

Useful Method for the Preparation of Low-Coordinate Nickel(I) Complexes via Transformations of the Ni(I) Bis(amido) Complex $K\{Ni[N(SiMe_3)(2,6\text{-}i\text{-}Pr_2\text{-}C_6H_3)]_2\}$

Michael I. Lipschutz and T. Don Tilley*

Department of Chemistry, University of California–Berkeley, Berkeley, California 94720, United States

S Supporting Information

ABSTRACT: A convenient method of preparing two- and three-coordinate Ni(I) complexes of the form $L-Ni^I-X$ ($L = P^tBu_3$, P^iPr_3 , DPPE, NHC; $X = -N(SiMe_3)(2,6\text{-}i\text{-}Pr\text{-}C_6H_3)$, $-O(2,6\text{-}i\text{-}Bu_2\text{-}4\text{-}Me\text{-}C_6H_2)$) is reported. Protonation of the easily prepared anionic Ni(I) bis(amido) complex $K\{Ni[N(SiMe_3)(2,6\text{-}i\text{-}Pr\text{-}C_6H_3)]_2\}$ in the presence of an appropriate L-type ligand results in loss of $HN(SiMe_3)(2,6\text{-}i\text{-}Pr\text{-}C_6H_3)$ and trapping of the resulting neutral Ni(I)-amido fragment to yield neutral, paramagnetic, two- and three-coordinate Ni(I) complexes. Protonation of these neutral amido complexes by the bulky phenol $HO(2,6\text{-}i\text{-}Bu_2\text{-}4\text{-}Me\text{-}C_6H_2)$ results in loss of the second amido moiety and trapping by the resulting phenoxide to yield Ni(I)- $O(2,6\text{-}i\text{-}Bu_2\text{-}4\text{-}Me\text{-}C_6H_2)$ complexes. The hapticity of the phenoxide ligand is influenced by the π -accepting ability of the L-type ligand. Where $L = P^tBu_3$, a poor π -acceptor, the phenoxide acts as a π -acceptor and adopts a η^5 -bonding mode through dearomatization of the phenyl ring. When $L = NHC$, a competent π -acceptor, the phenoxide acts as a π -donor, adopting a η^1 -bonding mode through the O atom. The modular nature of this synthetic strategy allows variation of both the L- and X-type ligands of the complex in a stepwise fashion and should be extendable to a wide variety of ligand types for new Ni(I) complexes.



INTRODUCTION

Two-coordinate transition metal complexes are a unique class of compounds that possess interesting chemical,¹ magnetic,² and redox³ properties. Recent reports from this laboratory describe the catalytic C–C cross-coupling and hydrosilylation activities of the two-coordinate nickel bis(amido) complex $Ni[N(SiMe_3)DIPP]_2$ (**1**) and suggest that two-coordinate first-row metal complexes hold significant promise as cheap, earth-abundant catalysts.^{4,5} Analysis of the mechanism of the nickel-mediated cross-coupling revealed several key transformations that leverage the unusual coordination environment and redox properties of the two-coordinate structure. Related results from Hillhouse and co-workers demonstrate novel stoichiometric chemistry for several two- and three-coordinate nickel(I) complexes.⁶ Other nickel(I) complexes have been shown to catalyze C–C and C–N cross-coupling reactions or to serve as precursors to interesting Ni–E multiply bonded species.^{7,8} Despite their high reactivity,⁶ usefulness as synthetic precursors,^{7,8} and potential as cheap, earth-abundant catalysts,^{4,5} low-coordinate nickel(I) complexes have received little attention due to the lack of general synthetic methods for their preparation and the limited number of conveniently prepared nickel(I) starting materials.

Nickel(I) complexes of the type $L-Ni-X$ ($L = 1,3\text{-bis}(2,6\text{-diisopropylphenyl})\text{imidazol-2-ylidene}$ (IPr) and $1,2\text{-bis}(\text{di-tert-butylphosphino})\text{ethane}$ (dtbpe)) represent the most well-studied set of nickel(I) complexes. These complexes have been obtained from Sigman's dimer⁹ $[(IPr)NiCl]_2$ or from a related dimer reported by Hillhouse and co-workers, $[(dtbpe)-$

$NiCl]_2$.^{8a} These sterically demanding ligand platforms can accommodate a variety of X-type ligands in the nickel(I) oxidation state, including alkyls,^{6b,10–12} amides,^{6a,8a,13} phosphides,^{8b} hydrides,¹⁴ and silyls.¹⁵ However, the incorporation of additional L-type ligands is limited by the lack of appropriate L_nNi^I-X starting materials. These Ni(I) halide complexes are typically prepared and isolated from one-electron reduction of the parent Ni(II) halide, $L_nNi^{II}X_2$,^{8a,16} or via comproportionation between appropriate Ni(II) and Ni(0) sources.⁹ Both of these approaches are limited to a few examples and often result in over-reduction to Ni(0) and complex mixtures of products. Herein we report a convenient method for the preparation of two- and three-coordinate nickel(I) compounds from the recently reported complex $K\{Ni[N(SiMe_3)DIPP]_2\}$ (**2**).³ This method allows access to nickel(I) complexes of the form $L-Ni-X$, where both the L and X ligands can be varied.

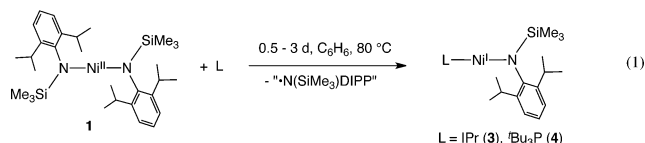
RESULTS AND DISCUSSION

Reactions of $Ni[N(SiMe_3)DIPP]_2$ (1**) with Sterically Hindered Donors.** Initial investigations of the coordination chemistry of **1** demonstrated that small L-type donors such as MeCN and DMAP (*p*-dimethylaminopyridine) simply add to the nickel center to form T-shaped, three-coordinate Ni(II) complexes.⁵ Attempts to extend this chemistry to larger L-donors, such as bulky N-heterocyclic carbenes (NHCs),

Received: August 22, 2014

Published: October 1, 2014

resulted in no reaction at room temperature. For example, IPr and **1** did not react in benzene-*d*₆ over the course of 24 h at 23 °C. However, at 80 °C, 1 equiv of IPr reacted with **1** in benzene to form the two-coordinate Ni(I) species (IPr)Ni[N(SiMe₃)-DIPP] (**3**; 61% isolated yield), rather than a three-coordinate Ni(II) adduct (eq 1).⁵ This interesting process, in which the



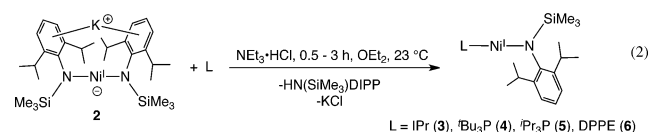
metal is reduced and the IPr formally displaces an equivalent of [•]N(SiMe₃)DIPP from **1**, is similar to the early preparation of (Ph₃P)₂Ni^I[N(SiMe₃)₂] from (Ph₃P)₂Ni^{II}Cl₂ and LiN(SiMe₃)₂ by Bradley and Welch, where the Ni is reduced and an equivalent of [•]N(SiMe₃)₂ is lost.¹⁷ Given these results, the reaction of **1** with sterically hindered donors appeared to represent a promising and general synthetic route to two-coordinate Ni(I) compounds.

In an attempt to evaluate the generality of this ligand-induced reduction, complex **1** was treated with the sterically demanding phosphine ^tBu₃P (1 equiv) in benzene at 80 °C over 3 days. Workup of the reaction mixture provided a low isolated yield (18%) of the new nickel(I) complex (^tBu₃P)Ni[N(SiMe₃)-DIPP] (**4**), isolated as orange crystals from hexanes. Other sterically demanding ligands such as ⁱPr₃P, Mes₃P, 1,2-diphenylphosphinoethane (DPPE), and 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (IMes) resulted only in the formation of HN(SiMe₃)DIPP upon reaction with **1**. No Ni(I) species could be isolated from these reactions, and no such species were observable by ¹H NMR spectroscopy. Thus, this simple synthetic route to two-coordinate Ni(I) complexes, based on the direct reaction of **1** with a two-electron donor, appears to be limited in scope. For this reason, an alternative approach to the synthesis of two-coordinate nickel(I) complexes, based on the stepwise combination of reduction and ligand-exchange reactions, was pursued.

Synthetic Route to Neutral, Two- and Three-Coordinate Ni(I) Complexes. Homolytic metal–ligand bond cleavages related to that shown in eq 1 are potentially interesting in the context of synthesis, catalysis, and biochemistry and exhibit a diverse range of mechanistic pathways.¹⁸ Given the low to moderate yields associated with the conversions of eq 1, it has proven difficult to probe the mechanism of this interesting, ligand-induced homolytic cleavage. However, it seemed that this process might involve separate reduction and ligand displacement steps. The formal reduction of Ni(II) to Ni(I) is consistent with the previously reported redox properties of **1**. As reported elsewhere,³ **1** undergoes a reversible reduction in 1,2-difluorobenzene at –1.28 V vs Fc/Fc⁺ and is readily reduced in high yield (89%) by KC₈ to the anionic Ni(I) complex K{[Ni[N(SiMe₃)DIPP]₂} (**2**). Thus, it was of interest to investigate reactions of **2** with mild acids HX, which were anticipated to result in loss of HN(SiMe₃)DIPP and KX to produce a neutral Ni(I) fragment that might be subsequently trapped by an L-type donor. Indeed, such transformations were found to provide convenient access to the two- and three-coordinate Ni(I) complexes **3–6**.

Compounds **3–6** were prepared from **2** via the same method. This procedure involves treatment of a cold (–30 °C) diethyl ether solution of **2** and the donor ligand L (L = IPr,

^tBu₃P, ⁱPr₃P, DPPE) with 1 equiv of NEt₃·HCl, followed by warming to room temperature over 0.5–3 h (eq 2). The

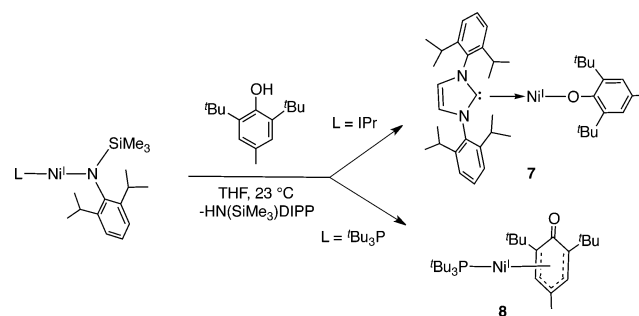


reactions result in elimination of KCl and HN(SiMe₃)DIPP and trapping of the resulting neutral Ni^I[N(SiMe₃)DIPP] fragment by L to provide the nickel(I) amido complexes **3–6** in 69–91% yield after recrystallization. While compound **3** is indefinitely stable at room temperature, compounds **4–6** are thermally unstable and decompose over weeks (**4** and **5**) or days (**6**) at ambient temperature. All compounds show no signs of decomposition after 3 months at –30 °C.

This synthetic method for the preparation of nickel(I) amido complexes of the form L–Ni^I–N(SiMe₃)DIPP appears to be limited only by the ability of the L-donor to support the resulting two- or three-coordinate nickel(I) complex. Strong σ-donors, such as phosphines and N-heterocyclic carbenes, are effective in this regard, whereas weaker, but similarly bulky σ-donors such as the aniline 2,6-Mes₂C₆H₂NH₂ result in reduction of NEt₃·HCl to hydrogen, with formation of **1** and no reaction of the donor (e.g., the aniline). The low oxidation state of the nickel center and the π-donating amido ligand suggest that the Ni^I–N(SiMe₃)DIPP fragment might be stabilized by good π-accepting ligands. However, use of 1,4-cyclooctadiene, 1,2-bis(trimethylsilyl)acetylene, and 2-butyne in the procedure of eq 2 resulted only in the formation of hydrogen and **1** (by ¹H NMR spectroscopy). Presumably, these π-accepting ligands are not efficient at trapping or stabilizing the Ni^I fragment, which may result from protonation of **2**.

The utility of the nickel(I) anionic complex **2** in providing access to neutral, two-coordinate complexes prompted an examination of further transformations of **3–6** involving simple ligand substitutions. In principle, it should be possible to substitute the basic amido ligand in these complexes with a variety of suitably bulky ligands, to produce a range of new L–Ni(I)–X complexes via proton-transfer reactions. Initial attempts to demonstrate this synthetic method involved the preparation of new aryloxide complexes **7** and **8** (Scheme 1).

Scheme 1. Synthesis of **7 and **8** from **3** and **4****



Treatment of **3** and **4** with 1 equiv of 2,6-di-*tert*-butyl-4-methylphenol (dtbmp) in THF at ambient temperature resulted in the loss of HN(SiMe₃)DIPP and incorporation of the –O(2,6-^tBu₂-4-Me-C₆H₂) ligand to give complexes **7** and **8** in 80% and 72% yields, respectively, after recrystallization.

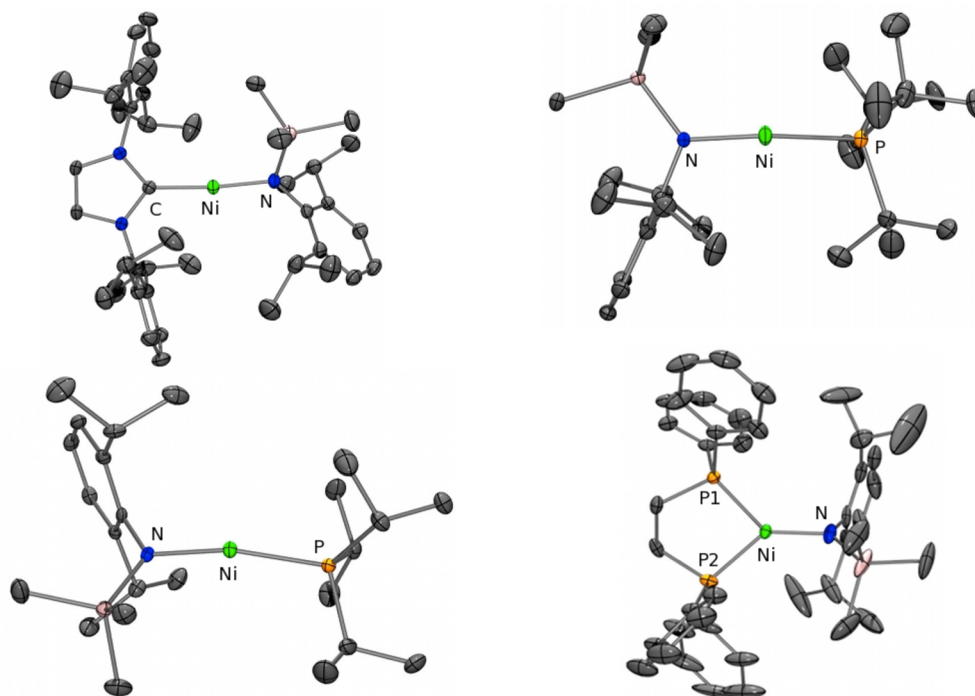


Figure 1. ORTEP diagrams of compounds **3** (top left), **4** (top right), **5** (bottom left), and **6** (bottom right) with all thermal ellipsoids shown at 50% probability. Selected bond lengths (Å) and angles (deg): **3**: Ni–N, 1.8271(2); Ni–C, 1.9123(2); N–Ni–C, 173.01(7). **4**: Ni–N, 1.8250(2); Ni–P, 2.2006(1); N–Ni–P, 165.6(1). **5**: Ni–N, 1.8407(2); Ni–P, 2.1992(7); N–Ni–P, 164.09(6). **6**: Ni–N, 1.875(2); Ni–P1, 2.1978(8); Ni–P2, 2.1922(8); P1–Ni–P2, 87.68(3).

Structural Properties. The X-ray crystal structures of compounds **3–6** are shown in Figure 1. All four compounds feature similar Ni–N bond lengths (1.8250(2)–1.875(2) Å) that are consistent with comparable values previously reported for nickel(I) amido complexes.^{6a,8a,13} The diphosphine compound **6** displays a distorted trigonal planar geometry with the Ni, N, and P atoms all occupying the same plane (sum of angles around Ni is 360°). Compounds **3–5** are two-coordinate and linear with slight bending of the primary bond axis. The N–Ni–C bond angle of **3** is 173.01(7)°, while the N–Ni–P angles of **4** and **5** are 167.6(2)° and 164.09(6)°, respectively. While there is some variation in specific bond distances and angles between these compounds, previous reports of two-coordinate Ni(I) complexes show that both electronic factors¹² and crystal-packing forces^{6a} can have a significant effect on these parameters.

Like compounds **3–5**, compound **7** possesses a linear, two-coordinate geometry with some bending along the primary bond axis. The solid-state structure of **7** (Figure 2) reveals three crystallographically independent molecules that display substantial variations in metrical parameters. The O–Ni–C bond angles vary from 162.19(9)° to 173.3(1)° and the Ni–O bond distances vary from 1.7612(2) to 1.8374(2) Å. An area of particularly significant structural variation between the three molecules is found in the geometry about the O atom. The C_{Ar}–O–Ni bond angle varies from nearly linear (168.2(2)°), as would be expected for an sp-hybridized oxygen, to highly bent (131.82(2)°) and more consistent with sp²-hybridization. Thus, compound **7** appears to be a particularly illustrative example of the effects that crystal-packing forces can have on the solid-state geometry of a compound and underscores the care that must be taken in the interpretation of such structures in terms of electronic structure and other chemical properties.

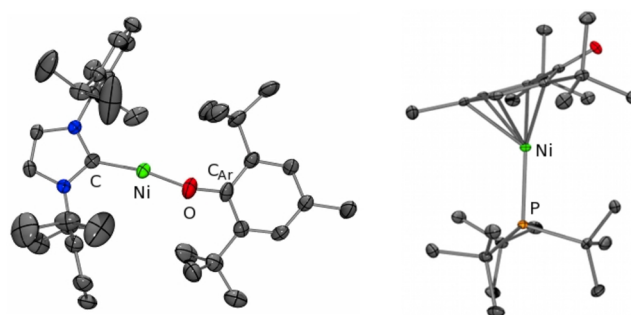


Figure 2. ORTEP diagrams of compounds **7** (left) and **8** (right) with thermal ellipsoids shown at 50% probability. For compound **7**, bond lengths and angles vary drastically among the crystallographically inequivalent molecules in the unit cell (see Supporting Information). Selected bond length (Å) for compound **7**: Ni–P, 2.2333(4) Å.

Attempted preparation of the tBu₃P analogue of **7** from **4** unexpectedly resulted in compound **8**, with dearomatization and η⁵-coordination of the dtbnp ligand to the Ni center (Figure 2). This complex is best characterized as possessing a pentadienyl ligand that is part of a six-membered ring also containing a ketonic carbonyl group. This type of bonding mode for a 2,6-substituted aryl oxide ligand is relatively rare, but a few examples of rhodium, ruthenium, iron, and nickel complexes are known.¹⁹ The five carbons comprising the pentadienyl fragment all lie between 2.1701(1) and 2.2534(1) Å from the Ni atom, while the carbon directly bound to the oxygen clearly lies out of the plane of the other five carbon atoms and is farther away from the Ni center (2.4648(1) Å). The intraligand bond distances further support this characterization of the bonding, as the C–C distances within the pentadienyl fragment fall between 1.4037(2) and 1.410(2) Å.

and are therefore consistent with a delocalized π -system. Furthermore, the C–C distances to the ketonic carbon are much longer, at 1.4707(2) and 1.4721(2) Å, and consistent with a C–C single bond. Finally, the C–O bond distance of 1.2570(2) Å reflects double-bond character.

The difference in binding modes for the dtbnp ligands in compounds 7 and 8 seems somewhat surprising, since it appears to be associated with the L-donors in these complexes (IPr and ^tBu₃P, respectively), which are both strong, bulky σ -donors. This difference in hapticity might be attributed to the differing abilities of IPr and ^tBu₃P to participate in π -back-bonding. When bound to a metal center through the oxygen atom in an η^1 fashion, the dtbnp ligand is a π -donor through the lone pairs on the oxygen, whereas when bound η^5 through the π -system, it may serve as a π -acceptor. The bonding mode of the dtbnp ligand changes to complement the nature of the L-donor, acting as a π -donor when L is a competent π -acceptor (IPr) and as a π -acceptor when L is not (^tBu₃P).

While phosphines are capable of acting as π -acceptor ligands through a σ^* -orbital, trialkylphosphines such as ^tBu₃P have been shown through a variety of experimental and computational methods to be very poor π -acceptors.²⁰ On the other hand, the π -acidity of N-heterocyclic carbenes, which formally have a vacant carbon p-orbital capable of accepting electron density, can vary greatly depending upon the substitution pattern and conjugation of the imidazole ring.²¹ In the case of IPr, structural comparison of the isosteric amido and alkyl compounds (IPr)Ni–N(SiMe₃)₂^{6a} and (IPr)Ni–CH(SiMe₃)₂^{6b} provides insight into the significance of π -back-bonding in these types of complexes. In the amido complex, where π -donation from the nitrogen lone pair would be expected to increase the degree of back-bonding, the Ni–C_{NHC} bond length is 1.879(2) Å. This is somewhat shorter than the Ni–C_{NHC} bond distance in the alkyl complex, 1.910(2) Å, suggesting that IPr can participate in π -back-bonding interactions with Ni(I). In the case of compound 7, the Ni–C_{NHC} bond lengths of the three crystallographically independent units range from 1.880(2) to 1.863(3) Å and suggest stabilization from π -back-bonding to favor the η^1 conformation of the dtbnp ligand. The poorer π -acidity of ^tBu₃P (relative to IPr) appears to favor participation of the dtbnp ligand as a π -acceptor in the η^5 -bonding mode.

Magnetic Properties. The magnetic moments of compounds 2–8 were measured using Evans' method²² and are given in Table 1. All seven compounds have moments

value of 1.53 μ_B . Compounds 2 and 7 exhibit magnetic moments very close to the expected values (1.66 and 1.80 μ_B , respectively). The magnetic moments of two-coordinate transition metal complexes are known to deviate substantially from the spin-only value, due to contributions from unquenched spin–orbit coupling. Examples of both higher-^{2a,b} and lower-than-expected^{2c} magnetic moments due to the contribution from spin–orbit coupling have been observed, and such effects are likely responsible for deviations from the spin-only values observed in complexes 2–8.

CONCLUSIONS

The easily prepared nickel(I) anion K{Ni[N(SiMe₃)DIPP]₂} has been shown to be a convenient and versatile starting material for the synthesis of two- and three-coordinate nickel(I) compounds. This method allows for the sequential substitution of both amido ligands, to give unsymmetrical L–Ni(I)–X type complexes in a modular fashion. The ability to prepare these previously inaccessible nickel(I) complexes will allow the further exploration of their chemical, structural, and electronic properties.

EXPERIMENTAL SECTION

General Considerations. Unless otherwise stated, all reactions and manipulations were carried out in an MBraun Lab Master DP glovebox or using standard Schlenk techniques under a nitrogen atmosphere. Pentane, toluene, and 1,2-difluorobenzene were purchased from Sigma-Aldrich. Diethyl ether was purchased from Honeywell, and tetrahydrofuran was purchased from Macron Chemicals. Pentane, toluene, tetrahydrofuran, diethyl ether, and 1,2-difluorobenzene were dried and degassed using a JC Meyers Phoenix SDS solvent purification system. C₆D₆ was purchased from Cambridge Isotope Laboratories, dried over Na/K alloy, and then degassed by four freeze–pump–thaw cycles. All NMR spectra were collected at ambient temperature (ca. 22 °C) on a Bruker AVB-400, AV-500, AV-600, or AVQ-400 NMR spectrometer, each equipped with a 5 mm BB probe, and referenced to the residual proteo solvent signals. Solution magnetic susceptibilities were determined by ¹H NMR spectroscopy using Evans' method.²² Elemental analyses were performed by the UC Berkeley College of Chemistry Microanalytical facility. The abbreviation “DIPP” refers to a 2,6-diisopropylphenyl moiety. The abbreviation “DPPE” refers to 1,2-(bis(diphenylphosphino)ethane). The abbreviation “IPr” refers to the N-heterocyclic carbene *N,N'*-1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene. DPPE and P^tBu₃ were purchased from Sigma-Aldrich and used as received. NEt₃·HCl was purchased from Sigma-Aldrich and sublimed before use. PⁱPr₃ was purchased from Strem Chemicals and used as received. 2,6-Di-*tert*-butyl-4-methylphenol was purchased from Pfaltz and Bauer and used as received. IPr was prepared according to the standard literature procedure.²³ Representative procedures for nickel complexes (3 and 7) are given below; those for the other complexes are contained in the Supporting Information.

(IPr)Ni–N(SiMe₃)DIPP (3). To a 20 mL scintillation vial were added 2 (0.100 g, 0.168 mmol), IPr (0.066 g, 0.170 mmol), and 6 mL of Et₂O, forming a yellow solution. To a separate 20 mL scintillation vial were added NEt₃·HCl (0.023 g, 0.168 mmol) and a magnetic stir bar, and both vials were cooled to –30 °C. The chilled solution of 2 and IPr was then transferred to the vial containing the NEt₃·HCl, and the resulting suspension was stirred while warming to room temperature for 1 h, during which the color of the mixture changed from yellow to dark orange-brown. The mixture was then filtered, and the volatile components were removed under reduced pressure. The resulting residue was dissolved in 1.5 mL of dimethoxyethane, upon which was layered 6 mL of pentane. The layered solution was then placed in a –30 °C freezer overnight, yielding 0.106 g of 3 (91%) as yellow-orange plates, which were isolated by decantation, washed with 4 aliquots of 2 mL of –30 °C pentane, and dried in vacuo. Full

Table 1. Magnetic Moments of Compounds 2–8 As Measured by Evans' Method

compound	μ_{eff} (μ_B)
K{Ni[N(SiMe ₃)DIPP] ₂ } (2)	1.66
(IPr)Ni[N(SiMe ₃)DIPP] (3)	2.12
(^t Bu ₃ P)Ni[N(SiMe ₃)DIPP] (4)	2.35
(ⁱ Pr ₃ P)Ni[N(SiMe ₃)DIPP] (5)	2.55
(DPPE)Ni[N(SiMe ₃)DIPP] (6)	1.53
(IPr)Ni[OAr] (7)	1.80
(^t Bu ₃ P)Ni[η^5 -OAr] (8)	2.29

consistent with the presence of one unpaired electron. However, there are substantial deviations from the expected spin-only value of 1.73 μ_B for the magnetic moment, with some moments falling substantially above or below that value. Compounds 3, 4, 5, and 8 have higher than expected values, ranging from 2.12 μ_B (3) to 2.55 μ_B (4), while 6 exhibits a low

characterization data for **3** are available in a prior publication. For convenience, its spectroscopic properties are reproduced here.³ ¹H NMR (400 MHz, C₆D₆, 21 °C): δ 22.20 (2H), 10.93 (4H), 9.37 (2H), 8.37 (p-Ar-H, 1H), 4.17 (4H), 3.99 (2H), 3.82 (–Si(CH₃)₃, 9H), 3.56 (Ar–CH(CH₃)₂, 12H), 1.88 (Ar–CH(CH₃)₂, 12H), –0.65 (Ar–CH(CH₃)₂, 6H), –6.27 (Ar–CH(CH₃)₂, 6H), –11.69 (2H). Assignment of shifts to particular protons is given where integration allows unambiguous assignment. $\mu_{\text{eff}} = 2.12 \mu_{\text{B}}$ (C₆D₆, 21 °C, Evans' method).

(IPr)Ni(2,6-di-*tert*-butyl-4-methyl)C₆H₂O (**7**). To a 20 mL scintillation vial were added **3** (0.135 g, 0.194 mmol) and 6 mL of THF, forming a yellow-orange solution. To this stirring solution at ambient temperature was added a solution of 2,6-di-*tert*-butyl-4-methylphenol (0.043 g, 0.194 mmol) in 4 mL of THF, resulting in an immediate color change from yellow-orange to red. Stirring was continued for 30 min; then the mixture was filtered and the volatile components were removed under reduced pressure. The resulting residue was dissolved in 2.5 mL of toluene, upon which was layered 8 mL of pentane. The layered solution was placed in the –30 °C freezer overnight, yielding 0.107 g of **7** (80%) as large red blocks, which were isolated by decantation and dried in vacuo. After extensive drying in this manner (>8 h), approximately 0.25 equiv of toluene of crystallization remained in the sample (quantified by ¹H NMR spectroscopy using an internal standard). The yield listed above accounts for the presence of this toluene. ¹H NMR (400 MHz, C₆D₆, 24 °C): δ 21.38 (12H), 18.82 (4H), 16.69 (2H), 11.18 (2H), 6.80 (3H), 2.84 (12H), –0.94 (4H), –3.49 (2H), –7.09 (18H). $\mu_{\text{eff}} = 1.80 \mu_{\text{B}}$ (C₆D₆, 20 °C, Evans' method). Anal. Calcd for C₄₂H₅₉N₂NiO + 0.25(C₇H₈): C, 76.19; H, 8.92; N, 4.06. Found: C, 76.54; H, 9.12; N, 3.72. Crystals suitable for single-crystal X-ray diffraction studies were obtained from the workup described above.

■ ASSOCIATED CONTENT

■ Supporting Information

Additional experimental procedures, crystallographic data, and spectral characterization are available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: tdtilley@berkeley.edu.

Notes

The authors declare no competing financial interests.

■ ACKNOWLEDGMENTS

We gratefully acknowledge funding from the National Science Foundation for this work under grant no. CHE-1265674. We also acknowledge the National Institutes of Health for funding of the ChexRay X-ray crystallographic facility (College of Chemistry, University of California, Berkeley) under grant no. S10-RR027172.

■ REFERENCES

- (1) Power, P. P. *Chem. Rev.* **2012**, *112*, 3482–3507.
- (2) (a) Reiff, W. M.; LaPointe, A. M.; Witten, E. H. *J. Am. Chem. Soc.* **2004**, *126*, 10206–10207. (b) Merrill, W. A.; Stitch, T. A.; Brynda, M.; Yeagle, G. J.; Fetting, J. C.; De Hont, R.; Reiff, W. M.; Schulz, C. E.; Britt, R. D.; Power, P. P. *J. Am. Chem. Soc.* **2009**, *131*, 12693–12702. (c) Boynton, J. N.; Guo, J.-D.; Fetting, J. C.; Melton, C. E.; Nagase, S.; Power, P. P. *J. Am. Chem. Soc.* **2013**, *135*, 10720–10728. (d) Zadrozny, J. M.; Xiao, D. J.; Atanasov, M.; Long, G. J.; Grandjean, F.; Neese, F.; Long, J. R. *Nat. Chem.* **2013**, *5*, 577–581. (e) Bryan, A. M.; Merrill, W. A.; Reiff, W. M.; Fetting, J. C.; Power, P. P. *J. Am. Chem. Soc.* **2012**, *134*, 3366–3373. (f) Zadrozny, J. M.; Atanasov, M.; Bryan, A. M.; Lin, C.-Y.; Rekken, B. D.; Power, P. P.; Neese, F.; Long, J. R. *Chem. Sci.* **2013**, *4*, 125–138.
- (3) Lipschutz, M. I.; Yang, X.; Chatterjee, R.; Tilley, T. D. *J. Am. Chem. Soc.* **2013**, *135*, 15298–15301.
- (4) Lipschutz, M. I.; Tilley, T. D. *Angew. Chem., Int. Ed.* **2014**, *53*, 7290–7294.
- (5) Lipschutz, M. I.; Tilley, T. D. *Chem. Commun.* **2012**, *48*, 7146–7148.
- (6) (a) Laskowski, C. A.; Hillhouse, G. L. *J. Am. Chem. Soc.* **2008**, *130*, 13846–13847. (b) Laskowski, C. A.; Bungum, D. J.; Baldwin, S. M.; Del Ciello, S. A.; Iluc, V. M.; Hillhouse, G. L. *J. Am. Chem. Soc.* **2013**, *135*, 18272–18275. (c) Anderson, J. S.; Iluc, V. M.; Hillhouse, G. L. *Inorg. Chem.* **2010**, *49*, 10203–10207.
- (7) Cross-coupling: (a) Miyazaki, S.; Koga, Y.; Matsumoto, T.; Matsubara, K. *Chem. Commun.* **2010**, *46*, 1932–1934. (b) Zhang, K.; Conda-Sheridan, M.; Cooke, S. R.; Louie, J. *Organometallics* **2011**, *30*, 2546–2552. (c) Nagao, S.; Matsumoto, T.; Koga, Y.; Matsubara, K. *Chem. Lett.* **2011**, *40*, 1036–1038.
- (8) Ni–E multiple bonds: (a) Mindiola, D. J.; Hillhouse, G. L. *J. Am. Chem. Soc.* **2001**, *123*, 4623–4624. (b) Melenkivitz, R.; Mindiola, D. J.; Hillhouse, G. L. *J. Am. Chem. Soc.* **2002**, *124*, 3846–3847. (c) Iluc, V. M.; Miller, A. J. M.; Anderson, J. S.; Monreal, M. J.; Mehn, M. P.; Hillhouse, G. L. *J. Am. Chem. Soc.* **2011**, *133*, 13055–13063. (d) Kogut, E.; Wiencko, H. L.; Zhang, L.; Cordeau, D. E.; Warren, T. H. *J. Am. Chem. Soc.* **2005**, *127*, 11248–11249.
- (9) Dibble, B. R.; Sigman, M. S.; Arif, A. M. *Inorg. Chem.* **2005**, *44*, 3774–3776.
- (10) Hruszkewycz, D. P.; Wu, J.; Green, J. C.; Hazari, N.; Schmeter, T. J. *Organometallics* **2012**, *31*, 470–485.
- (11) Kitiachvili, K. D.; Mindiola, D. J.; Hillhouse, G. L. *J. Am. Chem. Soc.* **2004**, *126*, 10554–10555.
- (12) Wu, J.; Nova, A.; Balcells, D.; Brudwig, G. W.; Dai, W.; Guard, L. M.; Hazari, N.; Lin, P.-H.; Pokhrel, R.; Takese, M. K. *Chem.—Eur. J.* **2014**, *20*, 5327–5337.
- (13) Laskowski, C. A.; Morello, G. R.; Saouma, C. T.; Cundari, T. R.; Hillhouse, G. L. *Chem. Sci.* **2013**, *4*, 170–174.
- (14) Bach, I.; Goddard, R.; Kopiske, C.; Seevogel, K.; Pörschke, K.-R. *Organometallics* **1999**, *18*, 10–20.
- (15) Iluc, V. M.; Hillhouse, G. L. *J. Am. Chem. Soc.* **2010**, *132*, 11890–11892.
- (16) (a) Aresta, M.; Nobile, C. F.; Sacco, A. *Inorg. Chim. Acta* **1975**, *12*, 167–178. (b) Dapporto, P.; Fallani, G.; Sacconi, L. *Inorg. Chem.* **1974**, *13*, 2847–2850. (c) Krüger, C.; Betz, P. *J. Organomet. Chem.* **1990**, *387*, 113–121. (d) Bai, G.; Wei, P.; Stephan, D. W. *Organometallics* **2005**, *24*, 5901–5908. (e) Holland, P. L.; Cundari, T. L.; Perez, L. L.; Eckert, N. A.; Lachicotte, R. J. *J. Am. Chem. Soc.* **2002**, *124*, 14416–14424.
- (17) Bradley, D. C.; Hursthouse, M. B.; Smallwood, R. J.; Welch, A. J. *J. Chem. Soc., Chem. Commun.* **1972**, *15*, 872–873.
- (18) (a) Ke, M.; Rettig, S. J.; James, B. R.; Dolphin, D. J. *Chem. Soc., Chem. Commun.* **1987**, 1110–1112. (b) He, M.; Dowd, P. J. *Am. Chem. Soc.* **1998**, *120*, 1133–1137. (c) Randaccio, L. *Comments Inorg. Chem.* **1999**, *21*, 327–376. (d) Jensen, K. P.; Ryde, U. *J. Am. Chem. Soc.* **2005**, *127*, 9117–9128. (e) Finke, R. G.; Hay, B. P. *Inorg. Chem.* **1984**, *23*, 3041–3043. (f) Wayland, B. B.; Ba, S.; Sherry, A. E. *J. Am. Chem. Soc.* **1991**, *113*, 5305–5311.
- (19) (a) Dahlenburg, L.; Hock, N. *J. Organomet. Chem.* **1985**, *284*, 129–138. (b) Wallasch, M.; Wolmershäuser, G.; Sitzmann, H. *Angew. Chem., Int. Ed.* **2005**, *44*, 2597–2599. (c) Cámpora, J.; Reyes, M. L.; Hackl, T. *Organometallics* **2000**, *19*, 2950–2952. (d) Loren, S. D.; Campion, B. K.; Heyn, R. H.; Tilley, T. D.; Bursten, B. E.; Luth, K. W. *J. Am. Chem. Soc.* **1989**, *111*, 4712–4718.
- (20) (a) Marynick, D. N. *J. Am. Chem. Soc.* **1984**, *106*, 4064–4065. (b) Pacchioni, G.; Bagus, P. S. *Inorg. Chem.* **1992**, *31*, 4391–4398. (c) Mitoraj, M. P.; Michalak, A. *Inorg. Chem.* **2010**, *49*, 578–582.
- (21) Khranov, D. M.; Lynch, V. M.; Bielawski, C. W. *Organometallics* **2007**, *26*, 6042–6049.
- (22) Evans, D. F. *J. Chem. Soc.* **1959**, 2003–2005.
- (23) Jafarpour, L.; Stevens, E. D.; Nolan, S. P. *J. Organomet. Chem.* **2000**, *606*, 49–54.