# Normal-to-Abnormal Rearrangement and NHC Activation in Three-Coordinate Iron(II) Carbene Complexes

Benjamin M. Day,[†] Thomas Pugh,[†] Daniël Hendriks,[||] Célia Fonseca Guerra,[||] David J. Evans,[‡] F. Matthias Bickelhaupt,*[,||,#] and Richard A. Layfield*[,†]

[†]School of Chemistry, The University of Manchester, Manchester, M13 9PL, U.K.

[‡]Department of Chemistry, University of Hull, Hull, HU6 7RX, U.K.

[||]Department of Theoretical Chemistry, Amsterdam Center for Multiscale Modeling, VU University Amsterdam, NL-1081 HV Amsterdam, The Netherlands

[#]Radboud University Nijmegen, Institute for Molecules and Materials, NL-6525 AJ Nijmegen, The Netherlands

**S** *Supporting Information*

**ABSTRACT:** The 'normal' three-coordinate iron−NHC complex $[(IPr)Fe(N'')_2]$ (N″ = N(SiMe₃)₂) rearranges to its abnormal NHC analogue $[(aIPr)Fe(N'')_2]$ (6) on heating, providing a rare abnormal iron−aNHC complex, and the first such three-coordinate complex. The *tert*-butyl-substituted complex $[(I^tBu)Fe(N'')_2]$ (4) undergoes a thermal decomposition that has not previously been observed in iron−NHC chemistry, resulting in the bis(imidazole) complex $[(^tBuIm)_2Fe(N'')_2]$ (7). A mechanism that involves consecutive C−H and C−N activation is proposed to account for the formation of 7.

Iron complexes of N-heterocyclic carbene (NHC) ligands are currently attracting much attention,[1] yet their chemistry is still surprisingly under-developed compared to late transition-metal NHC chemistry.[2] Notwithstanding the considerable fundamental interest in iron−NHC chemistry, recent studies have dealt with applications in biomimetic chemistry and, in particular, catalysis.[3−5] In many instances, progress in iron chemistry has been enabled specifically through the use of NHC ligands, whereas analogous phosphine systems have produced different outcomes.

Three-coordinate iron(II)−NHC complexes have been the focus of recent studies, partly because of the intrinsic interest in low-coordinate iron and also because of their potential applications in catalysis, however stable complexes of the type $[(NHC)FeX_2]$ are still rare. Bulky substituents are typically required to stabilize the three-coordinate iron, with notable examples including a cyclic bent allene iron(II) complex reported by Stephan et al.,[6] and NHC-ligated complexes of the type $[(NHC)FeX_2]$ (X = aryl, benzyl, CH₂SiMe₃).[7,8] We recently reported the three-coordinate iron NHC complexes $[(IPr)Fe(N'')_2]$ (1) and $[(IMes)Fe(N'')_2]$ (2), where N″ = N(SiMe₃)₂, IPr = 1,3-bis(diisopropylphenyl)imidazolylidene), and IMes =1,3-bis(mesityl)imidazolylidene.[9] Although 1 and 2 are stable as solids, density functional theory (DFT) revealed that the Fe−C bond energy decreases dramatically as the steric bulk of the NHC substituents increases. The influence of ligand sterics in these systems was underscored by a study of the model complex $[(H_2Im)Fe(N'')_2]$ (3), containing an unsub-

stituted imidazolylidene ligand, which produced more substantial Fe−C bond dissociation energies.

We now report on the reactivity and thermal stability of 1 and the new three-coordinate complex $[(I^tBu)Fe(N'')_2]$ (4) (I^tBu = 1,3-bis(*tert*-butyl)imidazol-2-ylidene). In the case of 1, a remarkably facile rearrangement to give the first three-coordinate abnormal iron carbene complex $[(aIPr)Fe(N'')_2]$ (6) occurs in refluxing toluene. Applying the same conditions to 4 results in a thermal decomposition to give the tetrahedral bis(*tert*-butylimidazole) complex $[(^tBuIm)_2Fe(N'')_2]$ (7). Our study provides the first evidence that the NHC ligands in three-coordinate iron−NHC complexes are capable of substituent-dependent 'non-innocent' reactivity.

In light of the weak Fe−C bond in 1, our initial hypothesis was that the Fe−C bond could be strengthened by modifying the amido ligand framework, while retaining a three-coordinate iron environment. Thus, we targeted complexes in which the iron center is part of a moderately bulky, strained, four-membered chelate ring, i.e., 5 in Scheme 1. However, whereas transamination reactions of Fe(N″)₂ are well-known,[10] 1 does not react with *N,N′*-dimesityl-1,1-dimethylsilanediamine.[11] When conducted at room temperature, only starting materials are recovered, but refluxing 1 in toluene for three hours

**Scheme 1**
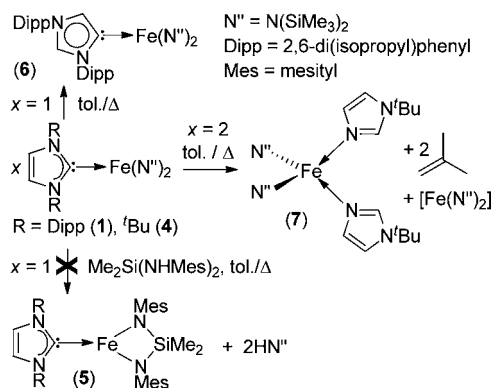


Received: August 19, 2013
Published: August 26, 2013

produces a rearrangement from the C2-bonded, normal NHC (nNHC) complex to the corresponding C5-bonded abnormal NHC (aNHC) complex **6** (Scheme 1). The possible influence of $Me_2Si(NHMes)_2$ in the rearrangement was excluded by refluxing **1** alone in toluene and again observing the formation of **6**.

Complex **6** forms as green crystals, and X-ray crystallography revealed a planar three-coordinate iron(II) center, with an Fe–C bond length of 2.117(2) Å and Fe–N(3) and Fe–N(4) bond lengths of 1.949(2) and 1.974(2) Å, respectively (Figure 1).
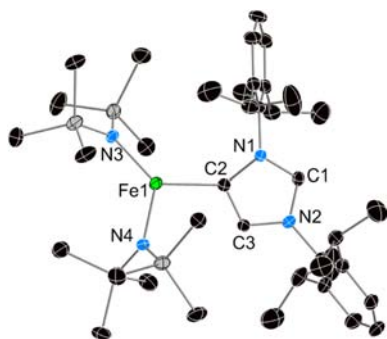


**Figure 1.** Molecular structure of **6** (50% thermal ellipsoids).

The lack of a bulky substituent on C(3) results in a relatively wide C(2)–Fe–N(3) angle of 129.83(7)°, whereas the C(2)–Fe–N(4) angle is much more acute at 104.01(7)°. The N(3)–Fe–N(4) angle is 125.77(7)°, hence the sum of the angles around iron is 359.6°. The carbene carbon C(2) also resides in a low-symmetry environment, with the C(3)–C(2)–Fe, N(1)–C(2)–Fe, and C(3)–C(2)–N(1) angles being 116.4(1)°, 140.8(1)° and 102.4(1)°, respectively. The ¹H NMR spectrum of **6** in toluene at 298 K shows resonances due to C(1)H and C(3)H at 40.09 and −50.76 ppm, respectively (Figure S1). Resonances for the aromatic protons occur at 13.02, 10.18, 9.62, and 8.92 ppm, with the magnetically inequivalent isopropyl protons occurring at 4.73, 0.04, −2.57, −8.73, and −10.20 ppm and the $SiMe_3$ group at −2.03 ppm.

The ⁵⁷Fe Mössbauer spectra of **1** and **6** were collected at 80 K (Figures S2 and S3). The isomer shifts (i.s.) of **1** and **6** are, at 0.60(1) and 0.51(1) mm/s, respectively, typical of three-coordinate iron(II), with $S = 2$ configurations.[12] Notably, the i.s. of the nNHC complexes **1** and **4** (see below) are essentially identical, whereas that of the aNHC complex **6** is significantly lower, by ∼0.10 mm/s. The lower i.s. for **6** can be interpreted as an increase in the population of the iron s-orbitals, which occurs through an increase in σ-donation by the aNHC ligand in **6** relative to the nNHC ligand in **1**. This explanation is consistent with the generally accepted picture proposed by Bertrand et al. that aNHC ligands are much stronger Lewis bases than their nNHC isomers.[13] To the best of our knowledge, this property has not previously been demonstrated by Mössbauer spectroscopy.

Complex **6** is the first three-coordinate abnormal iron NHC complex. It is noteworthy that the 'normal' C2 carbene carbon in **6** (labeled C(1) in Figure 1) is unprotected, i.e., the carbon substituent is a hydrogen atom. Although many stable, C2-unprotected aNHC complexes of late transition metals are known, protection of C2 is often an important consideration for the rational synthesis of such complexes.[14] Indeed, conversion of the aNHC into the nNHC is thermodynamically favored based on relative $pK_a$ values of the respective C–H

bonds.[15] We have found no evidence for the conversion of **6** back into **1**, either in the solid state or in toluene. The development of abnormal NHCs (aNHCs), or so-called mesionic carbenes (MICs), has introduced fascinating new possibilities for organometallic synthesis and catalysis.[14] Metal complexes of aNHC ligands, and in particular of late 4d and 5d transition metals, have been known since 2001, however their use is still much less widespread than that of nNHC ligands, possibly due to the lack of general synthetic routes to isolable aNHCs. Only two iron–aNHC complexes have been structurally characterized.[16,17] Of particular note is Grubbs' di-iron cyclo-octatetraenyl (COT) complex [(aNHC)Fe(μ-COT)Fe(COT)]: the unique properties of the aNHC ligand are thought to enable isolation of an intermediate complex in the NHC-catalyzed transformation of [Fe(COT)₂] into a range of unusual iron–COT complexes.[16]

The rearrangement of **1** to **6** occurs despite the higher energy of abnormal IPr relative to its normal isomer. This process is most likely driven by the relief of steric congestion, whereby the aNHC complex **6** features a carbene carbon that is bonded to only one bulky {N(Dipp)} group, as opposed to two such groups in **1**. Furthermore, the Fe–C bond in **6** is shorter than that in **1** by 0.065 Å, hence it should be stronger and therefore help to drive the rearrangement. To gain insight into the energetics of this process, relativistic DFT computations at the ZORA-BLYP/TZ2P level were carried out, using COSMO to simulate the toluene solvation.[18] Complex **6** is computed to be more stable than **1**, with an exothermic rearrangement energy of $\Delta E_{rear} = -7.6$ kcal/mol. We also find that the 'free' abnormal carbene aIPr, with an energy $E(aIPr)$, is 12.5 kcal/mol less stable than nIPr, with energy $E(nIPr)$. Through eq 1, generalized for any NHC, these results imply that the Fe–C bond dissociation energy in **6** ($BDE_{FeC}^a$) is 20.1 kcal/mol higher than that in **1** ($BDE_{FeC}^n$).

$$\Delta E_{rear} = [BDE_{FeC}^n - BDE_{FeC}^a] + [E(aNHC) - E(nNHC)] \tag{1}$$

Further insight into the role of steric factors in the normal-to-abnormal rearrangement was obtained through computations of the model complexes [(nIMe)Fe(N″)₂] and [(aIMe)Fe(N″)₂] (IMe = 1,3(dimethyl)imidazolylidene), in which the NHC nitrogen atoms carry nonbulky methyl substituents. In the IMe complexes, the rearrangement is computed to be overall endothermic, with $\Delta E_{rear} = +8.1$ kcal/mol. The origins of the significant difference in stability relative to **1**/**6** can be traced to the much smaller difference in the Fe–C bond dissociation energies, $[BDE_{FeC}^n - BDE_{FeC}^a]$, which for the IMe complexes is only −5.9 kcal/mol. In contrast, the difference in the stability of the methyl-substituted abnormal and normal NHCs, $[E(aIMe) - E(nIMe)]$, is 14.0 kcal/mol, i.e., similar to the analogous energy difference for **1**/**6**.

The computations provide further evidence that aNHC ligands are not only intrinsically more basic, and better donors, than their nNHC isomers but also that the preference for **6** over **1** requires an enhancement of 14 kcal/mol from steric factors to drive the rearrangement. The role of sterics in the formation of **6** is broadly consistent with a recent study on a series of palladium complexes of chelating NHC-amidate ligands, which can also form in normal and abnormal modes.[19] Additional support for the role of sterics comes from an analysis of the computed molecular structures of **1**, **6**, [(nIMe)Fe(N″)₂], and [(aIMe)Fe(N″)₂]. The Fe–C bond in **6**

(2.120 Å) is much shorter than that in **1** (2.200 Å) by 0.080 Å, which agrees well with the experimental difference of 0.065 Å. The Fe−C distances in $[(n\text{IMe})\text{Fe}(\text{N}'')_2]$ (2.148 Å) and $[(a\text{IMe})\text{Fe}(\text{N}'')_2]$ (2.115 Å) are significantly shorter than the analogous distances in the Dipp-substituted complexes because of the reduced steric bulk, and the difference between them is now only 0.033 Å, hence the difference in their bond dissociation energies is much smaller.

To investigate the possibility that bulky NHC ligands in three-coordinate iron−NHC complexes might be generally amenable to the normal-to-abnormal rearrangements, we synthesized the $^t$Bu-substituted complex **4** (Scheme 1). The structure of **4** is similar to that of **1** and features a planar, three-coordinate iron center, a long Fe(1)−C(1) bond of 2.151(2) Å (CSD average = 1.994 Å),[20] and Fe(1)−N(1) and Fe(1)−N(2) bond lengths of 1.9611(19) and 1.9713(18) Å. The C−Fe−N angles are 115.47(8)° and 113.19(8)°, and the N−Fe−N angle is 131.02(8)°. The $^1$H NMR spectrum (Figure S4) of **4** in toluene at 298 K features resonances at 32.75 and 2.94 ppm, corresponding to the imidazolylidene and SiMe$_3$ protons, respectively. The $^t$Bu methyl groups are inequivalent on the NMR time scale at 298 K and occur as two overlapping resonances at −11.21 and −13.94 ppm. Thus, the solid-state structure is retained in solution. The $^{57}$Fe Mössbauer spectrum of **4** (Figure S5) features an isomer shift of 0.59(1) mm/s, which confirms that the iron(II) center is three-coordinate with $S = 2$.

Heating **4** in toluene to 80 °C in a sealed NMR tube for 3 h produces additional resonances in the $^1$H NMR spectrum relative to that of **4**, implying the formation of a second species, however the NMR spectrum is still dominated by resonances due to **4**. In contrast, heating solutions of **4** for 24 h resulted in the $^1$H NMR resonances characteristic of **4** being replaced by the new set of resonances (Figure S6). A scale-up of the reaction produced a light-brown solution, and storing the concentrated toluene solution at −30 °C overnight produced colorless crystals of $[(^t\text{BuIm})_2\text{Fe}(\text{N}'')_2]$ (**7**) ($^t$BuIm = *tert*-butylimidazole) (Scheme 1, Figure 2). Molecules of **7** contain
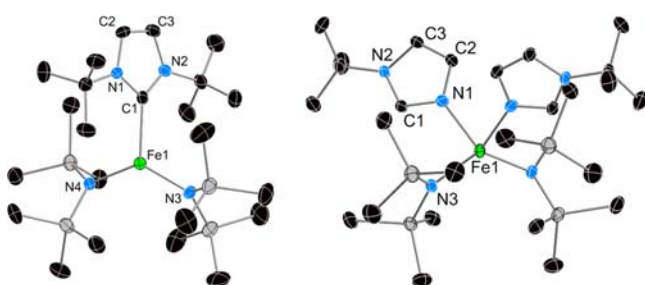


**Figure 2.** Molecular structures of **4** (left) and **7** (right) (50% thermal ellipsoids).

an iron(II) center in a distorted tetrahedral environment, with a $C_2$-axis bisecting the N(1)−Fe−N(1A) angle and with N−Fe−N angles in the range 91.33(8)−127.76(8)° (average 107.8°). The N(3)−Fe−N(3A) angle of 127.76(8)° between the amido ligands is relatively wide, whereas the N(1)−Fe−N(1A) angle of 91.33(8)° involving the imidazole ligands is much narrower due to the bulk of the SiMe$_3$ substituents. The Fe−N(1/1A) bonds to the imidazole ligands are, at 2.149(2) Å, markedly longer than the Fe−N(3/3A) bonds to the amido ligands, which are 2.009(2) Å. With a relatively large quadrupole splitting (q.s.) of 1.74 mm/s and an i.s. 0.85(1) mm/s, the

Mössbauer spectrum of **7** is diagnostic of four-coordinate iron(II) with $S = 2$. The byproducts that accompany the formation of **7** were identified in the $^1$H NMR spectrum as isobutene ($\delta = 4.72$ ppm and 1.60 ppm)[21] and Fe(N$''$)$_2$ ($\delta = 61.16$ ppm).[22] To assist with assigning the $^t$BuIm hydrogens, complex **7** was also synthesized by the direct addition of $^t$BuIm to Fe(N$''$)$_2$: The $^1$H NMR spectrum of an analytically pure sample of **7** formed from this reaction (Figures S7, S8) is different to that of **7** acquired after the thermal rearrangement of **4**. In the $^1$H NMR spectrum of **7** formed in the direct addition reaction, the *tert*-butyl group occurs at $\delta = 1.61$ ppm, the SiMe$_3$ groups occur as a broad resonance at $\delta = 5.98$ ppm, and the imidazole hydrogen atoms occur as weak, broad resonances at 34.89, 33.50, and 41.90 ppm. The NMR spectrum of **7** obtained after heating **4** features the *tert*-butyl group at $\delta = 0.59$ ppm and the SiMe$_3$ groups as a broad resonance centered on $\delta = 1.95$ ppm; the imidazole hydrogen atoms occur as weak resonances at 40.61, 48.10, and 51.33 ppm. The different NMR spectra indicate that the $^t$BuIm ligands in toluene solutions of Fe(N$''$)$_2$ and **7** are exchanging between iron(II) centers.

A mechanism for the transformation of **4** into **7** is proposed in Scheme 2. Intramolecular deprotonation of a methyl group

**Scheme 2**
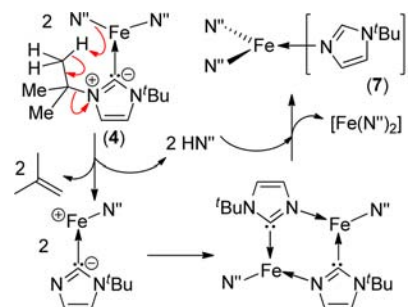


by $[(\text{Me}_3\text{Si})_2\text{N}]^-$ ligand occurs first, which produces (Me$_3$Si)$_2$NH and eliminates isobutene. The resulting intermediate iron complex can then form a dimer, and finally, the NHC is protonated by (Me$_3$Si)$_2$NH, producing **7** and Fe(N$''$)$_2$.

The C−H/C−N activation shown by the *tert*-butyl substituents in **4** has not previously been observed in an iron−NHC complex. Rhodium(I), iridium(I), and nickel(0) activate an I$^t$Bu C−H bond via oxidative addition, producing metal hydrido-alkyl complexes,[23,24] but such a pathway is improbable in **4**. In a study of the reaction of [Ni(COD)$_2$] with I$^t$Bu, Cloke et al. also observed C−N activation upon addition of excess carbene, after exposure of the complex to sunlight.[24] Whittlesey et al. have reported on the C−H/C−N activation of an isopropyl-substituted NHC ligand by octahedral ruthenium-(II), followed by tautomerism to give an N-bound imidazole complex, where the isopropyl activation involves cyclo-metalated species and requires addition of imidazolium chloride to give the C−N activated product.[25] The precise mechanism of the conversion of **4** into **7** and of the conversion of **1** into **6** will be the subject of a detailed computational study and reported in a future article.

In summary, the NHC ligands in the three-coordinate complexes [(NHC)Fe(N$''$)$_2$] show non-innocent reactivity. In the diisopropylphenyl-substituted normal NHC complex **1**, the steric pressure in the complex is, on heating, relieved via a rearrangement to the abnormal NHC complex **6**. Complex **6** is

a rare example of an iron−*a*NHC complex and the first such three-coordinate complex. The *tert*-butyl-substituted complex **4** is prone to a thermal decomposition reaction that has not previously been observed in iron−NHC chemistry, resulting in the bis(imidazole)iron complex **7**. A mechanism involving consecutive C−H and C−N activation, which is distinct from the mechanisms proposed for I^tBu activation by late transition metals, may account for this transformation.

The NHC activation reactions reported herein are unlikely to be unique to our three-coordinate iron systems. This chemistry probably also occurs in catalytic reactions of iron−NHC complexes, especially at elevated temperatures, and this presumably has implications for the 'well-defined' nature of the active iron−NHC species.

## ■ ASSOCIATED CONTENT

### ⓢ Supporting Information

Synthetic, spectroscopic and computational details. Crystallographic data in cif format. This material is available free of charge via the Internet at http://pubs.acs.org.

## ■ AUTHOR INFORMATION

### Corresponding Authors

Richard.Layfield@manchester.ac.uk
F.M.Bickelhaupt@vu.nl

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

## ■ REFERENCES

(1) Ingleson, M. J.; Layfield, R. A. *Chem. Commun.* **2012**, *48*, 3579.

(2) (a) Gaillard, S.; Cazin, C. S. J.; Nolan, S. P. *Acc. Chem. Res.* **2012**, *45*, 778. (b) Valente, C.; Çalimsiz, S.; Hoi, K. H.; Mallik, D.; Sayah, M.; Organ, M. G. *Angew. Chem., Int. Ed.* **2012**, *51*, 3314. (c) Radius, U.; Bickelhaupt, F. M. *Coord. Chem. Rev.* **2009**, *253*, 678.

(3) Scepaniak, J. J.; Vogel, C. S.; Khusniyarov, M. M.; Heinemann, F. W.; Meyer, K.; Smith, J. M. *Science* **2011**, *331*, 1049.

(4) (a) Pulukkody, P.; Kyran, S. J.; Bethel, R. D.; Hsieh, C. H.; Hall, M. B.; Darensbourg, D. J.; Darensbourg, M. Y. *J. Am. Chem. Soc.* **2013**, *135*, 8423. (b) Hsieh, C. H.; Darensbourg, M. Y. *J. Am. Chem. Soc.* **2010**, *132*, 14118. (c) Liu, T.; Darensbourg, M. Y. *J. Am. Chem. Soc.* **2007**, *129*, 7008. (d) Deng, L.; Holm, R. H. *J. Am. Chem. Soc.* **2008**, *130*, 9878.

(5) (a) Bézier, D.; Sortais, J. B.; Darcel, C. *Adv. Synth. Catal.* **2013**, *355*, 19. (b) Li, H.; Misal Castro, L. C.; Zheng, J.; Roisnel, T.; Dorcet, V.; Sortais, J. B.; Darcel, C. *Angew. Chem., Int. Ed.* **2013**, *52*, 8045. (c) Hashimoto, T.; Urban, S.; Hoshino, R.; Ohki, Y.; Tatsumi, K.; Glorius, F. *Organometallics* **2012**, *31*, 4474.

(6) Pranckevicius, C.; Stephan, D. W. *Organometallics* **2013**, *32*, 2693.

(7) (a) Xiaojie, W.; Mo, Z.; Xiao, J.; Deng, L. *Inorg. Chem.* **2013**, *52*, 59. (b) Mo, Z.; Zhang, Q.; Deng, L. *Organometallics* **2012**, *31*, 6158. (c) Xiang, L.; Xiao, J.; Deng, L. *Organometallics* **2011**, *30*, 2018.

(8) (a) Danopoulos, A. A. *Chem.—Eur. J.* **2013**, *19*, 450. (b) Danopoulos, A. A.; Braunstein, P.; Wesolek, M.; Monakhov, K. Y.; Rabu, P.; Robert, V. *Organometallics* **2012**, *31*, 4102. (c) Danopoulos, A. A.; Braunstein, P.; Stylianides, N.; Wesolek, M. *Organometallics* **2011**, *30*, 6514.

(9) Layfield, R. A.; McDouall, J. J. W.; Scheer, M.; Schwarzmaier, C.; Tuna, F. *Chem. Commun.* **2011**, *47*, 10623.

(10) (a) Lappert, M.; Protchenko, A.; Power, P.; Seeber, A. *Metal Amide Chemistry*, J. Wiley and Sons Ltd.: Hoboken, NJ, 2009; Chapter 6. (b) Sulway, S. A.; Collison, D.; McDouall, J. J. W.; Tuna, F.; Layfield, R. A. *Inorg. Chem.* **2011**, *50*, 2521.

(11) Chen, H.; Bartlett, R. A.; Dias, H. V. R.; Olmstead, M. M.; Power, P. P. *Inorg. Chem.* **1991**, *30*, 2487.

(12) Evans, D. J.; Hughes, D. L.; Silver, J. *Inorg. Chem.* **1997**, *36*, 747.

(13) Aldeco-Perez, E.; Rosenthal, A. J.; Donnadieu, B.; Parameswaran, P.; Frenking, G.; Bertrand, G. *Science* **2009**, *326*, 556.

(14) (a) Schuster, M.; Yang, L.; Raubenheimer, H. G.; Albrecht, M. *Chem. Rev.* **2009**, *109*, 3445. (b) Albrecht, M. *Chem. Commun.* **2008**, 3601. (c) Crabtree, R. H. *Coord. Chem. Rev.* **2013**, *257*, 755. (d) Arnold, P. L.; Pearson, S. *Coord. Chem. Rev.* **2007**, *251*, 596.

(15) (a) Magill, A. M.; Yates, B. F. *Aust. J. Chem.* **2004**, *57*, 1205. (b) Magill, A. M.; Kavell, K. J.; Yates, B. F. *J. Am. Chem. Soc.* **2004**, *126*, 8717. (c) Sini, G.; Eisenstein, O.; Crabtree, R. H. *Inorg. Chem.* **2002**, *41*, 602.

(16) Lavallo, V.; El-Batta, A.; Bertrand, G.; Grubbs, R. H. *Angew. Chem., Int. Ed.* **2011**, *50*, 268.

(17) Danopoulos, A. A.; Tsoureas, N.; Wright, J. A.; Light, M. E. *Organometallics* **2004**, *23*, 166.

(18) (a) te Velde, G.; Bickelhaupt, F. M.; Baerends, E. J.; Fonseca Guerra, C.; van Gisbergen, S. J. A.; Snijders, J. G.; Ziegler, T. *J. Comput. Chem.* **2001**, *22*, 931. (b) *Computer code ADF 2013.01*; SCM: Amsterdam; see http://www.scm.com. (c) van Lenthe, E.; Baerends, E. J.; Snijders, J. G. *J. Chem. Phys.* **1994**, *101*, 9783. (d) de Jong, G. T.; Bickelhaupt, F. M. *J. Chem. Theory Comput.* **2006**, *2*, 322. (e) Klamt, A. *J. Phys. Chem.* **1995**, *99*, 2224. (f) Swart, M.; Rösler, E.; Bickelhaupt, F. M. *Eur. J. Inorg. Chem.* **2007**, 3646.

(19) Tan, K. V.; Dutton, J. L.; Skelton, B. W.; Wilson, D. J. D.; Barnard, P. J. *Organometallics* **2013**, *32*, 1913.

(20) *CSD ConQuest*, version 1.15; Cambridge Crystallographic Data Centre: Cambridge. Accessed August 1, 2013.

(21) Jordan, A. Y.; Meyer, T. Y. *J. Organomet. Chem.* **1999**, *591*, 104.

(22) Olmstead, M. M.; Power, P. P.; Shoner, S. C. *Inorg. Chem.* **1991**, *30*, 2547.

(23) (a) Scott, N. M.; Pons, V.; Stevens, E. D.; Heinekey, D. M.; Nolan, S. P. *Angew. Chem., Int. Ed.* **2005**, *44*, 2512. (b) Scott, N. M.; Dorta, R.; Stevens, E. D.; Correa, A.; Cavallo, L.; Nolan, S. P. *J. Am. Chem. Soc.* **2005**, *127*, 3516.

(24) Caddick, S.; Cloke, F. G. N.; Hitchcock, P. B.; Lewis, A. K. de. K. *Angew. Chem., Int. Ed.* **2004**, *43*, 5824.

(25) (a) Burling, S.; Mahon, M. F.; Powell, R. E.; Whittlesey, M. K.; Williams, J. M. J. *J. Am. Chem. Soc.* **2006**, *128*, 13702. (b) Häller, L. J. L.; Page, M. J.; Erhardt, S.; Macgregor, S. A.; Mahon, M. F.; Naser, M. A.; Vélez, A.; Whittlesey, M. K. *J. Am. Chem. Soc.* **2010**, *132*, 18408.

13341

dx.doi.org/10.1021/ja408589p | *J. Am. Chem. Soc.* 2013, 135, 13338−13341