Phosphaalkynes from Acid Chlorides via P for O(Cl) Metathesis: A Recyclable Niobium Phosphide (P³⁻) Reagent that Effects C−P Triple-Bond Formation

Joshua S. Figueroa and Christopher C. Cummins*

Room 2-227, Department of Chemistry, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, Massachusetts 02139-4307

Received June 29, 2004; E-mail: ccummins@mit.edu

With the advent of niobaziridine-hydride Nb(H)(t-Bu(H)C=NAr)(N[Np]Ar)₂ (**1**, Np = neopentyl, Ar = 3,5-Me₂C₆H₃)[1] has emerged new potential for P-atom transfer stemming from the ability of **1** to serve as a synthon for the reactive Nb(N[Np]Ar)₃ fragment.[2] As shown in Figure 1, white phosphorus (P₄) reacts with **1** to provide the μ-P₂ diniobium complex **2**. The latter is cleaved reductively by sodium amalgam in THF to provide the [Na(THF)$_x$]⁺ salt of the terminal niobium phosphide anion, [PNb(N[Np]Ar)₃]⁻ (**3**). The latter sequence (reactions i and ii in the synthetic cycle at left in Figure 1) was reported recently.[1,2] Featured in the present communication is the fact that phosphide anion **3** serves to transform acid chlorides into corresponding phosphaalkynes via four-membered metallacyclic intermediates, examples of which have been isolated and fully characterized. The transformation represents a new, mild method for access to phosphaalkynes, the high inherent reactivity of which has led to their implementation in organic,[3,4] polymer,[5] and coordination chemistry.[6]

Treatment of [Na(THF)$_x$]**3** with either pivaloyl chloride (t-BuC-(O)Cl) or 1-adamantoyl chloride (1-AdC(O)Cl) in cold THF solution elicits a color change from dark yellow to red over a period of 1.0 h. A standard workup followed by crystallization from Et₂O produced the cherry-red metallacyles, (t-BuC(O)P)Nb(N[Np]Ar)₃ (**4**-t-Bu) and (1-AdC(O)P)Nb(N[Np]Ar)₃ (**4**-1-Ad), in yields of 70 and 80%, respectively (reaction iii, Figure 1). Crystallographic structure determination of both derivatives **4**[7] revealed the presence of four-membered, Nb−P−C−O rings containing both Nb−P and Nb−O linkages (an ORTEP rendering of **4**-1-Ad is included in Figure 1, top right). Whereas metallacycles **4** might be viewed as acylphosphinidenes[8] (Nb=PC(=O)R) with bending at phosphorus[9] and carbonyl oxygen coordination, we suggest that they are best formulated as heteroatom-substituted, niobacyclobutene (Nb−P=C(−O)R) complexes. Significant electronic rearrangement is thus brought about by acylation of the phosphide (M−P triple bond[10]) moiety.[2] Structural parameters in support of this formulation for **4**-1-Ad include a C−O distance of 1.314(4) Å and a (short) P−C distance of 1.757(7) Å. The latter parameter is in the range typical for phosphaalkene P−C double bonds,[11] while the former parameter exceeds the maximum value expected for a carbonyl group. Furthermore, the Nb−P distance of 2.491(2) Å is substantially longer than expected for a doubly bound terminal phosphinidene,[9] more closely approximating a Nb−P single bond.[12]

The foregoing description of metallacycles **4** finds further support by way of spectroscopic signatures. In C₆D₆ solution, the ³¹P{¹H} NMR resonances for **4**-t-Bu (261 ppm) and **4**-1-Ad (258 ppm) are upfield of the chemical shift range characteristic of early transition metal, terminal phosphinidene complexes,[9] while lying in a range typical of phosphaalkenes.[11] The ¹³C{¹H} NMR resonances of 260 ppm (**4**-t-Bu and **4**-1-Ad) for the metallacyclic carbon,[13] with associated large $^1J_{PC}$ coupling constants of 113 Hz (**4**-t-Bu) and 107

Hz (**4**-1-Ad), are likewise strongly suggestive of the presence of P−C multiple bonding in these niobacycles. In addition, the increase in P−C bond order at the expense of carbonyl C=O bonding is reflected in the infrared spectrum of complexes **4**, where carbonyl stretching vibrations in the usual energy range are not observed.[14]

Niobacycles **4** are valence-isoelectronic to the metallacyclic intermediates postulated by Chisholm in explanation of NW(O-t-Bu)₃-catalyzed nitrogen atom exchange between PhCN and MeC¹⁵N.[15] Accordingly, metallacycles **4** have been found to readily undergo retro [2 + 2]-fragmentation in solution, leading smoothly to known phosphaalkynes[3] **5** (t-BuCP or 1-AdCP) along with oxoniobium-(V) complex[1] **6** (reaction iv in Figure 1). Cherry red C₆D₆ solutions of either **4**-t-Bu or **4**-1-Ad left standing at room temperature are observed to pale in color, becoming yellow over several hours. Intermittent assay of these solutions by either ¹H or ³¹P{¹H} NMR spectroscopy revealed the disappearance of **4** concomitant with formation of oxo **6** and either t-BuCP (**5**-t-Bu) or 1-AdCP (**5**-1-Ad). Phosphaalkynes **5** are readily identified by their characteristic resonances[3,16] in both ¹H and ³¹P{¹H} NMR spectra of the reaction mixtures, and the reaction can be conveniently monitored as a function of time.

Figure 1 includes (bottom, right) a stacked plot of the ³¹P{¹H} NMR spectrum as a function of time corresponding to the **4**-t-Bu → **5**-t-Bu + **6** conversion at 45 °C in C₆D₆ solution. Clearly evident is the smooth decay of the resonance at 261 ppm (**4**-t-Bu) simultaneous with the appearance of a resonance located at −64 ppm (**4**-t-Bu, lit. (20 °C) = −69 ppm). At 45 °C, phosphaalkyne formation is complete in ca. 4 h, and it is noteworthy that no additional signals are observed in the ³¹P{¹H} NMR spectrum over the range +700 to −300 ppm during the reaction. Upon complete thermolysis, solutions containing equimolar amounts of **5**-t-Bu and **6** stored at room temperature do not revert back to **4**-t-Bu when monitored for several weeks. Thus, the retro [2 + 2]-fragmentation reaction is irreversible under the conditions probed. Preliminary kinetic studies for the **4**-t-Bu → **5**-t-Bu + **6** reaction over the temperature range 308−338 K in C₆D₆ solution are consistent with a first-order fragmentation process. Activation parameters $\Delta H^{\ddagger}$ = 24.9 ± 1.4 kcal/mol and $\Delta S^{\ddagger}$ = 2.4 ± 4.3 cal/mol K were obtained over this range, with the small entropic barrier adding weight to the notion of niobacycles **4** as intermediates on the phosphalkyne formation pathway, requiring little reorganization to reach the transition state for fragmentation.

For synthetic purposes, thermolysis of solutions containing **4**-t-Bu or **4**-1-Ad at 85 °C provides **6** and the corresponding phosphaalkyne within 30 min. After thermolysis of a solution containing **4**-t-Bu, colorless solutions of the pure phosphaalkyne, **5**-t-Bu, are obtained by simple vacuum transfer. The yield of **5**-t-Bu obtained in this fashion is greater than 90%, on scales from 20 to 200 mg of
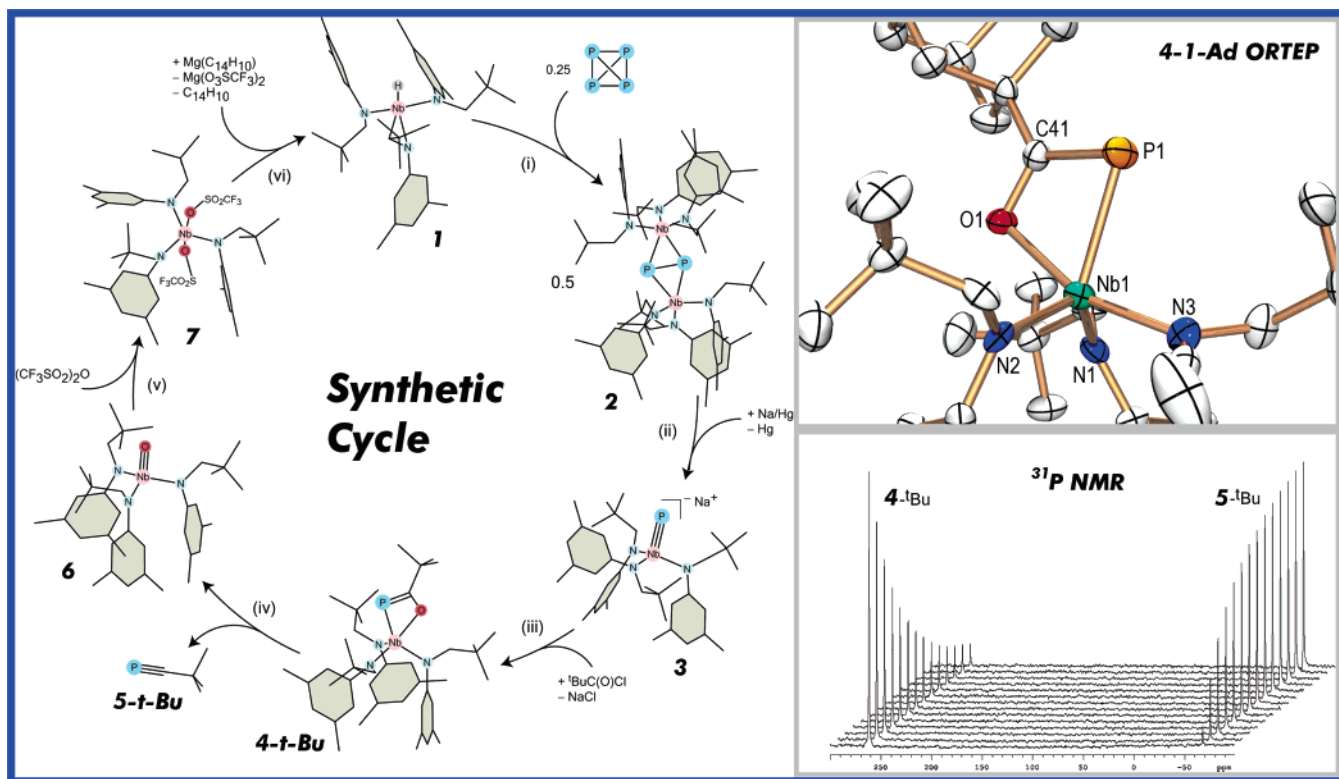
Figure 1. Shown at left is a synthetic cycle for P$_4$ activation, terminal phosphide acylation, phosphaalkyne elimination, and reactive metal complex regeneration. At upper right is an enlarged 50% thermal ellipsoid rendering of intermediate **4**-1-Ad; at lower right is shown ^{31}P{^{1}H} NMR monitoring of the **4**-*t*-Bu → **5**-*t*-Bu + **6** transformation. All line drawings of niobium complexes pictured above were generated from crystallographically determined structure coordinates.

4-*t*-Bu, as assayed by ^{1}H NMR integration relative to an internal standard.

Golden yellow oxo **6** is recovered quantitatively after removal of *t*-BuCP by vacuum transfer, and we find that it can be converted to the bistriflate complex Nb(OTf)$_2$(N[Np]Ar)$_3$ (**7**, reaction v) upon treatment with 1.0 equiv of the potent electrophile triflic anhydride[17] (Tf$_2$O, Tf = O$_2$SCF$_3$) in Et$_2$O. Bistriflate **7** is a bright orange, ether-insoluble, crystalline solid isolated in 90% yield by filtration of the reaction mixture. Whereas early transition metal, terminal oxo moieties have been reported to be moderately nucleophilic,[18,19] their smooth incorporation into a good leaving group has rarely been documented.[20] Furthermore, bistriflate **7** serves as an ideal synthetic precursor to niobaziridine-hydride **1**. As indicated in Figure 1, reduction of bistriflate **7** with magnesium anthracene[21] (reaction vi) proceeds with high-yield formation of **1**, the complex being readily separable from the magnesium triflate and anthracene byproducts.

Thus is completed a synthetic cycle for element (P$_4$) activation, phosphaalkyne synthesis by metathetical P-atom transfer, and deoxygenative recycling of the ultimate niobium oxo product. As demonstrated previously for C−C[22] and C−N[15,23,24] triple bonds, C−P triple-bond formation is now shown to be available via metathetical exchange on a low-coordinate, d^0 transition metal platform.

Supporting Information Available: Full experimental details for all new compounds, representative spectra for thermolysis reactions, kinetic data, and X-ray structural information for complexes **4**-*t*-Bu, **4**-1-Ad, and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Figueroa, J. S.; Cummins, C. C. *J. Am. Chem. Soc.* **2003**, *125*, 4020.
(2) Figueroa, J. S.; Cummins, C. C. *Angew. Chem., Int. Ed.* **2004**, *43*, 984.
(3) Regitz, M.; Binger, P. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1484.
(4) Märkl, G.; Seidl, E.; Trötsch, I. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 879.
(5) Loy, D. A.; Jamison, G. M.; McClain, M. D.; Alam, T. M. *J. Polym. Sci. A* **1999**, *37*, 129.
(6) Nixon, J. F. *Coord. Chem. Rev.* **1995**, *145*, 201.
(7) Key metrical parameters for **4**-1-Ad and **4**-*t*-Bu are essentially identical.
(8) Bohle, D. S.; Clark, G. R.; Rickard, C. E. F.; Roper, W. R. *J. Organomet. Chem.* **1988**, *353*, 355.
(9) Cowley, A. H. *Acc. Chem. Res.* **1997**, *30*, 445.
(10) Johnson, B. P.; Balazs, G.; Scheer, M. *Top. Curr. Chem.* **2004**, *232*, 1.
(11) Regitz, M.; Scherer, O. J.; Eds. *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Thieme Verlag: New York, 1990.
(12) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960; Chapter 11, p 405.
(13) Synthesis and spectroscopic characterization of **4**-1-Ad utilizing 1-Ad^{13}C-(O)Cl confirmed that the niobacyclic carbon atom originated from the acyl chloride carbonyl group. See Supporting Information.
(14) Difference FTIR spectroscopy experiments on **4**-1-Ad and its ^{13}C-labeled isotopomer failed conclusively to establish the identity of the CO vibrations in these molecules.
(15) Chisholm, M. H.; Delbridge, E. E.; Kidwell, A. R.; Quinlan, K. B. *Chem. Commun.* **2003**, 126.
(16) NMR parameters (^{1}H, ^{13}C, and ^{31}P) for phosphaalkynes **5** obtained here are in excellent agreement with the literature values. See Supporting Information.
(17) Baraznenok, I. L.; Nenajdenko, V. G.; Balenkova, E. S. *Tetrahedron* **2000**, *56*, 3077.
(18) Freundlich, J. S.; Schrock R. R. *Inorg. Chem.* **1996**, *35*, 7459.
(19) Cheng, J. Y. K.; Cheung, K.-K.; Chan, M. C. W.; Wong, K.-Y.; Che, C.-H. *Inorg. Chim. Acta* **1998**, *272*, 176.
(20) Triflic anhydride has been used for conversion of Ph$_3$SbO to Ph$_3$Sb-(OTf)$_2$: Niyogi, D. G.; Singh, S.; Verma, R. D. *J. Fluor. Chem.* **1995**, *70*, 237. See also ref 17.
(21) Magnesium anthracene reductant was employed as its orange, crystalline, tris-THF complex: Freeman, P. K.; Hutchinson, L. L. *J. Org. Chem.* **1983**, *48*, 879.
(22) Schrock, R. R. *Chem. Rev.* **2002**, *102*, 145.
(23) Clough, C. R. Greco, J. B.; Figueroa, J. S.; Diaconsecu, P. L.; Davis, W. M.; Cummins, C. C. *J. Am. Chem. Soc.* **2004**, *126*, 7742.
(24) Brask, J. K.; Durà-Vilà, V.; Diaconescu, P. L.; Cummins, C. C. *Chem. Commun.* **2002**, 902.

JA0461522