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Synthesis and Reactivity of Two-Coordinate Ni(I) Alkyl and Aryl Complexes

Carl A. Laskowski,[‡] Donald J. Bungum,[§] Steven M. Baldwin, Sarah A. Del Ciello, Vlad M. Iluc,[†] and Gregory L. Hillhouse*

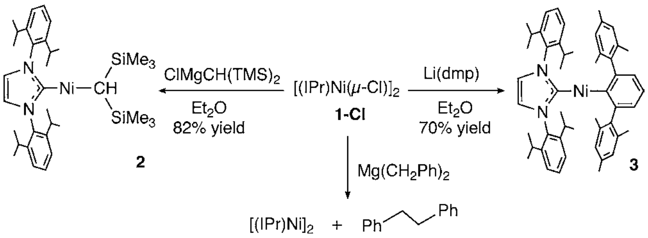
Gordon Center for Integrative Science, Department of Chemistry, The University of Chicago, Chicago, Illinois 60637, United States

Supporting Information

ABSTRACT: Reaction of $[(\mathrm{IPr})\mathrm{Ni}(\mu\text{-Cl})]_2$ (**1-Cl**; IPr = 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene) with $\mathrm{ClMg\{CH(SiMe_3)_2\}\cdot Et_2O}$ affords $\mathrm{(IPr)Ni\{CH(SiMe_3)_2\}}$ (**2**), a two-coordinate Ni(I) alkyl complex. An analogous two-coordinate aryl derivative, (IPr)Ni(dmp) (dmp = 2,6-dimesitylphenyl), can be similarly prepared from Li(dmp) and **1-Cl**. Reaction of **2** with alkyl bromides gives the three-coordinate Ni(II) alkyl halide complex $\mathrm{(IPr)Ni\{CH(SiMe_3)_2\}Br}$. Evidence for a radical mechanism is presented to explain the reaction of **2** with alkyl halides.

Nickel-based alkyl−alkyl coupling has emerged as a powerful tool for the formation of C−C bonds.[1] In contrast to Pd, for which β-hydride elimination is facile, Ni alkyls show decreased propensity to β-hydride eliminate,[2] possibly due to a thermodynamic preference for alkyl complexes over olefin hydrides.[3] The recent development of Ni-based stereoconvergent alkyl−alkyl coupling reactions strongly suggests a more complicated mechanism is occurring than the "simple" Pd-based oxidative addition/transmetalation/reductive elimination mechanism often proposed.[4] One could envision a radical mechanism proceeding from either a Ni(II) or Ni(I) alkyl. While Ni(II) alkyls are plentiful and their reactions with alkyl halides have been studied,[5,6] Ni(I) alkyls are quite rare. We have had previous success isolating reactive low-coordinate Ni(I) species, including one of the few structurally characterized Ni(I) alkyls.[7] Here we report the synthesis of two-coordinate Ni(I) alkyl and aryl complexes supported by the *N*-heterocyclic carbene (NHC) ligand 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene (IPr). IPr and related NHCs have recently been shown to support Ni-based alkyl coupling reactions;[8] IPr therefore seemed to present a relevant scaffold for preparing a Ni(I) alkyl complex and studying its coupling reactivity with alkyl halides.

Scheme 1



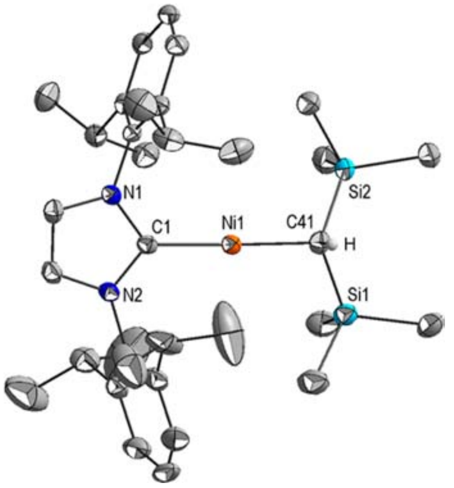


Figure 1. Thermal ellipsoid plot of **2** with all hydrogen atoms removed for clarity except on C(41). Ellipsoids shown at 50% probability. Selected metrical parameters for **2**: Ni−C(1) = 1.910(2), Ni−C(41) = 1.968(3) Å; C(1)−Ni−C(41) = 174.81(10)°.

It has been demonstrated that Sigman's d^9-d^9 dimer $[(\mathrm{IPr})\mathrm{Ni}(\mu\text{-Cl})]_2$ (**1-Cl**)[9] can serve as a precursor to two-coordinate d^9 Ni amides.[10] Attempts to use an analogous salt-metathesis strategy with **1-Cl** to prepare two-coordinate Ni(I) alkyls incorporating small alkyl groups lacking β-hydrogens proved ineffective. For example, reaction of **1-Cl** with $\mathrm{Mg(CH_2Ph)_2}$ gave only the homocoupled product dibenzyl and the known Ni(0) dimer $[(\mathrm{IPr})\mathrm{Ni}]_2$ (Scheme 1).[11] Use of a more sterically encumbered alkyl proved capable of avoiding the homocoupling reaction. Combination of **1-Cl** with $\mathrm{ClMg\{CH(SiMe_3)_2\}\cdot Et_2O}$ in a 1:2 stoichiometric fashion ($\mathrm{Et_2O}$ solution) affords the two-coordinate Ni(I) alkyl complex $\mathrm{(IPr)Ni\{CH(SiMe_3)_2\}}$ (**2**) as a yellow powder in 82% isolated yield (Scheme 1). ^{1}H NMR analysis revealed a paramagnetic spectrum consistent with the solution magnetic moment of 1.9 μ_B as measured via Evans's method. X-ray-quality crystals of **2** were grown from hexamethyldisiloxane (HMDSO) and confirmed the identification of **2** as a two-coordinate complex (Figure 1). The crystal structure of **2** reveals a nearly linear C−Ni−C core (174.81(10)°) and Ni−C bond lengths of 1.910(2) and 1.968(3) Å for the IPr and alkyl groups, respectively. The alkyl bond length in **2** is somewhat shorter than those found in the three-coordinate Ni(I) alkyl complexes $(\mathrm{PPh_3})\mathrm{Ni}[(C,N{:}\kappa^2\text{-}\mathrm{C(SiMe_3)_2}$-

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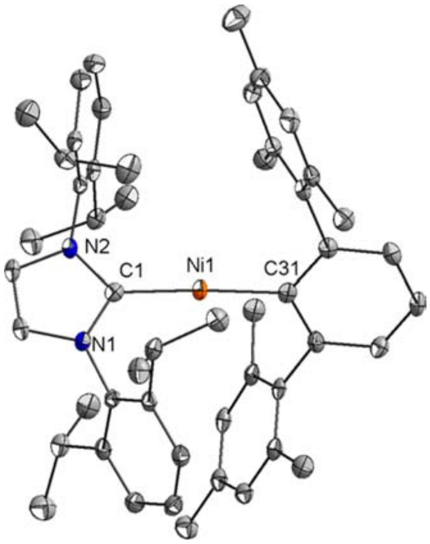


Figure 2. Thermal ellipsoid plot of $3\cdot(C_7H_8)$ with all hydrogen atoms and toluene of solvation removed for clarity. Ellipsoids shown at 50% probability. Selected metrical parameters for **3**: Ni−C(1) = 1.923(2), Ni−C(31) = 1.944(2) Å; C(1)−Ni−C(31) = 175.97(8)°.

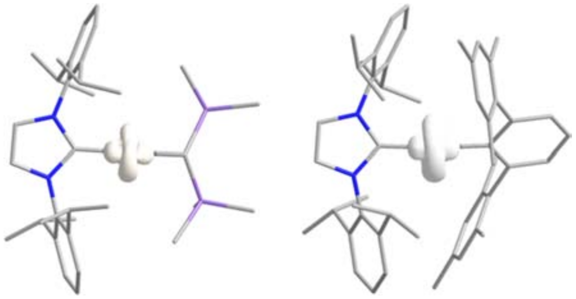


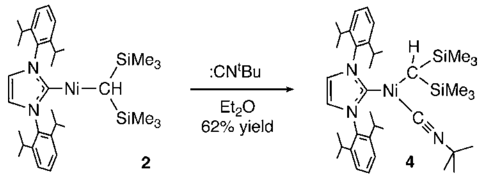
Figure 3. Unpaired-spin density plots for **2** (left) and **3** (right).

$(SiMe_2\text{-}2\text{-}C_5H_4N)]$ (2.025(4) Å)[7a] and $(^tBu_2PCH_2CH_2P^tBu_2)Ni(CH_2CMe_3)$ (1.982(3) Å).[7b] A related Ni(I) silyl complex, $(^tBu_2PCH_2CH_2P^tBu_2)Ni(SiHMes_2)$, has also been reported.[12] There is no agostic interaction in **2** between Ni and the α-CH moiety (which was located in the electron density map), as indicated by the long 2.26(3) Å Ni−H distance.

Analogous metathesis chemistry leads to the formation of a two-coordinate Ni(I) terphenyl complex. Reaction of **1-Cl** with Li(dmp) (dmp = 2,6-dimesitylphenyl) afforded (IPr)Ni(dmp) (**3**) as a bright-yellow solid in 70% isolated yield. The solution magnetic moment of **3** (1.80 μ_B) is indicative of a one-electron paramagnet. Crystals of **3** were obtained from HMDSO solution and revealed a nearly linear C−Ni−C angle of 175.97(8)° (Figure 2). The Ni−C bond lengths of 1.923(2) and 1.944(2) Å for the NHC and aryl substituents are similar to those observed in **2**, with only a slightly contracted $Ni-C_{aryl}$ bond and corresponding elongation of the $Ni-C_{NHC}$ bond.

Inasmuch as other formally "Ni(I)" alkyl complexes have been shown, upon inspection, to be in fact Ni(II) complexes with reduced ligands,[5g,h,13] DFT studies (B3LYP/LANL2DZ) of **2** and **3** were undertaken to examine their electronic structures and confirm the assignments as Ni(I) alkyl and aryl complexes. Single-point calculations on the geometries obtained from the X-ray structures revealed SOMOs that are localized on Ni composed of Ni $3d(z^2)$ mixed with Ni 4s. The Ni in each complex dominates the unpaired-spin density, with Mulliken spin densities of 1.01 and 1.00 for **2** and **3**, respectively (Figure 3). No other atom in either case has an unpaired-spin density >0.01. The pure Ni character of the SOMO is consistent with assignment as Ni(I) and likely contributes to the stabilities of **2** and **3**.

Scheme 2



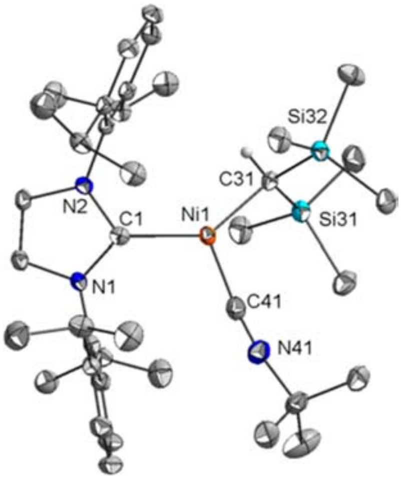
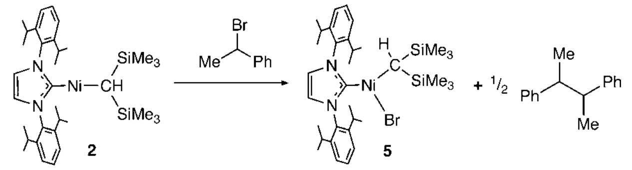


Figure 4. Thermal ellipsoid plot of **4** with all hydrogen atoms removed for clarity except on C(31). Ellipsoids shown at 50% probability. Selected metrical parameters for **4**: Ni−C(1) = 1.950(2), Ni−C(41) = 1.855(2), Ni−C(31) = 2.008(3) Å; C(1)−Ni−C(31) = 135.12(8), C(1)−Ni−C(41) = 108.23(9), C(31)−Ni−C(41) = 116.35(9)°.

Although **2** is sterically protected from dimerization, it reacts with the small Lewis base pivaloisocyanide to afford the three-coordinate Ni(I) alkyl complex, $(IPr)Ni(CN^tBu)\{CH(SiMe_3)_2\}$ (**4**), in 62% isolated yield as an orange solid (Scheme 2). Complex **4** is paramagnetic, with a solution magnetic moment of 2.10 μ_B as determined via Evans's method. X-ray-quality crystals were grown from diethyl ether solution and revealed a distorted trigonal planar geometry with the sum of angles at Ni = 360° (Figure 4). A slight elongation of the $Ni-C_{NHC}$ bond to 1.950(2) Å and of the $Ni-C_{alkyl}$ bond to 2.008(3) Å was observed when compared with **2**. The ability of the 13-electron Ni(I) alkyl complex **2** to coordinate a third ligand is consistent with its electron-deficient character.

Reactions of **2** with secondary alkyl halides were investigated since they might shed mechanistic light on the stereospecificity of cross-coupling reactions previously reported.[4a−j] Addition of 1-bromo-1-phenylethane to a solution of **2** resulted in immediate reaction yielding a dark, inky-turquoise solution. No cross coupling to yield 1,1-bis(trimethylsilyl)-2-phenylpropane was observed, but GC-MS and ^1H NMR spectroscopic analysis of the organic products revealed the homocoupled product, 2,3-diphenylbutane (Scheme 3). NMR analysis also revealed a new diamagnetic IPr-containing product inconsistent with either $[(IPr)Ni]_2$ or **1-Br**. X-ray-quality crystals of the new IPr-containing product were grown via diffusion of hexanes into a benzene solution, and analysis of the blue crystals revealed the product to be a three-coordinate Ni(II) alkyl complex,

Scheme 3



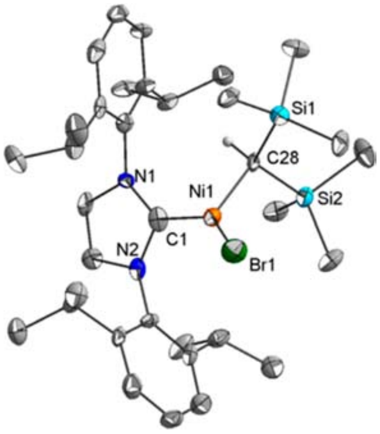


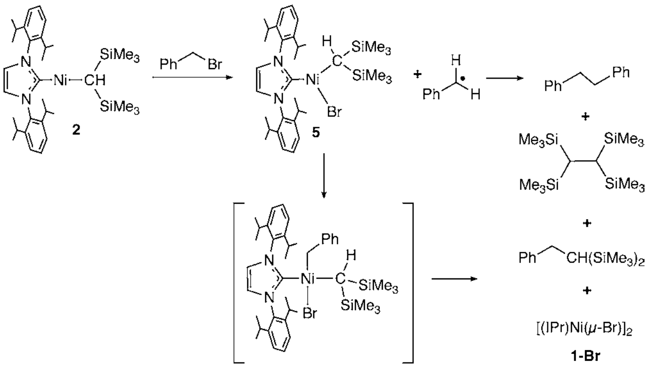
Figure 5. Thermal ellipsoid plot of **5**·0.5C_6H_6 with all hydrogen atoms (except on C(28)) and molecules of solvation removed for clarity. Ellipsoids shown at 50% probability. Selected metrical parameters for **5**: Ni−C(1) = 1.814(8), Ni−C(28) = 1.902(8), Ni−Br(1) = 2.247(2) Å; C(1)−Ni−C(28) = 93.8(4), C(1)−Ni−Br(1) = 141.0(3), C(28)−Ni−Br(1) = 124.9(2)°.

(IPr)NiBr{$CH(SiMe_3)_2$} (**5**, Figure 5). **5** exhibits a distorted Y-shaped geometry in which the Br forms the stem of the Y. Compared with **2**, significant shortening of the NHC (1.814(8) Å) and alkyl (1.902(8) Å) Ni−C bonds is observed, which likely arises from two complementary factors: first, a decrease in bond lengths upon going from Ni(I) to Ni(II), and second, the loss of the *trans* influence of the alkyl ligand upon going from two- to three-coordinate. The other structurally characterized example of a Ni bis(trimethylsilyl)methyl complex is $(PMe_3)_2NiCl\{CH(SiMe_3)_2\}$,[14] with Ni−C at 1.972(8) Å, and while the Ni−C_{alkyl} bond in **5** is significantly shorter, it is comparable to those in other three-coordinate Ni(II) alkyls,[10,15] which are T-shaped complexes with the alkyl group forming the stem of the T in all cases. The T-shaped configuration has been calculated to be the electronically preferred geometry for d^8 three-coordinate metal complexes with σ-donor ligands,[16] but the large steric profiles of the ligands in **5** are likely responsible for its observed Y-shaped geometry.

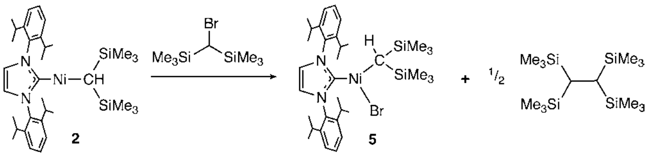
The isolation of **5** along with 2,3-diphenylbutane suggests a radical mechanism for oxidative addition of alkyl halides. The ability of the phenyl group to stabilize a radical would allow the radical to persist long enough for homocoupling to occur. Without the stabilization, the radical could react with **5** to either abstract $^\bullet CH(SiMe_3)_2$ and form the heterocoupled product, or form a Ni−C bond to generate a dialkyl Ni(III) complex, from which reductive elimination to form the heterocoupled product could occur. To probe this further, other alkyl bromides were examined.

Reaction of **2** with benzyl bromide resulted in a mixture of products (Scheme 4). Among the Ni-containing products were obtained **1-Br** and **5** in a ~4:1 ratio. Analysis of the organic products revealed the expected heterocoupled product 1,1-bis(trimethylsilyl)-2-phenylethane as the major product, but also dibenzyl and 1,1,2,2-tetra(trimethylsilyl)ethane as byproducts (~4:2:1 relative ratio). Benzyl bromide would form a less stable radical than (1-bromoethyl)benzene as it forms a primary instead of a secondary radical. Additionally, the smaller steric profile of a benzyl radical would make formation of a four-coordinate Ni intermediate more facile. Therefore, a mixture of products is reasonable from the reaction of benzyl bromide.

Scheme 4



Scheme 5



The formation of the tetrakis(trimethylsilyl)ethane was somewhat surprising. One explanation for its formation would be that a species such as a Ni(III) dialkyl bromide complex eliminates $(Me_3Si)_2CHBr$, which subsequently reacts with another equivalent of **2** to yield the homocoupled product (and either **1-Br** or **5**, depending on the mechanism). To test this hypothesis, **2** was directly reacted with $(Me_3Si)_2CHBr$ under the standard reaction conditions. Clean, rapid conversion of **2** to **5** was observed, along with formation of 1,1,2,2-tetrakis(trimethylsilyl)ethane (Scheme 5). Silicon is known to stabilize both α- and β-radicals, with estimates of this effect being ~1−3 kcal/mol for an α-Si radical.[17] In addition, Si has been shown to increase the rate of α-Br abstraction 3.3× for $^nBu_3Ge^\bullet$ and 6.6× for $^nBu_3Sn^\bullet$ relative to a bromoalkane.[18] This effect would likely be enhanced by the presence of two α-Si groups, as the effect of Si substitution has been shown to be additive;[17c] even when one α-Si is proposed to have no stabilization effect on α-radicals, two α-Si groups were found to be stabilizing.[19] Therefore, halogen abstraction from $(Me_3Si)_2CHBr$ by **2** is expected to be rapid, while oxidative addition or S_N2 displacement would be strongly inhibited by the very bulky $SiMe_3$ groups. The possibility of bromide abstraction to form a carbocation seems unlikely, as silicon tends to destabilize α-cations, and this reaction type is observed only when the cation is stabilized.[20]

To investigate the possibility of alkyl group scrambling during the course of reaction of **2** with alkyl halides, **2** was reacted with $(Me_3Si)_2CDBr$ prepared from $CDBr_3$ according to the literature synthesis of $(Me_3Si)_2CHBr$.[21] Reaction with **2** afforded **5-*d*$_0$** and 1,1,2,2-tetrakis(trimethylsilyl)ethane-d_2. No alkyl scrambling was observed, ruling out the transient formation of a dialkyl Ni(III). Bimolecular oxidative addition, which was recently proposed in another system,[22] is also ruled out, as no monodeuterio homocoupling products are observed.

Further evidence for a radical pathway was seen in the reaction of **2** with the unactivated alkyl bromides. Reaction of a primary alkyl bromide, 1-bromobutane, with **2** resulted in slow consumption of the alkyl bromide over the course of 2 days with formation of **1-Br**. The major organic product from this reaction was $(Me_3Si)_2CH_2$, with 0.7 equiv of butene isomers formed. 2-Bromobutane reacts slowly over the course of hours to give a 2:1 mixture of **1-Br** and **5** along with $(Me_3Si)_2CH_2$ and 0.8 equiv of butene isomers relative to **1-Br**. Menthyl bromide reacts over the course of 4 days, yielding **1-Br** as the major Ni-containing product. Once again $(Me_3Si)_2CH_2$ is formed; however, the other organic products were not identified. For none of these unactivated alkyl bromides was a cross-coupled product observed. The isolation of a Ni(II) alkyl bromide from reaction of **2** with alkyl bromides is strong evidence for a radical oxidative addition mechanism. The fact that alkyl bromides capable of forming stabilized radicals react faster than simple alkyl halides further supports this suggestion.

In conclusion, the first two-coordinate Ni alkyl and aryl complexes have been synthesized and crystallographically characterized. Study of the reactivity of **2** has led to the isolation and crystallographic characterization of a three-coordinate Ni(II) alkyl complex. These reactivity studies strongly implicate a radical mechanism for the reaction of Ni(I) alkyl complexes with alkyl halides. How these findings relate to Ni-catalyzed alkyl−alkyl coupling is less clear since the large steric profiles of the ligands in this particular system could bias its reactivity.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental, spectroscopic, computational, and analytical details; crystallographic data (CIF) for **2**−**5**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

g-hillhouse@uchicago.edu

Present Addresses

‡3M Corporate Research Materials Laboratory, St. Paul, MN
§Department of Philosophy, St. Louis University, St. Louis, MO
†Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, IN

Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Netherton, M. R.; Fu, G. C. *Adv. Synth. Catal.* **2004**, *346*, 1525. (b) Terao, J.; Kambe, N. *Acc. Chem. Res.* **2008**, *41*, 1545. (c) Phapale, V. B.; Cárdenas, D. J. *Chem. Soc. Rev.* **2009**, *38*, 1598. (d) Rudolph, A.; Lautens, M. *Angew. Chem., Int. Ed.* **2009**, *48*, 2656. (e) Jana, R.; Pathak, T. P.; Sigman, M. S. *Chem. Rev.* **2011**, *111*, 1417. (f) Hu, X. *Chem. Sci* **2011**, *2*, 1867. (g) Heravi, M. M.; Hajiabbasi, P. *Monatsh. Chem.* **2012**, *143*, 1575. (h) Wang, Z. X.; Liu, N. *Eur. J. Inorg. Chem.* **2012**, 901. (i) Han, F. S. *Chem. Soc. Rev.* **2013**, *42*, 5270.

(2) Ittel, S. D.; Johnson, L. K.; Brookhart, M. *Chem. Rev.* **2000**, *100*, 1169.

(3) Breitenfeld, J.; Vechorkin, O.; Corminboeuf, C.; Scopelliti, R.; Hu, X. L. *Organometallics* **2010**, *29*, 3686.

(4) (a) Arp, F. O.; Fu, G. C. *J. Am. Chem. Soc.* **2005**, *127*, 10482. (b) Fischer, C.; Fu, G. C. *J. Am. Chem. Soc.* **2005**, *127*, 4594. (c) Son, S.; Fu, G. C. *J. Am. Chem. Soc.* **2008**, *130*, 2756. (d) Lou, S.; Fu, G. C. *J. Am. Chem. Soc.* **2010**, *132*, 5010. (e) Zultanski, S. L.; Fu, G. C. *J. Am. Chem. Soc.* **2011**, *133*, 15362. (f) Lu, Z.; Wilsily, A.; Fu, G. C. *J. Am. Chem. Soc.* **2011**, *133*, 8154. (g) Binder, J. T.; Cordier, C. J.; Fu, G. C. *J. Am. Chem. Soc.* **2012**, *134*, 17003. (h) Choi, J. W.; Fu, G. C. *J. Am. Chem. Soc.* **2012**, *134*, 9102. (i) Perez Garcia, P. M.; Di Franco, T.; Orsino, A.; Ren, P.; Hu, X. L. *Org. Lett.* **2012**, *14*, 4286. (j) Wilsily, A.; Tramutola, F.; Owston, N. A.; Fu, G. C. *J. Am. Chem. Soc.* **2012**, *134*, 5794. (k) Cordier, C. J.; Lundgren, R. J.; Fu, G. C. *J. Am. Chem. Soc.* **2013**, *135*, 10946.

(5) (a) Barefield, E. K.; Carrier, A. M.; Sepelak, D. J.; Van Derveer, D. G. *Organometallics* **1985**, *4*, 1395. (b) Bräunlich, G.; Fischer, R.; Nestler, B.; Walther, D. *Z. Chem.* **1989**, *29*, 417. (c) Schönecker, B.; Walther, D.; Fischer, R.; Nestler, B.; Bräunlich, G.; Eibisch, H.; Droescher, P. *Tetrahedron Lett.* **1990**, *31*, 1257. (d) Fischer, R.; Walther, D.; Bräunlich, G.; Undeutsch, B.; Ludwig, W.; Bandmann, H. *J. Organomet. Chem.* **1992**, *427*, 395. (e) Kauffmann, T.; Nienaber, H. *Synthesis-Stuttgart* **1995**, 207. (f) Matsunaga, P. T.; Mavropoulos, J. C.; Hillhouse, G. L. *Polyhedron* **1995**, *14*, 175. (g) Anderson, T. J.; Jones, G. D.; Vicic, D. A. *J. Am. Chem. Soc.* **2004**, *126*, 8100. (h) Jones, G. D.; McFarland, C.; Anderson, T. J.; Vicic, D. A. *Chem. Commun.* **2005**, 4211. (i) Liang, L. C.; Chien, P. S.; Lin, J. M.; Huang, M. H.; Huang, Y. L.; Liao, J. H. *Organometallics* **2006**, *25*, 1399. (j) Csok, Z.; Vechorkin, O.; Harkins, S. B.; Scopelliti, R.; Hu, X. L. *J. Am. Chem. Soc.* **2008**, *130*, 8156.

(6) Related allylnickel halide reactions: (a) Corey, E. J.; Semmelhack, M. F. *J. Am. Chem. Soc.* **1967**, *89*, 2755. (b) Baker, R. *Chem. Rev.* **1973**, *73*, 487. (c) Billington, D. C. *Chem. Soc. Rev.* **1985**, *14*, 93. (d) Shrestha, R.; Dorn, S. C. M.; Weix, D. J. *J. Am. Chem. Soc.* **2013**, *135*, 751.

(7) (a) Eaborn, C.; Hill, M. S.; Hitchcock, P. B.; Smith, J. D. *Chem. Commun.* **2000**, 691. (b) Kitiachvili, K. D.; Mindiola, D. J.; Hillhouse, G. L. *J. Am. Chem. Soc.* **2004**, *126*, 10554.

(8) (a) Joshi-Pangu, A.; Wang, C. Y.; Biscoe, M. R. *J. Am. Chem. Soc.* **2011**, *133*, 8478. (b) Zell, T.; Radius, U. *Z. Anorg. Allg. Chem.* **2011**, *637*, 1858.

(9) Dible, B. R.; Sigman, M. S.; Arif, A. M. *Inorg. Chem.* **2005**, *44*, 3774.

(10) Laskowski, C. A.; Hillhouse, G. L. *J. Am. Chem. Soc.* **2008**, *130*, 13846.

(11) Lee, C. H.; Laitar, D. S.; Mueller, P.; Sadighi, J. P. *J. Am. Chem. Soc.* **2007**, *129*, 13802.

(12) Iluc, V. M.; Hillhouse, G. L. *J. Am. Chem. Soc.* **2010**, *132*, 11890.

(13) Jones, G. D.; Martin, J. L.; McFarland, C.; Allen, O. R.; Hall, R. E.; Haley, A. D.; Brandon, R. J.; Konovalova, T.; Desrochers, P. J.; Pulay, P.; Vicic, D. A. *J. Am. Chem. Soc.* **2006**, *128*, 13175.

(14) Belderraín, T. R.; Paneque, M.; Sernau, V.; Carmona, E.; Gutíerrez, E.; Monge, A. *Polyhedron* **1996**, *15*, 3501.

(15) (a) Tamaki, T.; Nagata, M.; Ohashi, M.; Ogoshi, S. *Chem.—Eur. J.* **2009**, *15*, 10083. (b) Tamaki, T.; Ohashi, M.; Ogoshi, S. *Chem. Lett.* **2011**, *40*, 248.

(16) (a) Burdett, J. K. *Inorg. Chem.* **1975**, *14*, 375. (b) Elian, M.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 1058. (c) Komiya, S.; Albright, T. A.; Hoffmann, R.; Kochi, J. K. *J. Am. Chem. Soc.* **1976**, *98*, 7255.

(17) (a) Doncaster, A. M.; Walsh, R. *J. Chem. Soc., Faraday Trans. 1* **1976**, *72*, 2901. (b) Davidson, I. M. T.; Barton, T. J.; Hughes, K. J.; Ijadi-Maghsoodi, S.; Revis, A.; Paul, G. C. *Organometallics* **1987**, *6*, 644. (c) Brinkman, E. A.; Berger, S.; Brauman, J. I. *J. Am. Chem. Soc.* **1994**, *116*, 8304.

(18) (a) Wilt, J. W.; Belmonte, F. G.; Zieske, P. A. *J. Am. Chem. Soc.* **1983**, *105*, 5665. (b) Wilt, J. W.; Lusztyk, J.; Peeran, M.; Ingold, K. U. *J. Am. Chem. Soc.* **1988**, *110*, 281.

(19) Zhang, S. Z.; Zhang, X. M.; Bordwell, F. G. *J. Am. Chem. Soc.* **1995**, *117*, 602.

(20) Jenkins, C. L.; Kochi, J. K. *J. Am. Chem. Soc.* **1972**, *94*, 856.

(21) Wiberg, N.; Wagner, G. *Chem. Ber.* **1986**, *119*, 1455.

(22) Breitenfeld, J.; Ruiz, J.; Wodrich, M. D.; Hu, X. *J. Am. Chem. Soc.* **2013**, *135*, 12004.