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Cycloaddition of Phosphaalkynes to High-Oxidation-State Metal Alkylidenes: Synthesis and Characterization of a Unique Phosphametallacyclobutene via an Alkoxide Ligand Shift

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*Summary: The phosphametallacycle **3**, [ArN][RO]Mo═C-(t-Bu)P(OR)C(H)(t-Bu) (Ar = 2,6-(i-Pr)$_2$-C_6H_3, R = CMe-$(CF_3)_2$), is formed from the cycloaddition of tert-butylphosphaacetylene to the high-oxidation-state molybdenum alkylidene [ArN]$[RO]_2$Mo═C(H)(t-Bu), accompanied by an alkoxide metal-to-ligand shift. The 1-phospha-3-molybdacyclobut-2-ene has been characterized by multinuclear NMR spectroscopy and its molecular structure determined by X-ray crystallographic analysis.*

Recent reactivity studies of phosphaalkynes[1] indicate the predominance of the P−C triple bond in determining the course of their reactions with unsaturated organic and organometallic[2] reagents. Numerous organotransition-metal complexes have been employed in the cyclooligomerization of *t*-BuC≡P (**1**) to form stabilized cyclic dimers,[3] trimers,[4] and higher polycyclics;[5] a handful of unusual phosphametallacycles, arising from the apparent [2 + 2] cycloaddition of the phosphaalkyne triple bond to the organometal $d_\pi-p_\pi$ bond, have recently been reported.[6] Typically, these cycloadducts reflect hetero-"head-to-head" regiochemistry.[7]

The isolobal relationship[8] of phosphaalkynes and organic alkynes RC≡CR led us to investigate the reactivity of phosphaalkyne **1** with potential oligomerization catalysts. High-oxidation-state transition-metal complexes such as **2** have been established as effective olefin ROMP catalysts.[9] Here we report the synthesis and characterization of **3**, the first 1-phospha-3-molybdacyclobut-2-ene, an isolable complex formally derived

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(7) Spectroscopic detection of a 1-phospha-3-titanacyclobut-1-ene constitutes the only reported details of a "head-to-tail" phosphaalkyne cycloaddition to an unsaturated mononuclear organometallic compound.[6c] Other reports of phosphaalkyne head-to-tail cycloaddition include details of the cycloaddition of **1** to a bridging methylidyne,[6a] mention of the isolation and characterization of the tungsten d^0 complex [*t*-BuO]$_2$(*t*-Bu)C═W═C(*t*-Bu)P(O-*t*-Bu) with no supporting data,[18] and the inferred formation of a cycloadduct in the *tert*-butylphosphaacetylene annelation with (alkoxynaphthylcarbene)chromium.[19]

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(13) [ArN][$(F_3C)_2$MeCO]Mo═C(*t*-Bu)P(OCMe$(CF_3)_2$)C(H)(*t*-Bu) (**3**): Under an argon atmosphere (glovebox), a 25 mL scintillation vial was charged with a magnetic stirbar, 0.075 g (0.107 mmol) of [ArN][$(F_3C)_2$-MeCO]$_2$Mo═C(H)(*t*-Bu) (**2**), and 1.0 mL of dry Et_2O. At 25 °C, 12 μL (0.128 mmol) of *tert*-butylphosphaacetylene (**1**) was added and the vial was capped; the catalyst solution changed from yellow to red-orange. After it was stirred for 5 h, solvent removal under vacuum left an orange residue which was dissolved in a minimum of dry pentane. Cooling at −40 °C yielded 0.075 g of orange crystals (87% yield based on starting molybdenum alkylidene **2**).

(14) Spectroscopic data for **3**: ^{1}H NMR (300 MHz, C_6D_6) δ 7.01 (s, 3H, [(2,6-(i-Pr)$_2C_6H_3$)N]Mo), 4.72 (d, 1H, $^2J_{P-H} = 7$ Hz, Mo−C(*H*)-(C$(CH_3)_3$), 3.76 (septet, 2H, $^3J_{H-H} = 7$ Hz, [(2,6-(*i-Pr*)$_2C_6H_3$)N]Mo), 1.75 (s, 3H, P(OCC*H*$_3(CF_3)_2$)), 1.38 (s, 3H, [$(F_3C)_2$C*H*$_3$CO]Mo), 1.35 (s, 9H, Mo(═C(C(C*H*$_3)_3$))), 1.32, 1.16 (each a d, 12H, $^3J_{H-H} = 7$ Hz, [(2,6-(*i-Pr*)$_2C_6H_3$)N]Mo), 0.91 (s, 9H, Mo−C(H)(C(C*H*$_3)_3$)); ^{13}C NMR (75 MHz, C_6D_6) δ = 251.9 (d, $^1J_{C-P} = 85$ Hz, Mo(═*C*(C$(CH_3)_3$), 154.1, 145.2, 128.3, 123.6 ([(2,6-(*i*-Pr)$_2$*C*$_6H_3$)N]Mo), 124.0, 122.9 (q, $^1J_{C-F} = 284$ Hz, P(OCCH$_3$(*C*F$_3)_2$), [(F$_3$*C*)$_2$CH$_3$CO]Mo), 120.4 (d, $^2J_{C-P} = 69$ Hz, Mo−*C*(H)-(C$(CH_3)_3$), 80.6 (septet, $^2J_{C-F} = 29$ Hz, [$(F_3C)_2CH_3$*C*O]Mo), 78.5 (doublet of septets, $^2J_{C-F} = 30$ Hz, $^2J_{P-C} = 4$ Hz, P(O*C*CH$_3(CF_3)_2$), 45.8 (d, $^2J_{C-P} = 25$ Hz, Mo(═C(*C*$(CH_3)_3$))), 38.2 (d, $^2J_{C-P} = 17$ Hz, Mo−C(H)-(*C*$(CH_3)_3$)), 33.4, 33.3 (both doublets, $^3J_{C-P} = 15$, 18 Hz, Mo(═C-(C(*C*H$_3)_3$)) and Mo-C(H)(C(*C*H$_3)_3$)), 28.2, 24.3, 23.9 (all singlets, [(2,6-(*i-Pr*)$_2C_6H_3$)N]Mo), 18.8 (s, [$(F_3C)_2$*C*H$_3$CO]Mo), 15.3 (d, $^1J_{C-P} = 21$ Hz, P(OC*C*H$_3(CF_3)_2$)); ^{31}P NMR (121.4 MHz, C_6H_6, external H_3PO_4) δ −105.7 (s); IR (C_6D_6) ν 2962, 2927, 2868, 1261, 1216, 1172, 1088, 1015, 870 cm^{-1}. Anal. Calcd for $C_{30}H_{42}NO_2F_{12}PMo$: C, 44.84; H, 5.27; N, 1.74. Found: C, 45.05; H, 5.19; N, 1.79.

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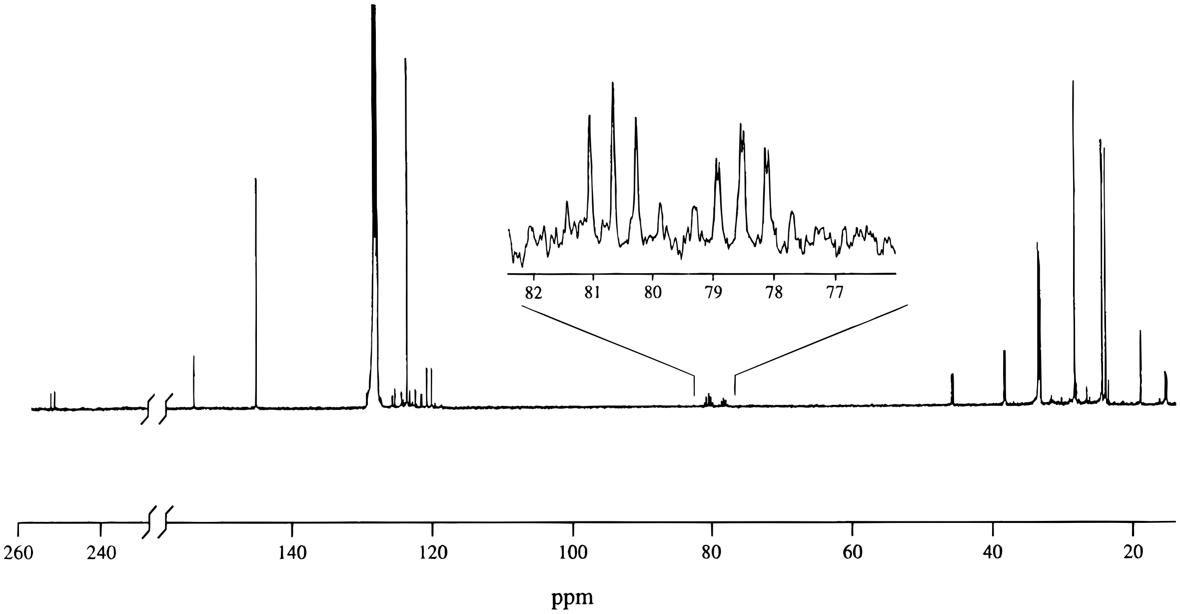
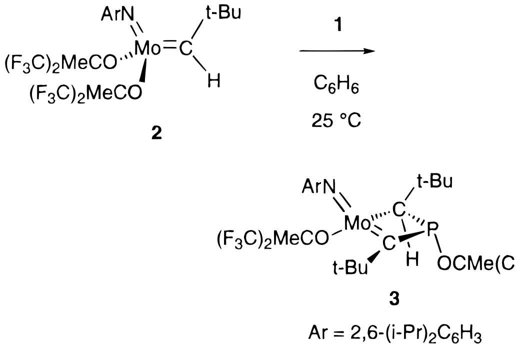


Figure 1. ^{13}C NMR spectrum of phosphamolybdacyclobutene **3** (in C_6D_6). The inset shows resonances for C(23) and C(27) (see numbering scheme in Figure 2).

from head-to-tail phosphaalkyne cycloaddition to a metal—carbon double bond. The formation of **3** constitutes the first reported instance of a characterized metal-to-phosphorus ligand migration in the growing number of organometallic phosphaacetylene cycloadducts.[10]

Upon addition of a slight excess of **1**[11] to a solution of **2** (in benzene, 25 °C),[12] a gradual color change from yellow to red-orange was observed over 5 min (eq 1).[13] Quantitative conversion (^{1}H NMR, C_6D_6) of the alkylidene/phosphaalkyne mixture to the single product **3** was confirmed by the disappearance of the low-field alkylidene proton resonance at δ 12.06 and the singlet resonance of **1** at δ 1.15. After the mixture was stirred for 5 h at room temperature, quantitative isolation of **3** was achieved by removing volatiles *in vacuo*. The reaction can also be conducted in diethyl ether.



(1)

A single ^{1}H NMR doublet resonance at δ 4.72 is attributed to the phosphametallacyclobutene ring C*H* proton, and the isopropyl C*H* septet appears at δ 3.76.[14] Two distinct singlets at δ 1.75 and 1.38 are attributed to the metal- and phosphorus-bound hexafluoro-*tert*-butoxy ligands, which now reside in very different molecular environments. Salient ^{13}C NMR features include two resonances strongly coupled to phosphorus: a low-field *tert*-butylcarbene doublet appears at δ 251.9 ($^1J_{P-C}$ = 85 Hz), and an upfield doublet at δ 120.4 ($^1J_{P-C}$ = 69 Hz) can be assigned to the carbon nuclei of the phosphametallacyclobutene subunit (C(6) and C(1), respectively; see numbering scheme in Figure 2). Two fluorine-coupled quaternary hexafluoro-*tert*-butoxy carbon signals are distinguishable at δ 80.6 and 78.5, the latter of which is also coupled to phosphorus ($^2J_{P-C}$ = 4 Hz; Figure 1). ^{31}P {^{1}H} NMR spectroscopy reveals a single resonance at δ −105.7 (external H_3PO_4 reference).

Upon slow cooling for 10 days at −40 °C in toluene, orange crystals suitable for X-ray diffraction analysis were isolated. Structural analysis of crystalline **3** verifies the 1-phospha-3-metallacyclobut-2-ene heterocyclic structure and the unusual regiochemistry of the product (Figure 2).[15] Phosphaalkyne cycloaddition has taken place with the dominant *syn* isomer of alkylidene **2**.[16] The geometry about the molybdenum atom is approximately tetrahedral, with a C(1)—Mo(1)—C(6) bond angle reduced from an ideal 109° to 87.4(3)° and an expanded bond angle O(1)—Mo(1)—N(1) of 114.6(2)°. A Mo(1)—C(6) bond length of 1.894(6) Å is consistent with a formal molybdenum—carbon double bond.[17] Approximate sp^2 hybridization at C(6) is confirmed by the bond angle summation about C(6) of 358.8°. A molybdenum—carbon single bond (Mo(1)—C(1) = 2.092(6) Å)

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(15) Crystal structure analysis of **3** at 163 K: orange prisms, 0.23 × 0.33 × 0.36 mm, $C_{30}H_{42}NO_2F_{12}PMo$: mol wt 803.6, monoclinic, space group $P2_1$, a = 9.630(1) Å, b = 14.958(1) Å, c = 12.945(1) Å, β = 110.12(1)°, Z = 2, V = 1750.9(3) Å^3, ρ_{calcd} = 1.524 g cm^{-3}, μ(Mo Kα) = 5.12 cm^{-1}. Data were collected on a Siemens P4 diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.7107 30 Å) using the $\theta-2\theta$ scan type ($2\theta_{max}$ = 45°), resulting in 2558 measured reflections (2258 observed; $F > 4.0\sigma(F)$). The structure was solved by direct methods. Full-matrix least-squares refinement gave residuals of R = 0.030 and R_w = 0.035 for 278 parameters. Hydrogen atoms were included using a riding model with d(C—H) = 0.96 Å and U(iso) = 0.06 Å^2. All crystallographic calculations were performed using the UCI-modified version of the UCLA Crystallographic Computing Package (UCLA Crystallographic Computing Package, University of California, Los Angeles, 1981: Strouse, C. Personal communication) and the SHELXTL PLUS program set (PC version: Sheldrick, G. SHELXTL PLUS program set; Siemens Analytical X-Ray Instruments: Madison, WI, 1990).

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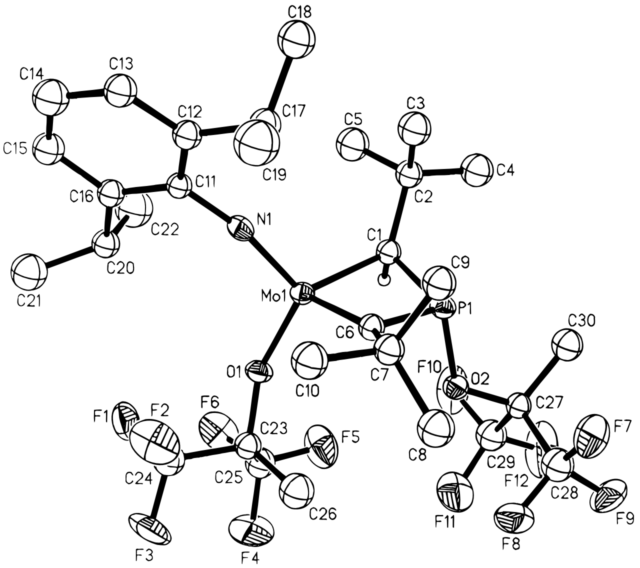

Figure 2. Molecular structure of complex **3**. Selected bond lengths (Å) and angles (deg): Mo(1)−O(1) = 1.930(4), Mo(1)−N(1) = 1.751(4), Mo(1)−C(6) = 1.894(6), Mo(1)−C(1) = 2.092(6), P(1)−C(1) = 1.841(9), P(1)−C(6) = 1.803(6), P(1)−O(2) = 1.693(4), C(1)−C(2) = 1.54(1); N(1)−Mo(1)−O(1) = 114.6(2), O(1)−Mo(1)−C(1) = 111.9(2), O(1)−Mo(1)−C(6) = 112.8(2), N(1)−Mo(1)−C(1) = 117.3(2), N(1)−Mo(1)−C(6) = 109.9(2), C(1)−Mo(1)−C(6) = 87.4(3), Mo(1)−C(1)−P(1) = 82.3(3), C(1)−P(1)−C(6) = 98.3(3), Mo(1)−C(6)−P(1) = 89.1(3), Mo(1)−C(6)−C(7) = 147.3(4), P(1)−C(6)−C(7) = 122.4(5), C(6)−P(1)−O(2) = 104.2(3), C(1)−P(1)−O(2) = 106.0(2).

exists between the molybdenum and sp^3-hybridized ring carbon, which presumably originates from the alkylidene catalyst. The difference in hybridization at C(1) and C(6) can be seen in their bond distances to the phosphorus nucleus (P(1)−C(6) = 1.803(6) Å; P(1)−C(1) = 1.841(9) Å). A Mo(1)−P(1) interatomic distance of 2.594 (2) Å is too long to constitute any phosphorus coordination to the molybdenum center. There is a significant deviation from planarity in the four-membered-ring complex, with a 17.8° dihedral angle defined by the Mo(1)−C(6)−P(1) and Mo(1)−C(1)−P(1) planes.

Bond angles at phosphorus confirm the tetrahedral geometry at P(1); an alkoxide ligand is bound to phosphorus with a P(1)−O(2) single-bond distance of 1.693(4) Å. The alkoxide is directed away from the bulky *tert*-butyl group attached to C(1), presumably to minimize nonbonding steric interactions with the *tert*-butyl methyl groups.

It is interesting to consider how metallacycle **3** is formed, and its implications regarding the potential for metathesis polymerization of phosphaalkynes to polyphosphaacetylenes. Substantial precedent exists for phosphaalkyne [2 + 2] cycloaddition to metal alkylidenes; however, isolated products from [phosphaalkyne + (transient) carbene] cycloadditions typically display regiochemistry *opposite* to that of **3**, with direct metal-to-phosphorus bonding.[6,7] Should subsequent 1,3-alkoxide migration to phosphorus follow initial head-to-tail [2 + 2] cycloaddition in the case reported here, inhibition of such a migration may allow for ring opening to a new molybdenum alkylidene. Head-to-head cycloaddition followed by ring opening would yield a terminal metal phosphinidene complex, which might be expected to be less electrophilic and therefore less apt to participate in subsequent cycloadditions than the alkylidene.[20]

Current investigations involve identification of a valid reaction mechanism for **3** and more suitable catalysts to promote phosphaalkyne oligomerization.

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Supporting Information Available: Text giving synthetic details and spectroscopic data for **3** and tables giving the structure determination summary, atomic coordinates, thermal parameters, and bond distances and angles for **3** (12 pages). Ordering information is given on any current masthead page.

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