Titanium(II) Synthon

Deutsche Ausgabe: DOI: 10.1002/ange.201607441
Internationale Ausgabe: DOI: 10.1002/anie.201607441

$C(sp^3)$–H Oxidative Addition and Transfer Hydrogenation Chemistry of a Titanium(II) Synthon: Mimicry of Late-Metal Type Reactivity

*J. Rolando Aguilar-Calderón, Alejandro J. Metta-Magaña, Bruce Noll, and Skye Fortier**

Abstract: *Two-electron reduction of the* Ti^{IV} *compound* $(^{ket}guan)(Im^{Dipp}N)Ti(OTf)_2$ *(**3**) gives the arene-masked complex* $(^{ket}guan)(\eta^6\text{-}Im^{Dipp}N)Ti$ *(**1**) in excellent yield. Upon standing in solution, **1** converts to a* Ti^{IV} *metallacycle (**4**) through dehydrogenation of a pendant isopropyl group. Spectroscopic evidence shows this transformation initially proceeds via the oxidative addition of a* $C(sp^3)$*–H bond and can be reversed upon exposure of **4** to* H_2*. Interestingly, treatment of **1** with cyclohexene gives cyclohexane and **4** via a titanium-mediated transfer hydrogenation reaction, a process that can be extended to catalytically hydrogenate other unsaturated hydrocarbons under mild conditions. These results, rare for the early-metals, suggest **1** possesses chemical characteristics reminiscent of noble, late-metals.*

Catalytic alkane dehydrogenation, proceeding via a formal H_2 transfer mechanism, was first achieved by Crabtree and Felkin, independently, using iridium and rhenium phosphine complexes and olefin co-reagents as hydrogen acceptors.[1] In these reactions, the critical step is the oxidative addition of a C–H bond to a coordinatively unsaturated metal center.[1b,2] Arguably, of the known C–H bond activation mechanisms (oxidative addition, σ-bond metathesis, electrophilic substitution, etc.), the oxidative addition of C–H bonds to low-valent late-metals (e.g. palladium, iridium) has shown the most success and versatility.[3] Of course, a major disadvantage of using precious metals is their associated cost and toxicity.

The redox neutral activation of C–H bonds by early-metal complexes through σ-bond metathesis is well-known.[4] However, in very rare instances, low-valent early-metal (i.e. Groups 4 and 5) complexes have been shown capable of effecting alkane C–H bond activation via oxidative addition pathways.[5] Efforts by Brintzinger and Bercaw to isolate titanocene, Cp_2Ti ($Cp = \eta^5\text{-}C_5H_5$), were unsuccessful as the complex undergoes ring hydrogen transfer to give the Ti^{III} fulvene dimer $(\mu\text{-}\eta^5{:}\eta^5\text{-}C_{10}H_8)[(Cp)Ti(\mu\text{-}H)]_2$.[5g,6] Rothwell et al. demonstrated that the two-electron reduction of the Nb^V aryloxide $Nb(ODipp)_3Cl_2$ (Dipp = 2,6-diisopropylphenyl) resulted in the formation of the cyclometalated Nb^V complex $Nb(OC_6H_3\text{-}^iPr\text{-}\eta^2\text{-}MeCCH_2)(ODipp)_2(THF)$.[5c] It is postulated that the reaction proceeds via a three-coordinate, $d^2\text{-}Nb^{III}$ intermediate which undergoes intramolecular oxidative addition of an isopropyl C–H bond followed by H_2 elimination. In support of this, Wolczanski and co-workers have shown that the isolable Ta^{III} complex $Ta(OSi^tBu_3)_3$ gradually cyclometalates to give the Ta^V alkyl hydride $Ta(H)(OSi^tBu_2CH_2)(OSi^tBu_3)_2$ in low yield.[5b] Notably, in all of the aforementioned cases, the observed C–H bond activation involves the putative formation of a coordinatively unsaturated d^2-metal species. These examples, although extremely limited, are noteworthy as they showcase that C–H oxidative addition chemistry is not the sole province of precious metals but can be performed under certain circumstances by abundant and non-toxic early-metals.

In line with this, we describe the synthesis, characterization, and reactivity of the 16-electron Ti^{II} synthon $(^{ket}guan)(\eta^6\text{-}Im^{Dipp}N)Ti$ (**1**). In solution, **1** slowly transforms into a new cyclometalated product from the intramolecular dehydrogenation of two $C(sp^3)$–H bonds through an oxidative addition step and subsequent loss of H_2. Notably, this transformation can be utilized to perform intermolecular transfer hydrogenation chemistry to convert cyclohexene to cyclohexane. Furthermore, we demonstrate that our system is capable of catalytically hydrogenating alkenes under mild conditions. This combined reactivity is unprecedented for early-metal systems but akin to the hydrocarbon chemistry observed with late, precious metals.

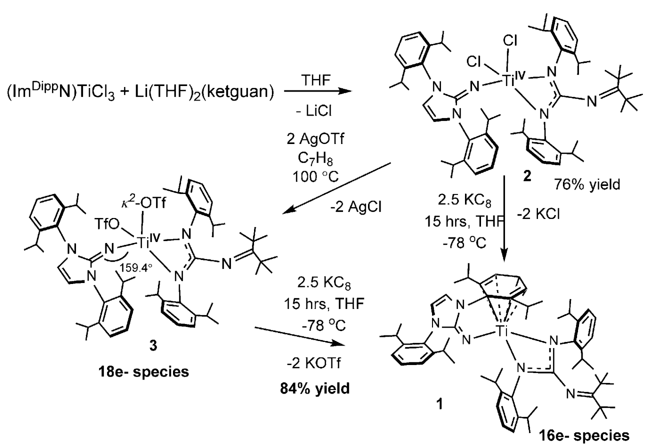
In an attempt to probe and explore the intriguing reactivity of coordinatively unsaturated early-metals in low oxidation states, that is, $\geq d^2$, we have been endeavoring to synthesize reduced but low-coordinate complexes of titanium. To maximize our chances for success, we chose to use a three-coordinate ligand base with sterically encumbering Dipp substituents for kinetic stabilization. To enhance the electron richness at the metal center and thus its reductive capabilities, we selected a ketimine-guanidinate $[(^tBu_2C{=}N)C(NDipp)_2]^-$ ($^{ket}guan^-$) and 1,3-bis(Dipp)imidazolin-2-iminato ($Im^{Dipp}N^-$) ligand combination as both are competent σ- and π-donors capable of donating up to 6 electrons each via 2σ–1π and 1σ–2π bonds, respectively.[7,8]

Addition of $[Li(THF)_2][^{ket}guan]$ to $(Im^{Dipp}N)TiCl_3$ in THF gives $(^{ket}guan)(Im^{Dipp}N)TiCl_2$ (**2**) in 76% as a dark red material (Scheme 1). Complex **2** is only partially soluble in aromatic and polar solvents but solubility can be dramatically improved through chloride-for-triflate metathesis using 2.1 equiv of AgOTf to give $(^{ket}guan)(Im^{Dipp}N)Ti(OTf)_2$ (**3**) which is highly soluble in THF and aromatic solvents. It

---

[*] J. R. Aguilar-Calderón, Dr. A. J. Metta-Magaña, Prof. Dr. S. Fortier
Department of Chemistry, University of Texas at El Paso
El Paso, TX 79968 (USA)
E-mail: asfortier@utep.edu
Homepage: http://utminers.utep.edu/asfortier/
Dr. B. Noll
Bruker AXS Inc.
5465 East Cheryl Parkway, Madison, WI 53711 (USA)

Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under http://dx.doi.org/10.1002/anie.201607441.



Scheme 1. Routes for the synthesis of **1**.

should be noted that Kempe has reported the synthesis of the related complex [(Et$_2$N)C(NDipp)$_2$](Im$^{\text{Dipp}}$N)TiCl$_2$, but its reduction chemistry has not been explored.[9]

The reduction of a suspension of **2** in THF with 2.5 equiv of KC$_8$ at −75 °C for 15 h results in the formation of a complicated product mixture from which we were able to isolate single crystals of **1** in trace amounts. We attribute the failure to cleanly reduce **2** to the heterogeneity of the reaction conditions. Accordingly, the treatment of **3**, fully dissolved in THF, with 2.5 equiv of KC$_8$ at low temperature smoothly produces **1** in 84 % yield (Scheme 1).

Complex **1** can be synthesized on a multigram scale and is isolated as a golden-brown solid that is partially soluble in non-polar solvents, such as hexane, but fully soluble in aromatics and Et$_2$O. Crystals of **1** can be grown from a saturated hexane or Et$_2$O solution stored for three days at −25 °C, and its solid-state structure is shown in Figure 1. Most notably, the titanium center is capped by an η^6-bonded aryl substituent of the Im$^{\text{Dipp}}$N ligand with a significantly bent Ti–N–C$_{\text{Im}}$ bond angle and elongated Ti–N$^{\text{Dipp}}$Im bond distance (Ti1–N1–C1 118.8(2)°; Ti1–N1 1.927(2) Å) which accommodates the masking interaction. Inspection of the metrical parameters within the capping arene moiety reveals severe ring distortions indicative of aromaticity loss and presence of a prominent 1,4-cyclohexadiene dianion resonance form. For example, the sp^3-character of the *ipso* and *para* carbons results in a ring fold angle of 10° at their vertex, while the endocyclic bond metrics show two localized π-bonds in the 1,4-positions (Figure 1).[10] Accordingly, the *meta* and *ortho* proton resonances of the masking ring shift upfield from the aromatic region, appearing as a triplet and a doublet at 4.62 and 2.99 ppm, respectively, in the ^{1}H NMR spectrum of **1** in C$_6$D$_6$.[8]

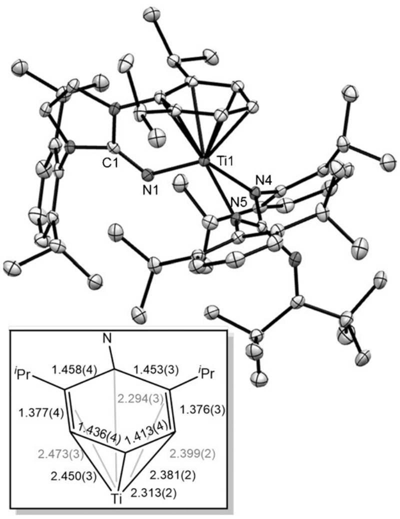
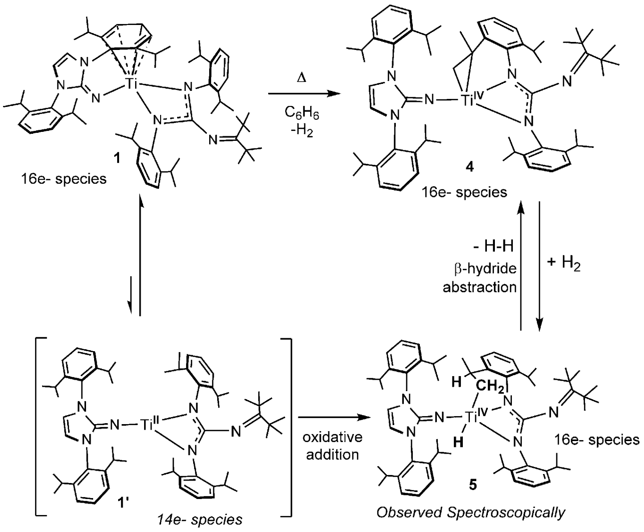


Figure 1. Solid-state structure of **1**·Et$_2$O and corresponding bond distances [Å] within its masking ring. Co-crystallized Et$_2$O removed for clarity.

Consequently, these features are consistent with predominant Ti$^{\text{IV}}$ resonance character,[11] as opposed to a Ti$^{\text{II}}$ canonical form. Nonetheless, masked early-metal complexes have been shown to be rich electron reservoirs of which **1** is no exception.[12]

Complex **1** can be stored indefinitely as a solid or in non-polar solutions at −25 °C. Yet, at room temperature, benzene solutions of **1** are observed to slowly transform to a new, diamagnetic product over the course of many days.[8] Warming these solutions to 60 °C accelerates the transformation resulting in complete conversion within hours, the product of which we have identified as the intramolecularly cyclometalated (Im$^{\text{Dipp}}$N)[(2,6-^{i}Pr$_2$C$_6$H$_3$N)(2-^{i}PrC$_6$H$_3$-6-(η^2-CH$_3$*CCH$_2$*)-N)C(NC^{t}Bu$_2$)]Ti (**4**) (Scheme 2) via X-ray crystallographic (Figure 2) and NMR spectral analyses.



Scheme 2. Proposed formation of **4** via a Ti$^{\text{II}}$ intermediate.

Complex **4** exhibits many salient features. For instance, aromaticity is restored to the once-masking aryl group of the Im$^{\text{Dipp}}$N ligand, traded in place for the intramolecular C–H activation of the guanidine ligand. Specifically, two of the carbon atoms from a flanking isopropyl group of the guanidine are seen to engage the titanium in an η^2-interaction. The Ti–C (Ti1–C8 2.141(2) and Ti1–C9 2.008(2) Å) and C–C

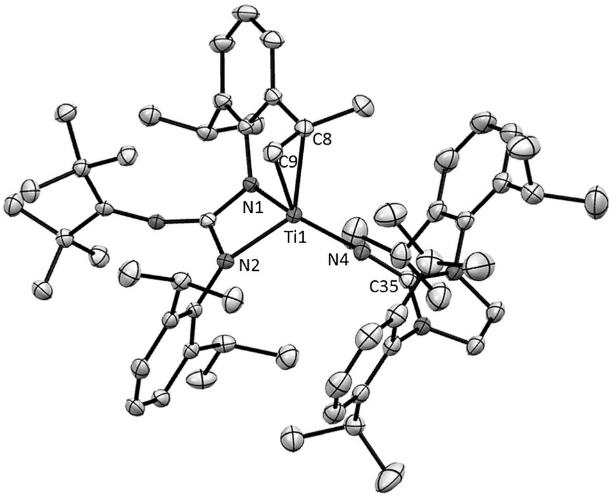
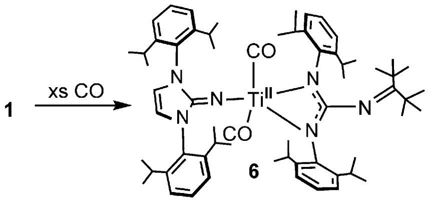


Figure 2. Solid-state structure of $\mathbf{4}\cdot C_6H_{14}$. Hexane solvate not shown.

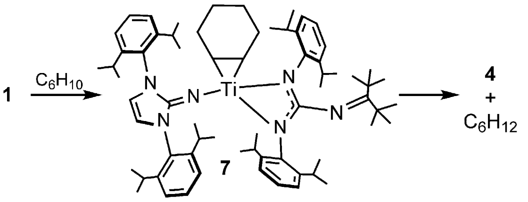
(C8–C9 1.476(3) Å) bond distances are consistent with that of a Ti^{IV} metallacyclopropane,[13] indicating partial dehydrogenation of the alkyl moiety via formal loss of H_2. The proton resonances of the diastereotopic hydrogen atoms of the metallacyclopropane η^2-(Me-*C*-*CH*$_2$) fragment appear as two doublets at 3.03 and 2.66 ppm in a 1:1 ratio in the ^1H NMR spectrum.

Following the transformation of **1** to **4** by NMR spectroscopy, the presence of an intermediate can be detected in trace amounts. This species is unstable and fully converts to **4** with time. We postulated that this intermediate was the Ti^{IV} product $(Im^{Dipp}N)[(2,6\text{-}^iPr_2C_6H_3N)(2\text{-}^iPrC_6H_3\text{-}6\text{-}(\eta^1\text{-}CH_2CH\text{-}CH_3)N)C(NC^tBu_2)]TiH$ (**5**) (Scheme 2) formed by oxidative addition of a C–H bond of a pendant isopropyl methyl group. In an attempt to trap **5** by reversing the reaction equilibrium, a C_6D_6 solution of **4** was exposed to an atmosphere of H_2 at ambient temperature. This generates **5** in nearly quantitative yield offset by the formation of **1** in small amount (Figure S25 in the Supporting Information)—the latter indicating full reversibility of the C–H activation process from **4** back to **1**. Complex **5** is indefinitely stable in the presence of H_2, but efforts to isolate **5** have been unsuccessful as it quickly converts back to **4** within minutes of removing the H_2 headspace (Figure S26). Nonetheless, we have fully elucidated its solution-phase structure via NMR correlation spectroscopy (COSY, dqCOSY, TOCSY, DEPT-135, HMQC).[8] The NMR correlation experiments confirmed our initial assignment of **5** as a Ti^{IV} alkyl hydride. In line with this, the ^1H NMR spectrum displays a singlet at 8.60 ppm, which lacks carbon atom correlation in the HMQC spectra, that is attributable to the Ti–H hydride resonance (Figure S29). Based upon these observations and supported by the earlier findings of Rothwell and Wolczanski,[5b–e] we contend, that in solution, **1** is in equilibrium with a coordinatively and electronically unsaturated d^2-Ti^{II}, 14-electron species (**1′**) that oxidatively adds across a dangling C–H bond, yielding **4** upon the concomitant release of H_2 via β-hydride abstraction (Scheme 2). In support of this, exposure of **2** to CO results in the quantitative formation of the Ti^{II} carbonyl complex $(Im^{Dipp}N)(^{ket}guan)Ti(CO)_2$ (**6**) [Eq. (1)] (Figure S4), unequivocally demonstrating the ability of **2** to perform as a Ti^{II} synthon.



(1)

In a preliminary exploration of the chemistry of **1** with unsaturated molecules, addition of excess cyclohexene to a C_6D_6 solution results in the formation of a new product which we have formulated as the metallacycle $(Im^{Dipp}N)(^{ket}guan)Ti(\eta^2\text{-}C_6H_{10})$ (**7**) [Eq. (2)].[8] Curiously, while olefin and alkynyl adducts of titanium are well known and isolable,[14] **7** is not persistent in solution and slowly converts to **4** with concomitant evolution of 1 equiv of cyclohexane over two days at room temperature.[8] Even more surprisingly, we have found that solutions of **7** are unstable under reduced pressure and quantitatively give **4** upon drying in vacuo.



(2)

Remarkably, in these reactions, the olefin mediates the clean conversion of **1** to **4** by acting as a terminal hydrogen acceptor. As such, this hydrogenation chemistry is effectuated through a C–H bond activation pathway, the source of the hydrogen being the C–H bonds of the aliphatic isopropyl group. This stands in stark contrast to the long established hydrogenation chemistry of unsaturated hydrocarbons by titanocenes which necessitates external hydrogen sources.[15] The transfer hydrogenation that occurs between **1** and cyclohexene is notable as this reactivity is akin to that known of the late-metals,[1c,16] and to the best of our knowledge, is the first instance of such chemistry with titanium or any other early-metal.

These observations prompted us to investigate the ability of our system to perform catalytic hydrogenation chemistry. Treatment of **5** with 5 equiv of cyclohexene under 1 atm of H_2 results in full hydrogenation to cyclohexane within five days at room temperature (Figure S34). Based upon this, the catalytic activity of our system towards other unsaturated hydrocarbons was examined under mild conditions (2 atm H_2, 55 °C), and the results are summarized in Table 1.[8] Of note, using 1,5-cyclooctadiene (1,5-COD) as a substrate led to the expected formation of cyclooctane and cyclooctene after short reaction times; however, prolonging the experiment appears to instead favor 1,5-COD to 1,3-COD isomeriza-

Table 1: Catalytic hydrogenation of select unsaturated hydrocarbons.[a]

Substrate	Equiv.[b]	Product	t [h][c]	TON[d]	TOF [h^{-1}][e]
cyclohexene	77	cyclohexane	3.5	5	1.4
cycloheptene	45	cycloheptane	5	2	0.4
cyclooctene	70	cyclooctane	2	4	2
1,5-COD	24	cyclooctane/ cyclooctene	5	1/5	0.2/1
1,5-COD	24	cyclooctane/ cyclooctene/ 1,3-COD	17	2/8/12	0.1/0.5/0.7
1-octene	32	–			
1-octyne	22	–			

[a] Reactions conducted using solutions of **1** (0.1 mmol, 14 mM, 0.7 mL) with >20 equiv of substrate at 55 °C under H_2 (2 atm) in C_6D_6. [b] Substrate equivalents. [c] Reaction time. [d] Turnover number. [e] Average turnover frequency.

tion.[17] The reason behind this phenomenon is not known at present and is currently under investigation.

In comparison to other titanocene hydrogenation catalysts,[15] the catalytic activity of our system is admittedly low with the best performance observed with cyclic olefins. Nonetheless, our results demonstrate that our system can effect alkene hydrogenation using modest H_2 pressures and temperatures, and further optimization of the reaction conditions or modifications to the ligand manifold may improve catalytic competency.[18] At this time, the mechanism by which this chemistry occurs, whether by transfer hydrogenation or other classic pathways, is not known, but we have discovered that regardless of catalyst source—i.e., starting with either **1**, **4** or **5**—the presence of **5** in the reaction mixtures is critical for successful hydrogenation catalysis.

In conclusion, using a strongly electron-donating, three-coordinate and sterically encumbered N-donor ligand base, we have succeeded in synthesizing the reduced titanium complex (^{ket}guan)(η^6-Im^{Dipp}N)Ti (**1**) which features a metal center capped by a pendant arene group of the Im^{Dipp}N ligand. While bond metrics support a formal Ti^{IV} oxidation state assignment, **1** behaves as a masked form of low-coordinate Ti^{II}. Notably, **1** effects the intramolecular dehydrogenation of a peripheral isopropyl group upon standing in solution to give (Im^{Dipp}N)[(2,6-$^iPr_2C_6H_3N$)(2-$^iPrC_6H_3$-6-(η^2-$CH_3\mathit{CCH_2}$)N)C(NC^tBu_2)]Ti (**4**)—a transformation that can be reversed upon addition of H_2. Spectroscopic evidence points to a rare instance of C(sp^3)–H oxidative addition across titanium as a key step. Moreover, treatment of **1** with cyclohexene gives **4** and cyclohexane via transfer hydrogenation. This dual reactivity is unprecedented for the early-metals, but well-established for the later d-block elements, thus suggesting that our titanium system can mimic the chemical characteristics of late metals. This implies that through judicious molecular design and reduction chemistry, precious-metal type reactivity can be elicited from inexpensive, non-toxic base metals such as titanium. To this end, we are currently exploring the reduction chemistry of related platforms whereby the "reactive" isopropyl groups have been removed in an attempt to evoke intermolecular C–H bond activation chemistry.

Acknowledgements

S.F. thanks the University of Texas at El Paso, NSF PREM Program (DMR-1205302), and the UT STARS award for support of this work.

Keywords: C–H activation · N ligands · reduction · titanium · transfer hydrogenation

How to cite: *Angew. Chem. Int. Ed.* **2016**, *55*, 14101–14105
Angew. Chem. **2016**, *128*, 14307–14311

---

[1] a) D. Baudry, M. Ephritikhine, H. Felkin, R. Holmes-Smith, *J. Chem. Soc. Chem. Commun.* **1983**, 788–789; b) M. J. Burk, R. H. Crabtree, C. P. Parnell, R. J. Uriarte, *Organometallics* **1984**, *3*, 816–817; c) J. Choi, A. H. MacArthur, M. Brookhart, A. S. Goldman, *Chem. Rev.* **2011**, *111*, 1761–1779.

[2] a) R. H. Crabtree, J. M. Mihelcic, J. M. Quirk, *J. Am. Chem. Soc.* **1979**, *101*, 7738–7740; b) R. H. Crabtree, M. F. Mellea, J. M. Mihelcic, J. M. Quirk, *J. Am. Chem. Soc.* **1982**, *104*, 107–113; c) M. J. Burk, R. H. Crabtree, *J. Am. Chem. Soc.* **1987**, *109*, 8025–8032; d) A. H. Janowicz, R. G. Bergman, *J. Am. Chem. Soc.* **1982**, *104*, 352–354.

[3] X. Chen, K. M. Engle, D. H. Wang, J. Q. Yu, *Angew. Chem. Int. Ed.* **2009**, *48*, 5094–5115; *Angew. Chem.* **2009**, *121*, 5196–5217.

[4] R. Waterman, *Organometallics* **2013**, *32*, 7249–7263.

[5] a) M. Tayebani, K. Feghali, S. Gambarotta, G. Yap, *Organometallics* **1998**, *17*, 4282–4290; b) R. E. Lapointe, P. T. Wolczanski, J. F. Mitchell, *J. Am. Chem. Soc.* **1986**, *108*, 6382–6384; c) J. S. Yu, P. E. Fanwick, I. P. Rothwell, *J. Am. Chem. Soc.* **1990**, *112*, 8171–8172; d) B. D. Steffey, L. R. Chamberlain, R. W. Chesnut, D. E. Chebi, P. E. Fanwick, I. P. Rothwell, *Organometallics* **1989**, *8*, 1419–1423; e) P. N. Riley, J. R. Clark, P. E. Fanwick, I. P. Rothwell, *Inorg. Chim. Acta* **1999**, *288*, 35–39; f) J. E. Bercaw, R. H. Marvich, L. G. Bell, H. H. Brintzinger, *J. Am. Chem. Soc.* **1972**, *94*, 1219–1238; g) H. Brintzinger, J. E. Bercaw, *J. Am. Chem. Soc.* **1970**, *92*, 6182–6185; h) L. Messerle, *Chem. Rev.* **1988**, *88*, 1229–1254; i) J. W. Pattiasina, C. E. Hissink, J. L. Deboer, A. Meetsma, J. H. Teuben, *J. Am. Chem. Soc.* **1985**, *107*, 7758–7759; j) M. Tayebani, S. Gambarotta, G. Yap, *Organometallics* **1998**, *17*, 3639–3641.

[6] a) A. Davison, S. S. Wreford, *J. Am. Chem. Soc.* **1974**, *96*, 3017–3018; b) S. I. Troyanov, H. Antropiusová, K. Mach, *J. Organomet. Chem.* **1992**, *427*, 49–55.

[7] a) A. K. Maity, A. J. Metta-Magaña, S. Fortier, *Inorg. Chem.* **2015**, *54*, 10030–10041; b) A. Glöckner, T. Bannenberg, C. G. Daniliuc, P. G. Jones, M. Tamm, *Inorg. Chem.* **2012**, *51*, 4368–4378; c) A. G. Trambitas, J. Yang, D. Melcher, C. G. Daniliuc, P. G. Jones, Z. Xie, M. Tamm, *Organometallics* **2011**, *30*, 1122–1129; d) M. Tamm, D. Petrovic, S. Randoll, S. Beer, T. Bannenberg, P. G. Jones, J. Grunenberg, *Org. Biomol. Chem.* **2007**, *5*, 523–530; e) M. Tamm, S. Randoll, T. Bannenberg, E. Herdtweck, *Chem. Commun.* **2004**, 876–877; f) X. Wu, M. Tamm, *Coord. Chem. Rev.* **2014**, *260*, 116–138; g) T. Ochiai, D. Franz, S. Inoue, *Chem. Soc. Rev.* **2016**, DOI: 10.1039/C1036CS00163G.

[8] See the Supporting Information for Details.

[9] I. Haas, C. Hübner, W. P. Kretschmer, R. Kempe, *Chem. Eur. J.* **2013**, *19*, 9132–9136.

[10] a) O. V. Ozerov, B. O. Patrick, F. T. Ladipo, *J. Am. Chem. Soc.* **2000**, *122*, 6423–6431; b) J. R. Hagadorn, J. Arnold, *Angew. Chem. Int. Ed.* **1998**, *37*, 1729–1731; *Angew. Chem.* **1998**, *110*, 1813–1815; c) D. J. Arney, P. A. Wexler, D. E. Wigley, *Organometallics* **1990**, *9*, 1282–1289.

[11] J. N. Boynton, J.-D. Guo, F. Grandjean, J. C. Fettinger, S. Nagase, G. J. Long, P. P. Power, *Inorg. Chem.* **2013**, *52*, 14216–14223.

[12] B. L. Tran, M. Singhal, H. Park, O. P. Lam, M. Pink, J. Krzystek, A. Ozarowski, J. Telser, K. Meyer, D. J. Mindiola, *Angew. Chem. Int. Ed.* **2010**, *49*, 9871 – 9875; *Angew. Chem.* **2010**, *122*, 10067 – 10071.

[13] M. G. Thorn, J. E. Hill, S. A. Waratuke, E. S. Johnson, P. E. Fanwick, I. P. Rothwell, *J. Am. Chem. Soc.* **1997**, *119*, 8630 – 8641.

[14] a) F. Sato, H. Urabe, S. Okamoto, *Chem. Rev.* **2000**, *100*, 2835 – 2886; b) U. Rosenthal, V. V. Burlakov, P. Arndt, W. Baumann, A. Spannenberg, *Organometallics* **2003**, *22*, 884 – 900; c) S. A. Cohen, P. R. Auburn, J. E. Bercaw, *J. Am. Chem. Soc.* **1983**, *105*, 1136 – 1143.

[15] a) H. S. Lee, H. Y. Lee, *Bull. Korean Chem. Soc.* **2000**, *21*, 451 – 452; b) W. D. Bonds, C. H. Brubaker, E. S. Chandrasekaran, C. Gibbons, R. H. Grubbs, L. C. Kroll, *J. Am. Chem. Soc.* **1975**, *97*, 2128 – 2132; c) R. L. Halterman, K. P. C. Vollhardt, M. E. Welker, D. Blaser, R. Boese, *J. Am. Chem. Soc.* **1987**, *109*, 8105 – 8107; d) J. Pinkas, R. Gyepes, I. Císařová, J. Kubišta, M. Horáček, K. Mach, *Organometallics* **2014**, *33*, 3399 – 3413; e) J. F. Harrod, *Coord. Chem. Rev.* **2000**, *206*, 493 – 531.

[16] a) D. Wang, D. Astruc, *Chem. Rev.* **2015**, *115*, 6621 – 6686; b) G. Brieger, T. J. Nestrick, *Chem. Rev.* **1974**, *74*, 567 – 580.

[17] a) M. J. Butler, A. J. P. White, M. R. Crimmin, *Angew. Chem. Int. Ed.* **2016**, *55*, 6951 – 6953; *Angew. Chem.* **2016**, *128*, 7065 – 7067; b) Y. L. Qian, J. Q. Lu, W. H. Xu, *J. Mol. Catal.* **1986**, *34*, 31 – 38.

[18] F. Kallmeier, T. Irrgang, T. Dietel, R. Kempe, *Angew. Chem. Int. Ed.* **2016**, *55*, 11806 – 11809; *Angew. Chem.* **2016**, *128*, 11984 – 11988.

Received: August 1, 2016
Revised: September 12, 2016