

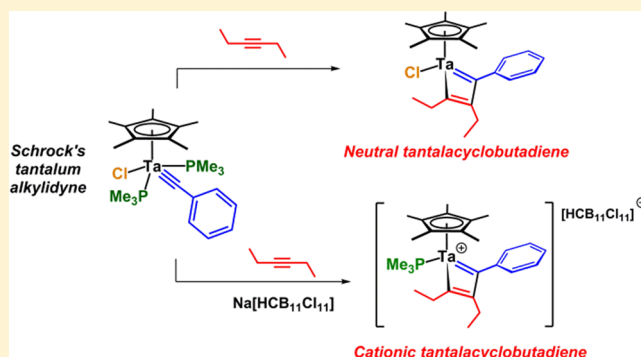
Cycloaddition and C–H Activation Reactions of a Tantalum Alkylidyne

Rodrigo Ramírez-Contreras, Nattamai Bhuvanesh, and Oleg V. Ozerov*

Department of Chemistry, Texas A&M University, College Station, Texas 77842, United States

S Supporting Information

ABSTRACT: The alkylidyne complex $(C_5Me_5)Ta(\equiv CPh)(PMe_3)_2Cl$ (**1**) was first reported by Schrock in 1978, but little if any follow-up work on **1** or other group 5 metal alkylidynes has been reported. This work discloses two avenues of reactivity of **1**. Treatment of **1** with 3-hexyne resulted in the formation of a tantalacyclobutadiene. Abstraction of chloride from **1** led to a mixture of products that included isomers of $[(C_5Me_5)Ta(\equiv CHPh)(CH_2PMe_2)(PMe_3)]^+$ (**4**), in which a C–H bond of a PMe_3 ligand was added across the Ta≡C bond. The C–H activation was found to be reversible, and the equilibrium mixture functioned as an equivalent of a cationic Ta alkylidyne in reaction with 3-hexyne, producing a cationic tantalacyclobutadiene (**6**). Compounds **4** and **6** were structurally characterized in the solid state by XRD methods, with **6** being the first structurally characterized metallacyclobutadiene in group 5.

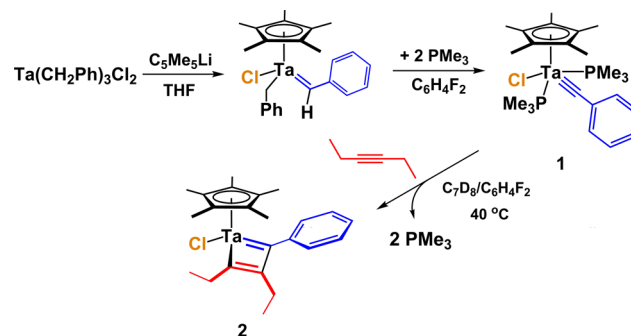


Compounds with transition metal–carbon triple bonds (i.e., $M\equiv CR$),¹ typically termed carbyne or alkylidyne complexes,^{2,3} are of particular importance as intermediates and catalysts in the metathesis of carbon–carbon triple bonds.^{4,5} They are most common in the chemistry of Mo and W (group 6),⁶ which function as capable alkyne and nitrile metathesis catalysts.^{7,8} Metal–carbon triple bonds are also well established for Re (group 7),^{9,10} with some examples of alkyne metathesis,¹¹ as well as Ru¹² and Os¹³ (group 8), while Rh¹⁴ and Ir (group 9)¹⁵ offer only a few examples. Isolated compounds of metal–carbon triple bonds are unknown for metals of groups 3 and 4 and are rare for group 5. For purely hydrocarbyl CR ligands (alkylidynes) only one family of NacNac-based compounds is known for V,¹⁶ none for Nb, and only the 1978 report¹⁷ from the Schrock group describing $Cp'Ta(PMe_3)_2Cl(\equiv CPh)$ (where $Cp' = \eta^5-C_5H_5$ or $\eta^5-C_5Me_5$) for Ta. The Lippard group reported a series of V, Nb, and Ta siloxycarbyne complexes containing $M\equiv COSiX_3$ moieties that resulted from silylation of metal carbonylate anions.¹⁸ Li and co-workers described Nb¹⁹ and Ta²⁰ phosphoniomethylidynes with a $M\equiv CPPH_3$ substructure. Several bridging alkylidyne complexes are known in group 5, including homobimetallic dimetallacyclobutadienes^{21,22} and alkylidynes bridging between Ta and Li,²³ as well as Ta and Zn.²⁴

We were interested by the scarcity of group 5 terminal alkylidynes reported in the literature and by the fact that they have not been studied experimentally²⁵ in the context of alkyne metathesis, even though $Cp'Ta(PMe_3)_2Cl(\equiv CPh)$ could potentially be a viable candidate for this type of reactivity. To the best of our knowledge, the only observation (*in situ*) of a [2+2] cycloaddition to yield a tantalacyclobutadiene comes

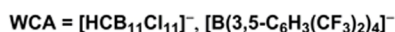
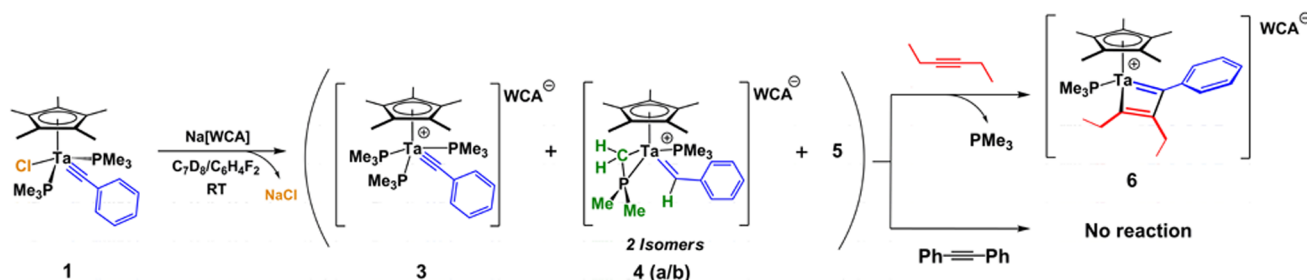
from the 1985 report by Pasman et al.,²⁶ describing the conversion of a trimetallic Ta_2Zn bridging alkylidyne to cyclopentadienyls in reactions with alkynes. We set out to revisit Schrock's $(C_5Me_5)Ta(PMe_3)_2Cl(\equiv CPh)$ (**1**).¹⁷ Our synthesis of **1** largely followed the original procedure (Scheme 1).¹⁷ Treatment of **1** with 3-hexyne resulted in the formation of tantalacyclobutadiene complex **2**. The net reaction to form **2** entails replacement of 2 equiv of PMe_3 by 1 equiv of 3-hexyne. Around 95% conversion to **2** required repeated removal of volatiles (including free PMe_3) and readdition of 3-hexyne. Compound **2** was identified on the basis of the relevant NMR data in solution, especially the signature metallacyclobutadiene

Scheme 1. Treatment of **1** with 3-Hexyne Yields the Neutral Metallacyclobutadiene **2** as the Only Reaction Product



Received: March 11, 2015

Published: April 2, 2015

Scheme 2. Reversible C–H Bond Activation at PMe_3 in Response to Chloride Abstraction from **1**^a

^a PMe_3 ligand distribution to form compound **3** is concomitant with formation of a small amount of an unidentified compound **5**. Treatment of the mixture with 3-hexyne afforded the metallacyclobutadiene **6** as the only product.

¹³C NMR resonances at 154.7, 207.2, and 212.9 ppm. We observed no NMR-detectable amounts of the potential metathesis product (1-phenylbutyne) in the formation of **2**.

In light of this result and based on our previous experience with highly reactive cations,²⁷ we speculated that abstraction of chloride from it may lead to a more reactive complex. Abstraction of chloride was performed using excess $\text{Na}[\text{BARF}]$ ($\text{BARF} = [\text{B}(3,5\text{-C}_6\text{H}_3(\text{CF}_3)_2)_4]^-$), which was dried following the Bergman procedure.²⁸ In some reactions, especially for the purposes of isolation of pure solids, we used equimolar amounts of $\text{Na}[\text{HCB}_{11}\text{Cl}_{11}]$ or $\text{Na}[n\text{-BuCB}_{11}\text{Cl}_{11}]$,²⁹ which can be safely dried by heating *in vacuo*. A 3:2 mixture of toluene-*d*₈ and *protio*-1,2-difluorobenzene (ODFB) was our solvent of choice for *in situ* NMR studies. This mixture provides a reasonable compromise in terms of cost, the solubility of organometallic BARF or carborane salts, and the ability to collect quality ¹H NMR spectra (with the exception of the aromatic region). Treatment of **1** with 2.5 equiv of $\text{Na}[\text{BARF}]$ resulted in a mixture of four apparent products (Scheme 2). The same mixture of organometallic cations was observed when 1.0 equiv of $\text{Na}[\text{BARF}]$, $\text{Na}[\text{HCB}_{11}\text{Cl}_{11}]$, or $\text{Na}[n\text{-BuCB}_{11}\text{Cl}_{11}]$ was used, along with the free anion resonances. We were able to identify the nature of three components of the mixture. One is the tris-phosphine complex **3**. It was isolated in 84% yield as a BARF salt in an analytically pure solid form from a reaction with three additional equivalents of PMe_3 (Scheme 2). NMR data supported the assignment, with a 2:1 doublet:triplet pattern in the ³¹P{¹H} NMR spectrum and a ¹³C{¹H} resonance at 365.6 ppm for the alkyldiene carbon (dt, ²*J*_{C-P} = 29.9 Hz, ²*J*_{C-P} = 9.2 Hz).

Two other components of the mixture appear to be isomers of the cyclometalated complex **4**. Each of the isomers displayed a pair of doublets in the ³¹P{¹H} NMR spectrum, and the ¹H NMR spectra of the mixture contained resonances assignable to two sets of cyclometalated Me_2PCH_2 fragments, in addition to the corresponding unactivated PMe_3 and C_5Me_5 signals. The isomers **4a/4b** are products of the net addition of a C–H bond in PMe_3 across the $\text{Ta}\equiv\text{C}$ bond, in the unobserved intermediate $[(\text{C}_5\text{Me}_5)\text{Ta}(\text{CPh})(\text{PMe}_3)_2]^+$. Compounds **4a/4b** and **3** are clearly related by equilibrium with PMe_3 . Addition of extra PMe_3 to the mixture increased the content of **3** after sitting overnight at 40 °C. Additionally, treatment of **3** with $\text{B}(\text{C}_6\text{F}_5)_3$ to trap PMe_3 as $\text{Me}_3\text{P-B}(\text{C}_6\text{F}_5)_3$ ³⁰ led to the clean conversion to the mixture of **4a/4b** only. This demonstrates the facile reversibility of C–H activation by $\text{Ta}\equiv\text{C}$ under the reaction conditions.

We were not able to identify the fourth, minor component (<2%) of the mixture corresponding to the singlet in the ³¹P{¹H} NMR spectrum. Its content in the mixture was not affected by addition or removal of PMe_3 , suggesting that compound **5** is not related to **3** and **4** simply by PMe_3 loss. We considered whether it might be a product of adventitious hydrolysis, but carefully measured addition of small quantities of water to a mixture of **3**, **4**, and **5** did not result in the increase of the content of **5**.

The mass balance for the chloride abstraction reaction is not fully clear. Naturally, the P:Ta ratio of **3** for compound **2** and of **2** for compound **3** necessitates the formation of another co-product with a lower P:Ta ratio. It is possible that the unknown **5** contains only one P per Ta or that formation of a small quantity of P-free Ta complex(es) takes place. Chloride abstraction in the presence of mesitylene as an internal integration standard showed retention of C_5Me_5 and PMe_3 ¹H resonance intensity in solution within the likely 10% error of measurement, but this margin of error may be enough to provide for the extra PMe_3 release needed to form **5**.

Our efforts to isolate **4a/4b** separately or as a pure isomeric mixture on a preparative scale have not been successful. However, we obtained an X-ray quality single crystal from the reaction of **1** with $\text{Na}[n\text{-BuCB}_{11}\text{Cl}_{11}]$, and an XRD study confirmed the proposed connectivity (Figure 1). The $\text{CH}_2\text{-P}$ bond of the cyclometalated phosphine is in the same plane as the Ta–P bond to the unaffected PMe_3 , with the CH_2 group

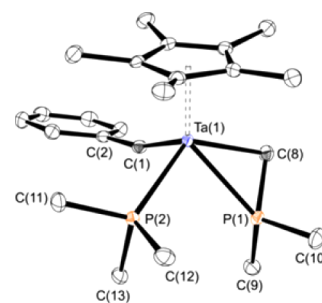


Figure 1. ORTEP diagram of one of the isomers of **4**. Thermal ellipsoids are set to 50% probability. Hydrogen atoms and $[n\text{-BuCB}_{11}\text{Cl}_{11}]^-$ anion are omitted for clarity. Selected distances (Å) and angles (deg): Ta(1)–C(1) 1.918(2), Ta(1)–C(8) 2.262(2), Ta(1)–(P1) 2.5729(6), Ta(1)–(P2) 2.5680(6), P(1)–C(8) 1.762(2), P(1)–C(9) 1.808(2), P(1)–C(10) 1.817(2); Ta(1)–C(1)–C(2) 164.24(18), P(2)–Ta(1)–P(1) 82.065(19).

tilted toward the C_5Me_5 ring. The two Ta–P distances are nearly the same, and the Ta–CH₂ bond length of 2.262(2) Å is normal for a single Ta–C single bond. The overall geometry of the Ta–P(Me)₂–CH₂ fragment is very similar to that in (Me₃P)₄W(CH₂PMe₂)(H), except that M–P and M–C distances are shorter for M = W.³¹ The Ta=C bond in the alkylidene fragment of 1.918(2) Å is at the shorter end of the Ta=C bond length range, but is longer than the 1.849(8) Å Ta≡C bond in **1**. The Ta=C–C angle of ca. 164° is quite typical for agostic Ta alkylidenes.¹⁷ The alkylidene formulation of **4a/4b** is further supported by the observation of two downfield resonances (δ 234.6 and 244.7 ppm) in the ¹³C NMR spectrum of the reaction mixture showing low ¹J_{C–H} values of 76–77 Hz. The closest Ta structural analogue of **4** is (C₅Me₅)Ta(C₂H₄)(PMe₃)(=CHCMe₃),³² where the Ta–(C₂H₄) metallacyclopropane is positioned similarly to Ta–(CH₂PMe₂) in **4**. The two isomers of **4** likely reflect a switch of the CH₂ and PMe₂ positions in **4**. While we cannot rule out other possibilities, this explanation is consistent with markedly different ²J_{P–P} values in **4a/4b** (14 and 54 Hz), as would be expected for different P–Ta–P angles. Addition of C–H bonds across metal–element multiple bonds has rich precedent.³³ The most closely related example is the chemistry of C–H activation by an unobserved Ti alkylidyne extensively studied by the Mindiola group.³⁴

(C₅H₅)Ta(PMe₃)₂(Cl)(≡CPh) underwent a transformation to an apparently analogous mixture upon treatment with Na[BARF], based on NMR spectroscopic data. We have not pursued full characterization or isolation of Cp complexes. The details of the *in situ* observations are given in the SI.

We then set out to examine reactions of the mixture of compounds **2** and **4a/4b** with alkynes (Scheme 2). Treatment of this mixture with 3-hexyne resulted in a clean reaction, forming **6** in >95% purity (NMR evidence) *in situ* and in 68% isolated yield. In contrast, addition of diphenylacetylene gave no evidence of metallacycle formation. Treatment of the mixture of **2** and **4a/4b** with a mixture of 3-hexyne and diphenylacetylene gave only **6**. We saw no evidence of formation of the cross-metathesis product (1-phenyl-1-butyne).

The molecular structure of **5** in the solid state was established by an X-ray diffraction study (Figure 2).

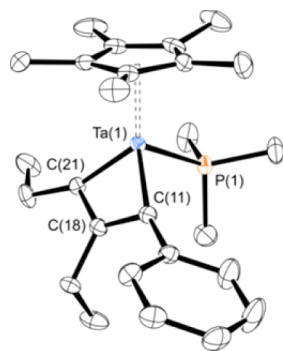


Figure 2. ORTEP diagram (50% probability ellipsoids) of **6**. Selected atom labeling is shown. Thermal ellipsoids are set to 50% probability. Hydrogen atoms and the [HCB₁₁Cl₁₁][−] anion are omitted for clarity. Selected distances (Å) and angles (deg): Ta(1)–C(11) 1.956(4), Ta(1)–C(21) 1.948(4), Ta(1)–C(18) 2.179(3), C(11)–C(18) 1.461(5), C(18)–C(21) 1.481(5), Ta(1)–P(1) 2.5602(10), C(21)–Ta(1)–C(11) 82.51(15), C(21)–C(18)–C(11) 122.1(3).

Compound **6** exhibits a geometry that is distorted away from the ideal three-legged piano stool configuration, due to the geometric restrictions imposed by the tantalacyclobutadiene. The Ta–C(21) (1.948(4) Å) and Ta–C(11) (1.956(4) Å) distances are not significantly different and are within the range of Ta–C double bonds.¹ The two C–C distances within the TaC₃ ring are quite similar, as well, and fall between the typical range of C–C double bonds (1.33 Å in ethylene)³⁵ and single bonds (1.54 Å in ethane).³⁶ While there are no other structurally characterized tantalacyclobutadienes for comparison, the metrics in the C₃Et₂Ph ligand in **5** and the near-symmetric binding to the metal are similar to those reported for the tungstacyclobutadiene W(C^tBuCMeCMe)Cl₃ (**7**).³⁷ Structurally characterized tungstacyclobutadienes vary in how symmetric the C₃ fragment is.³⁸ Distances M–C_α Ta(1)–C(11) and Ta(1)–C(21) in **6** (1.956(4), 1.948(4) Å) were in the same range as analogous distances in compound **7** (1.861(9), 1.864(8) Å). Similarly, C_α–C_β bond lengths C(11)–C(18) and C(18)–C(21) (1.461(5), 1.481(5) Å) in **6** are comparable to related bonds in **7** (1.455(13), 1.478(12) Å).³⁷ Finally, compound **6** displays an obtuse C_α–C_β–C_{α'} angle of 122.1(3)°, which is comparable to the analogous angle in **7** (118.9(8)°). The three metallacyclic carbons in **5** were observed at 170.7, 236.2, and 240.8 ppm in the ¹³C NMR spectrum. The pattern of two more downfield (>200 ppm) C_α resonances and one more upfield (C_β) is common for trisubstituted metallacyclobutadienes of W,^{37,38} Mo,³⁹ and Re.⁴⁰

In summary, we have examined the reactivity of a Ta alkylidyne moiety, which has been hardly explored previously. A cationic Ta alkylidyne has been characterized, along with products of C–H addition across the Ta≡C bond. Cycloaddition with 3-hexyne produced a tantalacyclobutadiene that was ostensibly stable to cycloreversion.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details; crystallographic data in the form of a CIF file. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: ozzerov@chem.tamu.edu.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We are grateful for support of this research by the U.S. Department of Energy, Office of Basic Energy Sciences (grant DE-FG02-06ER15815), and the Welch Foundation (grant A-1717).

■ REFERENCES

- (1) Schrock, R. R. *Chem. Rev.* **2002**, *102*, 145.
- (2) Fischer, H.; Hofmann, P.; Kreißl, F. R.; Schrock, R. R.; Schubert, U.; Weiss, K.; *Carbyne Complexes*; VCH Verlag: Weinheim, 1988.
- (3) Schrock, R. R. *J. Chem. Soc., Dalton Trans.* **2001**, 254.
- (4) Fürstner, A. *Angew. Chem., Int. Ed.* **2013**, *52*, 2794.
- (5) Schrock, R. R.; Czekelius, C. *Adv. Synth. Catal.* **2007**, *349*, 55.
- (6) Schrock, R. R. *Acc. Chem. Res.* **1986**, *19*, 342.
- (7) Schrock, R. R. *Angew. Chem., Int. Ed.* **2006**, *45*, 3748.

- (8) Geyer, A. M.; Wiedner, E. S.; Gary, J. B.; Gdula, R. L.; Kuhlmann, N. C.; Johnson, M. J. A.; Dunietz, B. D.; Kampf, J. W. *J. Am. Chem. Soc.* **2008**, *130*, 8984.
- (9) Toreki, R.; Vaughan, G. A.; Schrock, R. R.; Davis, W. M. *J. Am. Chem. Soc.* **1993**, *115*, 127.
- (10) Ozerov, O. V.; Watson, L. A.; Pink, M.; Caulton, K. G. *J. Am. Chem. Soc.* **2007**, *129*, 6003.
- (11) Schrock, R. R.; Weinstock, I. A.; Horton, A. D.; Liu, A. H.; Schofield, M. H. *J. Am. Chem. Soc.* **1988**, *110*, 2686.
- (12) (a) Caskey, S. R.; Stewart, M. H.; Ahn, Y. J.; Johnson, M. J. A.; Rowsell, J. L. C.; Kampf, J. W. *Organometallics* **2007**, *26*, 1912. (b) Shao, M.; Zheng, L.; Qiao, W.; Wang, J.; Wang, J. *Adv. Synth. Catal.* **2012**, *354*, 2743.
- (13) Jia, G. *Coord. Chem. Rev.* **2007**, *251*, 2167.
- (14) Rappert, T.; Nürnberg, O.; Mahr, N.; Wolf, J.; Werner, H. *Organometallics* **1992**, *11*, 4156.
- (15) Luecke, H. F.; Bergman, R. G. *J. Am. Chem. Soc.* **1998**, *120*, 11008.
- (16) (a) Basuli, F.; Bailey, B. C.; Brown, D.; Tomaszewski, T.; Huffman, J. C.; Baik, M. H.; Mindiola, D. J. *J. Am. Chem. Soc.* **2004**, *126*, 10506. (b) Adhikari, D.; Basuli, F.; Orlando, J. H.; Gao, X.; Huffman, J. C.; Pink, M.; Mindiola, D. J. *Organometallics* **2009**, *28*, 4115.
- (17) McLain, S. J.; Wood, C. D.; Messerle, L. W.; Schrock, R. R.; Hollander, F. J.; Youngs, W. J.; Churchill, M. R. *J. Am. Chem. Soc.* **1978**, *100*, 5962.
- (18) (a) Protasiewicz, J. D.; Lippard, S. J. *J. Am. Chem. Soc.* **1991**, *113*, 6564. (b) Protasiewicz, J. D.; Bronk, B. S.; Masschelein, A.; Lippard, S. J. *Organometallics* **1994**, *13*, 1300. (c) Vrtis, R. N.; Rao, C. P.; Warner, S.; Lippard, S. J. *J. Am. Chem. Soc.* **1988**, *110*, 2669. (d) Vrtis, R. N.; Liu, S.; Rao, C. P.; Bott, S. G.; Lippard, S. J. *Organometallics* **1991**, *10*, 275.
- (19) Li, X.; Sun, H.; Harms, K.; Sundermeyer, J. *Organometallics* **2005**, *24*, 4699.
- (20) (a) Nazhen Liu, N.; Zhu, G.; Sun, H.; Li, X. *Inorg. Chem. Commun.* **2013**, *27*, 36. (b) Li, X.; Wang, A.; Wang, L.; Sun, H.; Harms, K.; Sundermeyer, J. *Organometallics* **2007**, *26*, 1411.
- (21) (a) Gambarotta, S.; Edema, J. J. H.; Minhas, R. K. *J. Chem. Soc., Chem. Commun.* **1993**, 1503. (b) Shaver, M. P.; Johnson, S. A.; Fryzuk, M. D. *Can. J. Chem.* **2005**, *83*, 652.
- (22) (a) Riley, P. N.; Profflet, R. D.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1996**, *15*, 5502. (b) Riley, P. N.; Profflet, R. D.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1996**, *15*, 5502. (c) Riley, P. N.; Thorn, M. G.; Vilardo, J. S.; Lockwood, M. A.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1999**, *18*, 3016. (d) Riley, P. N.; Profflet, R. D.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1996**, *15*, 5502.
- (23) Guggenberger, L. J.; Schrock, R. R. *J. Am. Chem. Soc.* **1975**, *97*, 2935.
- (24) (a) Rietveld, M. H. P.; Lohner, P.; Nijkamp, M. G.; Grove, D. M.; Veldman, N.; Spek, A. L.; Pfeffer, M.; van Koten, G. *Chem.—Eur. J.* **1997**, *3*, 817. (b) Abbenhuis, H. C. L.; Feiken, N.; Henk, F.; Haarman, H. F.; Grove, D. M.; Horn, E.; Spek, A. L.; Pfeffer, M.; van Koten, G. *Organometallics* **1993**, *12*, 2227.
- (25) Computational study: Suresh, C.; Frenking, G. *Organometallics* **2012**, *31*, 7171.
- (26) van der Heijden, H.; Gal, A. W.; Pasma, P. *Organometallics* **1985**, *4*, 1847.
- (27) (a) DeMott, J. C.; Bhuvanesh, N.; Ozerov, O. V. *Chem. Sci.* **2013**, *4*, 642. (b) Douvris, C.; Nagaraja, C. M.; Chen, C.-H.; Foxman, B. M.; Ozerov, O. V. *J. Am. Chem. Soc.* **2010**, *132*, 4946.
- (28) Yakelis, N. A.; Bergman, R. G. *Organometallics* **2005**, *24*, 3579.
- (29) Ramírez-Contreras, R.; Ozerov, O. V. *Dalton Trans.* **2012**, *41*, 7842.
- (30) Chase, P. A.; Masood, P.; Piers, W. E. *Acta Crystallogr., Sect. E* **2006**, *62*, o5181.
- (31) Gibson, V. C.; Graimann, C. E.; Hare, P. M.; Green, M. L. H.; Bandy, J. A.; Grebenik, P. D.; Prout, K. *J. Chem. Soc., Dalton Trans.* **1985**, 2025.
- (32) Schultz, A. J.; Brown, R. K.; Williams, J. M.; Schrock, R. R. *J. Am. Chem. Soc.* **1981**, *103*, 169.
- (33) (a) Schafer, D. F.; Wolczanski, P. T.; Lobkovsky, E. B. *Organometallics* **2011**, *30*, 6518. (b) Schafer, D. F.; Wolczanski, P. T.; Lobkovsky, E. B. *Organometallics* **2011**, *30*, 6539. (c) Cundari, T. R.; Klinckman, T. R.; Wolczanski, P. T. *J. Am. Chem. Soc.* **2002**, *124*, 1481. (d) Schaller, C. P.; Cummins, C. C.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1996**, *118*, 591. (e) Schaller, C. P.; Wolczanski, P. T. *Inorg. Chem.* **1993**, *32*, 131. (f) Baillie, R. A.; Legzdins, P. *Acc. Chem. Res.* **2013**, *47*, 330. (g) Lefèvre, G. P.; Baillie, R. A.; Fabulyak, D.; Legzdins, P. *Organometallics* **2013**, *32*, 5561.
- (34) Bailey, B. C.; Fan, H.; Huffman, J. C.; Baik, M.-H.; Mindiola, D. J. *J. Am. Chem. Soc.* **2007**, *129*, 8781.
- (35) Bartell, L. S.; Bonham, R. A. *J. Chem. Phys.* **1957**, *27*, 1414.
- (36) Hansen, G. E.; Dennison, D. M. *J. Chem. Phys.* **1952**, *20*, 313.
- (37) Edwards, D. S.; Schrock, R. R. *J. Am. Chem. Soc.* **1982**, *104*, 6808.
- (38) (a) Churchill, M. R.; Ziller, J. W.; McCullough, L.; Pedersen, S. F.; Schrock, R. R. *Organometallics* **1983**, *2*, 1046. (b) Schrock, R. R.; Pedersen, S. F.; Churchill, M. R.; Ziller, J. W. *Organometallics* **1984**, *3*, 1574. (c) Churchill, M. R.; Ziller, J. W.; Freudenberger, J. H.; Schrock, R. R. *Organometallics* **1984**, *3*, 1554. (d) Freudenberger, J. H.; Schrock, R. R.; Churchill, M. R.; Rheingold, A. L.; Ziller, J. W. *Organometallics* **1984**, *3*, 1563. (e) Beer, S.; Hrib, C. G.; Jones, P. G.; Brandhorst, K.; Grunenberg, J.; Tamm, M. *Angew. Chem., Int. Ed.* **2007**, *46*, 8890. (f) Beer, S.; Brandhorst, K.; Hrib, C. G.; Wu, X.; Haberlag, B.; Grunenberg, J.; Jones, P. G.; Tamm, M. *Organometallics* **2009**, *28*, 1534.
- (39) (a) Schrock, R. R.; Jamieson, J. Y.; Araujo, J. P.; Bonitatebus, P. J., Jr.; Sinha, A.; Lopez, L. P. H. *J. Organomet. Chem.* **2003**, *684*, 56. (b) McCullough, L. G.; Schrock, R. R.; Dewan, J. C.; Murdzek, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 5987.
- (40) Schrock, R. R.; Weinstock, I. A.; Horton, A. D.; Liu, A. H.; Schofield, M. H. *J. Am. Chem. Soc.* **1988**, *110*, 2686.