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Double Phosphaalkyne Insertion to a Tungsten Alkylidene: Formation of a Diphosphametallabicyclobutane

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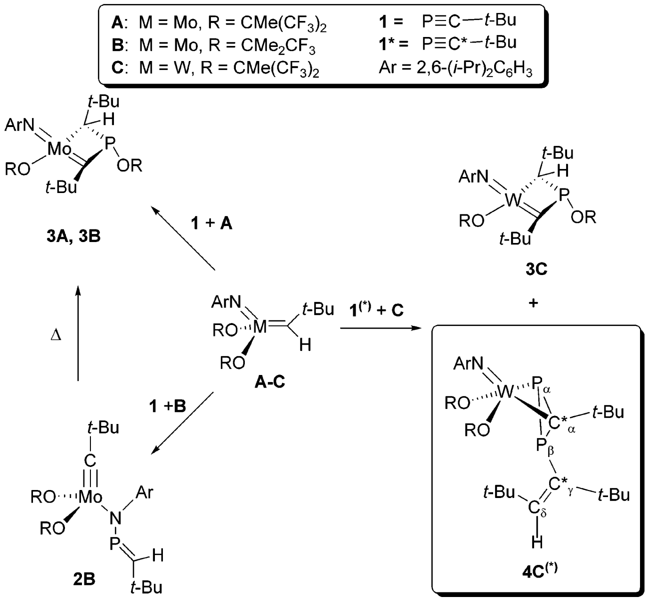
Summary: A unique diphosphametallabicyclobutane complex results from the reaction of the Schrock tungsten neopentylidene with excess $P\equiv C$-t-Bu, in contrast to phosphaalkyne reaction products with similar molybdenum alkylidenes. A mechanistic rationalization for the complex, which has been structurally characterized by NMR spectroscopy and single-crystal X-ray analysis, is postulated in terms of a ring-opening metathesis-like mechanism.

A widely accepted mechanism for metal-initiated alkyne polymerization is the Masuda “alkylidene” mechanism,[1] by which propagation involves [2 + 2] cycloaddition at the metal−carbon multiple bond of metal alkylidenes ($L_nM = CR_2$)[2] or metal vinylidenes ($L_nM = C{=}CHR$)[3] to form metallacyclobutenes, followed by productive ring opening to form a new, active metal−carbon double bond. In contrast, the cycloaddition chemistry of phosphaalkynes,[4] specifically *tert*-butylphosphaalkyne **1**, with discrete metal vinylidenes and alkylidenes gives isolable 1:1 cycloadducts; no polymers have been isolated. Whereas high-oxidation-state metal vinylidenes add to **1** to form 1-phospha-2-metallacyclobutenes with a new M−P bond,[5] we recently reported the unusual head-to-tail cycloaddition of **1** with Schrock molybdenum alkylidenes[6] to generate alkoxide-shifted 1-phospha-3-metallacyclobutenes (Scheme 1).[7,8] Manipulation of alkylidene electrophilicity permits isolation of alkylidyne intermediates and unprecedented cleavage/re-formation of the phosphaalkyne P−C bond in these mononuclear systems.[9] Here we apply the tungsten alkylidene **C** as a potential phosphaalkyne polymerization catalyst and describe the isolation and characterization of a unique diphosphametallabicyclobutane complex whose formation may be rationalized in terms of an operative alkylidene mechanism involving **1**.[10]

Scheme 1. Reactions of 1 with Metal Alkylidenes A−C



Introduction of 1.5 equiv of $P\equiv C$-*t*-Bu (**1**)[11] to a benzene solution of **C**[12] at room temperature induces a

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color change to dark yellow and partial consumption of **C**, as followed by ^{1}H NMR (attenuation of the characteristic alkylidene signal at 8.84 ppm). Two products are formed in an approximate 1:1 ratio, requiring 3 equiv of **1** to consume **C**; excess **1** does not change the constitution or ratio of the two reaction products. By ^{1}H NMR one set of product signals was identified as the organotungsten analogue of a previously described family of 1-phospha-3-molybdacyclobutenes, **3C**. The second product displays a distinguishing ^{1}H NMR doublet at δ 6.26 and was assigned to complex **4C** following more complete characterization (vide infra). Molybdenum analogues **4A** and **4B** have not been detected or isolated. Fractional crystallization from cold pentane isolates **3C** as a yellow crystalline solid mixed with red microcrystals of **4C**; a second recrystallization of the impure red crystals from cold pentane yields crystalline **4C** in 16% yield.

Heteronuclear NMR features of bicycle **4C** include ^{13}C NMR doublet resonances at δ 134.2 (${}^{1}J_{\mathrm{P-C}} = 120$ Hz) and δ 154.1 (${}^{2}J_{\mathrm{P-C}} = 20$ Hz), assigned to the phosphorus-bound (C_γ) and terminal (C_δ) olefinic carbons, respectively (Scheme 1). The quaternary bridgehead carbon C_α could not be resolved without ^{13}C labeling. A phosphorus doublet (δ −174.2) and doublet of quartets (δ −184.8 (${}^{1}J_{\mathrm{P-P}} = 162$ Hz, ${}^{6}J_{\mathrm{P-F}} = 16$ Hz)) are assigned to P_α and P_β, respectively. These data compare favorably with large upfield chemical shifts found in 1,2- and 1,3-diphosphabicyclobutanes reported by Niecke[13] and for a heavily substituted 1,2,3-triphosphabicyclobutane.[14]

Crystallographic analysis[15] reflects the formal incorporation of two phosphaacetylenes in **4C** and reveals a highly puckered bicyclobutane core with a 87.7° dihedral angle defined by the C(1)−W(1)−P(1) and C(1)−P(1)−P(2) planes (Figure 1). This establishes approximate tetrahedral geometry at the bridging phosphorus and carbon nuclei (mutually bound through a short single bond: (P(1)−C(1) = 1.838(6) Å).[14,16] Acute angles at P(1) and a W(1)−P(1) interatomic distance of 2.456(2) Å unambiguously define P(1) as an organophosphide ligand.[17,18] Other interatomic distances and angles within the bicyclobutane moiety are consistent with single bonding. A W(1)−P(2) interatomic distance of 2.777(2) Å exceeds that accepted for a coordinating phosphine ligand.[19]

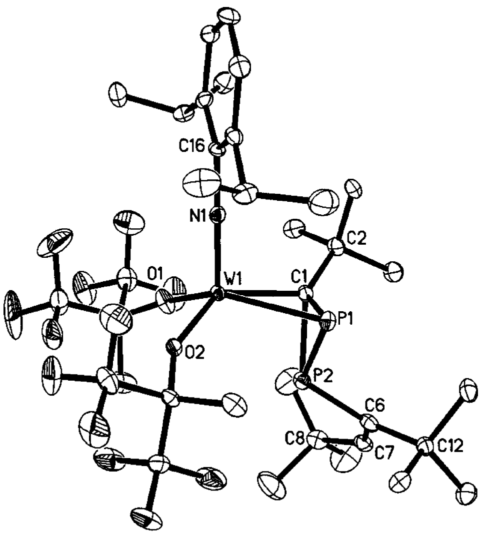

Figure 1. Molecular structure of complex **5**. For clarity, 50% probability thermal ellipsoids are shown only for selected atoms. Selected bond lengths (Å) and angles (deg): W(1)−N(1) = 1.724(5), W(1)−C(1) = 2.117(6), W(1)−P(1) = 2.456(2), C(1)−P(1) = 1.838(6), C(1)−P(2) = 1.873(6), P(1)−P(2) = 2.187(2), P(2)−C(6) = 1.865(6), C(6)−C(7) = 1.315(8); C(16)−N(1)−W(1) = 177.6(4), C(1)−W(1)−P(1) = 46.7(2), W(1)−C(1)−P(1) = 76.4(2), W(1)−P(1)−C(1) = 56.9(2), W(1)−P(1)−P(2) = 73.2(6), P(1)−C(1)−P(2) = 72.2(2), C(1)−P(1)−P(2) = 54.6(2), C(1)−P(2)−P(1) = 53.2(2), P(2)−C(6)−C(7) = 117.9(5), C(7)−C(6)−C(12) = 120.3(6), P(2)−C(6)−C(12) = 120.4(4), C(6)−C(7)−C(8) = 135.7(6).

Isolation of, and spectral data from 99% ^{13}C site-specifically labeled **4C*** (99% α-^{13}C-enriched P≡C*-*t*-Bu, prepared from ${}^{13}\mathrm{CO}_2$ by literature methods[20]) support a Masuda-like mechanism and unambiguously define the terminal olefinic group in **4C*** as being derived from the starting tungsten alkylidene complex; ^{13}C NMR of **4C*** reflects the signal enhancement expected for the C_γ doublet at 134.2 ppm and also allows assignment of the bridging C_α resonance at 118.7 ppm as a doublet of doublets with ^{183}W satellites (${}^{1}J_{\mathrm{P-C}} =$ 89 and 70 Hz, ${}^{1}J_{\mathrm{W-C}} = 70$ Hz).

We postulate a mechanism for formation of **3C** and **4C** which reflects a competing regiochemical preference of P≡C-*t*-Bu for head-to-tail (leading to **3C**) or head-to-head cycloaddition to the W═C double bond of **C** (Scheme 2). Initial formation of the [2 + 2] head-to-tail cycloadduct **5** followed by 1,3-alkoxide migration to phosphorus is an attractively simple explanation for generation of **3C**. This explanation has gained favor in arguments for products derived from phosphaalkyne metathesis by high-oxidation-state dinuclear tungsten complexes.[21]

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(10) The formal insertion of 2 equiv of **1** into a metal−hydride bond has been reported by Hill: Hill, A. F.; Jones, C.; Wilton-Ely, J. D. E. T. *Chem. Commun.* **1999**, 451.

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(15) Crystal data for **4C** at 163 K: red crystal, monoclinic, space group *C*2/*c*, $a = 42.110(5)$ Å, $b = 10.6323(9)$ Å, $c = 20.577(2)$ Å, $\beta = 117.670(6)°$, $Z = 8$, $R = 0.032$ and $R_\mathrm{w} = 0.065$ for 4385 reflections with $I > 2.0\sigma(I)$ and 478 parameters, GOF = 1.060.

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(18) Instances of higher order bonding between disubstituted phosphorus and transition metals invoke phosphinidene-like character and have been described: see: (a) Zanetti, N. C.; Schrock, R. R.; Davis, W. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2044. (b) Rocklage, S. M.; Schrock, R. R.; Churchill, M. R.; Wasserman, H. J. *Organometallics* **1982**, *1*, 1332.

(19) During the review process it was noted that **4C** could be also be structurally interpreted as a tungsten η^2-diphosphirene complex, presumably derived from insertion of **1** into the W═P bond of a tungsten phosphinidene intermediate (vide infra).

(20) 99% α-^{13}C-enriched P≡C*-*t*-Bu was prepared by starting from labeled pivalic acid (see: *Organic Syntheses*; Wiley: New York, 1932; Collect. Vol. 1, p 524).

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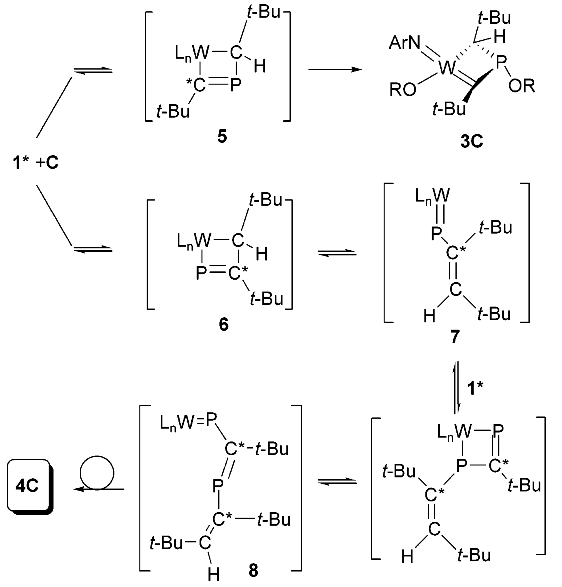
Scheme 2



L_n = [(ArN)(RO)$_2$]; Ar = 2,6-(*i*-Pr)$_2$C$_6$H$_3$, R = CH$_3$(CF$_3$)$_2$C

Formation of **4C** may be mechanistically interpreted in terms of sequential cycloaddition/ring opening, which is consistent with ^{13}C NMR spectral data of **4C*** and highlights the potential for linear oligomerization of suitably substituted phosphaalkynes under appropriate conditions. Head-to-head cycloaddition of **1** to **C** followed by ring opening of the resultant phosphametallacyclobutene **6** would yield the intermediate, high-oxidation-state vinylphosphinidene complex **7**, which we anticipate should support W=P multiple bonding and reflect reactivity as such.[22,23] Cycloaddition of a second equivalent of **1** to phosphinidene **7** followed by ring opening would yield the new phosphinidene **8**.[24] Rearrangement of the acyclic diphosphametallahexatriene **8** to the bicyclic complex **4C** may be energetically favorable, in light of the established reactivity of phosphaalkene P=C double bonds and the relaxed ring strain energies inherent in **4C** (vis-à-vis the organic bicyclobutane → butadiene system).[25] Similar rearrangements have been invoked to explain the formation of diphosphabicyclobutanes from 2,3-diphosphabutadienes.[13]

It is attractive to consider complex **4C** as a catalyst resting state, potentially capable of inserting additional phosphaalkyne at the tungsten center. Current efforts are underway to activate **4C** for further uptake of phosphaalkyne **1** and to identify other potential catalysts for phosphaalkyne oligomerization.

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Supporting Information Available: Text giving synthetic details and spectroscopic and analytical data for **3C** and **4C** and a CIF file giving crystallographic data for **4C**. This material is available free of charge via the Internet at http://pubs.acs.org.

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