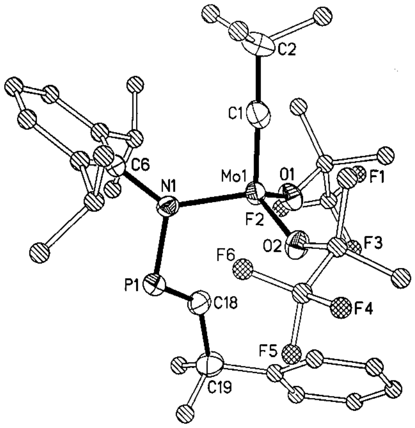

Figure 1. Molecular structure of complex **3b**. For clarity, 50% probability thermal ellipsoids are shown only for selected atoms. Selected bond lengths (Å), angles (deg), and dihedral angles (deg): Mo(1)−O(1) = 1.883(3), Mo(1)−O(2) = 1.883(3), Mo(1)−C(1) = 1.739(6), Mo(1)−N(1) = 1.952(4), C(1)−C(2) = 1.516(8), N(1)−P(1) = 1.735(4), N(1)−C(6) = 1.434(6), P(1)−C(18) = 1.663(6), C(18)−C(19) = 1.521(8); O(1)−Mo(1)−O(2) = 112.6(2), O(1)−Mo(1)−C(1) = 107.6(2), O(2)−Mo(1)−C(1) = 109.0(2), O(1)−Mo(1)−N(1) = 113.2(2), O(2)−Mo(1)−N(1) = 113.0(2), C(1)−Mo(1)−N(1) = 100.6(2), Mo(1)−C(1)−C(2) = 177.4(4), Mo(1)−N(1)−C(6) = 132.7(3), Mo(1)−N(1)−P(1) = 108.9(2), C(6)−N(1)−P(1) = 117.6(3), N(1)−P(1)−C(18) = 102.9(2), P(1)−C(18)−C(19) = 125.7(5); Mo(1)−N(1)−P(1)−C(18) = 51.9, N(1)−P(1)−C(18)−C(19) = 173.1.

Addition of excess **2**[7] to molybdenum alkylidene **1b**[8] at room temperature generates a dark yellow solution within 10 min (Scheme 1) and leads to quantitative consumption (^{1}H NMR) of **1b** within 6 h. Low-temperature recrystallization from pentane affords large, dark yellow crystals of **3b** from an isomeric mixture[9] in 72% yield.

[⊗] Abstract published in *Advance ACS Abstracts,* July 1, 1996.

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[2] (a) Nixon, J. F. *Coord. Chem. Rev.* **1995**, *145*, 201. (b) Streubel, R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 436.

[3] (a) Binger, P.; Haas, J.; Herrmann, A. T.; Langhauser, F.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 310. (b) Beckhaus, R.; Strauss, I.; Wagner, T. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 688.

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[5] (a) Scheer, M.; Schuster, K.; Budzichowski, T. A.; Chisholm, M. H.; Streib, W. E. *J. Chem. Soc., Chem. Commun.* **1995**, 1671. (b) Becker, G.; Becker, W.; Knebl, R.; Schmidt, H.; Hildenbrand, U.; Westerhausen, M. *Phosphorus Sulfur Relat. Elem.* **1987**, *30*, 349.

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[7] Becker, G.; Schmidt, H.; Uhl, G.; Uhl, W. *Inorg. Synth.* **1990**, *27*, 249.

[8] Oskam, J. H.; Fox, H. H.; Yap, K. B.; McConville, D. H.; O'Dell, R.; Lichtenstein, B. J.; Schrock, R. R. *J. Organomet. Chem.* **1993**, *459*, 185.

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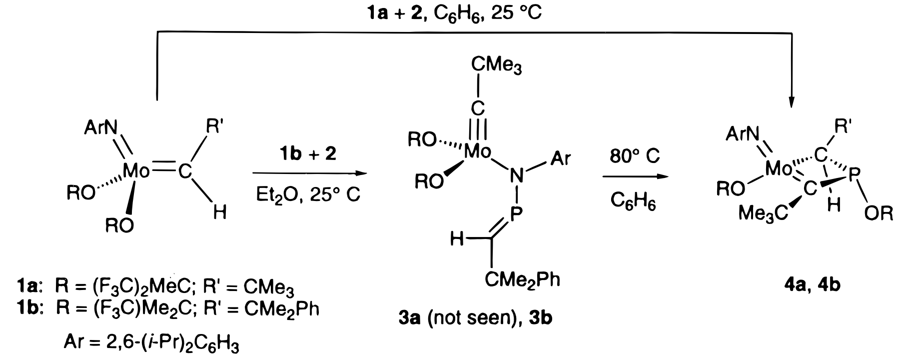
Scheme 1



Molybdenum alkylidyne **3b** is characterized by a ^{1}H NMR doublet at δ 8.48 ($^2J_{\mathrm{P-H}}$ = 14 Hz) and a ^{13}C NMR resonance at δ 180.0 ($^1J_{\mathrm{P-C}}$ = 52 Hz),[10] which are diagnostic for the aminophosphaalkene functionality.[11a] A second distinguishing feature in the ^{13}C NMR spectrum is a doublet at δ 314 ppm ($^3J_{\mathrm{P-C}}$ = 4 Hz), attributable to the terminal neopentylidyne ligand. The ^{31}P NMR of **3b** displays a resonance at δ 260.7 (C_7D_{14}, 25 °C), again typical of phosphaalkene σ^2,λ^3-P nuclei bearing phosphorus-bound amino substituents.[11b−d]

An X-ray crystallographic analysis of **3b**[12] confirms C_s symmetry and the remarkable connectivity in the mononuclear complex (Figure 1). Cleavage of the phosphaalkyne triple bond is reflected by the separate Mo−neopentylidyne (Mo(1)−C(1) = 1.739(6) Å, Mo(1)−C(1)−C(2) = 177.4(4)°) and (phosphaalkenyl)amido ligands bound to the pseudotetrahedral molybdenum center. The complete dissociation of the (initially) triply bound phosphaacetylene nuclei can be viewed as another example of metal alkylidyne mediated triple-bond cleavage. Important examples of these are the recent discovery of dinitrogen reductive cleavage[13] and both alkyne and nitrile metathesis.[14,15] Under the reaction conditions which lead to **3b**, alkylidene complex **1b** does *not* react with pivalonitrile, as determined by ^{1}H NMR.

Coordination of the planar nitrogen (bond angle summation at N(1) 359.2(1)°) to molybdenum is consistent with the bonding parameters of other amido ligands bound to low-valent metal centers through a formal double bond (Mo(1)−N(1) = 1.952(4) Å)[16] and suggests strong interaction of the nitrogen lone electron pair with the zerovalent molybdenum center.

Structural features of the *N*-phosphaalkenyl moiety complement an amido ligand bonding interpretation. A qualitative indication of the intimate molybdenum−nitrogen double bonding (at the expense of nitrogen lone electron pair interaction with the phosphaalkene functionality) is the observation that the usual P=C double-bond shortening typical of *P*-amino-substituted phosphaalkenes[11d,17] is not evident in complex **3b**. A formal double bond exists between P(1) and C(18) (1.663(6) Å).[11a] Approximate sp^2 hybridization at C(18) is reflected in the P(1)−C(18)−C(19) bond angle of 125.7(5)°. Only a slight deviation from planarity of the *P*-amino and *C*-neophyl substituents exists about the phosphaalkene double bond (N(1)−P(1)−C(18)−C(19) = 173.1°). Twisting of the N(1)-P(1)-C(18) plane from the Mo(1)-N(1)-P(1) plane (51°) establishes a phosphaalkene π-system electronically isolated from the molybdenum-amido bond.

Upon heating of **3b** (sealed tube, C_6H_6, 80 °C, 8 h) quantitative conversion to the cycloadduct $[\mathrm{ArN}][(\mathrm{F_3C})\mathrm{Me_2CO}]\overline{\mathrm{Mo{=}C}(t\text{-}\mathrm{Bu})\mathrm{P}(\mathrm{OCMe_2(CF_3)})\mathrm{C}}(\mathrm{H})(\mathrm{CMe_2Ph})$ (**4b**) is observed by ^{1}H NMR. The reaction rate is independent of concentration, suggesting that the reaction is intramolecular. Isolation of **4b** as orange crystals is achieved by recrystallization from pentane at −40 °C. As with its *bis*-hexafluoro-*tert*-butoxy analogue **4a**,[4] **4b** is characterized by a ^{1}H NMR doublet at δ 4.88 ($^2J_{\mathrm{P-H}}$ = 7 Hz) and six distinct methyl singlets, assignable to three diastereotopic pairs of methyl groups. Distinguishing ^{13}C NMR features include resonances at δ 247.9 ($^1J_{\mathrm{P-C}}$ = 80 Hz) and δ 119.3 ($^1J_{\mathrm{P-C}}$ = 65 Hz) assigned respectively to the carbene C_α and sp^3-hybridized methine carbon of the $\overline{\mathrm{M{=}CPC}}$ core. Chemically distinct Mo- and P-bound alkoxides give rise to two fluorine-coupled quartets at δ 79.0 and 77.1 (respectively), attributed to their quaternary carbon nuclei; the latter displays coupling to the phosphorus nucleus as well ($^2J_{\mathrm{P-C}}$ = 7 Hz). ^{31}P NMR of **4b** shows a high-field singlet at δ −110.3.

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(9) The isomeric mixture may be either an *E*/*Z* phosphaalkene mixture or perhaps rotamers about either Mo−N or N−P bonds.

(10) Complete characterization and crystal structure details for **3b** and **4b** are provided in the Supporting Information.

(11) (a) Appel, R. In *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Regitz, M., Scherer, O. J., Eds.; Thieme: Stuttgart, Germany, 1990; p 157. (b) Niecke, E.; Böske, J.; Krebs, B.; Dartmann, M. *Chem. Ber.* **1985**, *118*, 3227. (c) Markovskii, L. N.; Romanenko, V. D.; Ruban, A. V.; Polyachenko, L. K. *Zh. Obshch. Khim.* **1986**, *56*, 1907. (d) Appel, R.; Kündgen, U.; Knoch, F. *Chem. Ber.* **1985**, *118*, 1352.

(12) Crystal data for **3b** at 168 K: yellow crystal, monoclinic, space group $P2_1/c$, a = 17.719(1) Å, b = 11.3585(8) Å, c = 18.753(4) Å, β = 91.68(1)°, Z = 4, R = 0.048, R_w = 0.114 for 4009 reflections with $I > 2.0\sigma(I)$ and 416 parameters, GOF = 1.097.

(13) (a) Laplaza, C. E.; Cummins, C. C. *Science* **1995**, *268*, 861. (b) Laplaza, C. E.; Johnson, A. R.; Cummins, C. C. *J. Am. Chem. Soc.* **1996**, *118*, 709.

(14) Alkynes: (a) Buhro, W. E.; Chisholm, M. H. *Adv. Organomet. Chem.* **1987**, *27*, 311. (b) Listemann, M. L.; Schrock, R. R. *Organometallics* **1985**, *4*, 74. Metal alkylidene catalyzed acetylene metathesis oligomerizations have been observed also: (c) Schlund, R.; Schrock, R. R.; Crowe, W. E. *J. Am. Chem. Soc.* **1989**, *111*, 8004. Nitriles: (d) Chisholm, M. H.; Folting-Streib, K.; Tiedtke, D. B.; Lemoigno, F.; Eisenstein, O. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 110 and references cited therein.

(15) Other examples of apparent phosphaacetylene metatheses with mononuclear alkylidynes include: (a) Hill, A. F.; Howard, J. A. K.; Spaniol, T. P.; Stone, F. G. A.; Szameitat, J. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 210. (b) Hill, A. F. *J. Mol. Catal.* **1991**, *65*, 85. See ref 5 for reports of bimetallic complex mediated phosphaacetylene metatheses.

(16) (a) Legzdins, P.; Rettig, S. J.; Ross, K. J. *Organometallics* **1993**, *12*, 2103. (b) Nugent, W. A.; Harlow, R. L. *Inorg. Chem.* **1980**, *19*, 777.

(17) (a) Chernega, A. N.; Ruban, A. V.; Romanenko, V. D.; Markovski, L. N.; Korkin, A. A.; Antipin, M. Y.; Struchkov, Y. T. *Heteroatom. Chem.* **1991**, *2*, 229. (b) Chernega, A. N.; Romanenko, V. D. *Zh. Obshch. Khim.* **1992**, *62*, 1257.

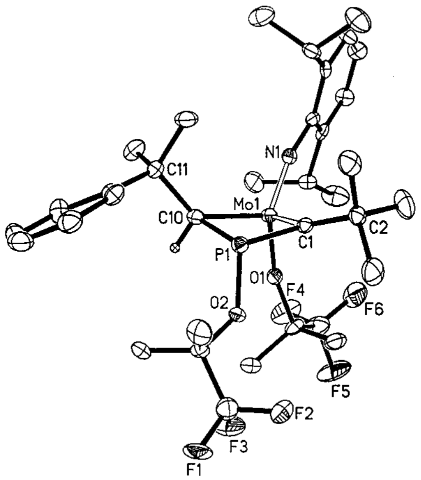

Figure 2. Molecular structure of complex **4b**; 50% probability thermal ellipsoids are shown. Selected bond lengths (Å), angles (deg), and dihedral angles (deg): Mo(1)−O(1) = 1.906(5), Mo(1)−N(1) = 1.767(6), Mo(1)−C(1) = 1.889(7), Mo(1)−C(10) = 2.110(7), P(1)−C(1) = 1.804(7), P(1)−C(10) = 1.854(8), C(1)−C(2) = 1.52(1), P(1)−O(2) = 1.662(5), C(10)−C(11) = 1.55(1); N(1)−Mo(1)−O(1) = 115.2(2), O(1)−Mo(1)−C(1) = 111.2(3), O(1)−Mo(1)−C(10) = 109.7(3), N(1)−Mo(1)−C(1) = 110.5(3), N(1)−Mo(1)−C(10) = 119.7(3), C(1)−Mo(1)−C(10) = 87.2(3), Mo(1)−C(1)−P(1) = 89.4(3), C(1)−P(1)−C(10) = 98.0(3), Mo(1)−C(10)−P(1) = 81.7(3), Mo(1)−C(1)−C(2) = 149.0(5), P(1)−C(1)−C(2) = 120.3(5), C(1)−P(1)−O(2) = 105.5(3), C(10)−P(1)−O(2) = 106.8(3); Mo(1)−C(1)−P(1)−C(10) = 19.9.

Crystallographic characterization of **4b**[18] shows a puckered phosphametallacyclobutene core in which the phosphorus and pseudotetrahedral molybdenum nuclei each bear one alkoxide group and are situated at the 1- and 3-positions, respectively (Figure 2). A Mo−C$_\alpha$ double bond (Mo(1)−C(1) = 1.889(7) Å)[19] and molybdenum−alkyl single bond (Mo(1)−C(10) = 2.110(7) Å) comprise the heterocyclobutene ring. Restoration of the arylimido ligand is evident (Mo(1)−N(1) = 1.767(6) Å, Mo(1)−N(1)−C(20) = 166.8(5)°),[19,20] as is bonding between the phosphorus and carbon nuclei of phosphaalkyne reagent **2**.

It is interesting to note that while molybdenum alkylidyne **3b** is the sole isolated product from the addition of **2** to **1b**, we are able to identify the formation of a transient species (δ 212.6 in C_7D_{14}) by low-temperature ^{31}P NMR experiments.[21] It is attractive to speculate that the observed transient may be a [2 + 2] cycloadduct between the alkylidene and phosphaalkyne (proposed in the cycloaddition reactions of phosphaalkynes with mononuclear metal alkylidynes and -vinylidenes)[5] from which ligand rearrangement can proceed to form **3b** or, per low-temperature ^{31}P NMR studies in the reaction of **1a** with **2**,[21] to generate **4b** directly.[22] Studies are underway to elucidate the nature of the transient species, to identify the relative influence of the alkylidene substituent and alkoxide ligands in determining the reaction course and kinetics, to determine the nature of alkylidyne isomers **3b**,[9] and to provide mechanistic details of the rearrangement of **3b** to **4b**.

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Supporting Information Available: Text and tables giving complete experimental procedures and characterization and X-ray structure details for complexes **3b** and **4b** and text and figures giving experimental details and ^{1}H NMR spectra of concentration kinetic studies and the reaction of **1b** with pivalonitrile (43 pages). Ordering information is given on any current masthead page.

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[18] (18) Crystal data for **4b** at 158 K: orange crystal, monoclinic, space group $P2_1/c$, $a = 9.971(1)$ Å, $b = 17.866(2)$ Å, $c = 20.897(2)$ Å, $\beta = 103.30(9)°$, $Z = 4$, $R = 0.055$, $R_w = 0.106$ for 2982 reflections with $I > 2.0\sigma(I)$ and 415 parameters, GOF = 1.157.

[19] (19) Schrock, R. R.; Murdzek, J. S.; Bazan, G. C.; Robbins, J.; DiMare, M.; O'Regan, M. *J. Am. Chem. Soc.* **1990**, *112*, 3875.

[20] (20) (a) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; Wiley: New York, 1988. (b) Wigley, D. E. *Prog. Inorg. Chem.* **1994**, *42*, 239.

[21] (21) Neither an analogous transient nor **3a** is observed in the reaction of **1a** with **2**. The electron-withdrawing bis(hexafluoro-*tert*-butoxy) substituents could activate reaction of an analogous transient too rapid to be observed on the NMR time scale.

[22] (22) It may be that the alkylidyne lies on the reaction coordinate between the reactants and the molybdacyclobutene. We are currently investigating both possibilities.