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Article

Phosphaalkenes as Long-Lived Phosphorus Cluster Surface Functional Groups: Intramolecular P=C Addition to a Niobium-Supported P_7 Cage

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The diniobium octaphosphorus complex $(P_8)[Nb(OC[^2Ad]Mes)_3]_2$ (**1**) (Ad = adamantylidene, Mes = $2,4,6\text{-}Me_3C_6H_2$) contains a reactive niobium phosphinidene moiety that can be exploited for metathetical scission of the Nb=P bond. When **1** is treated with aryl ketones, loss of $ONb(OC[^2Ad]Mes)_3(OEt_2)$ (**2**) is observed along with concomitant formation of the corresponding phosphaalkene $(RC_6H_4)_2C=PP_7Nb(OC[^2Ad]Mes)_3$ (**3-R**). Complexes **3-R** rearrange to incorporate the $(RC_6H_4)_2C=P$ unit into the phosphorus cage, thereby generating a saturated organo-phosphorus cluster complexed to the niobium *tris*-enolate platform, $(RC_6H_4)_2CP_8Nb(OC[^2Ad]Mes)_3$ (**4-R**). The structure of one such rearranged cluster **4-H**, as determined by X-ray crystallography, is briefly discussed. An Eyring analysis of the first-order rearrangement of **3-H** to **4-H** gives activation parameters of $\Delta H^\ddagger = 16.7$ kcal/mol and $\Delta S^\ddagger = -20.4$ eu. A Hammett analysis of the phosphaalkene rearrangement, **3-R** to **4-R**, with substitution varying at the *para* positions of the aryl rings, reveals a linear relationship between the σ values and the rearrangement rate constants. A concerted, asynchronous mechanism for the least-motion rearrangement of **3-H** to **4-H** is presented. When **1** is treated with alkyl ketones, similar loss of **2** and formation of the corresponding phosphaalkene is observed; however, the phosphaalkene complexes have considerably greater stability and are readily isolated.

Introduction

The activation of P_4 by transition-metal complexes is of interest for the discovery of processes for the synthesis of organophosphorus compounds that circumvent PCl_3 as an intermediate.[1-8] Incorporation of P_4-derived phosphorus atoms into organic molecules post transition metal activation of white phosphorus has been accomplished in select instances, but this area is developing and there is much room for exploration.[1,4] The first clear example of metal-mediated P–C bond formation originating from the direct transfer of an organic group to a metal-activated tetraphosphorus molecule was recently reported by Peruzzini and co-workers with their $(\text{triphos})Rh(\eta^{2:1}\text{-}P_4R)$ (R = Me, Et, Ph) complexes.[9] Direct reaction of the P_4 molecule with certain organic reagents, *sans* intervention by a transition-metal complex, is also contributing to the goal of direct functionalization of P_4. Bertrand and co-workers reported on the activation of P_4 by their cyclic alkyl(amino)carbenes that results in reactive products envisioned as synthons for the construction of P_4 containing molecules harboring P–C bonds.[10] Research in this general area of phosphorus activation continues apace with strides being made toward the synthesis of new and unusual phosphorus-containing molecules.[4-7,11-20]

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Scheme 1

(1)
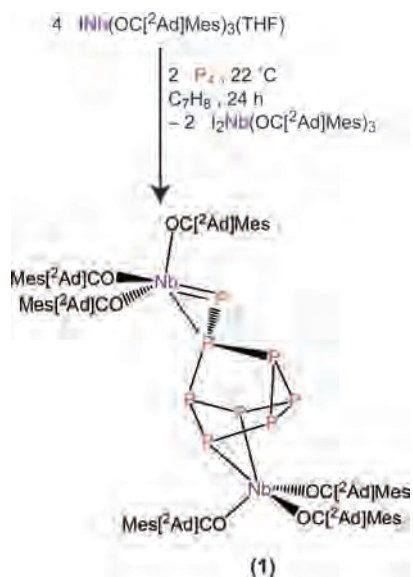
We have recently reported on a transition-metal platform for the generation of a diniobium octaphosphorus complex in a high yielding synthesis that takes place under mild conditions.[21] In that work, a niobium(IV) *tris*-enolate iodide molecule reductively couples two molecules of P_4 via a disproportionation mechanism to generate the diniobium octaphosphorus molecule $(P_8)[Nb(OC[^2Ad]Mes)_3]_2$ (**1**) and $I_2Nb(OC[^2Ad]Mes)_3$ (^2Ad = adamantylidene, Mes = 2,4,6-trimethylphenyl; Scheme 1). Complex **1** can be thought of as a Zintl-like P_7^{3-} unit that is decorated with a niobium phosphinidene moiety and a niobium trisenolate complex. The use of group 15 polyanions as ligands for transition metals is a diverse area of exploration. Such complexes are typically synthesized from the treatment of transition-metal precursors with Zintl ions formed through the prior activation of elemental molecules with alkali or alkaline-earth metals.[19,22−26] The synthesis of phosphorus polyanions via transition-metal activation of P_4 is efficient as it merges this two-step process into a single transformation. Furthermore, introducing functionality, particularly organic functionality, into traditional Zintl cages is uncommon in the literature,[27−29] and to our knowledge, conjugation of metal−ligand multiple bonds with Zintl ions is without precedent.

With the present work, our goal is to develop new methods for the functionalization of the octaphosphorus cluster in **1** with selective removal of a single niobium metal center as a recyclable entity. Ultimately, we hope to discover new routes to phosphorus-rich organic molecules. Herein we report a detailed mechanism by which an organic $C(C_6H_4R)_2$ moiety is incorporated into the phosphorus cluster of complex **1** with concomitant extrusion of one niobium *tris*-enolate fragment. The reactions presented herein do highlight the broader idea of phosphorus cluster functionalization, mediated by transition metal−phosphorus multiple bond chemistry, as a sequel to P_4 activation.

Experimental Section

General Considerations. All manipulations were performed in a Vacuum Atmospheres model MO-40 M glovebox under an inert atmosphere of purified N_2. Anhydrous-grade, oxygen-free tetrahydrofuran (THF) was purchased from Aldrich and further dried by passing through a column of molecular sieves and stirring with Na for at least 12 h prior to filtration through Celite to remove Na. All other solvents were obtained anhydrous and oxygen-free by bubble degassing (N_2) and purification through columns of alumina and Q5.[30] Deuterated solvents were purchased from Cambridge Isotope Laboratories. Benzene-d_6 and toluene-d_8 were degassed and stored over molecular sieves for at least 2 d prior to use. Celite 435 (EM Science) was dried by heating above 200 °C under a dynamic vacuum for at least 24 h prior to use. 4,4′-Bis(trifluoromethyl)benzophenone was prepared according to literature procedures using a CEM Explorer Series microwave reactor.[31] All other ketones were purchased from Aldrich chemical company and recrystallized once from THF or toluene prior to use. All metal starting materials were synthesized according to reported methods.[21] All glassware was oven-dried at temperatures greater than 170 °C prior to use. NMR spectra were obtained on Varian Inova 300 or 500, or Bruker Avance 400 instruments equipped with Oxford Instruments superconducting magnets and referenced to residual C_6H_5D (^1H = 7.16 ppm, ^{13}C = 128.06 ppm). ^{31}P NMR spectra were referenced externally to 85% H_3PO_4 (0 ppm). Elemental analyses were performed by Midwest Microlab LLC, Indianapolis, IN.

Independent Synthesis of ONb(OC[^2Ad]Mes)_3(OEt_2) (2). A suspension of $ONbCl_3(THF)_2$ (1.81 g, 5.04 mmol) in 140 mL of Et_2O was chilled to −116 °C in the glovebox cold-well. Upon removing from the cold-well, solid $KOC[^2Ad]Mes$ (5.0 g, 15.6 mmol) was added gradually in several portions. Upon warming, the color of the reaction mixture proceeded from white to gray/green to blue and finally to yellow-brown. After returning to 22 °C the solution was stirred an additional 2 h. The mixture was then concentrated and pentane added to help precipitate KCl. The

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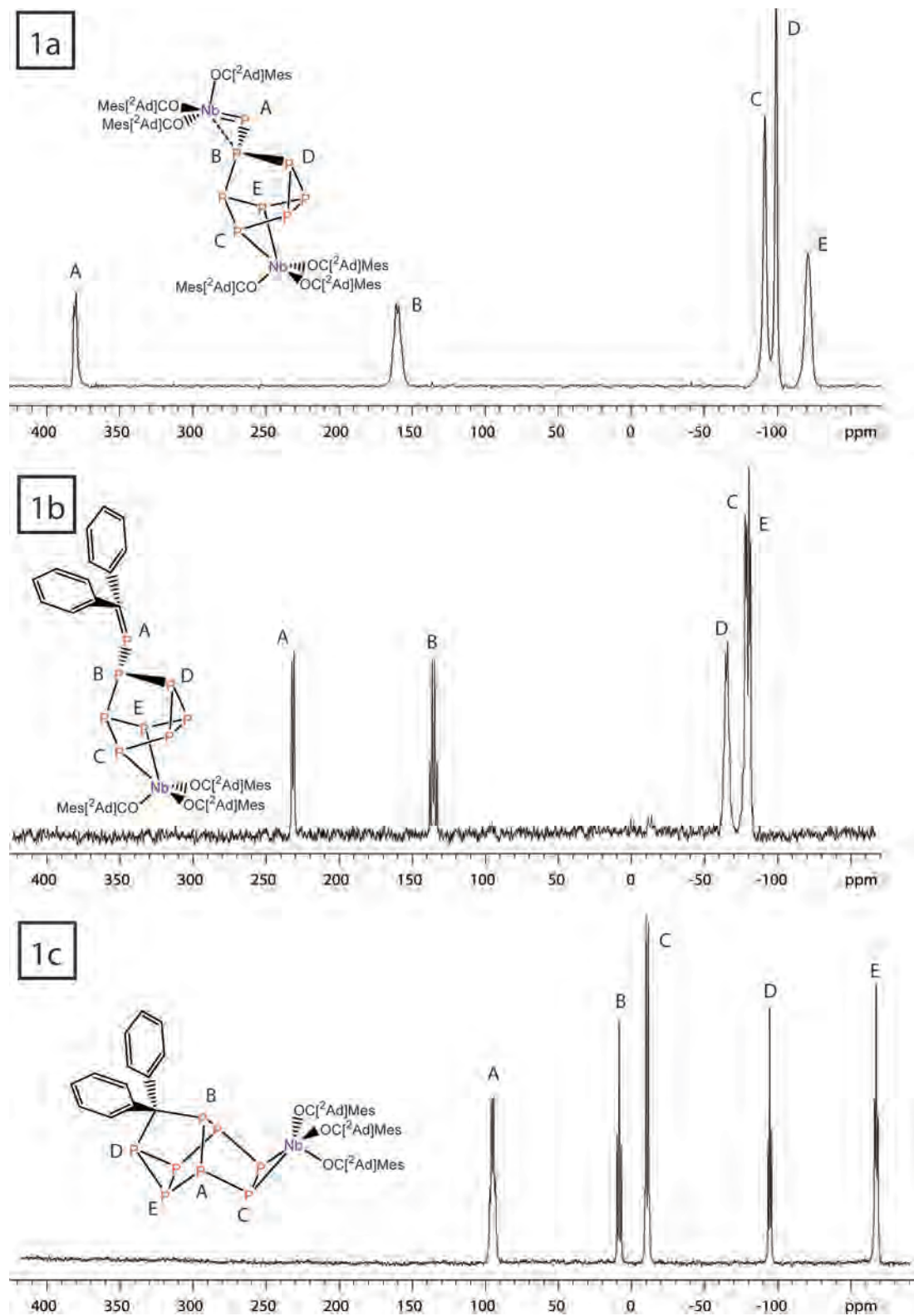
Figure 1. ^{31}P NMR spectrum shown with 50 Hz line broadening in benzene-d_6 of (a) diniobium octaphosphorus starting material, **1**, (b) phosphaalkene intermediate, **3**-H, and (c) final rearranged CP$_8$ complex, **4**-H.

solution was filtered through celite to remove KCl resulting in an amber colored solution. The filtrate was then dried, slurried once with cold pentane, concentrated and stored at −35 °C to recrystallize. After 16 h, a bright yellow crystalline material had formed. This material was isolated atop a sintered-glass frit and dried to constant mass (1.55 g, 1.51 mmol, 30% yield). X-ray quality crystals were grown from an Et$_2$O solution at −35 °C. ^{1}H NMR (20 °C,

benzene-d_6, 500 MHz): δ =1.43 (4H, broad, Et$_2$O), 1.60−2.19 (39H, multiple overlapping peaks, ^{2}Ad-H), 2.23 (9H, s, *p*-Me), 2.35 (18H, s, *o*-Me), 3.32 (3H, s, allylic H), 3.65 (6H, broad, Et$_2$O), 6.83 (6H, s, Ar−H). Elemental analysis calculated for C$_{64}$H$_{86}$Nb$_1$O$_5$: C 74.83, H 8.34; Found: C 75.04, H 8.34.

Synthesis of Ph$_2$CP$_8$Nb(OC[^{2}Ad]Mes)$_3$ (4-H). (Representative procedure for compounds **4** and **6**). To a 22 °C, bright orange Et$_2$O
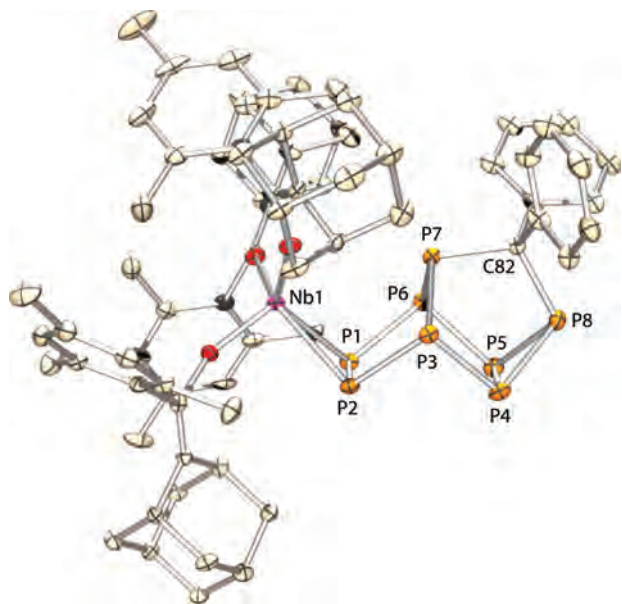
Figure 2. Molecular structure of **4**-H shown with 50% thermal ellipsoids. Hydrogen atoms have been omitted for clarity. Interatomic distances and angles: Nb–P2, 2.5404(8) Å; Nb–P1, 2.5685(8) Å; P1–P2, 2.2007(10) Å; P1–Nb–P2, 51.03(2)°; P7–C82–P8, 111.45(14)°.

solution (15 mL) of $(P_8)[Nb(OC[^2Ad]Mes)_3]_2$ (600 mg, 0.28 mmol) was added an Et_2O solution (5 mL) of benzophenone (52 mg, 0.28 mmol, 1 equiv) with stirring. Over the course of 1 h there was a brightening of the solution to a more vibrant red-orange color. This solution was allowed to stir for an additional 6 h during which time the solution darkened to yellow-brown. After this time the solvent was removed in vacuo and the residue was slurried in pentane (2 mL) and diethyl ether (10 mL) and placed in the glovebox freezer at −35 °C. After 10 h a copious tan colored precipitate formed. This material was collected by filtration on a glass frit and was washed with cold pentane (15 mL). The tan powder was then dried to constant mass (290 mg, 0.21 mmol, 76% yield). ^{31}P NMR (20 °C, benzene-d_6, 202.5 MHz): δ 94.75 (m, 2P), 7.81 (t, J = 297 Hz, 1P), −11.75 (apparent d, J = 316 Hz, 2P), −93.00 (t, J = 228 Hz, 1P), −167.95 (t, J = 238 Hz, 2P). ^1H NMR (20 °C, benzene-d_6, 500 MHz): δ 1.59−1.94 (multiple overlapping peaks, 36H, ^2Ad-H), 2.02 (s, 3H, allylic H), 2.18 (s, 9H, p-Me), 2.34 (s, 18H, o-Me), 3.48 (s, 3H, allylic H), 6.78 (s, 6H, aryl H enolate), 6.91 (t, 2H, J = 7 Hz, Ar–H CPh$_2$), 6.99 (t, 4H, J = 7 Hz, Ar–H CPh$_2$), 7.56 (d, 4H, J = 7 Hz, Ar–H CPh$_2$). ^{13}C NMR (20 °C, benzene-d_6, 125.8 MHz): δ 20.68 (CH$_3$), 21.29 (CH$_3$), 28.82 (CH), 31.00 (CH), 33.35 (CH$_2$), 37.28 (CH$_2$), 39.36 (m, **C**Ph$_2$), 100.18 (O–C=**C**), 127.83 (Ar), 127.52 (Ar), 128.35 (Ar), 129.17 (m, Ar), 129.96 (Ar), 133.52 (Ar), 137.01 (Ar), 137.64 (Ar), 148.83 (O–**C**=C). Elemental analysis calculated for $C_{73}H_{85}NbO_3P_8$: C, 64.89; H, 6.34; P, 18.34. Found: C, 64.68; H, 6.15; P, 18.48.

4-Me. The reaction mixture, prepared as described above, was stirred for 16 h prior to workup. The phosphorus containing material was separated from the niobium oxo by precipitation from 1:2 C_5H_{12}/Et_2O at −35 °C at an isolated yield of 68%. ^{31}P NMR (20 °C, benzene-d_6, 202.5 MHz): δ 94.82 (m, 2P), 7.23 (t, J = 293 Hz, 1P), −10.80 (apparent d, J = 318 Hz, 2P), −94.26 (t, J = 228 Hz, 1P), −167.92 (t, J = 228 Hz, 2P). ^1H NMR (20 °C, benzene-d_6, 500 MHz): δ 1.58−1.95 (multiple overlapping peaks, 39H), 2.03 (s, 6H), 2.18 (s, 9H), 2.36 (s, 18H), 3.50 (s, 3H), 6.79 (s, 6H),

6.79 (s, 6H), 6.89 (d, J = 8 Hz, 4H), 7.53 (d, J = 8 Hz, 4H). Elemental analysis calculated for $C_{74}H_{89}NbO_3P_8$: C, 65.29; H, 6.51; P, 17.98. Found: C, 64.96; H, 6.57; P, 18.11.

4-Cl. The reaction mixture, prepared as described above, was stirred for 5 h prior to workup. The phosphorus containing material was separated from the niobium oxo by precipitation from 1:2 C_5H_{12}/Et_2O at −35 °C at an isolated yield of 70%. ^{31}P NMR (20 °C, benzene-d_6, 202.5 MHz): δ 95.70 (m, 2P), 10.41 (t, J = 296 Hz, 1P), −13.62 (apparent d, J = 311 Hz, 2P), −90.46 (t, J = 221 Hz, 1P), −165.10 (t, J = 202 Hz, 2P). ^1H NMR (20 °C, benzene-d_6, 500 MHz): δ 1.53−2.05 (multiple overlapping peaks, 39H), 2.18 (s, 9H), 2.31 (s, 18H), 3.43 (s, 3H), 6.77 (s, 6H), 7.02 (d, J = 8.5 Hz, 4H), 7.29 (d, J = 8.5 Hz, 4H).

4-OMe. The reaction mixture, prepared as described above, was stirred for 12 h prior to workup. The phosphorus containing material was separated from the niobium oxo by precipitation from 1:2 C_5H_{12}/Et_2O at −35 °C at an isolated yield of 73%. ^{31}P NMR (20 °C, benzene-d_6, 202.5 MHz): δ 94.28 (m, 2P), 7.85 (t, J = 297 Hz, 1P), −11.20 (apparent d, J = 318 Hz, 2P), −94.84 (t, J = 229 Hz, 1P), −167.53 (t, J = 234 Hz, 2P). ^1H NMR (20 °C, benzene-d_6, 500 MHz): δ 1.50−2.05 (multiple overlapping peaks, 39H), 2.18 (s, 9H), 2.35 (s, 18H), 3.27 (s, 6H), 3.49 (s, 3H), 6.64 (d, J = 8.5 Hz, 4H), 6.79 (s, 6H), 7.53 (d, J = 8.5 Hz, 4H).

4-NMe₂. The reaction mixture, prepared as described above, was stirred for 16 h prior to workup. The phosphorus containing material was separated from the niobium oxo by precipitation from 1:2 C_5H_{12}/Et_2O at −35 °C at an isolated yield of 42%. ^{31}P NMR (20 °C, benzene-d_6, 202.5 MHz): δ 93.08 (m, 2P), 4.66 (t, J = 296 Hz, 1P), −9.39 (apparent d, J = 320 Hz, 2P), −99.96 (t, J = 230 Hz, 1P), −168.24 (t, J = 226 Hz, 2P). ^1H NMR (20 °C, benzene-d_6, 500 MHz): δ 1.60−2.00 (multiple overlapping peaks, 36H), 2.05 (s, 3H), 2.19 (s, 9H), 2.39 (s, 18H), 2.48 (s, 12H), 3.55 (s, 3H), 6.42 (d, J = 8.8 Hz, 4H), 6.80 (s, 6H), 7.57 (d, J = 8.5 Hz, 4H).

4-CF₃. The reaction mixture, prepared as described above, was stirred for 3.5 h prior to workup. The phosphorus containing material was separated from the niobium oxo by precipitation from 1:2 $O(SiMe_3)_2/Et_2O$ at −35 °C at an isolated yield of 43%. The appreciable solubility of this species in hydrocarbon solvents prevents isolation of more material free of niobium oxo. ^{31}P NMR (20 °C, benzene-d_6, 202.5 MHz): δ 95.05 (m, 2P), 13.15 (t, J = 303 Hz, 1P), −14.52 (apparent d, J = 323 Hz, 2P), −88.14 (t, J = 227 Hz, 1P), −166.33 (t, J = 246 Hz, 2P). ^1H NMR (20 °C, benzene-d_6, 500 MHz): δ 1.50−2.05 (multiple overlapping peaks, 39H), 2.16 (s, 9H), 2.30 (s, 18H), 3.41 (s, 3H), 6.76 (s, 6H), 7.27 (d, J = 8.4 Hz, 4H), 7.40 (d, J = 8.5 Hz, 4H). ^{19}F NMR (20 °C, benzene-d_6, 282.4 MHz): δ −62.7 (s, 6F).

6-iPr. The reaction mixture, prepared as described above, was stirred for 3 d prior to workup. The phosphorus containing material was separated from the niobium oxo by precipitation from 1:2 $O(SiMe_3)_2/Et_2O$ at −35 °C at an isolated yield of 43%. The appreciable solubility of this species in hydrocarbon solvents prevents isolation of more material free of niobium oxo. To effect a more rapid conversion to the phosphaalkene, 20 equiv of diisopropyl ketone may be used and the reaction mixture may be worked up after 5 h of stirring at 22 °C. Precipitation as described above results in 58% isolated yield of the bright orange phosphaalkene when the reaction is effected in this manner. ^{31}P NMR (20 °C, benzene-d_6, 202.5 MHz): δ 199.7 (d, J = 237 Hz, 1P), 114.98 (q, J = 266 Hz, 1P), −68.40 (m, 2P), −81.50 (m, 4P). ^1H

Scheme 2
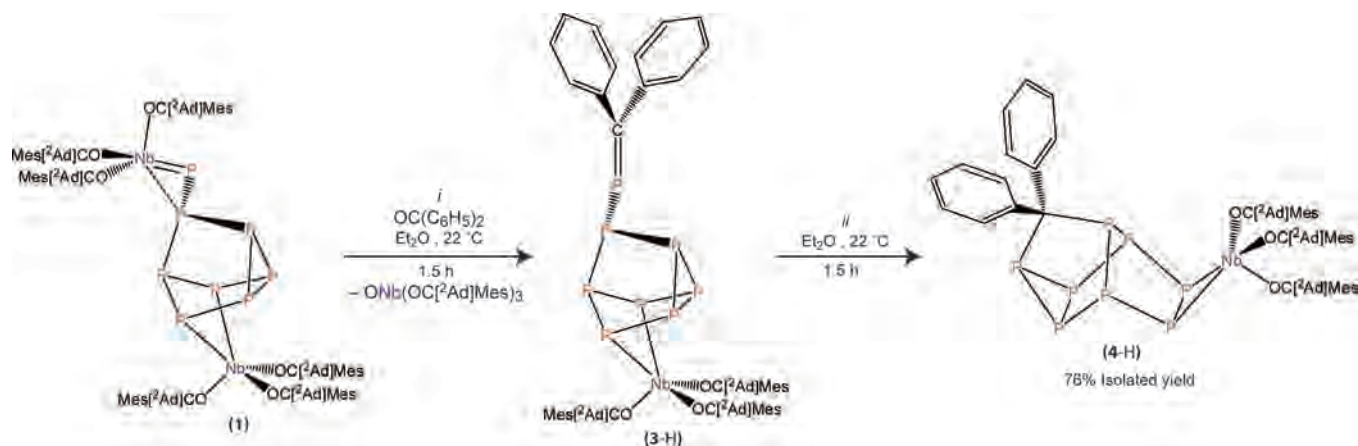
Table 1. First-Order Rate Constants for Rearrangement of **3**-H to **4**-H at Four Temperatures

temperature (°C)	average k (s⁻¹)
10	2.6(4) × 10⁻⁵
25	1.2(4) × 10⁻⁴
40	5.1(4) × 10⁻⁴
55	1.7(5) × 10⁻³

NMR (20 °C, benzene-d_6, 500 MHz): δ 0.89 (m, 12H), 1.48−2.14 (multiple overlapping peaks, 42H), 2.22 (s, 9H), 2.47 (s, 18H), 3.43 (s, 3H), 6.87 (s, 6H).

6-Cy. The reaction mixture was prepared using 20 equiv of dicyclohexyl ketone and was stirred for a total reaction time of 5 h. The phosphorus containing material was separated from the niobium oxo by precipitation from 1:2 O(SiMe₃)₂/Et₂O at −35 °C in 62% yield. ³¹P NMR (20 °C, benzene-d_6, 202.5 MHz): δ 201.70 (d, J = 260 Hz, 1P), 115.44 (q, J = 260 Hz, 1P), −67.50 (m, 2P), −82.80 (m, 4P). ¹H NMR (20 °C, benzene-d_6, 500 MHz): δ 0.77−2.15 (multiple overlapping peaks, 53H, *i*Pr and ad-H), 2.20 (s, 9H, *p*-Me), 2.47 (s, 18H, *o*-Me), 3.44 (s, 3H, allylic H), 6.88 (s, 6H, ar-H). ¹³C NMR (20 °C, benzene-d_6, 125.8 MHz): δ 231.0 (d, J_{CP} = 69 Hz). Elemental analysis calculated for C₇₃H₉₅NbO₃P₈: C, 64.39; H, 7.04; P, 18.21. Found: C, 64.92; H, 7.05; P, 18.42.

Kinetic Studies. A solution (2 mL) of (P₈)[Nb(OC[²Ad]Mes)₃]₂ (100 mg, 0. 047 mmol, 1 equiv) in C₆D₆ was added to solid benzophenone (10 mg, 0.056 mmol, 1.2 equiv). This solution was stirred for 30 s and placed in a sealable NMR tube equipped with a capillary containing PPh₃ in C₆D₆ as reference and was then chilled for transport to an NMR probe preset to the appropriate temperature as measured by a methanol or ethylene glycol NMR thermometer. ³¹P NMR spectra were collected every 300 s for 3−14 h depending on temperature on a Bruker Avance 400 spectrometer (162 MHz ³¹P). The integrals of the phosphaalkene resonances were monitored following complete consumption of the starting [Nb(OC[²Ad]Mes)₃]₂(P₈). The integrals of the phosphaalkene molecule as a function of time, corrected versus the PPh₃ standard, were fit to the first-order rate equation $I(t) = Ae^{-kt} + b$ using the automated curve fitting routine of Microcal OriginLab's *Origin 6.0*.[32]

X-ray Diffraction Studies. Diffraction-quality crystals of **4**-H were grown from toluene by slowly cooling from 70 to −10 °C over the course of several days. Diffraction-quality crystals of **2** were grown from Et₂O by cooling at −35 °C over the course of 2 days. The crystals were mounted in hydrocarbon oil on a nylon loop. Low-temperature (100 K) data were collected on a Siemens Platform three-circle diffractometer coupled to a Bruker-AXS Smart Apex CCD detector with graphite-monochromated Mo Kα radiation

(λ = 0.71073 Å) performing φ and ω scans. A semiempirical absorption correction was applied to the diffraction data using SADABS.[33] The structures were solved by direct methods using SHELXS[34] and refined against F^2 on all data by full-matrix least-squares with SHELXL-97.[35] All non-H atoms were refined aniso-tropically. All H atoms were included in the models at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all H atoms were fixed to 1.2 times the U value of the atoms they are linked to (1.5 times for methyl groups). There were no disorders or solvent molecules present in the structure of **4**-H; however, there were two disordered Et₂O molecules present in the structure of **2**. The disorders were refined within SHELXL with the help of rigid bond restraints as well as similarity restraints on the anisotropic displacement parameters for neighboring atoms and on 1,2- and 1,3-distances throughout the disordered components. The relative occupancies of disordered components were refined freely within SHELXL. Further details are available in the Supporting Information (Table S1 and a CIF file) and from the Cambridge Crystallographic Data Centre (CCDC) under deposition numbers 676572 and 676573.

Computational Studies. All calculations were carried out using ADF 2004.01 from Scientific Computing and Modeling (http://www.scm.com)[36,37] on an eight-processor Quantum Cube worksta-tion from Parallel Quantum Solutions (http://www.pqs-chem.com). In all cases, the LDA functional employed was that of Vosko, Wilk, and Nusair (VWM),[38] while the GGA part was handled using the functionals of Becke and Perdew (BP86).[39−41] In addition, all calculations were carried out using the zero-order regular ap-proximation (ZORA) for relativistic effects.[42−44] In all cases, the basis sets were triple-ζ with two polarization functions (TZ2P) as

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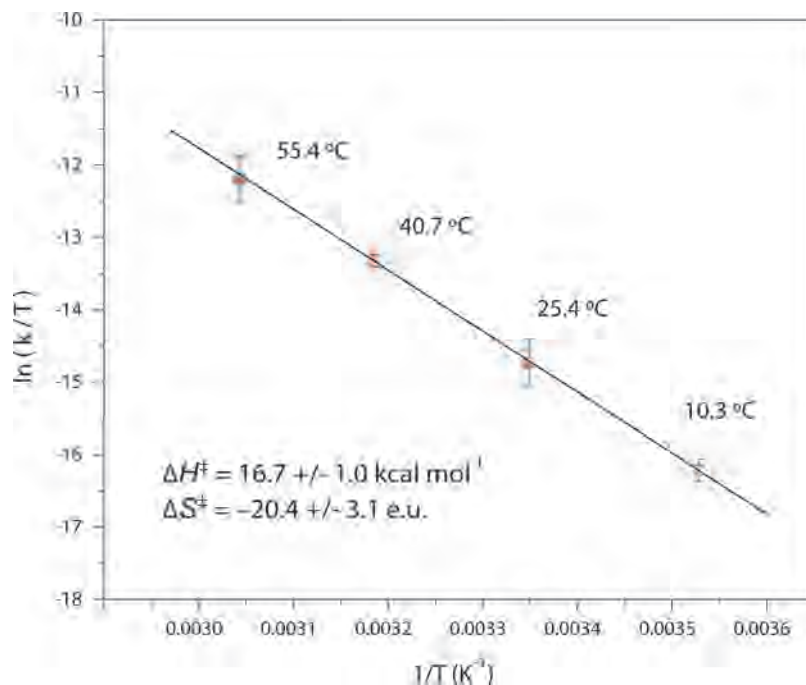(39) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098–3100.
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Figure 3. Eyring plot for rearrangement of **3**-H to **4**-H with error bars at a 95% confidence level.

Table 2. First-Order Decay Rate Constants for Rearrangement of **3**-R to **4**-R at 25 °C[a]

phosphaalkene	average k (s^{-1})
4-CF$_3$	4.0(1) × 10^{-4}
4-Cl	2.2(2) × 10^{-4}
4-CH$_3$	1.1(1) × 10^{-4}
4-OMe	8.7(4) × 10^{-5}
4-NMe$_2$	2.6(2) × 10^{-5}

[a] For **3**-H to **4**-H, see Table 1.

supplied with ADF. Chemical shielding tensors were calculated for the ^{31}P nuclei in the optimized structures by the GIAO method using the ADF package.[45−48] The functionals, basis sets, and relativistic approximations used were the same as those described above. The isotropic value of the chemical shielding was converted to a chemical shift downfield of 85% phosphoric acid using the series of compounds PMo(N[^{t}Bu]Ar)$_3$ (Ar = 3,5-dimethylphenyl), (OP)-Mo(N[^{t}Bu]Ar)$_3$, and (SP)Mo(N[^{t}Bu]Ar)$_3$ as a computational reference; their computed absolute shielding values were correlated with a chemical shift equal to their experimental value in dilute benzene solution.[49]

Results and Discussion

Synthetic entry into organophosphorus chemistry is provided by the diniobium octaphosphorus complex (P$_8$) [Nb(OC[^{2}Ad]Mes)$_3$]$_2$ (**1**). It is known that metal phosphinidenes (M=PR) may react with aldehydes to yield the corresponding metal oxo complex and phosphaalkenes.[50] This transformation is analogous to the olefination of carbonyl compounds by tantalum alkylidene complexes, a reaction thought to proceed via four-membered metal-

lacyclic intermediates.[51] The presence of a metal phosphinidene in **1** led us to investigate its reactivity with organic carbonyl compounds. Upon treating a stirring solution of complex **1** in diethyl ether with benzophenone, the orange color of the solution gradually increased in intensity over the course of 1.5 h at 22 °C. Probing the reaction mixture by ^{31}P NMR spectroscopy revealed the complete consumption of **1** with the formation of a new product having four resonances at 231.1, 136.0, −64.0, and −79.8 (2 overlapping peaks) ppm (Figure 1b). The resonance at 231.1 ppm provided evidence that a phosphaalkene moiety was formed during the reaction as phosphaalkenes have characteristic low field ^{31}P and ^{13}C NMR resonances.[20,52,53] The phosphaalkene carbon resonates at 230 ppm in the ^{13}C NMR spectrum and has a characteristic one-bond, carbon−phosphorus J-coupling ($^1J_{CP}$ = 70 Hz).[20,52]

However, the phosphaalkene complex Ph$_2$C=PP$_7$Nb(OC-[^{2}Ad]Mes)$_3$ (**3**-H) is not the final product of the reaction. Over the course of 6 h, **3**-H converts to a new species with a unique set of resonances in the ^{31}P NMR spectrum (Figure 1c). This observation is consistent with the well-established propensity of phosphaalkenes to undergo rearrangement or oligomerization reactions when not sterically protected.[20,52] The ^{1}H NMR spectrum of the final reaction mixture revealed two enolate environments corresponding to ONb(OC[^{2}Ad]-Mes)$_3$(OEt$_2$) (**2**, the identity of which was confirmed through independent synthesis and X-ray structure determination; see Supporting Information), and one new species.[21] The new species selectively precipitated from a Et$_2$O/C$_5$H$_{12}$ solution over 10 h at −35 °C, in 76% yield. The resulting tan colored precipitate was isolated and ^{31}P NMR spectroscopic analysis

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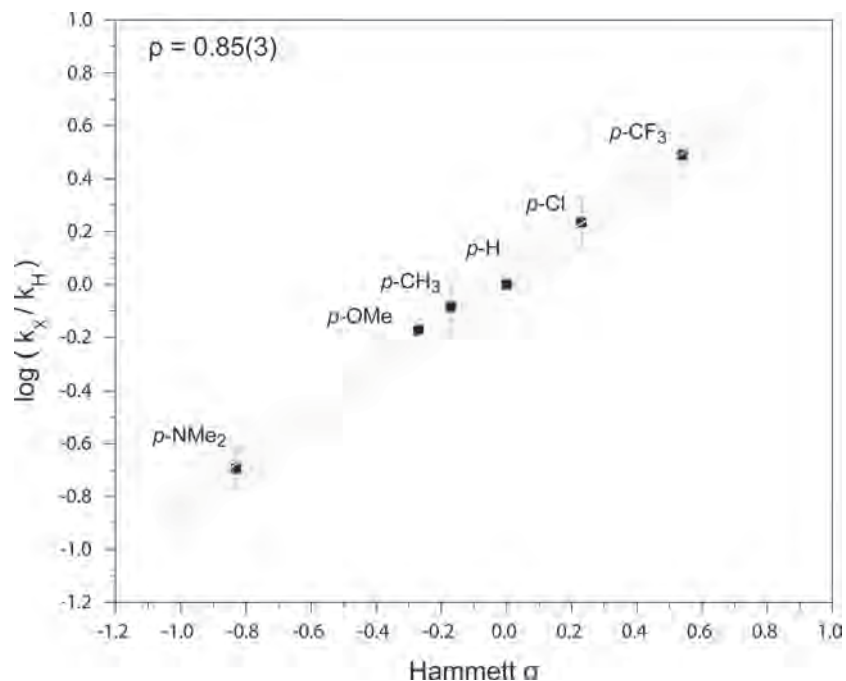(47) Wolff, S. K.; Ziegler, T. *J. Chem. Phys.* **1998**, *109*, 895–905.
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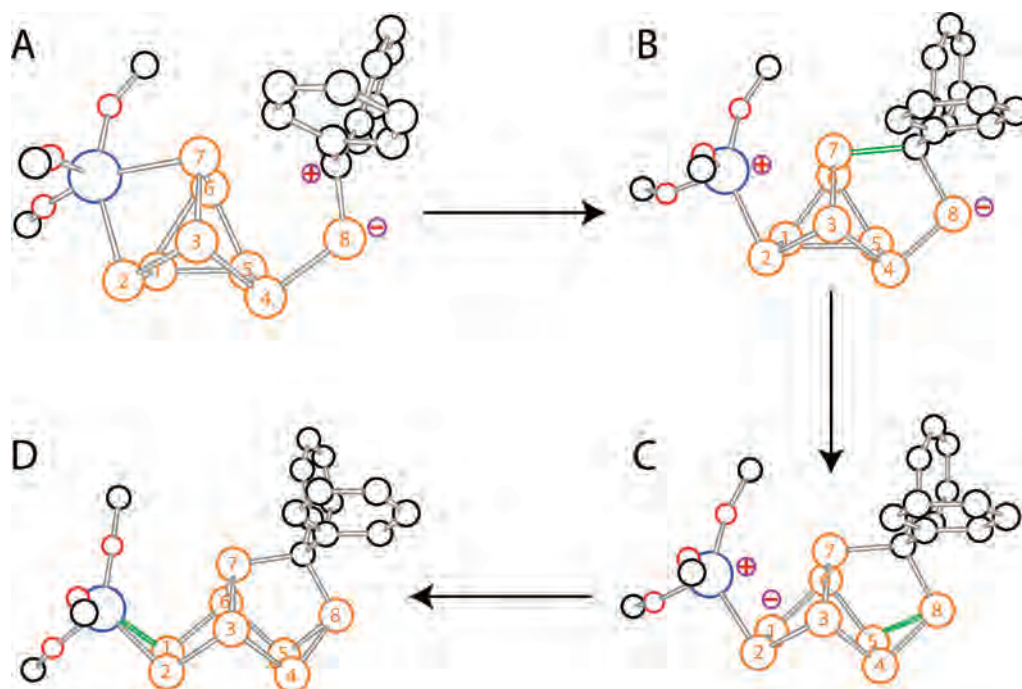(51) Schrock, R. R. *J. Am. Chem. Soc.* **1976**, *98*, 5399–5400.

Figure 4. Hammett analysis of rearrangement of **3**-R to **4**-R with error bars at a 95% confidence level.

Scheme 3. Snapshots along a Proposed Reaction Coordinate for 3-H → 4-H[a]

[a] Starting structure A is obtained by rotating about the C=P linkage to prepare the phosphaalkene for interaction with the P₇ cluster. Explicitly shown positive and negative charges in structures A−C are meant merely as a guide to the electron flow in the course of the addition reaction.

revealed it to be the phosphorus-containing product, $Ph_2CP_8Nb(OC[^2Ad]Mes)_3$ (**4**-H). Coproduct **2** may be isolated from the filtrate by crystallizing from Et_2O in 65% yield and can be recycled back to the starting material $I_2Nb(OC[^2Ad]Mes)_3$ in 72% yield by treatment with 1 equiv of trifluoroacetic anhydride and subsequent treatment with 2 equiv of $ISiMe_3$.[21]

The structure of **4**-H was elucidated through crystallographic studies, which revealed an unusual CP_8 cluster that incorporates the benzophenone-derived CPh_2 moiety into the cluster framework (Figure 2). Recently, Bertrand and co-workers described activation of white phosphorus by cyclic (alkyl)aminocarbenes to generate phosphorus chains and clusters with carbene substituents.[10,54] The synthesis of **4**-H is unique in that the organic carbene moiety is incorporated directly into the cluster framework in a post-P_4-activation

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step. As a result, the organic fragment can be varied through ketone selection, giving rise to a large number of possible product clusters.

In **4**-H, the Nb(OC[^{2}Ad]Mes)$_3$ unit binds to P1 and P2 at distances of 2.5404(8) and 2.5685(8) Å, respectively, with a P1—Nb—P2 angle of 51.03(2)°. The complex adopts the *exo* configuration relative to the P7 bridge, structurally hinting at a least-motion mechanism for the formation of the rearranged cluster (vide infra). The niobium—phosphorus interaction may be regarded as side-on coordination of a diphosphene (RP=PR) to a strongly π-donating d^2 niobium center, a viewpoint that may be fruitful when considering potential reactivity studies involving this complex.[7,55–61] This interpretation also highlights the formal exchange of the C—P π bond in **3**-H for a *complexed* P—P π bond in **4**-H.[62] The driving force for the **3**-H → **4**-H rearrangement can be traced tentatively to this extinguishing of P-unsaturation. All of the P—P distances in the new cluster are consistent with P—P single bonds and range between 2.180(1) Å and 2.229(1) Å. The P—C distances of 1.923(3) and 1.887(3) Å are as expected for P—C single bonds, and the P—C—P angle is near-tetrahedral at 111.45(14)°.

The chemistry of polycyclic phosphanes and their substituted derivatives is a relatively well-established field that came into its own with the pioneering work of Baudler.[29,63] Phosphorus cluster chemistry is rich with examples of P$_9$ clusters with a core identical to that of **4**-H except with a ninth phosphorus atom in place of C82 (Figure 2), but inclusion of heteroatoms (such as carbon!) into such cages is, to our knowledge, a new motif. The addition of the phosphaalkene P=C unit to the P7 core leads to the formation of a previously unknown CP$_8$ cluster (reaction ii, Scheme 2), and understanding the mechanism of such an addition reaction will aid in the design of similar transformations.

The reaction that generates **4**-H from **3**-H was found to follow a strict first-order kinetic profile, consistent with an intramolecular process. The decay of **3**-H was monitored by ^{31}P NMR spectroscopy at 10 °C, 25 °C, 40 °C, and 55 °C. The first-order rate constants obtained over this temperature range vary from 2.6(4) × 10^{-5} s^{-1} to 1.7(5) × 10^{-3} s^{-1} and are summarized in Table 1.

The enthalpy of activation, $\Delta H^{\ddagger}$, and the entropy of activation, $\Delta S^{\ddagger}$, were estimated from an Eyring analysis and were found to be 16.7 ± 1.0 kcal/mol and −20.4 ± 3.1 eu,

respectively (Figure 3).[64] Given that the rearrangement of **3**-H to **4**-H exhibits first-order kinetics, a mechanism involving an electrocyclic rearrangement in which the phosphaalkene P=C unit folds itself into the P$_7$ cluster seems most congruous. The process is not unlike an intramolecular Diels—Alder reaction, in which the diene and dienophile must preorganize prior to a 6e rearrangement. Given this interpretation, it is gratifying that the values for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are in accord with those of intramolecular Diels—Alder reactions.[65]

To further probe the mechanism of rearrangement, a linear free energy relationship was assessed by exploring various di-*para*-substituted benzophenones as substrates for reaction with (P$_8$)[Nb(OC[^{2}Ad]Mes)$_3$]$_2$.[66,67] Such a survey would also determine the tolerance of the system toward different functional groups. In all, six different benzophenone derivatives were investigated: parent benzophenone, 4,4′-dichlorobenzophenone, 4,4′-dimethylbenzophenone, 4,4′-dimethoxybenzophenone, 4,4′-bis(dimethylamino)benzophenone, and 4,4′-bis(trifluoromethyl)benzophenone. The rate of **3**-R to **4**-R rearrangement was measured at 25 °C, and the concentration of **4**-R plotted versus time and fit to an exponential equation of the form Ae^{-kt}. The first-order rate constants, k, so obtained, varied from 2.6(2) × 10^{-5} s^{-1} to 4.0(1) × 10^{-4} s^{-1} and are summarized in Table 2 and as a Hammett plot in Figure 4.

It should be noted that there is double substitution in these molecules, and the actual Hammett effect (given by ρ and generally thought of as additive) will be half of the observed effect since the Hammett constants only account for single substitution.[66] When moving to the more electron releasing substituents in the Hammett series we observe the effects of a divergent process for loss of the phosphaalkenes **3**-CH$_3$, **3**-OMe, and **3**-NMe$_2$. In fact, during the kinetics experiment probing the rearrangement of **3**-NMe$_2$, a new species (**5**-NMe$_2$) was observed. This new species is associated with phosphaalkene decay and is interpreted as an intermediate along an alternate, competing pathway for overall **3**-NMe$_2$ to **4**-NMe$_2$ conversion. (see Supporting Information for more details). This species, **5**-NMe$_2$, was observed to increase in concentration with concomitant consumption of **3**-NMe$_2$ and then to slowly convert to the final product **4**-NMe$_2$. This confounding factor leads to a nonlinear Hammett plot if rates of disappearance of **3**-R are compared (see Supporting Information). However, since the rate for conversion of **5**-R to **4**-R is much slower than the competing, direct **3**-R to **4**-R process, we can easily extract first-order rate information for the direct conversion of **3**-R to **4**-R by plotting the growth of **4**-R only for the reaction time period wherein **5**-R has not yet appreciably begun to decay.

The Hammett analysis of the kinetic data reveals a positive value for ρ, indicating more rapid rearrangement with more electron-withdrawing substituents. A 6e, asynchronous,

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concerted-electrocyclic rearrangement initiated by nucleophilic attack on the phosphaalkene carbon is shown in Scheme 3 and represents a plausible least-motion mechanism for the observed transformation. Density-functional theory (DFT) calculations suggest that such a pathway involves very little molecular motion, except for swinging the P=C moiety into proximity of the P$_7$ cluster, and would be energetically quite feasible.

All of the rate constants discussed above were obtained in C$_6$D$_6$. To address the effect of solvent polarity on the transformation rate, we conducted one set of kinetic measurements in THF (dielectric constant of 7.5[68]) at 25 °C. When **3**-H is allowed to form in THF, a new species is observed in addition to **4**-H, this new species **5**-H being identified with very similar spectral features to those observed with the NMe$_2$ substituted benzophenone (see Supporting Information for more details). Species **5**-H then slowly decays with growth of **4**-H. It is possible to fit the kinetic data obtained in THF to a model of two consecutive first-order reactions; however, this does not rule out a more complicated process. On the basis of the NMR data and DFT calculations, a tricyclooctaphosphane structure with a P$_8$ skeleton analogous to that of bisnoradamantane is proposed for **5**-R (see Supporting Information for more details).

Metathetical generation of phosphaalkene-substituted clusters by treating diniobium octaphosphorus complex **1** with ketones is not limited to the benzophenone class. When using diisopropyl or dicyclohexyl ketone as the Nb=P clipping reagent, the rate of niobium oxo formation is quite slow, taking 3 days at 22 °C to go to completion when carried out with 1 equiv of such a crowded ketone. This process is greatly accelerated to 5 hours by using 20 equiv of ketone in the reaction mixture. Interestingly, the new cluster phosphaalkenes, **6**-*i*Pr and **6**-Cy, are stable for as long as 5 days at 22 °C and for upward of 2 months at −35 °C. The stability of these alkyl-substituted phosphaalkenes may be a result of the electron-donating nature of the alkyl groups, in line with the notion that the first step in the mechanism of rearrangement involves a nucleophilic attack at the phosphaalkene, as discussed above. On the other hand, for these systems the phosphaalkene carbon is also more sterically shielded than is the case for the benzophenone-derived **3**-H system. Phosphaalkenes **6**-*i*Pr and **6**-Cy were isolated from Et$_2$O/(SiMe$_3$)$_2$O in 58% and 62% yield, respectively, as bright-orange powders. The appreciable solubility of both **6**-*i*Pr and **6**-Cy in hydrocarbon solvents has thus far limited the isolated yields of product from these otherwise clean reactions.

Conclusion

This work has developed a new class of niobium bound octaphosphorus clusters that include a single functionalized carbon atom within a saturated CP$_8$ cluster core. The "L$_3$NbP$_8$CR$_2$" molecules can be explained as having arisen via electrocyclic rearrangement from an observable phosphaalkene intermediate generated from the metathesis of ketones with the niobium phosphinidene moiety of **3**. We are presently making use of these monometallated CP$_8$ clusters as starting materials for the synthesis of phosphorus-rich organic molecules by exploiting the reactivity of the niobium-diphosphene interaction (vide supra). It is exciting to contemplate the developments that may arise from such a fusion of metal−ligand multiple bond chemistry with motifs more reminiscent of the field of the Zintl ions!

Supporting Information Available: Full crystallographic details are presented as well as more spectroscopic data and details on the rearrangement of **3**-NMe$_2$ in benzene and **3**-H in THF. This material is available free of charge via the Internet at http://pubs.acs.org.

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