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Methylidyne Transfer Reactions with Niobium

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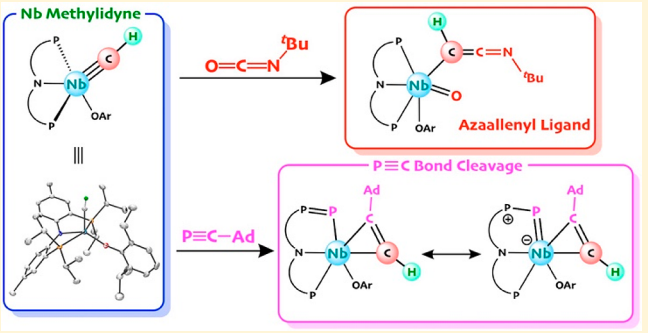
Supporting Information

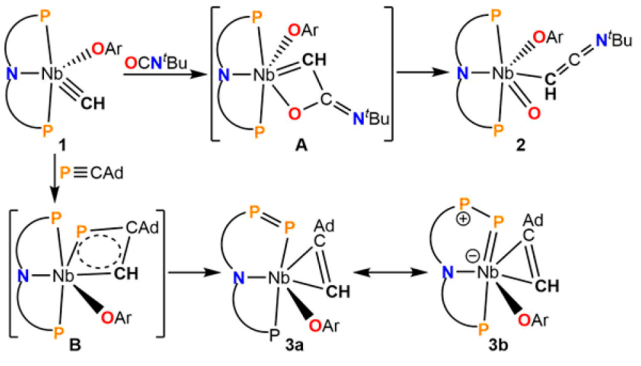
ABSTRACT: The mononuclear niobium methylidyne [(PNP)(ArO)Nb≡CH] (**1**; PNP$^-$ = N[2-P^{i}Pr$_2$-4-methylphenyl]$_2^-$, Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$) reacts with the isocyanate O=C=N^{t}Bu to form a mononuclear niobium oxo species with a rare example of an azaallenyl ligand, namely [(PNP)(ArO)Nb=O(CH=C=N^{t}Bu)] (**2**). When **1** is treated with the phosphaalkyne P≡CAd (Ad = 1-adamantyl), P≡C bond cleavage occurs to form a mononuclear complex where P−P coupling has occurred between the formal phosphaalkyne phosphorus atom and one phosphine arm from the PNP ligand, namely [(PNPP)(ArO)Nb(η^2-AdCCH)] (**3**). Solid-state structural studies and isotopic labeling experiments confirm C−C bond formation of the methylidyne group as well as provide conclusive evidence for the oxo ligand in **2** being terminal and the fate of the phosphorus atom from P≡CAd in complex **3**. Computational studies have been applied to understand the pathway involving the P−P bond forming reaction of **1** and P≡CAd.



High-valent (d^0) transition-metal methylidyne complexes are extremely rare and are generally confined to the heavier group 6 metals, such as ([N$_3$N]W≡CH) (N$_3$N^{3-} = [RNCH$_2$CH$_2$]$_3$N^{3-}, R = Me$_3$Si, Me$_2$PhSi, MePh$_2$Si, C$_6$F$_5$),[1] ([Me$_3$SiNCH$_2$CH$_2$]$_3$N)Mo≡CH,[2] [L$_n$W≡CH(H)(Cl)(X)] (L$_n$ = 2 (H$_3$C)$_2$PCH$_2$CH$_2$P(CH$_3$)$_2$, 4 P(CH$_3$)$_3$; X$^-$ = OTf$^-$, Cl$^-$),[3] (^{t}BuO)$_3$W≡CH(quinuclidine),[4] [(^{t}Bu$_3$SiO)$_3$W≡CH],[5] and [(Ar′^{t}BuN)$_3$Mo≡CH] (Ar′ = 3,5-Me$_2$C$_6$H$_3$).[6,7] As a result, the chemistry of the nucleophilic methylidyne moiety is largely unexplored despite its critical role as a precursor to metal carbides[6,7] and also in alkyne cross-metathesis reactions.[8] We recently reported the synthesis and characterization of the first mononuclear group 5 methylidyne complex [(PNP)(ArO)Nb≡CH] (**1**; PNP$^-$ = N[2-P^{i}Pr$_2$-4-methylphenyl]$_2^-$, Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$)[9] and now wish to showcase some preliminary reactivity involving methylidyne transfer with polar and unsaturated substrates such as O=C=N^{t}Bu and P≡CAd (Ad = 1-adamantyl). Herein we report metathesis reactions involving CH for O or P transfer and include isotopic labeling studies in addition to structural information for the products derived from these reactions. Theoretical studies have been applied to help us understand how **1** cleaves the P≡C bond in P≡CAd to ultimately form a P−P bond with the involvement of one arm of the PNP ligand.

Inspired by some of the metathesis reactivity reported by the Schrock and Veige groups involving the neopentylidyne complexes [^{t}BuC≡W(DME)Cl$_3$] (DME = 1,2-dimethoxyethane) and [(CF$_3$ONO)W≡C^{t}Bu(THF)$_2$] (CF$_3$ONO^{3-} = (MeC$_6$H$_3$[C-(CF$_3$)$_2$O])$_2$N^{3-}),[10,11] we explored the reactivity of **1** with the more sterically protected isocyanate substrate O=C=N^{t}Bu. Accordingly, treating **1** with 1 equiv of O=C=N^{t}Bu in toluene over 15 min resulted in clean formation of the mononuclear oxo complex [(PNP)(ArO)Nb=O(CH=C=N^{t}Bu)] (**2**), isolated in 65% yield as a reddish orange material (Scheme 1).[12] Performing the reaction with ^{13}C-enriched isotopomer [(PNP)(ArO)Nb≡^{13}CH] (**1**-^{13}C) clearly allowed for in identification of the azaallenyl ligand [^{13}CH=C=N^{t}Bu]$^-$ in **2**-^{13}C as a doublet at 4.6 ppm ($^1J_{CH}$ =

Scheme 1. Proposed Pathways for the Reaction of 1 with O=C=N^{t}Bu and P≡CAd to Form 2 and 3, Respectively[a]



[a]**3a** and **3b** characterize the two most likely resonances of **3**. The pincer ligand N[2-P^{i}Pr$_2$-4-methylphenyl]$_2^-$ has been simplified with a PNP caricature.

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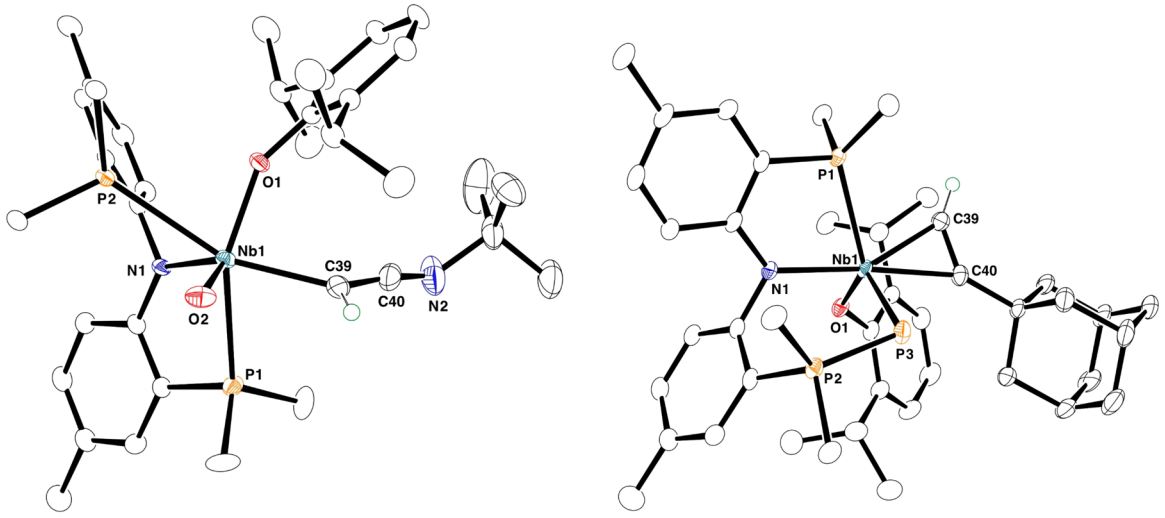

Figure 1. Solid-state structures of complexes **2** (left) and **3** (right) displaying thermal ellipsoids at the 50% probability level. H atoms (with the exception of the formal methylidyne group) and ^{i}Pr methyls on the PNP ligand have been omitted for clarity.

156 Hz) in the ^{1}H NMR spectrum, whereas the enriched ^{13}C{^{1}H} NMR resonance at 87.5 ppm was observed as a broad resonance ($\Delta\nu_{1/2}$ = 680 Hz) possibly due to coupling with the ^{93}Nb quadrupolar nucleus (I = 9/2, 100%).[12] A solid-state X-ray structure unequivocally confirms the presence of the azaallenyl (Nb−C, 2.224(3) Å; C═C, 1.314(4) Å; C═N, 1.235(4) Å) moiety, as well as the formation of a terminal oxo ligand (Nb═O, 1.7308(16) Å), as shown in the left side of Figure 1. The IR spectrum of **2** also shows a strong vibration, ν(C═C═N), at 1964 cm^{-1}; such a feature is consistent with a reported azaallenyl complex.[13] Akin to Veige's CO_2 reaction with a high-valent tungsten alkylidyne,[11] complex **2** is likely formed by a similar pathway involving a [2 + 2]-cycloaddition of the carbonyl group of isocyanate to produce the oxymetallacyclobutene intermediate [(PNP)(ArO)Nb-(CHCN^{t}BuO)] (**A**) followed by a [2 + 2]-retrocycloaddition to form the Nb═O and azaallenyl ligands (Scheme 1). In contrast to Schrock's report involving C−N bond metathesis between [^{t}BuC≡W(DME)Cl$_3$] and O═C═N(cyclohexyl),[10] the more sterically hindered environment around the Nb center (in addition to its oxophilicity) in **1** may result in the discrepancy in regioselectivity.

When **1** is treated with P≡CAd, metathesis also takes place but upon inspection of the final product it becomes clear that one of the phosphine groups of the pincer ligand has been involved in the reaction. Upon addition of P≡CAd to **1**, a gradual color change from green to reddish brown takes place when the mixture is heated at 50 °C over 18 h. Workup of the mixture results in the isolation of red crystals of the alkyne complex [(PNPP)(ArO)Nb(η^2-AdCCH)] (**3**) in 70% yield (Scheme 1).[12] A solid-state structure of a single crystal of **3** offered some surprises (Figure 1, right). Although a side-on terminal alkyne is observed with a high degree of back-bonding (C═C, 1.299(3) Å), the structure revealed insertion of the formal phosphaalkyne phosphorus into one of the phosphorus arms of the supporting PNP ligand (P−P, 2.1433(8) Å). In addition, the Nb−P distance (2.4161(6) Å) is exceptionally short, which in combination with the highly downfield resonance at 332.98 ppm tentatively implies there is metal−ligand multiple-bond character. As a result, we portray complex **3** as having two possible canonical forms with P═P (**3a**) or Nb═P bonding character (**3b**). Complex **3** most likely results from [2 + 2]-cycloaddition of P≡CAd across the Nb≡CH bond to form a phosphametallacyclobutadiene species (**B**) (Scheme 1). Although reductive splitting of the P≡C bond in phosphaalkynes has seldom been reported,[14] cross-metathesis reactions involving metal−carbon multiple bonds and a phosphaalkyne remain even rarer.[15]

Preparing the isotopologue **3**-^{13}C from **1**-^{13}C and P≡CAd allowed for conclusive assignment of the formal methylidyne carbon at 185.4 ppm in the ^{13}C{^{1}H} NMR, this being consistent with such a moiety being terminal alkyne like (inset in Figure 2).[16] The latter feature was further corroborated by

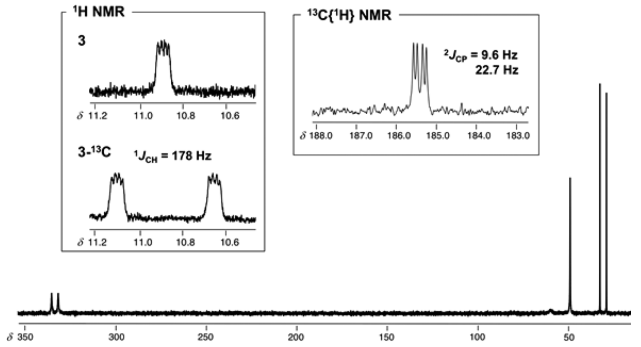

Figure 2. ^{31}P{^{1}H} NMR spectrum of complex **3** with inset showing ^{1}H (**3** and **3**-^{13}C) and ^{13}C{^{1}H} spectra (**3**-^{13}C).

the ^{1}H NMR spectrum, which revealed a multiplet at 10.9 ppm due to both $^{1}J_{CH}$ and $^{3}J_{PH}$ coupling (inset in Figure 2). Perhaps one of the most informative spectroscopic signatures in complex **3** is in the ^{31}P{^{1}H} NMR spectrum, displaying three inequivalent phosphorus environments, two of which can allow for the J_{PP} coupling to be resolved. The most downfield resonance was a broad doublet at 332.0 ppm ($^{1}J_{PP}$ = 570 Hz, $\Delta\nu_{1/2}$ = 97 Hz), followed by a broad resonance at 48.9 ppm ($\Delta\nu_{1/2}$ = 39 Hz), and another doublet at 30.6 ppm with a $^{1}J_{PP}$ value similar to that observed for the highly downfield resonance (Figure 2).

To shed light on the mechanism involving the formation of **3**, especially on how one of the phosphine ligands becomes

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involved during the metathesis reaction, density functional theory (DFT) calculations were performed using a slightly truncated model.[12] The most likely pathway for the reaction of **1** and P≡CAd to form **3** takes place in the singlet spin-state manifold and is illustrated in Figure 3. Other reasonable

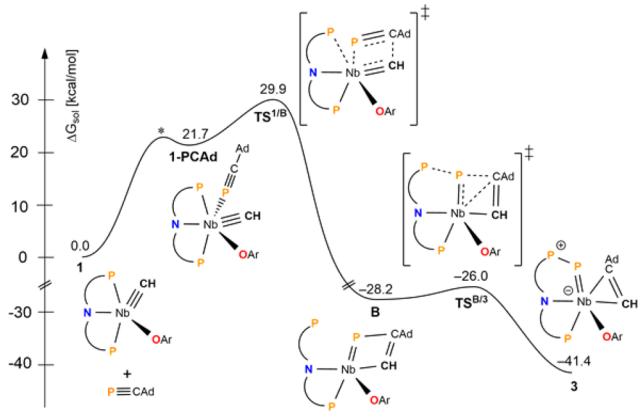

Figure 3. Solution-state free energy profile for the cross-metathesis reaction between **1** and P≡CAd. *The TS leading to **1-PCAd** was not located.

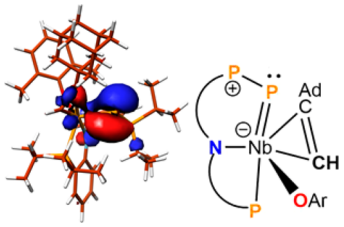

Figure 4. Highest occupied molecular orbital (HOMO) of **3** depicting the Nb−P π-type interaction (left) along with the proposed canonical form most likely dominant in this complex (**3b**, right). The isodensity is ±0.04 au.

pathways in both the singlet (S = 0) and triplet (S = 1) spin states were ruled out due to these being unreasonably high in energy. As Figure 3 shows, at the onset of the reaction P≡CAd binds to the Nb(V) center in an η^1 fashion to produce **1-PCAd** followed by [2 + 2]-cycloaddition traversing transition state $\mathbf{TS}^{1/B}$. The activation barrier for the latter event is 29.9 kcal mol^{-1}. Interestingly, one of the phosphine ligands of PNP ligand demetalates upon formation of phosphametallacyclobutadiene intermediate **B** (Nb−P_{PNP}, ∼3.89 Å) as well as of $\mathbf{TS}^{1/B}$. P−C bond cleavage of the formal phosphaalkyne via a [2 + 2]-retrocycloaddition step occurs concertedly via a low-energy transition state, $\mathbf{TS}^{B/3}$, that is essentially barrierless at 2.1 kcal mol^{-1} relative to **B**. Concurrently during the retrocycloaddition step the free phosphine arm of the PNP ligand approaches the phosphorus atom in the phosphametallacyclobutadiene in $\mathbf{TS}^{B/3}$ (P−P, 2.93 Å), inadvertently weakening the P−C bond (C−P, 2.16 Å). The calculated structure of the final product **3**, which has a solution-phase stability of −41.4 kcal mol^{-1}, reveals bond lengths (Nb−P, 2.42 Å; P−P, 2.18 Å) similar to those found in the crystallographic data (Nb−P, 2.4161 Å; P−P, 2.1433(8) Å). Consistent with our experimental conditions of elevated temperatures, the rate-determining step is [2 + 2]-cycloaddition of the phosphaalkyne across the Nb≡CH ligand. Natural bond orbital (NBO) and molecular orbital analyses clearly indicate a σ and π type (HOMO) bonding interaction taking place at the Nb═P linkage in **3**. On the basis of our calculations we suggest the electronic structure for **3** to be more realistic with resonance structure **3b** depicted in Figure 4, since there is a lone pair at the inserted phosphorus, while Wiberg bond order indices of 1.53 and 1.04 imply Nb═P and P−P bonding, respectively.

In conclusion, we have shown how a mononuclear niobium methylidyne can engage in cross-metathesis reactions with O═C═N^{t}Bu and P≡CAd, resulting in both O═C and P≡C bond cleavage. We are presently investigating the reactivity of complex **3** to achieve a terminal niobium phosphide species and also probing other phosphaalkyne substrates with **1**.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.8b00245.

Experimental details and crystallographic and spectroscopic data (PDF)

Cartesian coordinates for the calculated structures (XYZ)

Accession Codes

CCDC 1835374−1835375 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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