JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

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J. Am. Chem. Soc., **Just Accepted Manuscript** • Publication Date (Web): 06 Jun 2017

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Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

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Stable, Yet Highly Reactive Non-classical Iron(II) Polyhydride Pincer Complexes – Z-Selective Dimerization and Hydroboration of Terminal Alkynes

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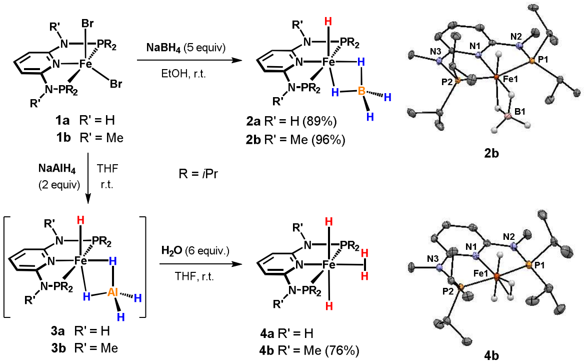
ABSTRACT: The synthesis, characterisation, and catalytic activity of non-classical iron(II) polyhydride complexes containing tridentate PNP pincer-type ligands is described. These compounds of the general formula $[Fe(PNP)(H)_2(\eta^2\text{-}H_2)]$ exhibit remarkable reactivity towards terminal alkynes. They efficiently promote the catalytic dimerization of aryl acetylenes giving the corresponding conjugated 1,3-enynes in excellent yields with low catalyst loadings. When the reaction is carried out in presence of pinacolborane vinyl boronates are obtained. Both reactions take place under mild conditions and are highly chemo-, regio- and stereoselective with up to 99% *Z*-selectivity.

Since the first discovery of a transition metal complex featuring a molecular hydrogen ligand by Kubas *et al* in 1984, dihydrogen complexes have been subject of considerable interest.[1] Among the huge number of well-defined dihydrogen complexes that have been reported over the past three decades, so-called polyhydrides, incorporating at least three hydrogens bound to the metal, have particularly stimulated intense research activities.[2] Apart from interesting structural features and their fluxional behavior, it is the potential loss of H_2 that can afford an unsaturated complex and might allow for the coordination and activation of a variety of other σ-bound molecules. For example, many polyhydride complexes based on Ru, Os, Rh or Ir are well-known to participate in catalytic reactions that involve the activation of H-E (E = C, B, Si) σ-bonds.[3] Among other groups,[4] we have been working on Fe(II) hydrido and dihydrido carbonyl complexes supported by PNP pincer ligands.[5] These complexes proved to be efficient catalysts in hydrogenation and dehydrogenation reactions.[4] Although CO is an inert co-ligand effectively stabilizing the Fe(II) metal center thereby maintaining a low-spin state, it blocks one of the coordination sites that might otherwise be available for the coordination and activation of incoming substrates. Moreover, as a strong π-acceptor, CO withdraws electron density from the metal center severely changing the basicity of hydride ligands.[6] Here, we describe a series of Fe(II) hydride complexes featuring η^2-BH_4, η^2-AlH_4, and η^2-H_2 co-ligands supported by PNP pincer ligands with a 2,6-diaminopyridine scaffold in which the phosphorous donors are connected via *N*-H or *N*-Me linkers to the pyridine ring that lack a supporting CO ligand. In particular Fe(II) dihydride dihydrogen complexes turned out to be stable enough to be isolated and yet highly active catalysts for the dimerization and hydroboration of terminal alkynes to yield Z-selectively enynes and vinylboronates, respectively. Since iron salts are readily available, inexpensive, and environmentally benign, the development of iron-based catalysts for organic transformations is currently a very active area of research.[7]

Scheme 1. Preparation of Iron Hydride Complexes and X-ray Structures of 2b and 4b



Treatment of $[Fe(PNP)Br_2]$ with excess $NaBH_4$ in ethanol afforded the hydrido borohydride complexes $[Fe(PNP)(H)(\eta^2\text{-}BH_4)]$ in 89 and 96 % isolated yields (Scheme 1). Milstein and coworkers reported a related hydrido borohydride complex $[Fe(PNP^{CH2})(H)(\eta^2\text{-}BH_4)]$ based on a lutidine ligand scaffold.[8] The terminal hydride ligands give rise to sharp triplet resonances (**2a**: -21.63 ppm, **2b**: -22.4 ppm), while two broad signals were found for the bridging (**2a**: -11.43/-27.32 ppm, **2b**: -12.04/-26.92 ppm) and another broad resonance in the positive spectral region for the non-coordinating borohydrides (**2a**: 4.80 ppm, **2b**: 4.76 ppm). A structural view of **2b** is depicted in Scheme 1. These compounds turned out to be surprisingly stable and unreactive towards various substrates including aldehydes, ketones and olefins.

In order to obtain more reactive species we envisaged the synthesis of analogue aluminum hydrides. Addition of 2 equiv of $NaAlH_4$ to a suspension of $[Fe(PNP)Br_2]$ in THF lead to the formation two novel compounds, tentatively assigned as hydrido alanate complexes $[Fe(PNP)(H)(\eta^2\text{-}AlH_4)]$ (**3**). This reaction is essentially quantitative as monitored by NMR spectroscopy. The $^{31}P\{^1H\}$ NMR spectra exhibit singlet resonances at 164.3 (**3a**) and 181.3 ppm (**3b**). Two broad signals (**3a**: -11.71/-25.12 ppm, **3b**: -

12.33/-24.47 ppm) as well as a slightly broadened triplet resonance (**3a**: -13.79 ppm, **3b**: -14.47 ppm) were found in the hydride region of the ^{1}H NMR spectra which strongly resemble those of the corresponding hydrido borohydride complexes. The handling of complexes **3** appeared to be extremely difficult, as they tend to decompose under formation of various intractable species upon removal of the solvent. Moreover, these species are highly sensitive towards moisture. Addition of water to THF solutions of **3a** and **3b** resulted in an immediate evolution of dihydrogen accompanied by the precipitation of aluminum salts together with the formation of well-defined complexes of the general formula $[Fe(PNP)(H)_2(\eta^2\text{-}H_2)]$ (Scheme 1). Complex **4b** could be isolated in pure form in 76% isolated yield upon removal of the solvent in a slight stream of H_2 (decomposition takes place under vacuum), while all attempts to isolate **4a** failed. This might be attributed to the presence of the acidic *N*-H moieties interacting with the basic hydride ligands. It is interesting to note that Chirik and co-workers observed the formation of the related complex $[Fe(PNP^{CH2})(H)_2(\eta^2\text{-}H_2)]$ obtained by displacement of a dinitrogen ligand in *cis*-$[Fe(PNP^{CH2})(H)_2(N_2)]$ under an atmosphere of dihydrogen.[9] However, a definitive characterization was hampered by the insufficient stability of this species, which, in analogy to **4a**, might be caused by the influence of the rather acidic CH_2 spacer groups. A related nonclassical Ru-polyhydride pincer complex $[Ru(PNP)(H)_2(\eta^2\text{-}H_2)]$ (PNP = 1,3-bis(di-*tert*-butylphosphinomethyl)pyridine) was reported recently by Leitner *et al.*[10] This complex was found to catalyze the addition of pinacolborane to terminal alkynes to yield selectively Z-vinylboronates. It has to be noted that Aresta *et al*[11] and the groups of Crabtree[12] and Caulton[13] described polyhydride complexes of the type $Fe(H)_2(\eta^2\text{-}H_2)(L)_3$ (L = tertiary phosphines). These molecules are highly fluxional and only one ^{1}H NMR signal was observed for all four metal-bound hydrogens even at low temperature. Most other nonclassical dihydrogen iron complexes are of the type $[Fe(L_4)(H)(\eta^2\text{-}H_2)]$ containing only one hydride ligand in conjunction with bi- tri-, and tetradentate ligands (L_4).[2d,6a,14] The solid state structure of **4b** was determined by single-crystal X-ray diffraction (Scheme 1) unequivocally establishing the *trans* arrangement of the hydride ligands. The data were of sufficient quality such that all of the hydrogens were located and refined.

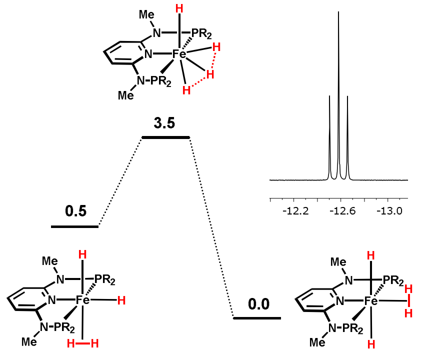


Figure 1. Free Energy Profile (in kcal/mol) Calculated (DFT) for the Interconversion of *cis*- and *trans*-$[Fe(PNP^{Me}\text{-}i Pr)(H)_2(\eta^2\text{-}H_2)]$ (**4b**). Inset: ^{1}H NMR Spectrum of **4b** (hydride region, 400 MHz, THF-d_8, 25°C).

Complexes **4** give rise to singlet resonances at 172.3 (**4a**) and 196.8 ppm (**4b**) in the $^{31}P\{^{1}H\}$ NMR spectrum as well as triplet resonances at -12.06 (**4a**) and -12.58 ppm (**4b**) in the ^{1}H NMR spectrum that both integrate to four hydrogen atoms (Figure 1). Owing to the fast exchange between classical and non-classical hydrides even at low temperature, it was not possible to determine separate resonance frequencies for the individual hydride ligands. DFT calculations[15] reveal that *trans*-$[Fe(PNP)(H)_2(\eta^2\text{-}H_2)]$ is slightly more stable by 0.5 kcal/mol than the respective *cis*-isomer. The transition state for their interconversion requires merely 3.5 kcal/mol being in line with the observed fluxional behavior even at low temperature. To further establish the nature of the hydride ligands, the minimum relaxation time T_1 (min) was measured with a 400 MHz NMR spectrometer. The T_1 (min) values for **4a** and **4b** were determined as 35 ms at -65°C and 39 ms at -80°C, respectively (the temperature-dependent evolution of T_1 is provided in the ESI). These values are typical for coordinated dihydrogen molecules,[2d] which is also confirmed by X-ray crystallography and DFT calculations where H-H bond distances of 0.97 and 0.90 Å, respectively, are obtained.

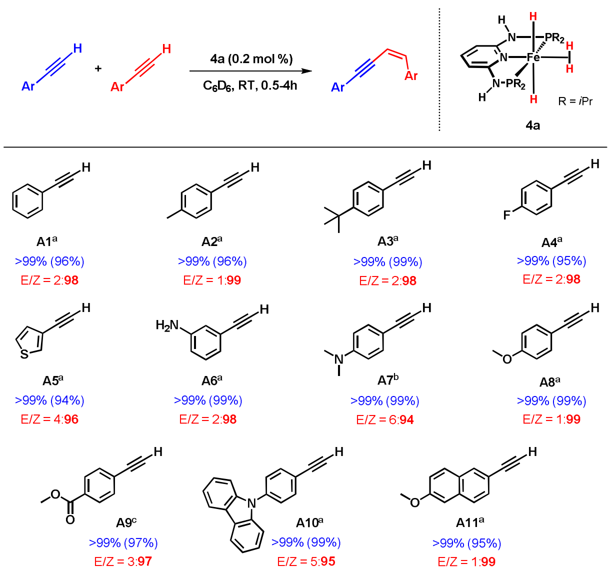
Since Fe borohydride and Ru polyhydride complexes were found to be active catalysts for the *Z*-selective head-to-head dimerization[16,17] and hydroboration[10] of terminal alkynes, it was of interest to us to study these transformations with the Fe catalysts **2** and **4**. Initial tests were carried out using HC≡CPh in benzene-d_6 and the progress of the reaction was continuously monitored by ^{1}H NMR. While the reactivity of **2a** (2 mol %) is comparable to Milstein's catalyst $[Fe(PNP^{CH2})(H)(\eta^2\text{-}BH_4)]$[8,16] which catalyzes also the dimerization of terminal alkynes to afford enynes with high Z selectivity (reaction time 12-15 h), **2b** was found to be much less active requiring up to 40 h in order to achieve quantitative formation of the product. On the other hand, the novel polyhydrides **4** exhibited a strongly enhanced catalytic activity. Using merely 0.2 mol% of **4a** under otherwise identical conditions, the starting material is converted to the respective *Z*-1,3-enyne within 30 min, while with **4b** the reaction was completed within 3 h.

On the basis of these initial results, we investigated the scope and limitations of the polyhydride pre-catalysts using various substrates (Table 1). In presence of 0.2 mol% of the *in situ* generated complex **4a** several aryl acetylenes were quantitatively converted into the corresponding enynes within 30 min at room temperature. A significantly lower reaction rate was observed for 4-ethynyl-N,N-dimethylaniline, apparently caused by the strong electron donating group in the *para*-position. All products could be isolated in high yields with 93-99% *Z*-selectivity. Moreover, the catalyst tolerates a wide range of functional groups including amines, esters and halides. On the other hand, aliphatic acetylene substrates as well as internal alkynes could not be converted.

We then investigated the reactivity of the polyhydride complexes **4** in presence of boranes. Addition of excess $BH_3 \cdot THF$ to a solution of **4b** resulted in the formation of the borohydride complex **2b** (Scheme 2). The respective complex $[Fe(PNP^{Me}\text{-}i Pr)(H)(\eta^2\text{-}H_2Bpin\}]$ (**5**) was obtained in 66% isolated yield when **4b** was reacted with pinacolborane. A structural view of **5** is depicted in Scheme 2. The related Ru complex $[Ru(PNP)(H)\{(\mu\text{-}H)_2Bpin\})]$ was reported by Leitner *et al* being also catalytically active for the hydroboration of terminal alkynes.[10]

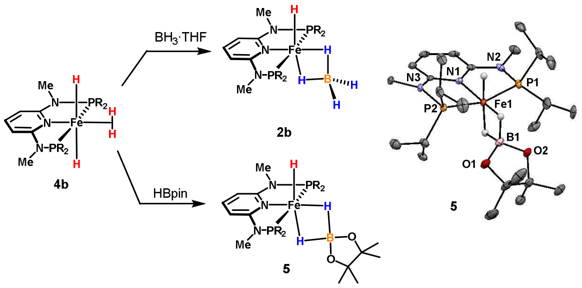
When HC≡CPh was added to a solution of **4b** or **5** (0.4 mol%) containing an equimolar amount of pinacolborane with respect to the alkyne, hydroboration of the terminal C-C triple bond was observed affording the respective vinyl boronate within 3 h. The reaction proceeded again with high *Z*-selectivity. This is remarkable since only a few systems are known that catalyze the *Z*-selective hydroboration of terminal alkynes.[10,18] The first base metal catalyzed hydroboration of terminal alkynes was recently described by Chirik and co-workers based on a bis(imino)pyridine Co catalyst.[19] In the case of **4a** catalyst deactivation occurs after a short time, which is apparently caused by the reaction of the borane with the NH linker of the PNP ligand. The borane complex **2b** is completely inactive in this reaction. DFT calculations on **2b** and **5** indicate that H_2Bpin is a better donor than BH_4 and forms quite stronger Fe-H bonds. For **5**, d(Fe-HB) = 1.57 and 1.63 Å (Wiberg index (WI) = 0.31, 0.17); for the **2b**, d(Fe-HB) = 1.67 and 1.70 Å (WI = 0.24, 0.13). As consequence, the metal is significantly electron richer in **5** (C_{Fe} = -0.42) than in **2b** (C_{Fe} = -0.28), and the Fe-hydride bond is weaker in **5**: WI = 0.56, vs. WI = 0.62 in **2b**, in line with the severe differences in reactivity.

Table1. Z-Selective Dimerization of Terminal Alkynes Catalyzed by 4a



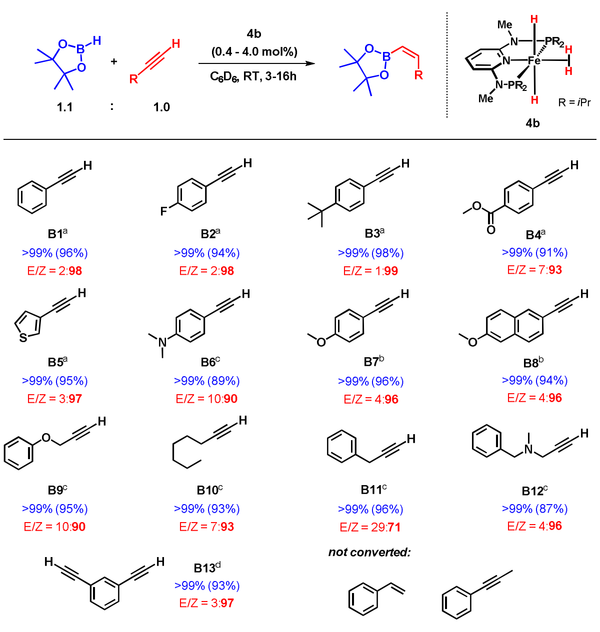
[a]Conditions: alkyne (1.0 mmol), **4a** (0.2 mol %, 50 µL of a 40 mM stock solution in THF), C_6D_6 (1 mL), r. t., 30 min, conversion and selectivity determined by ^{1}H NMR, isolated yields given in parenthesis; [b]4 h reaction time; [c]THF (2.0 mL) used as solvent.

Scheme 2. Reactions of 4b with Boranes and X-ray structure of 5.



Various substrates were tested in this reaction. In contrast to the hydroalkynylation, even aliphatic as well as propargylic substrates could be converted, which, however, required higher catalyst loadings and extended reaction times (Table 2). In most cases essentially quantitative conversion could be reached and the boronic esters could be isolated in high to excellent yields. The hydroboration is chemo-, regio- and stereoselective for terminal alkynes, since internal C-C triple bonds and olefins remain unaffected. For example, using phenyl acetylene in presence of an equimolar amount of 2-phenyl-1-propylene or styrene, only the terminal alkyne has been converted.

Table 2. Z-Selective Hydroboration of Terminal Alkynes Catalyzed by 4b



[a]Conditions: alkyne (1.0 mmol), HBpin (1.1 mmol), **4b** (0.4 mol %, 100 µL of a 40 mM stock solution in THF), C_6D_6 (1 mL), r. t., 3 h, conversion and selectivity determined by ^{1}H NMR, isolated yields given in parenthesis; [b]0.8 mol % of **4b**; [c]4.0 mol % of **4b**, 16 h; [d]0.8 mol % of **4b**, 2.2 mmol HBpin.

In conclusion, we describe here the synthesis and characterization of novel iron(II) polyhydride complexes that are supported by a PNP pincer ligand. These compounds are conveniently generated *in situ* from the corresponding hydrido alanate complexes by the addition of water. Along with the related hydrido borohydride complexes these compounds are catalysts for the regio- and stereoselective head-to-head dimerization of terminal alkynes giving enynes in high yields with up to 99% *Z*-selectivity. A comparison of the catalytic activity revealed a remarkable increase of the reaction rates in case of the novel polyhydrides. Moreover, these compounds are even capable of catalyzing the hydroboration of terminal alkynes in the presence of pinacolborane. Also this reaction exhibits a high degree of chemo-, regio- and stereoselectivity. The vinylboronates are obtained in high yields reaching a *Z*-selectivity between 90-99% for most substrates. For both reactions, the reactivity and selectivity may suggest that the underlying mechanisms involves vinylidene intermediates.[10,14,15] Detailed mechanistic experimental and theoretical studies, however, as well as further experimental studies to extend the scope of alkyne functionalizations are currently underway.

ASSOCIATED CONTENT

Supporting Information

The supporting information is available free of charge on the ACS Publications website at DOI: xxxxx

X-ray crystallographic data (CIF)
Synthetic procedures, ^{1}H, ^{13}C{^{1}H}, and ^{31}P{H} NMR spectra of all compounds, computational details and crystallographic data (PDF)
Optimized Cartesian coordinates for DFT-optimized structures (XYZ)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

NG and KK gratefully acknowledge the Financial support by the Austrian Science Fund (FWF) (Project No. P28866-N34). AMM and LV thank Dra. M. João Ferreira and Prof. Jose Ascenso for their valuable help with NMR measurements, and FCT, Portugal, for funding (UID/QUI/00100/2013 and SFRH/BPD/86815/2012)

REFERENCES

(1) Kubas, G. J.; Ryan, R. R.; Swanson, B. I.; Vergamini, P. J.; Wasserman, H. J. *J. Am. Chem. Soc.* **1984**, *106*, 451-452.

(2) (a) Kubas, G. J. *Metal Dihydrogen and σ-Bond Complexes*, Kluwer Academic Plenum Publishers, New York, 2001. (b) Kubas, G. J. *Chem. Rev.* **2007**, *107*, 4152-4205. (c) Kubas, G. J. *Proc. Natl. Acad. Sci.* **2007**, *104*, 6901-6907. (d) Crabtree, R. H. *Chem. Rev.* **2016**, *116*, 8750-8769.

(3) Esteruelas, M. A.; López, A. M.; Oliván, M. *Chem. Rev.* **2016**, *116*, 8770-8847.

(4) (a) Langer, R.; Leitus, G.. Ben-David, Y.; Milstein, D. *Angew. Chem., Int. Ed.* **2011**, *50*, 2120-2124. (b) Langer, R.; Diskin-Posner, Y.; Leitus, G.; Shimon, L. J. W.; Ben-David, Y.; Milstein, D. *Angew. Chem., Int. Ed.* **2011**, *50*, 9948-9952. (c) Zell, T.; Butschke, B.; Ben-David, Y.; Milstein, D. *Chem. Eur. J.* **2013**, *19*, 8068-8072. (d) Zell, T.; Ben-David, Y.; Milstein, D. *Angew. Chem. Int. Ed.* **2014**, *53*, 4685-4689. (e) Garg, J. A.; Chakraborty, S.; Ben-David, Y.; Milstein, D. *Chem. Commun.* **2016**, *52*, 5285-5288. (f) Alberico, E.; Sponholz, P.; Cordes, C.; Nielsen, M.; Drexler, H.-J.; Baumann, W.; Junge, H.; Beller, M. *Angew. Chem. Int. Ed.* **2013**, *52*, 14162-14166. (g) Bornschein, C.; Werkmeister, S.; Wendt, B.; Jiao, H.; Alberico, E.; Baumann, W.; Junge, H.; Junge, K.; Beller, M. *Nat. Commun.* **2014**, *5*, 4111. (h) Werkmeister, S.; Junge, K.; Wendt, B.; Alberico, E.; Jiao, H.; Baumann, W.; Junge, H.; Gallou, F.; Beller, M. *Angew. Chem. Int. Ed.* **2014**, *53*, 8722-8726. (i) Bielinski, E. A; Lagaditis, P. O.; Zhang, Y.; Mercado, B. Q.; Würtele, C.; Bernskoetter, W. H.; Hazari, N.; Schneider, S. *J. Am. Chem. Soc.* **2014**, *136*, 10234-10237. (j) Chakraborty, S.; Brennessel, W. W.; Jones, W. D. *J. Am. Chem. Soc.* **2014**, *136*, 10234-10237. (k) Chakraborty, S.; Lagaditis, P. O.; Förster, M.; Bielinski, E. A.; Hazari, N.; Holthausen, M. C.; Jones, W. D.; Schneider, S. *ACS Catal.* **2014**, *4*, 3994-4003. (l) Xu, R.; Chakraborty, S.; Bellows, S. M.; Yuan, H.; Cundari, T. R.; Jones, W. D. *ACS Catal.* **2016**, *6*, 2127-2135. (m) Peña-López, M.; Neumann, H.; Beller, M. *ChemCatChem* **2015**, *7*, 865-871. (n) Zhang, Y.; MacIntosh, A. D.; Wong, J. L.; Bielinski, E. A.; Williard, P. G.; Mercado, B. Q.; Hazari, N.; Bernskoetter, W. H. *Chem. Sci.* **2015**, *6*, 4291-4299. (o) Bielinski, E. A.; Förster, M.; Zhang, Y.; Bernskoetter, W. H.; Hazari, N.; Holthausen, M. C. *ACS Catal.* **2015**, *5*, 2404-2415. (p) Glüer, A.; Förster, M.; Celinski, V. R.; Schmedt auf der Günne, J.; Holthausen, M. C.; Schneider, S. *ACS Catal.* **2015**, *5*, 7214-7217. (q) Rezayee, N. M.; Samblanet, D. C.; Sanford, M. S. *ACS Catal.* **2016**, *6*, 7214-7217.

(5) (a) Gorgas, N.; Stöger, B.; Veiros, L. F.; Pittenauer, E.; Allmaier, G.; Kirchner, K. *Organometallics* **2014**, *33*, 6905-6914. (b) Gorgas, N.; Stöger, B.; Veiros, L. F.; Kirchner, K. *ACS Catal.* **2016**, *6*, 2664-2672. (c) Bertini, F.; Gorgas, N.; Stöger, B.; Peruzzini, M.; Veiros, L. F.; Kirchner, K.; Gonsalvi, L. *ACS Catal.* **2016**, *6*, 2889-2893. (d) Mellone, I.; Gorgas, N.; Bertini, F.; Peruzzini, M.; Kirchner, K.; Gonsalvi, L. *Organometallics* **2016**, *35*, 3344-3349.

(6) (a) Morris, R. H. *Chem. Rev.* **2016**, *116*, 8588–8654. (b) Wiedner, E. S.; Chambers, M. B.; Pitman, C. L.; Bullock, R. M.; Miller, A. J. M.; Appel, A. M. *Chem. Rev.* **2016**, *116*, 8655-8692.

(7)(a) Bauer, I.; Knölker, H.-J. *Chem. Rev.* **2015**, *115*, 3170-3387. (b) Fürstner, A. *ACS Cent. Sci.* **2016**, *2*, 778-789. (c) Robinson, S. J. C.; Heinekey, D. M. *Chem. Commun.* **2017**, *53*, 669-676.

(8) Langer, R.; Iron, M. A.; Konstantinovski, L.; Diskin-Posner, Y.; Leitus, G.; Ben-David, Y.; Milstein, D., *Chem. Eur. J.* **2012**, *18*, 7196-7209.

(9) Trovitch, R. J.; Lobkovsky, E.; Chirik, P. J. *Inorg. Chem.* **2006**, *45*, 7252-7260.

(10) Gunanathan, C.; Hölscher, M.; Pan, F.; Leitner, W. *J. Am. Chem. Soc.* **2012**, *134*, 14349-14352.

(11)Aresta, M.; Giannoccaro, P.; Rossi, M.; Sacco, A. *Inorg. Chim. Acta* **1971**, *5*, 115-118.

(12)Crabtree, R. H.; Hamilton, D. G. *J. Am. Chem. Soc.* **1986**, *108*, 3124-3125.

(13) Van der Sluys, L. S.; Eckert, J.; Eisenstein, O.; Hall, J. H.; Huffman, J. C.; Jackson, S. A.; Koetzle, T. F.; Kubas, G. J.; Vergamini, P.; J.; Caulton, K. G. *J. Am. Chem. Soc.* **1990**, *112*, 4831-4841.

(14) (a) Morris, R. H.; Sawyer, J. F.; Shiralian, M.; Zubkowski, J. *J. Am. Chem. Soc.* **1985**, *107*, 5581-5582. (b) Bianchini, C.; Peruzzini, M.; Zanobini, F. *J. Organomet. Chem.* **1988**, *354*, C19-22. (c) Fong, H.; Moret, M.-E.; Lee, Y.; Peters, J. C. *Organometallics* **2013**, *32*, 3053-3062.

(15) (a) Parr, R. G.; Yang, W. *Density Functional Theory of Atoms and Molecules*, Oxford University Press, New York, **1989**; (b) Calculations performed at the M06/(6-311++G**, PCM)//PBE0/(SDD, 6-31G**) level using the GAUSSIAN 09 package.

(16) (a) Jia, G.; Meek, D. W.; Gallucci, J. C. *Organometallics* **1991**, *10*, 403-410. (b) Conifer, C.; Gunanathan, C.; Rinesch, T.; Hölscher, M.; Leitner, W. *Eur. J. Inorg. Chem.* **2015**, *2015*, 333-339.

(17) Rivada-Wheelaghan, O.; Chakraborty, S.; Shimon, L. J. W.; Ben-David, Y.; Milstein, D. *Angew. Chemie Int. Ed.* **2016**, *55*, 6942-6945.

(18) Ohmura, T.; Yamamoto, Miyaura, N. *J. Am. Chem. Soc.* **2000**, *122*, 4990-4991.

(19) Obligacion, J. V.; Neely, J. M.; Yazdani, A. N.; Pappas, I.; Chirik, P. J. *J. Am. Chem. Soc.* **2015**, *137*, 5855-5858.

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