Reaction of Cp*(Cl)M(Diene) (M = Ti, Hf) with Isonitriles

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S *Supporting Information*

ABSTRACT: We have investigated the reaction of isonitriles (RNC) with electronically unsaturated diene complexes of Ti and Hf. Cp*(Cl)Ti(2,3-dimethyl-butadiene) (**1**) reacts with 2 equiv of RNC to give η^1,η^2-diimine complexes **2** (R = ^{t}Bu) and **3** (R = 1-adamantyl). Cp*(Cl)Ti(N,N-di-^{t}Bu-η^1,η^2-diimine) (**2**), in the presence of pyridine, fragments to Cp*(Cl)Ti(N^{t}Bu)(NC$_5$H$_5$) (**10**) and an α-methylene cyclopent-3-enimine (**11**). The hafnium analogue of **1**, Cp*(Cl)Hf(2,3-dimethyl-butadiene) (**14**), has been reported to give a cyclic amidine complex when treated with 2 equiv of 2,6-dimethylphenyl isonitrile. By X-ray crystallography, however, we find that **14** and 2,6-dimethylphenyl isonitrile give instead a 2,5-diazahafnacyclopentane that features a σ-interaction between the C−C bond of a cyclopropane ring and the Hf.

C heletropic cycloadditions like the [1,4]-addition of SO$_2$ to dienes (eq 1)[1] and that of CO to enynes (Pauson−Khand reaction, eq 2)[2] are very useful in synthesis.


(1)

(2)
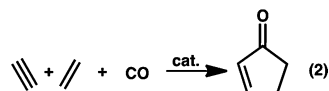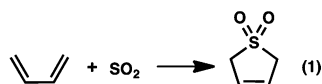
In 1972, Corey used a series of reactions to accomplish the addition of CO to a diene (eq 3),[3] but it has been problematic to carry out the reaction directly from CO and a diene. Chatani has noted that there are "no example[s] but stoichiometric".[2,4]


(3)
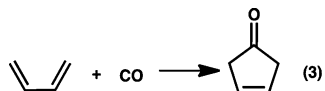
A potential replacement for CO in cycloaddition reactions is an isoelectronic isonitrile (RNC). The reactions of isonitriles do not need to be carried out under pressure, and their steric and electronic properties are easily varied by the use of different substituents R. The first [4+1] isonitrile cycloadditions, reported in 1982, involved the reaction of α,β-unsaturated carbonyl compounds in the presence of a stoichiometric amount of AlEtCl$_2$ (eq 4).[5] A catalytic version of the same reaction was reported by Chatani and co-workers in 2003,[6] and reviewed by Tobisu and Chatani in 2011.[7] The addition of RNC to an enyne was carried out stoichiometrically with

Ni(COD)$_2$ in 1988 (eq 5),[8] and catalytically with titanocene in 1994 (eq 6).[9]


(4)

(5)

(6)
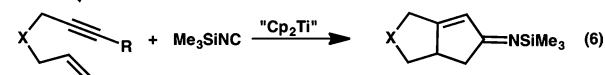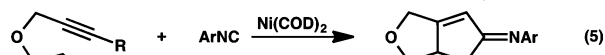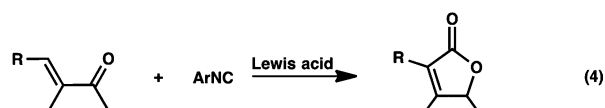
We have therefore examined the reaction of isonitriles with dienes. DFT calculations (B3LYP/6-311++G**)[10] show that eq 7 is over 10 kcal/mol more favorable in the gas phase than eq 3, and the advantages of an isonitrile are even greater in solution (a higher concentration is more easily achieved).

(7)
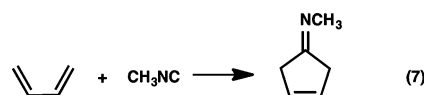
Dienes are easily coordinated to transition metals. Group 4 complexes of dienes[11] are particularly attractive for insertion reactions, because they are best described by metalla-cyclopentene resonance structures.
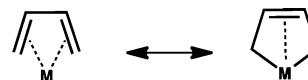
Treatment of **1** with ^{t}BuNC did not, however, result in one insertion but in two (eq 8). (The use of only 1 equiv of ^{t}BuNC gave a 1:1 mixture of **1** and the double insertion product **2**.)

(8)

2 R = ^{t}Bu
3 R = 1-adamantyl = 1-Ad
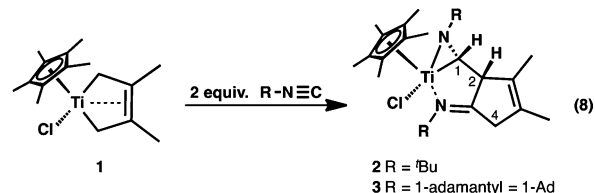
The ^{1}H NMR spectrum of **2** contains an AB pattern (δ 2.75 and 2.38 with $^2J_{HH}$ = 21.8 Hz) that we assign to the diastereotopic protons on C-4. COSY and HSQC experiments support the titanaaziridine structure we have drawn for **2**, with the methine protons on C-1 and C-2 at δ 2.50 and 2.98, respectively ($^3J_{HH}$ = 4.2 Hz). A ketimine group is coordinated to the Ti in an η^1 fashion, as demonstrated by the C=N stretching frequency of 1718 cm^{-1} and an imine ^{13}C NMR

Scheme 1. Proposed Mechanism for the Conversion of Titanacyclopentene 1 to Titanaaziridine 2 or 3
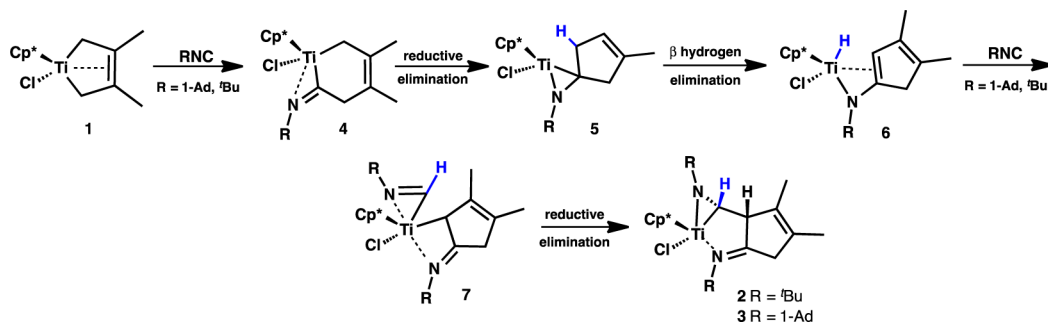
resonance at δ 192.[12] An aldimine is coordinated in an η^2 fashion, forming the titanaaziridine ring. Beckhaus and co-workers recently used $^{15}N,^1H$ HMBC experiments to determine the coordination mode of imines bound to Ti.[13] The same method shows that the aldimine and ketimine of 2 have similar ^{15}N chemical shifts (δ 296.5 and 299.1), although there is no practical way of determining which is which.

It was straightforward to isolate 2 as a green powder in 65–70% yield, but growing crystals of X-ray quality proved impossible. We therefore replaced ^tBuNC in eq 8 with its 1-adamantyl analogue. The resulting product 3 was isolated as a green powder in 70% yield. The NMR spectrum of 3 shows diastereotopic methylene resonances, presumably also on C-4, at δ 2.90 and 2.51, with $^2J_{HH}$ = 21.6 Hz. The methine proton on C-2 appears at δ 3.07, while that on C-1 is a doublet at δ 2.53; $^3J_{HH}$ between them is 5 Hz. The ^1H NMR spectra of 2 and 3 plainly demonstrate that they possess the same structure with different substituents R.
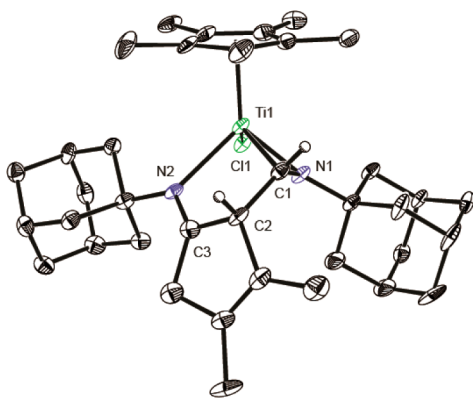

Figure 1. ORTEP view of one enantiomer of the titanaaziridine 3. The other enantiomer of 3 is shown in the Supporting Information. Thermal ellipsoids are drawn at 30% probability level. Selected hydrogen atoms are omitted for clarity. Selected bond lengths (Å) for this enantiomer: N1–C1, 1.407(11); N2–C3, 1.302(11). Bond lengths (Å) for the other enantiomer: N3–C41, 1.380(11); N4–C43, 1.290(11).

Crystallization of 3 at −35 °C from pentane permitted the collection of X-ray data. Their solution (one enantiomer of 3 is shown in Figure 1) confirmed the structure suggested in eq 8, with one C=N distance (N2–C3: 1.302(11) Å) reflecting the η^1 bonding of the ketimine to Ti and the other C=N distance (N1–C1: 1.407(11) Å) reflecting the η^2 bonding of the aldimine to Ti.

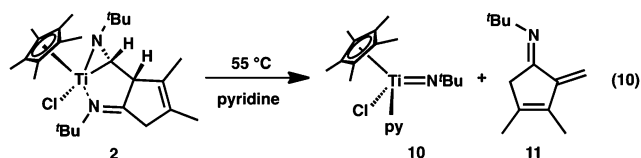The formation of 2 and 3 can be rationalized by the sequence in Scheme 1. Reductive elimination from 4 presumably leads to the titanaaziridine 5, just as a cyclopentenone complex of Ti is formed by the reaction of 1 with CO.[14] The facile epimerization at carbon of zirconaaziridines with β-hydrogens[15] suggests that titanaaziridines 5 will be easily transformed into 1-azaallyl titanium hydrides like 6. Insertion of the second RNC into the Ti–H bond,[16,17] followed by C,C reductive elimination, affords the titanaaziridines 2 and 3. The fact that no intermediates (4, 5, 6, or 7) can be observed implies that the first insertion (formation of 4) is rate determining. A similar isonitrile insertion is involved in the synthesis of titanaaziridines from dialkyl titanium complexes.[18]

The insertion of a second RNC, into the Ti–CH$_2$ bond of 4, apparently does not compete with the formation of 5 by reductive elimination. A bis(iminoacyl) titanacycle like 8 would be expected[19] to form a 2,5-diazametallacyclopentene like 9 (eq 9), and no 9 is observed. In contrast, Cp*$_2$M(1,3-diene) (M = Zr, Hf) complexes react with 2 equiv of CO to give enediolate complexes.[20]
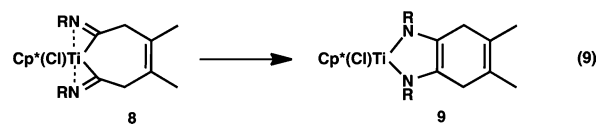

The 6 resulting from β-H elimination is presumably stabilized by conjugation with the other double bond. A similar mechanism, converting a metallaoxirane like 5 to a 1-oxaallyl metal hydride, has been invoked in the reaction of CO with Cp*(Cl)M(2,3-dimethylbutadiene) (M = Zr, Hf); Teuben and co-workers isolated an oxaallyl zirconium hydride from the reaction of CO with Cp*$_2$Zr(2,3-dimethylbutadiene).[14]

When heated to 55 °C in benzene with pyridine, 2 rearranges to the known titanium imido complex Cp*(Cl)Ti(N^{t}Bu)-(NC$_5$H$_5$) (10)[21] and the previously unknown α-methylene cyclopentenimine 11 (eq 10). The structure assigned to 11 is consistent with its ^1H NMR spectrum: two equivalent methylene protons appear as a singlet at δ 2.68, and exocyclic vinyl protons appear at δ 6.01 and 4.81 (J = 1.2 Hz). The C=N stretch at 1618 cm^{-1} in the IR spectrum of 11 is consistent with a cyclic secondary imine.

The conversion of the titanaaziridine 2 to 11 can be rationalized by the sequence in Scheme 2. A β-hydrogen

Scheme 2. Proposed Mechanism for the Fragmentation of Titanaaziridine 2 to 10 and 11
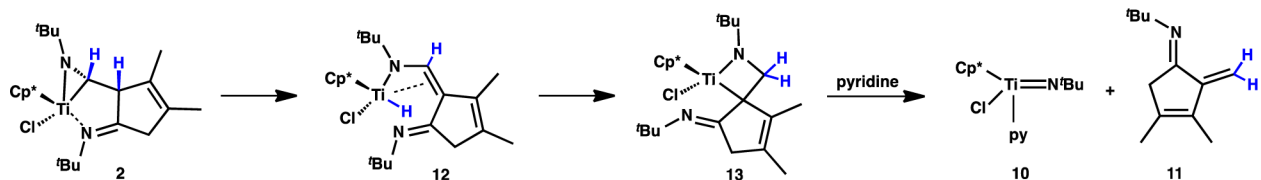

elimination converts **2** to a 1-azaallyl titanium hydride **12**, and addition of the Ti–H across the azaallyl double bond gives the azatitanacyclobutane **13**. Cycloreversion from **13** liberates **11** and Cp*(Cl)Ti(N^{t}Bu), which is trapped by the pyridine as **10**.[21]

The conversion of **1** to the cyclopentenimine **11** *includes* the formal [4+1] cycloaddition of an isonitrile to 2,3-dimethylbutadiene, but it also cleaves the triple bond of another isonitrile. Metal-mediated cleavage reactions of isonitriles, although rare, have been previously observed: under hydrogen (with W),[22] under protic conditions (with Ta, W, and Re),[22,23] and via cycloreversion (with Zr and Ta).[24] Cleavage of the CO triple bond by Cp*(Cl)Hf(2,3-dimethylbutadiene) has also been reported.[14]

The only previous report of the insertion of an isonitrile into the M–C bond of a group 4 diene complex (i.e., a metallacyclopentene) came from Teuben and co-workers in 1989.[25] These authors treated the hafnacyclopentene **14** with 2 equiv of 2,6-dimethylphenyl isonitrile and proposed that the product was **15** (which can be described as a cyclic amidine coordinated to Hf through a C=N and a C=C; eq 11).

(11)
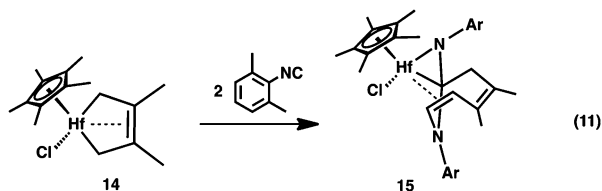
However, this structure assignment was based primarily on NMR spectroscopy, as the authors were unable to grow crystals suitable for X-ray crystallography. We were fortunate enough to be able to grow such crystals by slow evaporation of pentane from the product, and from the resulting structure determination (Figure 2) we learned that **15** is in fact **16** (eq 12).

(12)
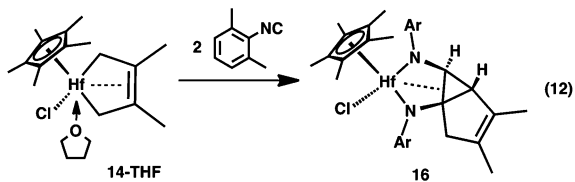
In hindsight, the NMR data are consistent with **16** (Figure 2). Two methine carbons, C-36 and C-35, have $^1J_{CH}$ = 184 and 168 Hz, respectively, values typical of cyclopropane rings.[26]

The X-ray results (the important distances are given in Table 1) show a C31–C36 distance in **16** (1.552(9) Å) that is substantially longer than that in cyclopropane (1.514(2) Å).[27] The Hf–C36 and Hf–C31 distances (2.490(7) and 2.527(7) Å, respectively) suggest that the C31–C36 bond of the cyclopropane is coordinated to the Hf, forming a "σ complex". Such complexes, although rare, are not unknown, and have been recently reviewed by Etienne.[28] The C–C bond lengths within the cyclopropane ring of **16** are similar to those in other
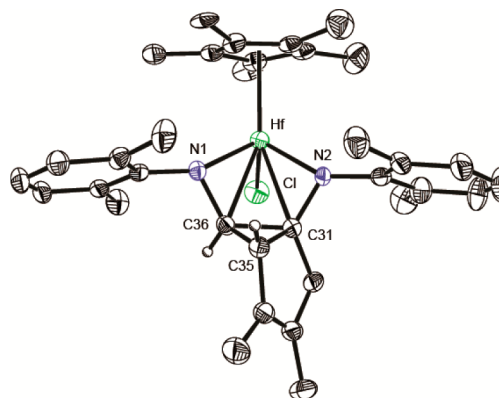

Figure 2. ORTEP view of diazahafnacyclopentane **16**. Thermal ellipsoids are drawn at 30% probability level. Selected hydrogen atoms are omitted for clarity. Selected bond lengths are given in Table 1.

Table 1. Selected Bond Lengths (Å) for the Diazahafnacyclopentane 16

Hf–N1	1.991(5)
Hf–N2	2.010(5)
Hf–C36	2.490(7)
Hf–C31	2.527(7)
N1–C36	1.444(8)
N2–C31	1.423(8)
C31–C36	1.552(9)
C31–C35	1.493(9)
C35–C36	1.507(9)

complexes with σ interactions between a cyclopropane C–C bond and the metal (Li[29] and Nb[30]).

The $^1J_{CC}$ values provide further evidence for an electronic interaction between a C–C bond and the metal center.[31] Preparation of the diazahafnacyclopentane **16** with ^{13}C from 2,6-Me$_2$PhN^{13}C allowed us to determine $^1J_{CC}$ between C31 and C36 as 1.1 Hz, which is an order of magnitude smaller than that in cyclopropane, where $^1J_{CC}$ = 12.4 Hz. The value of $^1J_{CC}$ in **16** compares well with the experimental and calculated $^1J_{CC}$ values for Tp^{Me_2}NbX(c-C$_3$H$_5$)(MeCCMe) (X = Cl, Ph, Me), all of which contain cyclopropyl C–C bonds that have σ interactions with Nb.[31] In all three Nb species, the experimentally determined upper limit for $|^1J_{CC}|$ is 3 Hz, and calculated values range from −1.3 to −2.1 Hz. We know of no previous examples of σ complex formation by one edge of a cyclopropane ring and a group 4 metal.

It seems likely that a Hf analogue of **2/3** is an intermediate in the formation of **16**, with the product resulting from insertion of the C=N in that intermediate (**17**) into its Hf–C bond (eq 13). This reaction, and this structure, are probably unavailable to titanium because of its size.

(13)
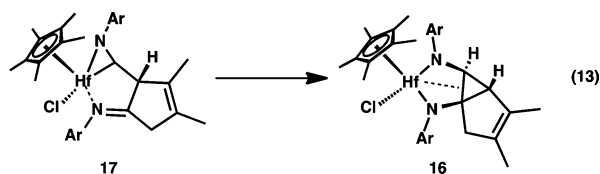
Thus, group 4 metals do mediate the cycloaddition of isonitriles to 2,3-dimethylbutadiene, although the product structure depends upon the nature of the group 4 metal. The preference we observe for the *double* insertion of isonitriles into the M−C bonds of Cp*(Cl)M(2,3-dimethylbutadiene) (M = Ti, Hf(THF)) will make it challenging to use these metals to catalyze [4+1] cycloadditions. Furthermore, the difficulty of transforming the Ti imido complex **10** back to the titana-cyclopentene **1** precludes the formation of **11** catalytically from 2,3-dimethylbutadiene and *tert*-butyl isonitrile. However, the chemistry we have observed offers an attractive route to more complex cyclic structures.

■ ASSOCIATED CONTENT

ⓢ Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b06654.

X-ray crystallographic data for **3** (CIF)
X-ray crystallographic data for **16** (CIF)
Synthetic procedures, compound characterization, NMR spectra, and crystallographic and structural results (PDF)

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Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

■ REFERENCES

(1) Vogel, P.; Turks, M.; Bouchez, L.; Markovic, D.; Varela-Alvarez, A.; Sordo, J. A. *Acc. Chem. Res.* **2007**, *40*, 931.
(2) Gibson, S. E.; Stevenazzi, A. *Angew. Chem., Int. Ed.* **2003**, *42*, 1800.
(3) Corey, E. J.; Walinsky, S. W. *J. Am. Chem. Soc.* **1972**, *94*, 8932.
(4) The carbonylation of 2,3-dimethylbutadiene has been reported in the patent literature, but the conditions are drastic and involve the use of an Ag-lined autoclave: Raasch, M. S.; Theobald, C. W. Chemical Process and Products. U.S. Patent 2,418,850, 1947.
(5) Ito, Y.; Kato, H.; Saegusa, T. *J. Org. Chem.* **1982**, *47*, 741.
(6) Tobisu, M.; Oshita, M.; Yoshioka, S.; Kitajima, A.; Chatani, N. *Pure Appl. Chem.* **2006**, *78*, 275.
(7) Tobisu, M.; Chatani, N. *Chem. Lett.* **2011**, *40*, 330.
(8) Tamao, K.; Kobayashi, K.; Ito, Y. *J. Am. Chem. Soc.* **1988**, *110*, 1286.
(9) Berk, S. C.; Grossman, R. B.; Buchwald, S. L. *J. Am. Chem. Soc.* **1994**, *116*, 8593.
(10) *Spartan '10*; Wavefunction, Inc., Irvine, CA, 2010.
(11) (a) Nakamura, A.; Mashima, K. *J. Organomet. Chem.* **2004**, *689*, 4552. (b) Erker, G.; Krüger, C.; Muller, G. *Adv. Organomet. Chem.* **1985**, *24*, 1.
(12) Cadierno, V.; Zablocka, M.; Donnadieu, B.; Igau, A.; Majoral, J. P.; Skowronska, A. *J. Am. Chem. Soc.* **1999**, *121*, 11086.
(13) Loose, F.; Plettenberg, I.; Haase, D.; Saak, W.; Schmidtmann, M.; Schafer, A.; Muller, T.; Beckhaus, R. *Organometallics* **2014**, *33*, 6785.
(14) Hessen, B.; Blenkers, J.; Teuben, J. H.; Helgesson, G.; Jagner, S. *Organometallics* **1989**, *8*, 2809.
(15) Cummings, S. A.; Tunge, J. A.; Norton, J. R. *J. Am. Chem. Soc.* **2008**, *130*, 4669.
(16) Parker, K. D. J.; Fryzuk, M. D. *Organometallics* **2014**, *33*, 6122.
(17) Boyarskiy, V. P.; Bokach, N. A.; Luzyanin, K. V.; Kukushkin, V. Y. *Chem. Rev.* **2015**, *115*, 2698.
(18) Thorn, M. G.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1999**, *18*, 4442.
(19) Chamberlain, L. R.; Durfee, L. D.; Fanwick, P. E.; Kobriger, L. M.; Latesky, S. L.; Mcmullen, A. K.; Steffey, B. D.; Rothwell, I. P.; Foltin, K.; Huffman, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 6068.
(20) Beckhaus, R.; Wilbrandt, D.; Flatau, S.; Bohmer, W. H. *J. Organomet. Chem.* **1992**, *423*, 211.
(21) Dunn, S. C.; Mountford, P.; Robson, D. A. *J. Chem. Soc., Dalton Trans.* **1997**, 293.
(22) Bernatis, P.; Laurie, J. C. V.; Dubois, M. R. *Organometallics* **1990**, *9*, 1607.
(23) (a) Galakhov, M. V.; Gomez, M.; Jimenez, G.; Royo, P.; Pellinghelli, M. A.; Tiripicchio, A. *Organometallics* **1995**, *14*, 1901. (b) Carvalho, M. F. N. N.; Pombeiro, A. J. L.; Schubert, U.; Orama, O.; Pickett, C. J.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1985**, 2079.
(24) (a) Scott, M. J.; Lippard, S. J. *Organometallics* **1997**, *16*, 5857. (b) Chamberlain, L. R.; Rothwell, I. P.; Huffman, J. C. *J. Chem. Soc., Chem. Commun.* **1986**, 1203. (c) Galakhov, M. V.; Gomez, M.; Jimenez, G.; Royo, P.; Pellinghelli, M. A.; Tiripicchio, A. *Organometallics* **1995**, *14*, 2843. (d) Matsuo, Y.; Mashima, K.; Tani, K. *Organometallics* **2002**, *21*, 138. (e) Xiang, L.; Mashima, K.; Xie, Z. W. *Chem. Commun.* **2013**, *49*, 9039.
(25) Hessen, B.; Blenkers, J.; Teuben, J. H.; Helgesson, G.; Jagner, S. *Organometallics* **1989**, *8*, 830.
(26) The reaction of **14**-PMe$_3$ with 2 equiv of ^{t}BuNC in C$_6$D$_6$ gives complete conversion to a compound that is structurally analogous to **16**, as demonstrated by its ^{1}H and ^{13}C NMR spectra (the two methine carbons have $^1J_{CH}$ = 178 and 165 Hz, respectively). Attempts to isolate this compound have been unsuccessful.
(27) de Meijere, A. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 809.
(28) (a) Etienne, M.; Weller, A. S. *Chem. Soc. Rev.* **2014**, *43*, 242. We feel, however, that the word "agostic" is not appropriately applied to a coordinated C−C, and note that the original article had proposed that term for "covalent interactions between carbon−hydrogen groups and transition metal centers": (b) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395.
(29) Goldfuss, B.; Schleyer, P. v R.; Hampel, F. *J. Am. Chem. Soc.* **1996**, *118*, 12183.
(30) (a) Jaffart, J.; Etienne, M.; Reinhold, M.; McGrady, J. E.; Maseras, F. *Chem. Commun.* **2003**, 876. (b) Besora, M.; Maseras, F.; McGrady, J. E.; Oulie, P.; Dinh, D. H.; Duhayon, C.; Etienne, M. *Dalton Trans.* **2006**, 2362.
(31) Boulho, C.; Keys, T.; Coppel, Y.; Vendier, L.; Etienne, M.; Locati, A.; Bessac, F.; Maseras, F.; Pantazis, D. A.; McGrady, J. E. *Organometallics* **2009**, *28*, 940.