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Communication

A Vanadium Methylidene

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ABSTRACT: Examples of stable 3d transition metal methylidene complexes are extremely rare. Here we report an isolable and stable vanadium methylidene complex, [(PNP)V(=NAr)(=CH_2)] (PNP = N[2-P^{i}Pr$_2$-4-methylphenyl]$^-$, Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$), via H atom transfer (HAT) from [(PNP)V(NHAr)(CH_3)] or [(PNP)V(=NAr)(CH_3)] using two or one equivalents of the TEMPO radical (TEMPO = (2,2,6,6-tetramethylpiperidin-1-yl)oxyl), respectively. Alternatively, the vanadium methylidene moiety can also be formed via the treatment of transient [(PNP)V=NAr] with the Wittig reagent, H_2CPPh_3. Structural and spectroscopic analysis, including ^{13}C enriched labeling of the methylidene ligand, unequivocally confirmed the terminal nature of a rare 3d methylidene complex, featuring a V=CH_2 bond distance of 1.908(2) Å and a highly downfield ^{13}C NMR spectral shift at 298 ppm. In the absence of the ylide, intermediate [(PNP)V=NAr] activates dinitrogen to form an end-on bridging N_2 complex, [(PNP)V(=NAr)]$_2$(μ_2-η^1:η^1-N_2), having a singlet ground state. Complex [(PNP)V(=NAr)(=CH_2)] reacts with H_3COTf to form [(PNP)V(=NAr)(OTf)], accompanied by the release of ethylene as evidenced by ^{1}H NMR spectroscopy, and reactivity studies suggest a β-hydride elimination pathway.

Transition metal alkylidenes are an important class of metal−ligand multiple bonds that play a pivotal role in a wide array of transformations, including olefin metathesis,[1] polymerizations,[2] and Fischer−Tropsch reactions.[3] The majority of these alkylidene complexes are substituted to offer kinetic stabilization to the reactive and polarized M=CR_n linkage.[4] Complexes bearing the simplest of carbenes, a methylidene "CH_2", however, remain considerably scarce, owing to the high reactivity of M=CH_2 unit.[5] This scarcity persists despite the pioneering discovery of the first methylidene complex, [Cp_2Ta=CH_2(CH_3)] by Schrock nearly half a century ago.[6] Coincidently, in 1974, the first Ti methylidene synthon, the Tebbe reagent [Cp_2Ti(μ-CH_2)(μ-Cl)Al(CH_3)$_2$], was also documented[7] and then reported in the literature.[8] Since the first report by Schrock, methylidene complexes have been shown to undergo bimolecular carbon−carbon bond-forming reactions to form ethylene.[9] Moreover, it has been proposed that group 5 metal methylidenes, supported on a silicon oxide surface, can dehydro-couple methane into ethylene and ethane.[10] However, preparing methylidene complexes of the 3d metals poses an even greater challenge since the carbene carbon could have radical character. Notably, among the 3d transition metals, only two systems bearing the parent carbene have been isolated and structurally characterized to date: The complex [(PN)$_2$Ti=CH_2][8] in 2017 by us and, more recently, the [Cp*(dppe)Fe(CH_2)][$BArF_{24}$][11] by Aghazada and Meyer et al. in 2021 (Figure 1). The vanadium methylidene moiety, in particular, has garnered considerable attention due to its proposed role as a critical intermediate in vanadium-catalyzed olefin metathesis reactions, such as ring-closing metathesis (RCM)[12] and cross metathesis (CM).[13] Such transient vanadium methylidene unit, [V=CH_2],[12a] has been postulated to undergo either bimolecular decomposition

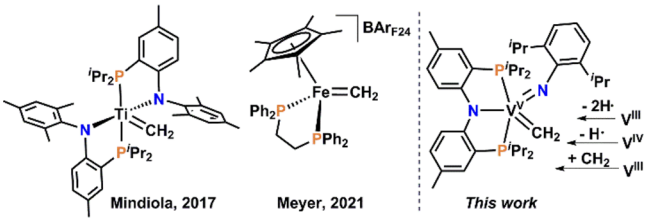

Figure 1. Known first-row transition metal terminal methylidene complexes, along with different routes to yield the mononuclear vanadium methylidene title complex reported in this work.

or [2 + 2] cycloaddition followed by β-hydride elimination, resulting in the deactivation of the initial vanadium alkylidene catalyst.[12,13] Given the dearth of 3d metal methylidenes, little is known about their properties or reactivity. We now report the isolation and characterization of a high-valent [V=CH_2] complex and explore some of its chemistry given the limited information on known 3d metal methylidenes, in particular for a metal ion like vanadium where low-valent and radical states (V^{III}, V^{IV}) are quite common.

Previously, the synthesis of terminal methylidene complexes of the heavier congeners of V, namely Nb and Ta, from their respective high oxidation state Nb^V or Ta^V precursors was reported.[14] This was achieved by utilizing the Wittig reagent, H_2CPPh_3, serving both as the methylene source and as the

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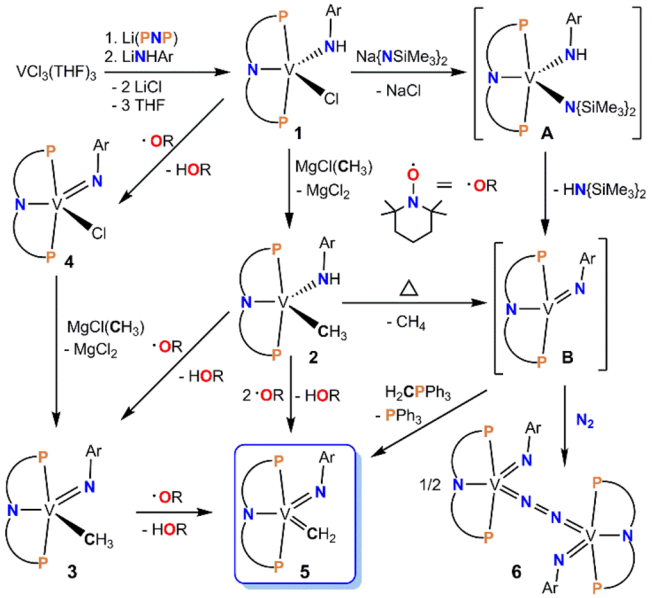
base[14a,b] or through the photolysis of the dimethyl precursors.[14c,15] However, due to vanadium's propensity to populate the low valent +3 oxidation state, our attempts to form a V methylidene directly from V^V precursors were met with challenges. Thus, we had to rely on a synthetic route to a V^V methylidene from a V^{III} precursor using a different approach; namely, by using hydrogen atom transfer (HAT) to convert the CH_3^- ligand to a CH_2^{2-} from either a V^{III} or V^{IV} precursor or by "CH_2" group transfer stemming from a phosphorus ylide using V^{III}. Furthermore, we also show preliminary reactivity of the $V^V{=}CH_2$ moiety.

Using the V^{III} precursor, [(PNP)VCl_2],[16] we sought to install a sterically encumbering robust ancillary ligand to offer more kinetic stabilization and discourage decomposition pathways. Accordingly, transmetalation of [(PNP)VCl_2] with Li(THF)(NHAr)[17] in toluene cleanly produced red crystals of [(PNP)V(NHAr)Cl] (**1**) in 79% crystalline yield (Scheme 1).

Scheme 1. Different Synthetic Routes to a Mononuclear Vanadium Complex Having a Terminal Methylidene and the Formation of 6[a]



[a]The PNP cartoon has been simplified by omitting the phenylene groups bridging the N and P and ^{i}Pr groups on P.

To install a methylidene, we then treated **1** with a Grignard $MgCl(CH_3)$ in toluene at room temperature to cleanly afford [(PNP)V(NHAr)(CH_3)] (**2**) in 80% yield (Scheme 1). Complexes **1** and **2** show typical characteristics for an $S = 1$ system with the ^{1}H NMR spectra featuring broad resonances between 22 and −1 ppm (Figures S1 and S2)[18] and a room temperature Evans method magnetic susceptibility of μ_{eff} = 2.80 and 2.96 μ_B, respectively. Complexes **1** and **2** are structurally isomorphous, based on *sc*-XRD analyses, with a skewed {(PNP)V} fragment due to the nonplanarity of the pincer ligand (Figure 2). The isotropically refined α-NH hydrogen atom in **1** and **2** is oriented at 90° with respect to N2−V1−Cl1, thus implying an α-hydrogen agostic interaction similar to the previously reported Sc-complex, [(PNP)Sc-(NHAr)Cl].[19]

Treatment of complex **2** with 1 equiv of TEMPO radical at room temperature in THF, resulted in the formation of the V^{IV} imido complex, [(PNP)V(=NAr)(CH_3)] (**3**) as red blocks in 58% isolated yield. Complex **3** can also be accessed in similar yields from the addition of TEMPO to **1** in THF to form [(PNP)V(=NAr)(Cl)] (**4**), followed by transmetalation of the latter with $MgCl(CH_3)$ in toluene (Scheme 1).[18] In addition to the broad features in the ^{1}H NMR spectrum, solution magnetic measurements are consistent with d^1 V^{IV} paramagnetic complexes **3** (μ_{eff} = 1.86 μ_B) and **4** (μ_{eff} = 1.92 μ_B). Notably, the room temperature CW X-band EPR spectra of **3** and **4**, observed in the liquid phase (g_{iso} = 1.995 and 1.996 respectively) show hyperfine coupling of the unpaired electron to the ^{51}V nucleus (I = 7/2, 99.75% nat. abundance, A_{iso} = 7.4 mT and 7.8 mT) and superhyperfine coupling to two ^{31}P (I = 1/2, 100% nat. abundance, A_{iso} = 2.7 mT and 2.6 mT) nuclei (Figure 3). A *sc*-XRD analysis (Figure 2) confirmed **3** and **4** to be more in line with a distorted square-pyramidal geometry (**3**: τ_5 = 0.20; **4**: τ_5 = 0.17),[20] with the respective V−N(imido) bond distances of 1.683(2) Å and 1.685(2) Å being essentially identical to each other.[16,21]

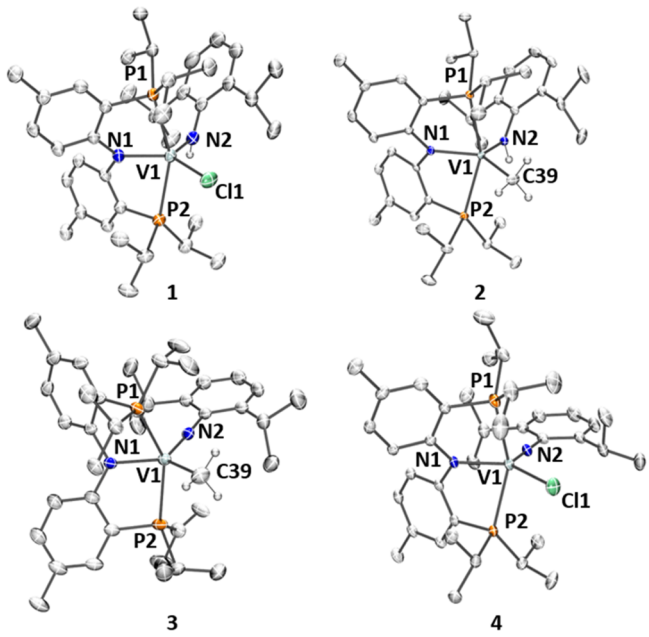


Figure 2. Molecular structures of **1**−**4**. Thermal ellipsoids are at 50% probability. H atoms and cocrystallized solvents, with the exception of α-hydrogens, are omitted for clarity.

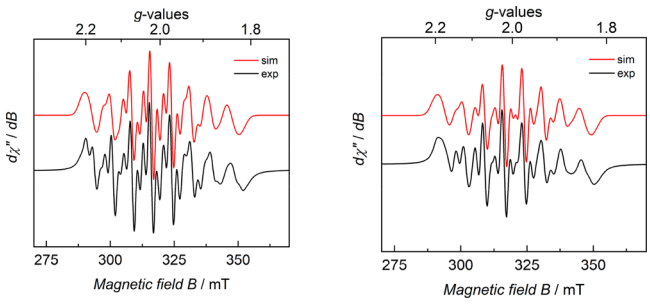


Figure 3. Left: CW X-band EPR spectrum of **3** recorded as a 1 mM solution in benzene at 293 K. Right: CW X-band EPR spectrum of **4** (exp. black trace, simulated red trace) under similar conditions. Experimental conditions: microwave frequency ν = 8.943 GHz, modulation amplitude = 0.5 mT, microwave power = 1.0 mW, modulation frequency = 100 kHz, time constant = 0.1 s.

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With complex **3** in hand, we abstracted a second H atom, but now from the methyl group using TEMPO, in order to form the target vanadium methylidene complex [(PNP)V(=NAr)(=CH_2)] (**5**) in 58% isolated yield. Complex **5** can also be alternatively prepared, in similar yields, using **2** and two equiv of TEMPO, thus circumventing the need to isolate the V^{IV} complex **4** (Scheme 1).[18] Complex **5** shows a broad signal at 52.7 ppm ($\Delta\nu_{1/2}$ = 46 Hz) by $^{31}P\{^1H\}$ NMR spectroscopy and two downfield resonances at 13.8 ($^3J_{HP}$ = 17.7, $^2J_{HH}$ = 6.1 Hz) and 12.6 ($^2J_{HH}$ = 6.6 Hz) ppm in the ^1H NMR spectrum each integrating to one hydrogen. The latter are consistent with the formation of a terminal vanadium methylidene complex having C_1 symmetry in solution. Furthermore, we prepared the isotopologue [(PNP)V(=NAr)(=$^{13}CH_2$)] (**5**-^{13}**C**)[18] and observed a highly downfield and broadened resonance at 298 ppm in the ^{13}C NMR spectrum (Figure S11) in accord with other reported methylidene complexes.[5a,8,14c,15] Notably, the latter downfield signal could be correlated to the methylidene resonances in the ^1H NMR spectrum via a $^1H-^{13}C$ HMQC experiment (Figure 4A), where the downfield

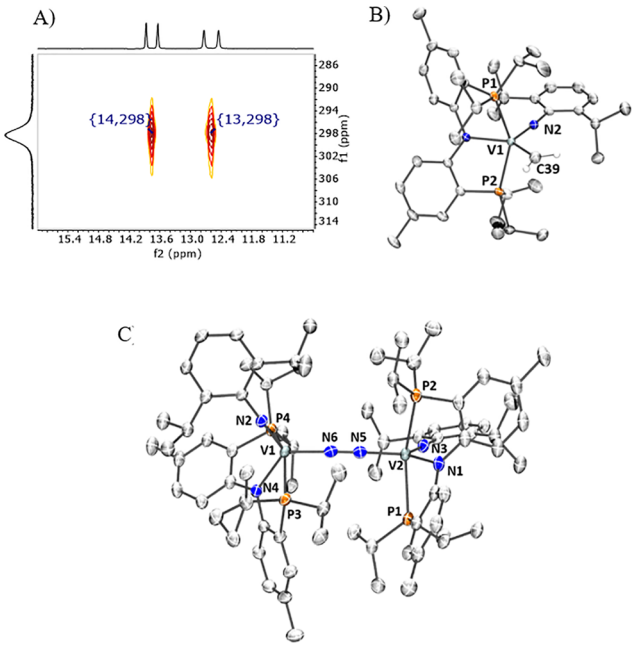

Figure 4. (A) Expanded $^1H-^{13}C$ HMBC spectrum of complex **5**-^{13}**C**. (B) Molecular structure of complex **5**. (C) Structure of complex **6** with 50% thermal ellipsoids. H atoms, and residual solvent, have been omitted for clarity.

methylidene resonances in the ^1H NMR further resolve into multiples ($^1J_{CH}$ = 114 and 139 Hz, Figure S12). The large $^1J_{CH}$ values and relatively minor disparity in their chemical shifts collectively imply the nonagostic nature of the methylidene hydrogens.[15,22] The ^1H NMR spectrum of **5** also featured broad resonances in the upfield region (0.6−3 ppm; Figure S5) that can be attributed to its fluxional behavior. To further explore this phenomenon, variable-temperature (VT) ^1H NMR spectra of **5** were collected between 298 and 248 K in THF-d_8. The stacked spectra show a notable shift in the methylidene resonances (Figure S13) as well as the resolution of broad resonances into distinct chemical shifts in the upfield region.[18] At 248 K, all resonances in **5** can be clearly observed and assigned (Figure S14). A *sc*-XRD study of a single crystal of **5**, grown from a concentrated pentane solution at −35 °C, shows a terminal methylidene group with a V=CH_2 bond distance of 1.908(2) Å and V=NAr bond distance of 1.679(1) Å (Figure 4B). The V=C bond length is significantly shorter in comparison to other PNP ligand-based methylidene complexes: [(PNP)Nb=CH_2(OAr)(OTf)] (1.962(2) Å, Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$), [(PNP)Ta(=CH_2)$_2$] (1.9385(17) Å), and [(PNP)Zr=CH_2(OAr)] (2.038(6) Å). Judging from the methylidene hydrogens, the π-bond is oriented along the P−V−P axis to minimize overlap with the imido and amide π-donors.

We explored the possibility of introducing [V=CH_2] by an independent route; for instance, by carbene transfer[23] using the ylide H_2CPPh_3. Accordingly, treatment of **1** with NaN{$SiMe_3$}$_2$, in the presence of H_2CPPh_3 in toluene for 4 h, revealed the formation of **5** (Scheme 1). Although complex **5** could be recrystallized in 66% yield from Et_2O at −35 °C, samples were marred with traces of PPh_3.[18] We propose this route to involve a V^{III} intermediate [(PNP)V(NHAr)(N{$SiMe_3$}$_2$)] [**A**], which undergoes α-H abstraction to furnish the transient imido [(PNP)V=NAr] [**B**] that is then oxidized by H_2CPPh_3 to form the methylidene ligand in **5** and free PPh_3 (Scheme 1).

To further assess how **5** is formed from CH_2 group transfer, complex **2** was heated under N_2 at 90 °C in C_6D_6 over 16 h, which resulted in the formation of CH_4 along with a new diamagnetic material (Figure S17) that contained broad chemical shifts in the $^{31}P\{^1H\}$ NMR spectrum at 58 ($\Delta\nu_{1/2}$ = 57 Hz) and 54 ($\Delta\nu_{1/2}$ = 50 Hz) ppm. Workup of the reaction mixture, followed by recrystallization from pentane at −35 °C, furnished dark brown needle-shaped crystals in 77% yield. A *sc*-XRD analysis revealed an end-on dinitrogen ligand in [(PNP)V(=NAr)]$_2$(μ_2-η^1:η^1-N_2) (**6**) with a V=NAr distance of 1.716(2) Å and an N−N bond distance of 1.181(2) Å (Figure 4C).[24] This substantiates the formation of intermediate **B** and its subsequent oxidation by H_2CPPh_3 to yield **5**.

Complex **5** reacts with H_3COTf, but does so very slowly, requiring 90 °C to reach completion. Monitoring the reaction by ^1H NMR spectroscopy revealed the formation of a paramagnetic complex along with resonances corresponding to ethylene (Figure S24).[18] Workup of the reaction and recrystallization from pentane at −35 °C formed red blocks of a new paramagnetic complex, [(PNP)V(=NAr)(OTf)] (**7**) in 58% yield (Scheme 2). Complex **7** displays characteristic features typical for a d^1 species (μ_{eff} = 1.91 μ_B), whereas a *sc*-XRD confirms this species to be in a distorted square-pyramidal geometry (τ_5 = 0.34) akin to **3** and **4** (Figure S44). We propose complex **7** to form via an ethyl intermediate [(PNP)V(=NAr)(CH_2CH_3)][OTf] (**C**) which undergoes β-H elimination to form [(PNP)V(H)(=NAr)][OTf] (**D**) and ethylene. Independently, we synthesized [(PNP)V(=NAr)(CH_2CH_3)] (**8**)[18] from **4** and oxidation with [$FeCp_2$][OTf] resulted in the formation of ethylene and **7** (Figure S27), thus corroborating our proposed β-H elimination in **C**.[18] The fate of the hydride in **D** is presently unknown but this likely decomposes to intractable products including PNPH. Since the ethyl moiety in **C** could undergo β-H abstraction to produce [(PNP)V(NHAr)(η^2-C_2H_4)][OTf] (**E**), lose H_2CCH_2, and subsequently α-H eliminate to **D**, we prepared [(PNP)V(NHAr)(OTf)] (**9**) independently from **1**,[18] and found not to convert to **7** (Scheme 2).

In conclusion, we show that a remarkably stable vanadium methylidene complex can now be readily assembled and

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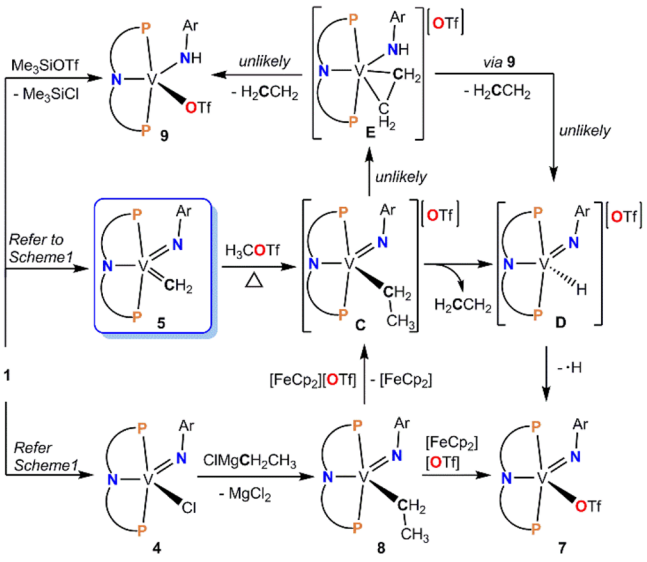
Scheme 2. Reactivity of the Methylidene Ligand in 5, Oxidation of 8 to 7, and Independent Synthesis of 9



structurally authenticated via a direct V^{III} to V^{V} oxidation using H_2CPPh_3 or sequential hydrogen atom abstraction of [(PNP)-V(NHAr)(CH_3)] using the TEMPO radical. We also show how a transient V^{III} imido can be trapped with N_2 and how the reactivity of V=CH_2 with H_3C^+ results in the formation of ethylene. We are currently exploring other transformations involving the V^{V} methylidene ligand in **5** as well as the wealth of redox chemistry offered by transient **B**.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.4c01906.

Synthetic procedures, NMR, IR, UV−vis, EPR, and X-ray crystallographic data (PDF)

Accession Codes

CCDC 2326846−2326848, 2326850−2326854, and 2347921 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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Author Contributions

The manuscript was written through the contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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■ ABBREVIATIONS

PN^- = (N-(2-(diisopropylphosphino)-4-methylphenyl)-2,4,6-trimethylanilide); Ar = 2,6-$^{i}Pr_2C_6H_3$; Cp = cyclopentadienyl; Cp* = pentamethylcyclopentadienyl; dppe = 1,2-bis-(diphenylphosphino)ethane; sc-XRD = single-crystal X-ray diffraction; HAT = hydrogen atom transfer; $^-BArF_{24}$ = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate; TEMPO = (2,2,6,6-tetramethylpiperidin-1-yl)oxyl); ^{i}Pr = *iso*-propyl; ^-OTf = $^-OSO_2CF_3$

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