ORGANOMETALLICS
Article
Cite This: *Organometallics* 2018, 37, 2945−2949
pubs.acs.org/Organometallics

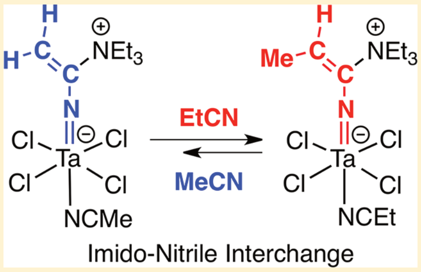
Imido Group Interchange in Reactions of Zwitterionic Tantalum(V) Vinylimido Complexes and Nitriles

Md. Mamdudur Rahman, Mark D. Smith, and Dmitry V. Peryshkov*

Department of Chemistry and Biochemistry, University of South Carolina, 631 Sumter Street, Columbia, South Carolina 29208, United States

Supporting Information

ABSTRACT: We report the imido group exchange transformation upon reactions with nitriles with the formation of a new vinylimido group from the incoming nitrile and a free nitrile from the initial imido group. Preliminary studies suggest the mechanism comprises elimination of triethylamine from the amminium group as the initial step, followed by the deprotonation of the incoming nitrile, followed by the rearrangement of its carbanion into an imido group at the tantalum center. The cationic group on the imido ligand can be replaced with another neutral nucleophile, which was demonstrated by NEt_3 to PPh_3 and NEt_3 to DMAP exchange reactions.



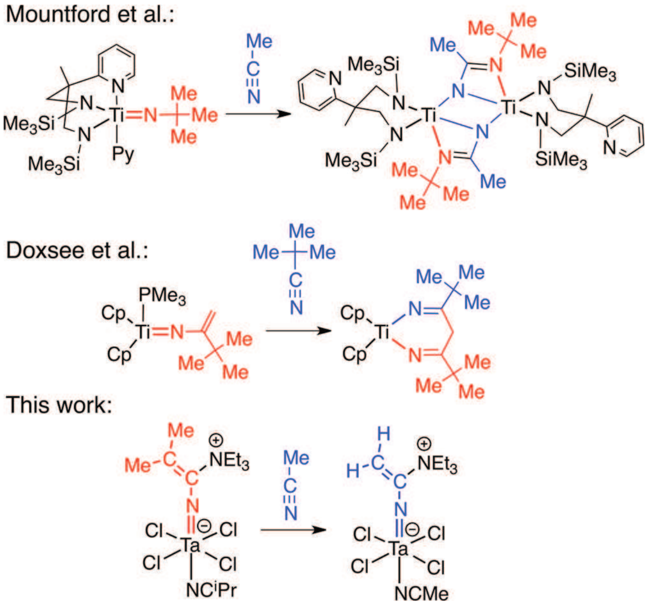
INTRODUCTION

Terminal imido groups have been used as ligands to high-valent early transition metal centers for several decades. In addition to being robust supporting ligands, these imido groups have been shown to participate in a wide range of stoichiometric reactions with unsaturated organic compounds, such as carbon dioxide, isocyanates, alkynes, alkenes, nitroso compounds, azides, and ketones.[1−8] Furthermore, there is a growing number of metathesis-type exchange reactions of high-valent imido complexes with carbodiimides, imines, amines, and, recently, isonitriles, in which the metal-containing product is also an imido complex, which often renders these transformations promising for catalysis.[9−14]

Somewhat surprisingly, imido groups bound to high-valent transition metals are often stable toward nitriles and, in fact, a number of nitrile adducts of metal imido complexes have been characterized.[15−22] At the same time, examples of imido group reactivity with nitriles have also been documented. For instance, Mountford and co-workers reported an addition of acetonitrile to a $Ti{=}N^tBu$ imido group to afford a doubly deprotonated *N-tert*-butylacetamidinate ligand (Scheme 1).[23] Interestingly, this transformation is reversible upon heating. Doxsee and co-workers reported that vinylimido complexes of Ti(IV) coupled through a formally [4 + 2] cycloaddition reaction with pivalonitrile or 1-adamantylnitrile to afford diazatitanacyclohexadienes (Scheme 1).[24]

Recently, we reported a novel activation mode of alkylnitriles coordinated to $TaCl_5$ in the presence of the weakly nucleophilic base, NEt_3.[25] This process resulted in the formation of a series of zwitterionic vinylimido complexes of Ta(V) through the initial deprotonation of the coordinated nitrile, bond rearrangement governed by the electrophilicity of the Ta(V) center, and the subsequent nucleophilic attack on the coordinated azaallene intermediate. These novel vinylimido complexes possess multiple potential reaction centers: the imido functionality, the vinyl group, and the cationic tetraalkylammonium fragment. Furthermore, facile ligand exchange was observed at the coordination site *trans*- to the imido group at the metal center. Herein, we report an unusual reactivity of these imido complexes with alkylnitriles that resulted in the complete imido group interchange under mild conditions (Scheme 1).

Scheme 1. Examples of Reactivity of Imido Complexes of Early Transition Metals with Nitriles[23,24]



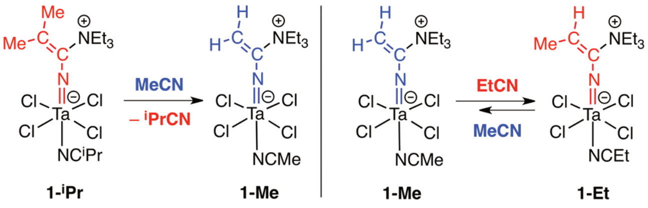
Received: April 18, 2018
Published: September 6, 2018

DOI: 10.1021/acs.organomet.8b00241
Organometallics 2018, 37, 2945−2949

RESULTS AND DISCUSSION

Heating a solution of the imido complex derived from isobutyronitrile [Ta(NCCMe$_2${NEt$_3$})Cl$_4$]($^{\mathrm{i}}$PrCN) (**1-$^{\mathrm{i}}$Pr**[25]) in the presence of excess MeCN at 40 °C in CD$_2$Cl$_2$ for 2 days resulted in the clean conversion to a vinylimido complex derived from acetonitrile [Ta(NCCH$_2${NEt$_3$})Cl$_4$](MeCN) (**1-Me**,[25] Scheme 2; see Figure S-1 in the Supporting Information (SI) for ^{1}H NMR spectra of the reaction mixture). The progress of the reaction can be easily tracked by ^{1}H NMR spectroscopy as characteristic singlets from two inequivalent methyl groups of **1-$^{\mathrm{i}}$Pr** gradually disappear and two doublets from the vinylimido group of **1-Me** grow in intensity (see the Supporting Information for details). No intermediates were observed in the spectra of the reaction mixture. The conversion is quantitative according to ^{1}H NMR data. The net outcome of the reaction is the interchange of the vinylimido group, including the migration of NEt$_3$ and the formation of free isobutyronitrile $^{\mathrm{i}}$PrCN, which was observed in the ^{1}H NMR spectrum of the crude mixture. An analogous metathesis reaction proceeded in the reaction of **1-$^{\mathrm{i}}$Pr** and an excess of propionitrile EtCN similarly producing the vinylimido complex [Ta(NCCHMe{NEt$_3$})Cl$_4$](EtCN) (**1-Et**,[25] Scheme 2; see Figure S-2 in the SI for ^{1}H NMR spectra of the reaction mixture).

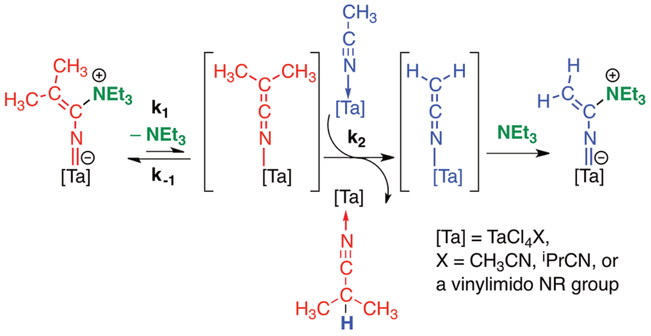
Scheme 2. Imido Group Interchange in Zwitterionic Ta(V) Vinylimido Complexes



The imido exchange reaction was found to proceed in both directions in the case of the MeCN/EtCN pair. Heating the imido complex **1-Me** with an excess (2 equiv) of propionitrile EtCN in CD$_2$Cl$_2$ at 45 °C for 2 days led to the quantitative formation of **1-Et** and free MeCN according to ^{1}H NMR data (see Figure S-3 in the SI). At the same time, the reverse transformation of **1-Et** to **1-Me** under similar conditions was found to be sluggish, resulting in ca. 50% conversion after 2 weeks at 50 °C according to ^{1}H NMR spectroscopy (Scheme 2; see Figure S-4 in the SI for the ^{1}H NMR spectrum of the reaction mixture). The starting imido complex **1-Et**, as synthesized from TaCl$_5$ and EtCN at room temperature, consists of a mixture of two isomers in a ratio *Z*:*E* = 1:4–6 (we found that this ratio varies depending on recrystallization conditions). The less abundant (and presumably less stable) *Z* isomer with the *cis*- mutual orientation of the methyl and triethylammonium groups reacts with acetonitrile at a significantly higher rate than the *E* isomer. Furthermore, only the *E* isomer of **1-Et** formed in the reaction of **1-$^{\mathrm{i}}$Pr** and EtCN.

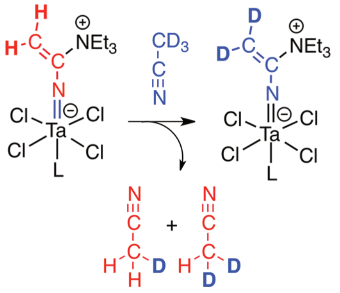
We propose that the transformation of **1-$^{\mathrm{i}}$Pr** to **1-Me** proceeds through the complete imido group interchange; in other words, the nitrogen of the incoming nitrile becomes a part of the new imido group. Elimination of triethylamine from the starting vinylimido group is likely the first step of the transformation (Scheme 3). The resulting coordinated azaallene fragment readily deprotonates the incoming nitrile molecule, especially if the nitrile ligand is coordinated to a metal center. This deprotonation may also happen through "shuttling" of a proton by the released triethylamine. The following rearrangement of the new deprotonated nitrile and nucleophilic attack by the amine proceeds analogously through the azaallene intermediate as during the formation of these zwitterionic vinylimido species.

Scheme 3. Proposed Mechanism of Imido Group Interchange on the Example of the 1-$^{\mathrm{i}}$Pr to 1-Me Conversion



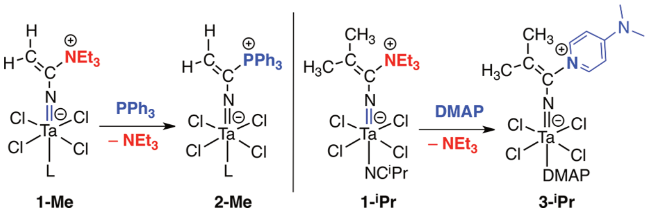
To support the proposed mechanism of the imido group exchange, we conducted a set of experiments with the observations listed below. First, the imido group metathesis occurred only with nitriles containing α-hydrogen atoms; for instance, pivalonitrile did not participate in an exchange reaction. Second, the reaction of [Ta(NCCH$_2${NEt$_3$})Cl$_5$]$^-$ (**1-Me′**) complex with excess CD$_3$CN in CD$_2$Cl$_2$ at 40 °C led to the formation of a deuterated imido complex [Ta(NCCD$_2$-{NEt$_3$})Cl$_5$]$^-$ (**1-Me′-d^2**) and the appearance of the signal from CD$_2$HCN in the ^{1}H NMR spectrum of the reaction mixture (Scheme 4, Figures S-5 and S-6 in the SI). This observation is congruous with the proton transfer from the incoming nitrile (CD$_3$CN) to the starting imido group (Ta═NCCH$_2${NEt$_3$}), resulting in its conversion to a nitrile (initially to CDH$_2$CN, which is likely to participate further in the imido interchange, eventually yielding CD$_2$HCN).

Scheme 4. Evidence of a Proton Transfer from a Nitrile to an Imido Group on the Example of the 1-Me′ to 1-Me′-d^2 Conversion



Finally, we attempted to carry out the replacement of the triethylammonium moiety of the imido group by another neutral nucleophile (see Scheme 5, Figure S-7 in the SI). The vinylimido complex **1-Me** reacted with PPh$_3$ at 45 °C in CD$_2$Cl$_2$ for 2 days with no other nitrile present. As expected, the reaction cleanly produced a new vinylimido complex [Ta(NCCH$_2${PPh$_3$})Cl$_4$](MeCN) **2-Me** by the exchange of NEt$_3$ and PPh$_3$ nucleophiles. We have independently prepared

Scheme 5. Replacement of the Ammonio Group by Triphenylphosphine (Left, 2-Me) or DMAP (Right, 3-^{i}Pr) in the Zwitterionic Vinylimido Complex 1-^{i}Pr



this imido complex in the direct reaction of MeCN and the $TaCl_5 \cdot PPh_3$ adduct.[26]

Similarly, the vinylimido complex **1-^{i}Pr** reacted with an excess of DMAP in CD_2Cl_2 at room temperature. Within 15 min, exchange of amine to pyridine at the imido group produced an orange crystalline solid $[Ta(NCCMe_2\{DMAP\})Cl_4](DMAP)$ (**3-^{i}Pr**). This interchange reaction opens the way for functionalization of these imido complexes with a broader range of nucleophilic groups as this DMAP-containing imido complex could not be obtained in the direct reaction of $TaCl_5(^iPrCN)$ and DMAP, which produced a simple unreactive adduct $TaCl_5(DMAP)$ instead. These nucleophile exchange reactions of vinylimido complexes particularly suggest that the elimination of triethylamine from the starting vinylimido group is the first step of the overall interchange transformation.

The single crystal X-ray diffraction experiment for a sample of **3-^{i}Pr** confirmed the expected molecular structure with the zwitterionic vinylimido group (Figure 1). The interatomic distances and angles are within typical ranges for the linear imido group at the Ta(V) center (Ta1≡N1 = 1.783(3) Å, Ta1≡N1−C1 = 169.2(2)°) and the carbon−carbon double bond of the vinylimido fragment (C1═C2 = 1.339(5) Å).

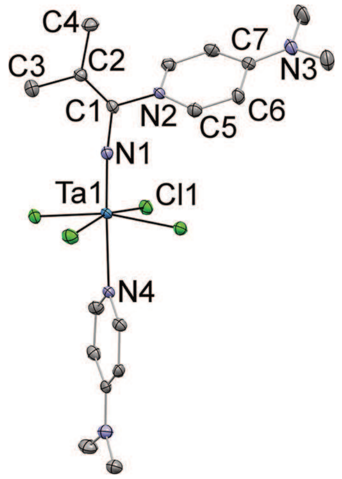


Figure 1. Displacement ellipsoid plot (50% probability) of **3-^{i}Pr**. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Ta1−N1 = 1.783(3), Ta1−N4 = 2.361(3), N1−C1 = 1.374(4), C1−C2 = 1.339(5), C1−N2 = 1.459(4), Ta1−N1−C1 = 169.2(2), N2−C1−C2 = 120.3(3).

The kinetics of the imido group interchange reaction was probed through initial rate studies with variable concentrations of an imido complex and a nitrile at 40 °C in dichloromethane (Figures S-10 and S-11 in the SI). The rate of conversion of **1-^{i}Pr** to **1-Et** was found to be the first order in the starting imido complex. At the same time, no dependence of the rate of the reaction on the concentration of propionitrile was found. Addition of 12 equiv of NEt_3 to the reaction mixture resulted in the slower reaction progression. Addition of 8 equiv of pivalonitrile also caused a significantly slower reaction rate. Similarly, the conversion of **1-^{i}Pr** to **1-Me** was found to exhibit the first order kinetics in the **1-^{i}Pr** imido complex and the zero order in acetonitrile. A comparison of reaction rates of **1-^{i}Pr** with CH_3CN and **1-^{i}Pr** with CD_3CN revealed the value of the kinetic isotope effect of 1.5. The reaction of **1-^{i}Pr** with EtCN was significantly faster than its reaction with MeCN ($k_{obs}(\mathbf{1\text{-}Et})/k_{obs}(\mathbf{1\text{-}Me}) = 4.2$).

These observations are compatible with the proposed mechanism shown in Scheme 3. The release of triethylamine from the starting vinylimido group is a slow reversible step of the reaction. This step is inhibited by added NEt_3. Notably, we were able to intercept the azaallene intermediate (not observed) in reactions with PPh_3 or DMAP (see above). Deprotonation of the coordinated nitrile by this intermediate is a faster step which is congruent with the apparent independence of the overall reaction rate on a nitrile concentration and the absence of the significant primary isotope effect. Deprotonation of an incoming nitrile is likely to occur only if it is coordinated to a tantalum center as these alkylnitriles do not react with NEt_3 without $TaCl_5$ present. This proposal is consistent with inhibition of the reaction in the presence of pivalonitrile that also coordinates to the metal center but lacks α-hydrogen atoms and therefore cannot be deprotonated and transformed to an imido group. Therefore, the second step is likely bimolecular in tantalum as it involves an interaction of the azaallene intermediate and a nitrile complex and does not depend on the concentration of a nitrile. The rate below can be derived using the steady-state approximation:

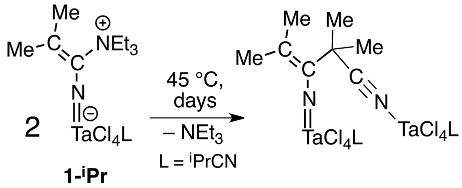
$$\frac{-d[\mathbf{1\text{-}^iPr}]}{dt} = \frac{k_1[\mathbf{1\text{-}^iPr}]k_2[\mathbf{1\text{-}^iPr}]}{k_{-1}[NEt_3] + k_2[\mathbf{1\text{-}^iPr}]}$$

However, if the proton transfer step is fast, the overall reaction rate would appear as the first order in the starting imido concentration under conditions used in our experiments. This is also consistent with the absence of the primary isotope effect for breaking C−H bonds of acetonitrile. In other words, if $k_2 \gg k_1$, then the derived rate law can be simplified and appears to be the first order in the starting imido:

$$\frac{-d[\mathbf{1\text{-}^iPr}]}{dt} = \frac{k_1[\mathbf{1\text{-}^iPr}]}{k_{-1}[NEt_3]}$$

Attempts to study kinetics of this transformation at higher temperatures in tetrachloroethane proved to be inconclusive due to formation of multiple products including insoluble species. We were able to identify one of these products due to its characteristic ^1H NMR spectra features as one containing a vinylimidocyanoalkyl group, featuring two isobutyronitrile-based fragments coupled through a C−C bond (Scheme 6). An analogous complex has been prepared earlier by deprotonation of isobutyronitrile by a sterically hindered Hunig's base $N(^iPr)_2Et$ in the presence of $TaCl_5$, which led to the subsequent C−C bond formation between deprotonated intermediates.[25] We also observed the appearance of signals from this vinylimidocyanoalkyl group during heating of **1-^{i}Pr** in CD_2Cl_2 at 45 °C for 4 days with no other nitrile present (except a coordinated ^{i}PrCN ligand in the starting imido

Scheme 6. Prevalent Decomposition Pathway for the Vinylimido Complex 1-^{i}Pr upon Prolonged Heating without an Added Nitrile



complex; see Figure S-12 in the SI). Under the conditions reported herein, the elimination of NEt_3 from the starting imido in **1-^{i}Pr** can lead to the bimolecular coupling of the nucleophilic deprotonated nitrile and the electrophilic azaallene intermediate at higher temperatures, resulting in the C−C coupling reaction similarly to the independent synthesis mentioned above.

CONCLUSIONS

Imido groups bound to high-valent transition metals are often stable toward nitriles as evidenced by a large number of reported nitrile adducts of metal imido complexes. The reactivity of zwitterionic vinylimido complexes of Ta(V) with nitriles described above is different from the reactions of nitriles with related vinylimido complexes of Ti(IV) or any other early transition metal imido species. Instead of previously reported cycloaddition reactions, in the case presented herein, elimination of the amine and subsequent proton transfer from a nitrile substrate to the former vinylimido fragment led to the formation of a new imido group. This is the first example of the reaction of an imido complex with a nitrile that results in the formation of a new imido group and a free nitrile in a metathesis-type transformation. Furthermore, the cationic group on the imido ligand can be replaced with other nucleophiles, which was demonstrated by NEt_3 to PPh_3 and NEt_3 to DMAP exchange reactions.

EXPERIMENTAL SECTION

All synthetic manipulations were carried out either in a nitrogen-filled drybox or on an air free dual-manifold Schlenk line.[27] Solvents were sparged with nitrogen, passed through activated alumina, and stored over activated 4 Å Linde-type molecular sieves. Chloroform-d^3, dichloromethane-d^2, and acetonitrile-d^3 (Cambridge Isotope Laboratories) were degassed and stored over activated 4 Å Linde-type molecular sieves. NMR spectra were recorded using Varian spectrometers at 400 MHz (^{1}H) and 100 MHz (^{13}C) and reported in δ (parts per million) and referenced to residual ^{1}H/^{13}C signals of a deuterated solvent or an external 85% phosphoric acid (^{31}P (δ): 0.0 ppm) standard. Midwest Microlab, Indianapolis, Indiana provided the elemental analysis results.

$TaCl_5$ (Strem) was used as received. NEt_3, CH_3CN, CD_3CN, EtCN, and ^{i}PrCN were degassed by freeze−pump−thaw technique and stored over 4 Å Linde-type molecular sieves. Starting **1-^{i}Pr**, **1-Me**, and **1-Et** were synthesized according to the previously published procedure.[25]

A typical imido group interchange experiment involved an addition of excess nitrile (2−30 equiv) to a solution of a vinylimido complex of Ta(V) in CD_2Cl_2 in an NMR tube with a J. Young valve. Reaction temperature varied from 22 to 50 °C; reaction time varied from 15 min to 2 weeks. Reaction progress was monitored by ^{1}H NMR spectroscopy.

Conversion of 1-^{i}Pr to 1-Me. This known compound[25] formed in the imido group interchange reaction. In a typical reaction, **1-^{i}Pr** was dissolved in CD_2Cl_2 and transferred into an NMR tube with the J. Young valve under nitrogen. Excess of MeCN was added. The solution was heated at 40 °C for 2 days. During that time, at least 95% of the **1-^{i}Pr** was converted into **1-Me** according to ^{1}H NMR spectroscopy.

Conversion of 1-^{i}Pr to 1-Et. This known compound[25] formed in the imido group interchange reaction. In a typical reaction, **1-^{i}Pr** was dissolved in CD_2Cl_2 and transferred into an NMR tube with the J. Young valve under nitrogen. Excess of EtCN was added. The solution was heated at 45 °C for 1 day. During that time, at least 99% of the **1-^{i}Pr** was converted into **1-Et** according to ^{1}H NMR spectroscopy.

Conversion of 1-Me to 1-Et. This known compound[25] formed in the imido group interchange reaction. In a typical reaction, **1-Me** was dissolved in CD_2Cl_2 and transferred into an NMR tube with the J. Young valve under nitrogen. Excess of EtCN was added. The solution was heated at 45 °C for 2 days. During that time, at least 99% of the **1-Me** was converted into **1-Et** according to ^{1}H NMR spectroscopy.

Conversion of 1-Et to 1-Me. This known compound[25] formed in the imido group interchange reaction. In a typical reaction, **1-Et** was dissolved in CD_2Cl_2 and transferred into an NMR tube with the J. Young valve under nitrogen. Excess of MeCN was added. The solution was heated at 50 °C for 2 weeks. During that time, at least 50% of the **1-Et** was converted into **1-Me** according to ^{1}H NMR spectroscopy.

Conversion of 1-Me to 2-Me. This known compound[26] formed in the imido group interchange reaction. In a typical reaction, **1-Me** (0.040 g, 0.007 mmol) was dissolved in CD_2Cl_2 and transferred into an NMR tube with the J. Young valve under nitrogen. A portion of PPh_3 (0.035 g, 0.013 mmol, 2 equiv) was added. The solution was heated at 45 °C for 2 days. During that time, at least 99% of the **1-Me** was converted into **2-Me** according to ^{1}H NMR spectroscopy.

Conversion of 1-^{i}Pr to 3-^{i}Pr. A portion of **1-^{i}Pr** (50 mg, 0.09 mmol) was dissolved in 2 mL of CH_2Cl_2. A solution of DMAP (0.021 mg, 0.17 mmol, 2 equiv) in CH_2Cl_2 (2 mL) was added. Within 15 min at room temperature, an orange precipitate formed. The precipitate was filtered, washed with 1 mL of CH_2Cl_2, and dried under vacuum (0.021 g, 0.03 mmol, 24%). **^{1}H NMR (400 MHz, CD_2Cl_2)**: δ 8.87 (d, 2H, $^3J_{HH}$ = 7 Hz, $NC_5H_4N(CH_3)_2$), 8.26 (d, 2H, $^3J_{HH}$ = 7 Hz, $NC_5H_4N(CH_3)_2$), 6.80 (d, 2H, $^3J_{HH}$ = 7 Hz, $NC_5H_4N(CH_3)_2$), 6.52 (d, 2H, $^3J_{HH}$ = 7 Hz, $NC_5H_4N(CH_3)_2$), 3.25 (s, 6H, $NC_5H_4N(CH_3)_2$), 3.05 s, 6H, $NC_5H_4N(CH_3)_2$), 2.69 (s, 3H, $NC{=}C(CH_3)_2$), 2.05 (s, 3H, $NC{=}C(CH_3)_2$). **^{13}C (100 MHz, CD_2Cl_2)**: δ 154.7 ($TaNC{=}C(CH_3)_2$), 151.4 ($NC_5H_4N(CH_3)_2$), 142.1 ($NC_5H_4N(CH_3)_2$), 129.8 ($TaNC{=}C(CH_3)_2$), 125.2 ($NC_5H_4N(CH_3)_2$), 123.8 ($NC_5H_4N(CH_3)_2$), 106.5 ($NC_5H_4N(CH_3)_2$), 105.5 ($NC_5H_4N(CH_3)_2$), 40.2 ($NC_5H_4N(CH_3)_2$), 39.0 ($NC_5H_4N(CH_3)_2$), 18.0 ($TaNC{=}C(CH_3)_2$), 17.7 ($TaNC{=}C(CH_3)_2$). Calcd. for $C_{18}H_{26}Cl_4N_5Ta$: C, 34.04; H, 4.13; N, 11.03. Found C, 34.38; H, 4.02; N, 11.35.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.8b00241.

NMR spectra and the crystal structure report (PDF)

Accession Codes

CCDC 1837033 contains 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.

AUTHOR INFORMATION

Corresponding Author

*E-mail: peryshkov@sc.edu.

ORCID

Md. Mamdudur Rahman: 0000-0003-4304-3927
Dmitry V. Peryshkov: 0000-0002-5653-9502

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This material is based in part upon work supported by the National Science Foundation under Award CHE-1654301.

■ REFERENCES

(1) Hazari, N.; Mountford, P. Reactions and Applications of Titanium Imido Complexes. *Acc. Chem. Res.* **2005**, *38* (11), 839−849.

(2) Schrock, R. R. Recent Advances in High Oxidation State Mo and W Imido Alkylidene Chemistry. *Chem. Rev.* **2009**, *109* (8), 3211−3226.

(3) Chao, Y. W.; Wexler, P. A.; Wigley, D. E. Preparation and Properties of Tantalum Imido Complexes and Their Reactions with Alkynes. Coordination Control through Multiple Metal-Ligand Bonding. *Inorg. Chem.* **1989**, *28* (20), 3860−3868.

(4) Cundari, T. R. Transition Metal Imido Complexes. *J. Am. Chem. Soc.* **1992**, *114* (20), 7879−7888.

(5) Polse, J. L.; Andersen, R. A.; Bergman, R. G. Reactivity of a Terminal Ti(IV) Imido Complex toward Alkenes and Alkynes: Cycloaddition vs C−H Activation. *J. Am. Chem. Soc.* **1998**, *120* (51), 13405−13414.

(6) Tomson, N. C.; Arnold, J.; Bergman, R. G. Halo, Alkyl, Aryl, and Bis(Imido) Complexes of Niobium Supported by the β-Diketiminato Ligand. *Organometallics* **2010**, *29* (13), 2926−2942.

(7) Helgert, T. R.; Zhang, X.; Box, H. K.; Denny, J. A.; Valle, H. U.; Oliver, A. G.; Akurathi, G.; Webster, C. E.; Hollis, T. K. Extreme π-Loading as a Design Element for Accessing Imido Ligand Reactivity. A CCC-NHC Pincer Tantalum Bis(Imido) Complex: Synthesis, Characterization, and Catalytic Oxidative Amination of Alkenes. *Organometallics* **2016**, *35* (20), 3452−3460.

(8) Obenhuber, A. H.; Gianetti, T. L.; Berrebi, X.; Bergman, R. G.; Arnold, J. Reaction of (Bisimido)Niobium(V) Complexes with Organic Azides: [3 + 2] Cycloaddition and Reversible Cleavage of β-Diketiminato Ligands Involving Nitrene Transfer. *J. Am. Chem. Soc.* **2014**, *136* (8), 2994−2997.

(9) Zuckerman, R. L.; Krska, S. W.; Bergman, R. G. Zirconium-Mediated Metathesis of Imines: A Study of the Scope, Longevity, and Mechanism of a Complicated Catalytic System. *J. Am. Chem. Soc.* **2000**, *122* (5), 751−761.

(10) Cantrell, G. K.; Meyer, T. Y. Catalytic CN Bond Formation by Metal-Imide-Mediated Imine Metathesis. *J. Am. Chem. Soc.* **1998**, *120* (32), 8035−8042.

(11) Ong, T.-G.; Yap, G. P. A.; Richeson, D. S. Catalytic CN Bond Metathesis of Carbodiimides by Group 4 and 5 Imido Complexes Supported by Guanidinate Ligands. *Chem. Commun.* **2003**, *20*, 2612−2613.

(12) Guiducci, A. E.; Boyd, C. L.; Mountford, P. Reactions of Cyclopentadienyl-Amidinate Titanium Imido Compounds with CS_2, COS, Isocyanates, and Other Unsaturated Organic Compounds. *Organometallics* **2006**, *25* (5), 1167−1187.

(13) Gianetti, T. L.; La Pierre, H. S.; Arnold, J. Group 5 Imides and Bis(Imide)s as Selective Hydrogenation Catalysts. *Eur. J. Inorg. Chem.* **2013**, *2013* (22−23), 3771−3783.

(14) Kriegel, B. M.; Bergman, R. G.; Arnold, J. Nitrene Metathesis and Catalytic Nitrene Transfer Promoted by Niobium Bis(Imido) Complexes. *J. Am. Chem. Soc.* **2016**, *138* (1), 52−55.

(15) La Pierre, H. S.; Arnold, J.; Bergman, R. G.; Toste, F. D. Carbon Monoxide, Isocyanide, and Nitrile Complexes of Cationic, d^0 Vanadium Bisimides: π-Back Bonding Derived from the π Symmetry, Bonding Metal Bisimido Ligand Orbitals. *Inorg. Chem.* **2012**, *51* (24), 13334−13344.

(16) Yuan, J.; Schrock, R. R.; Gerber, L. C. H.; Müller, P.; Smith, S. Synthesis and ROMP Chemistry of Decafluoroterphenoxide Molybdenum Imido Alkylidene and Ethylene Complexes. *Organometallics* **2013**, *32* (10), 2983−2992.

(17) Basuli, F.; Bailey, B. C.; Watson, L. A.; Tomaszewski, J.; Huffman, J. C.; Mindiola, D. J. Four-Coordinate Titanium Alkylidene Complexes: Synthesis, Reactivity, and Kinetic Studies Involving the Terminal Neopentylidene Functionality. *Organometallics* **2005**, *24* (8), 1886−1906.

(18) Townsend, E. M.; Kilyanek, S. M.; Schrock, R. R.; Müller, P.; Smith, S. J.; Hoveyda, A. H. High Oxidation State Molybdenum Imido Heteroatom-Substituted Alkylidene Complexes. *Organometallics* **2013**, *32* (16), 4612−4617.

(19) Duhacek, J. C.; Siddiquee, T. A.; Bennett, D. W.; Duncan, D. C. The Synthesis, Crystal, and Molecular Structure of Two Mononuclear Arylimido Tungsten Tetrachloride Complexes, $[WCl_4(4I\text{-}p)(CH_3CN)]$ and $[WCl_4(NC_6H_3\text{-}2,6\text{-}i\text{-}Pr\ _2)(CH_3CN)]$. *J. Chem. Crystallogr.* **2008**, *38* (6), 431−435.

(20) Basuli, F.; Huffman, J. C.; Mindiola, D. J. Reactivity at the β-Diketiminate Ligand Nacnac- on Titanium(IV) (Nacnac- = $[Ar]NC(CH_3)CHC(CH_3)N[Ar]$, Ar = $2,6\text{-}[CH(CH_3)_2]_2C_6H_3$). Diimine-Alkoxo and Bis-Anilido Ligands Stemming from the Nacnac-Skeleton. *Inorg. Chem.* **2003**, *42* (24), 8003−8010.

(21) Bolton, P. D.; Feliz, M.; Cowley, A. R.; Clot, E.; Mountford, P. Ti=NR vs Ti−R′ Functional Group Selectivity in Titanium Imido Alkyl Cations from an Experimental Perspective. *Organometallics* **2008**, *27* (23), 6096−6110.

(22) Lam, J. K.; Zhu, C.; Bukhryakov, K. V.; Müller, P.; Hoveyda, A.; Schrock, R. R. Synthesis and Evaluation of Molybdenum and Tungsten Monoaryloxide Halide Alkylidene Complexes for Z-Selective Cross-Metathesis of Cyclooctene and Z-1,2-Dichloroethylene. *J. Am. Chem. Soc.* **2016**, *138* (48), 15774−15783.

(23) Pugh, S. M.; Trösch, D. J. M.; Wilson, D. J.; Bashall, A.; Cloke, F. G. N.; Gade, L. H.; Hitchcock, P. B.; McPartlin, M.; Nixon, J. F.; Mountford, P. Cycloaddition Reactions of the Titanium Imide $[Ti(NBu^t)\{MeC(2\text{-}C_5H_4N)(CH_2NSiMe_3)_2\}(Py)]$ with Bu^tCP and MeCN. *Organometallics* **2000**, *19* (16), 3205−3210.

(24) Doxsee, K. M.; Farahi, J. B.; Hope, H. Synthesis and Formal [4 + 2] Cycloaddition Reactions of Vinylimido Complexes of Titanocene. *J. Am. Chem. Soc.* **1991**, *113* (23), 8889−8898.

(25) Rahman, M. M.; Smith, M. D.; Peryshkov, D. V. Formation of a Cationic Vinylimido Group upon C−H Activation of Nitriles by Trialkylamines in the Presence of $TaCl_5$. *Inorg. Chem.* **2016**, *55* (11), 5101−5103.

(26) Rahman, M. M.; Smith, M. D.; Amaya, J. A.; Makris, T. M.; Peryshkov, D. V. Activation of C−H Bonds of Alkyl- and Arylnitriles by the $TaCl_5$−PPh_3 Lewis Pair. *Inorg. Chem.* **2017**, *56* (19), 11798−11803.

(27) Shriver, D. F.; Drezdzon, M. A. *The Manipulation of Air-Sensitive Compounds*, 2nd ed.; Wiley-Interscience: New York, 1986.

DOI: 10.1021/acs.organomet.8b00241
Organometallics 2018, 37, 2945−2949