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Hydrosilylative Reduction of Tertiary Amides to Amines Catalyzed by *N*-(Phosphinoaryl)anilido Complexes of Iron and Cobalt

Dylan J. Hale,[a] Luke J. Murphy,[a] Robert McDonald,[b] Michael J. Ferguson[b] and Laura Turculet*[a]

Abstract: The synthesis and structural characterization of low-coordinate Fe(II) and Co(II) complexes supported by the monoanionic P,N-ligand *N*-(2-dicyclohexylphosphinophenyl)-2,6-diisopropylanilide are described. A three-coordinate (P,N)Fe-hexamethyldisilazide complex (**2**), and four-coordinate (P,N)Fe- (**3-Fe**) and (P,N)Co-alkyl (**3-Co**) complexes were evaluated as pre-catalysts for the hydrosilylative reduction of amides with $PhSiH_3$ (5 mol% pre-catalyst, 1 equiv. $PhSiH_3$, 80 °C, 1-24 h). The Fe complex **2** proved to be more broadly effective for the reduction of a variety of tertiary amide substrates, and was shown to mediate the reduction of *N*,*N*-dibenzylbenzamide at a loading of 1 mol%, to achieve near quantitative formation of tribenzylamine in 1 h (80 °C). Complex **2** also proved effective for the hydrosilylation of tertiary amides under ambient conditions (5 mol% Fe, 24 h), which is a unique example of room temperature amide hydrosilylation mediated by an Fe catalyst without the need for photochemical activation. Given the widespread use of amide reduction protocols in synthesis, the development of efficient Fe-based catalysts that operate under mild conditions is an important target.

Introduction

The reduction of amides to amines is a fundamental reaction of broad utility in organic synthesis.[1] While reactive alkali metal hydride or boron hydride reagents are commonly used as stoichiometric reductants in this regard, significant effort has been devoted to developing alternative routes that may prove less harsh and more selective, including transition metal catalyzed hydrosilylation.[1d] Notable examples of amide hydrosilylation catalyzed by platinum-group metals have been reported in recent years, including Ru-, Rh-, Ir-, and Pt-based catalysts.[2] However, the high cost and low abundance of such precious metals has inspired a broad effort to develop increasingly sustainable catalysts, including those that utilize earth-abundant 3*d* transition metals.[3] In this regard, Fe-based catalysts are particularly attractive, given the low cost, comparatively low toxicity, and high abundance of Fe.[1e, 4] In the context of amide hydrosilylation, early efforts towards this goal were reported concurrently by Beller[5] and Nagashima,[6] who demonstrated the utility of Fe carbonyl species in such catalysis under both thermal (6 - 30 mol% Fe, 100 °C, 24 h) and photochemical (10 mol% Fe, RT, 9 h) conditions. Since these initial reports, the groups of Sortais and Darcel,[7] Buitrago and Adolfsson,[8] and Driess[9] have each reported on the utility of Fe complexes supported by *N*-heterocyclic carbene ligation for amide hydrosilylation catalysis. Although the natural abundance of Fe makes it the top choice amongst the transition metals from the perspective of sustainability, a handful of noteworthy examples of amide hydrosilylation mediated by other base metals, such as Mn-,[10] Co-,[11] and Ni-,[12] as well as Cu-[13] and Zn-based [14] catalysts, have also been disclosed, and efforts to develop non-metal catalysts have also been undertaken.[15] These notwithstanding, such reports are still very few in comparison to related hydrosilylative reductions of carbonyl species such as ketones and aldehydes.[4d-g, 16]

In a collaborative effort, our group has recently reported on a versatile Mn catalyst featuring bidentate *N*-phosphinoamidinate ligation that is broadly useful for the hydrosilylation of carbonyl substrates under mild conditions, including rare examples of room temperature hydrosilylative reduction of tertiary amides with $PhSiH_3$ (5 mol% Mn, 75 °C, 1 h or 2 mol% Mn, 25 °C, 3 - 48 h).[10], [17] In a subsequent study, we evaluated the catalytic performance of structurally related *N*-phosphinoamidinate Mn, Fe, Co, and Ni pre-catalysts in amide hydrosilylation, and developed a new three-coordinate Ni pre-catalyst that proved to be particularly effective in such amide reduction chemistry.[12c] We further demonstrated that the consideration of ancillary ligation plays an important role in amide reduction catalysis, as *N*-phosphinoamidinate ligated complexes showed far superior reactivity in comparison with $M(N(SiMe_3)_2)_2$ (M = Mn, Fe, and Co) pre-catalysts.

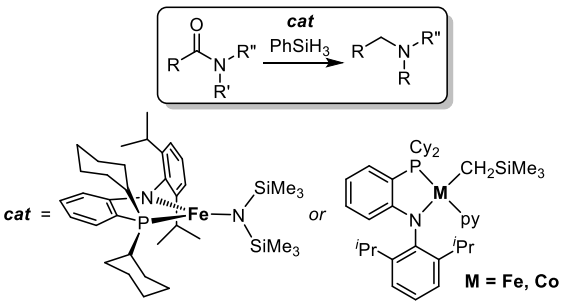

Figure 1. Fe and Co pre-catalysts reported herein for the reduction of amides to the corresponding amines with $PhSiH_3$.

[a] D. J. Hale, L. J. Murphy, Prof. Dr. L. Turculet
Department of Chemistry
Dalhousie University
6274 Coburg Rd., Halifax, Nova Scotia, B3H 4R2 (Canada)
E-mail: laura.turculet@dal.ca
[b] Dr. M. J. Ferguson, Dr. R. McDonald
X-Ray Crystallography Laboratory, Department of Chemistry
University of Alberta
11227 Saskatchewan Dr., Edmonton, Alberta, T6G 2G2 (Canada)

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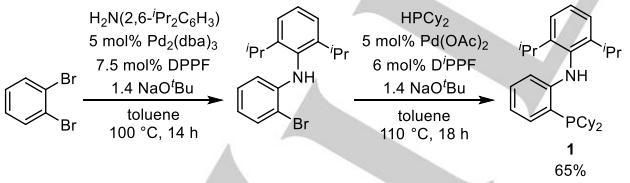
In an effort to further elaborate ancillary ligation strategies for reactive 3*d*-transition metal complexes that may be of catalytic utility in such transformations, we have also pursued alternative anionic P,N ligand motifs. Despite the rich chemistry of P,N ligands used in conjunction with various transition metals,[18] the specific class of *monoanionic* P,N ligands has received considerably less attention, particularly with respect to the first row transition metals. Phenylene-bridged anilido phosphine ligands are a structurally simple class of monoanionic P,N ligand that have not been widely explored in this regard.[19], [20] Herein we report a new anilido phosphine derivative (**1**) and evaluate complexes of Fe and Co supported by this bidentate ligand as pre-catalysts for the hydrosilylation of tertiary and secondary amides with $PhSiH_3$ (Figure 1). A three-coordinate Fe amido pre-catalyst of this type (**2**) was found to be superior to related four-coordinate Fe (**3-Fe**) and Co (**3-Co**) alkyl derivatives, enabling facile reduction of a variety of tertiary amide substrates, including more challenging sterically demanding substrates such as *N*,*N*-diisopropylbenzamide. The useful catalytic performance of **2** under relatively mild conditions, including examples of room temperature reactivity, is noteworthy given current interest in iron catalysis.

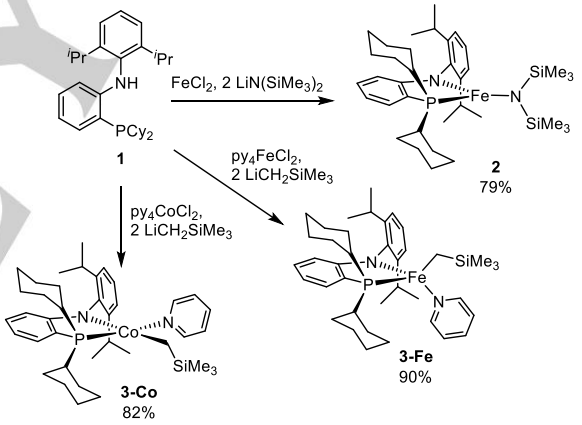
Results and Discussion

Synthesis of a P,N Ligand Precursor. The Liang group has previously reported the synthesis of bidentate, phenylene-bridged anilido phosphine ligands and their coordination chemistry with Ni and Zn.[19a-d] Examples of Cu and Ni complexes supported by similar ligands have also been reported by Peters[19e] and Mindiola,[19f] respectively. The closely related pro-ligand **1** featuring cyclohexyl-phosphino substitution was readily prepared on a multigram scale by the application of sequential C-N and C-P cross-coupling, starting from *o*-dibromobenzene (Scheme 1). Single crystal X-ray diffraction analysis (Figure 2a) and NMR spectroscopic data for **1** confirmed the formulation of this precursor.



Scheme1. Synthesis of the pro-ligand **1**.

Synthesis of an Fe(II) Amido Complex. Our previous work has identified Fe hexamethyldisilazide complexes as useful pre-catalysts for carbonyl hydrosilylation applications,[17f] possibly via reactive Fe-hydride intermediates generated under catalytic conditions.[17a] In an effort to access such a hexamethyldisilazide complex featuring anilido phosphine ancillary ligation, $FeCl_2$ was treated with two equiv. $LiN(SiMe_3)_2$ and subsequently with one equiv. of **1** (Scheme 2). The targeted three-coordinate hexamethyldisilazide Fe(II) complex **2** was isolated in 79% yield *via* this route. Solution magnetic moment measurements for **2** (Evans method,[21] benzene-d_6, 300K) resulted in a calculated μ_{eff} value of 4.9 μ_B, consistent with an $S = 2$ ground state, as was also observed for *N*-phosphinoamidinate analogues of **2**,[17f] and as is typically the case for related three-coordinate β-diketiminato Fe(II) complexes.[22] The solid state structure of **2** was determined by use of X-ray crystallographic techniques, and is consistent with the proposed formulation of **2** as a mononuclear hexamethyldisilazide complex featuring κ^2-*P*,*N* coordination of the diarylamido phosphine ligand (Figure 2b). The complex is planar at the Fe center ($\Sigma <_{\text{at Fe}} = 360°$) and adopts a coordination geometry that is somewhat closer to T-shaped (P-Fe-N1 84.90(6)°, N1-Fe-N2 153.09(9)°, P-Fe-N2 122.01(7)°) than previously observed for *N*-phosphinoamidinate analogues (*cf.* P-Fe-$N_{amidinate}$ 81.10(6)°, $N_{amidinate}$-Fe-N_{SiMe3} 144.15(9)°, P-Fe-N_{SiMe3} 132.86(6)° for an *N*-phosphinoamidinate analogue of **2** featuring P-^{t}Bu$_2$ and $N_{amidinate}$-2,6-^{i}Pr$_2$C$_6$H$_3$ substitution).[17f] The Fe-P and Fe-N1 distances of 2.4425(7) and 1.9409(19) Å, respectively, are comparable to those reported for related *N*-phosphinoamidinate Fe(II) species.[17f] Attempts to access the Co analogue of **2** using a similar synthetic route to that outlined in Scheme 2 were not successful.



Scheme 2. Synthesis of Fe(II) and Co(II) complexes.

Synthesis of Fe(II) and Co(II) Alkyl Complexes. We further sought to explore the feasibility of generating P,N-supported Fe(II) alkyl complexes that may function as pre-catalysts for carbonyl hydrosilylation applications. Towards this end, py_4FeCl_2 was treated with two equiv. of $LiCH_2SiMe_3$ and subsequently with one equiv. of **1**, which afforded the Fe alkyl complex **3-Fe** as a red, paramagnetic solid (Scheme 2).[23] Crystallographic characterization of **3-Fe** confirmed the formulation of this complex as a four-coordinate alkyl complex featuring distorted tetrahedral geometry at Fe, with κ^2-*P*,*N* coordination of the diarylamido phosphine ligand as well as an equiv. of pyridine coordinated to the Fe center (Figure 2c). The Fe-C7 distance of 2.045(3) Å is comparable to values reported previously for low-coordinate Fe(II)-CH_2SiMe_3 complexes.[24] Solution magnetic

moment measurements for **3-Fe** (Evans method,[21] benzene-d_6, 300K) resulted in a calculated μ_{eff} value of 5.2 μ_B, consistent with an S = 2 ground state, as anticipated for a high-spin d^6 metal center in tetrahedral geometry.[25]

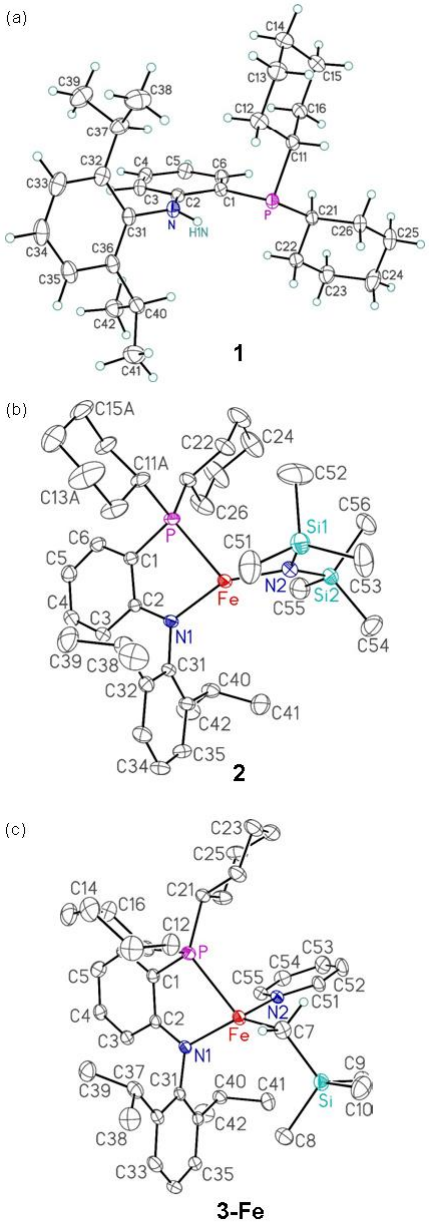


Figure 2. Crystallographically determined structures of (a) **1**, (b) **2**, and (c) **3-Fe**; most hydrogen atoms in (b) and (c) have been omitted for clarity. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 30% probability level. Selected interatomic distances (Å) and angles (°): for **1** P-C1 1.8406(11), P-C11 1.8651(12), P-C21 1.8529(12), N-C2 1.3857(14), N-C31 1.4279(14), C1-C2 1.4189(15); for **2** Fe-P 2.4425(7), Fe-N1 1.9409(19), Fe-N2 1.904(2), P-C1 1.812(2), N1-C2 1.398(3), C1-C2 1.422(3), P-Fe-N1 84.90(6), P-Fe-N2 122.01(7), N1-Fe-N2 153.09(9); for **3-Fe** Fe-P 2.4239(9), Fe-N1 2.007(2), Fe-N2 2.160(2), Fe-C7 2.045(3), P-C1 1.821(3), N1-C2 1.376(3), C1-C2 1.430(4), P-Fe-N1 82.86(7), P-Fe-N2 97.92(6), P-Fe-C7 117.56, N1-Fe-N2 105.50(9), N1-Fe-C7 135.05(11), N2-Fe-C7 110.06(11).

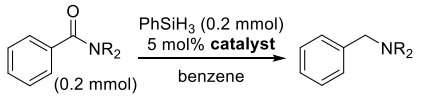
The analogous Co alkyl complex **3-Co** was also prepared using a similar synthetic route (Scheme 2). Thus treatment of py_4CoCl_2 with two equiv. of $LiCH_2SiMe_3$[26] and subsequently with one equiv. of **1** afforded dark red, paramagnetic **3-Co** in 82% yield. Unlike for **3-Fe**, solution magnetic moment measurements for **3-Co** (Evans method, benzene-d_6, 300K) resulted in a calculated μ_{eff} value of 2.3 μ_B, consistent with square-planar, low-spin (S = ½) Co(II).[27] A high quality X-ray crystal structure of **3-Co** has remained elusive. However, the connectivity and square-planar geometry in **3-Co** were unequivocally ascertained on the basis of a low resolution X-ray crystal structure (Figure S2 in the Supporting Information), whereby complete refinement was not feasible due to the lack of data at high diffraction angles.

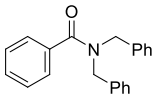
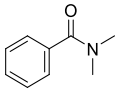
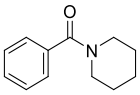
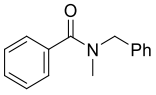
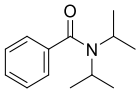
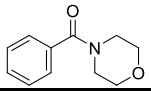
Complexes **3-Fe** and **3-Co** are among only a few reported Fe and Co alkyl complexes supported by bidentate P,N ligation. Some related examples of five- and six-coordinate Co^{II}- and Co^{III}-methyl complexes of 2-(diphenylphosphino)anilido ligands have been reported previously by Klein and co-workers.[19g] As well, examples of four-coordinate mono-alkyl complexes supported by *tridentate* bis(phosphine) amido PNP ligands have been reported for both Fe(II) and Co(II). Similar to the observations reported herein, $(PNP)MCH_2SiMe_3$ complexes (PNP = κ^3-$N(SiMe_2CH_2PPh_2)_2$, M = Fe or Co) were found to adopt tetrahedral high-spin configuration for M = Fe, and low-spin square planar configuration for M = Co.[25b, 27a]

Fe and Co-catalyzed Reduction of Amides. Having prepared mononuclear Fe and Co complexes supported by bidentate anilido phosphine ligation, the utility of these complexes as pre-catalysts for amide hydrosilylation was evaluated. The choice of $PhSiH_3$ as the reductant for this application was based on our previous observations that $PhSiH_3$ is effective for the reduction of ketones, aldehydes, esters, and amides by related *N*-phosphinoamidinate 3*d* metal complexes.[10, 12c, 17f] We initially chose to evaluate the efficacy of **2**, **3-Fe** and **3-Co** as catalysts for the hydrosilylation of a series of tertiary benzamide substrates using a pre-catalyst loading of 5 mol% and one equiv. of $PhSiH_3$ relative to amide (Table 1). Upon heating at 80 °C for 1 h, near quantitative (>99%) conversion of *N,N*-dibenzylbenzamide to tribenzylamine was observed for **2** and **3-Fe**, but only 48% conversion to product was obtained for **3-Co** (Table 1, Entry 1). Comparable reactivity was observed for similar substrates under these conditions, with the Fe-based pre-catalysts **2** and **3-Fe** generally outperforming **3-Co**. For the Co-based pre-catalyst **3-Co**, full conversion to product was observed only for 1-benzoylpiperidine (Table 1, Entry 3), while conversions for all other benzamides ranged from 55-83%. In the case of 4-benzoylmorpholine (Table 1, Entry 6), longer reaction times (18-23 h) were required to achieve >95% conversion to the amine product for both the Fe-based pre-catalysts. While **2** and **3-Fe** generally performed in a similar manner for this set of substrates, a significant divergence from this was observed in the reduction of *N,N*-diisopropylbenzamide (Table 1, Entry 5), which is a challenging substrate for all three pre-catalysts. After 24 h at 80 °C only **2** afforded >90% conversion to *N,N*-diisopropylbenzylamine (78% isolated yield), while use of **3-Fe** and **3-Co** resulted in 59 and 57% conversion

to product, respectively. In the case of *N*,*N*-dibenzylbenzamide (Table 1, Entry 1), the loading of **2** could be dropped to 1 mol% while still achieving near quantitative formation of tribenzylamine in 1 h.

Table 1. Reduction of tertiary benzamides to tertiary benzylamines.

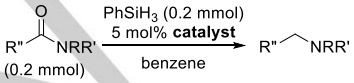


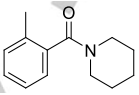
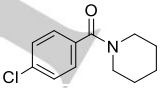
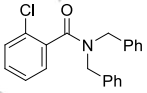
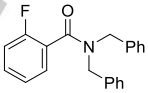
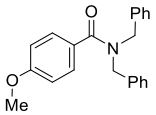
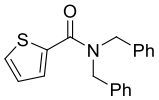
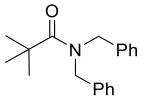
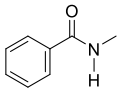
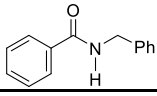
Entry	Amide	5 mol% **2**		5 mol% **3-Fe**		5 mol% **3-Co**	
		Yield (%)[a]	Time (h)	Yield (%)[a]	Time (h)	Yield (%)[a]	Time (h)
1		>99[b], 98[c] (74)	1	>99	1	48	1
2		>99, >99[c] (57)[d]	1	98	1	83	1
3		>99, >99[c] (74)	1	>99	1	98	1
4		>99, 66[c] (72)	1	93	1	80	1
5		94, 9[c] (78)	24	59	24	57	24
6		97 (78)	23	98	18	55	18

[a] Yield of product (average of two runs at 80 °C, unless otherwise stated) determined by use of gas chromatography against an internal standard (dodecane); in the case of incomplete reactions, the mass balance corresponds primarily to unreacted starting material. Numbers in parentheses are isolated yields following flash chromatography. [b] 1 mol % **2**, 80 °C, 1 h. [c] 5 mol% **2**, RT, 24 h. [d] Low isolated yield due in part to volatility of the amine product.

Expanding the substrate scope to include substituted benzamides (Table 2) further demonstrates that Fe-based pre-catalysts **2** and **3-Fe** are superior to the Co alkyl derivative **3-Co**. While the presence of an *ortho*-methyl substituent on the arene ring in 1-(*o*-toluoyl)piperidine does not appear to impact catalytic performance for **2** and **3-Fe** relative to the parent 1-benzoylpiperidine substrate, the conversion to product decreases substantially (from 98% conversion to 59%) in the case of **3-Co** (Table 2, Entry 1). The presence of electron donating (methoxy) or withdrawing (chloro) groups in the *para* position of the arene ring does not have a significant effect on reactivity (Table 2, Entries 2 and 5), though it should be noted that the reaction times necessary to achieve high conversion to product increased from 1 to 4 h for these substrates. The presence of halide substituents in the *ortho* position of the arene ring has a much greater impact on catalytic performance for all three pre-catalysts. In the case of an *ortho*-fluoro substituent (Table 2, Entry 4), increasing reaction times from 1 to 24 h facilitates >99% conversion to product for **2** (75% isolated yield), but **3-Fe** reaches only 65% conversion to the corresponding amine under these conditions. The presence of an *ortho*-chloro substituent also dramatically decreases catalytic performance (Table 2, Entry 3), such that only 64% conversion to product was achieved for **2** over 4 h, while **3-Fe** and **3-Co** achieve 13 and 27% conversion, respectively, under these conditions. Longer reaction times did not lead to higher yield of the amine product for this substrate. The Fe-based pre-catalysts can also tolerate thiophene- and pivalamide-derived substrates reasonably well (Table 2, Entries 6 and 7), with higher yields achieved in the case of **2**.

Table 2. Reduction of tertiary and secondary amides to amines.



Entry	Amide	5 mol% **2**		5 mol% **3-Fe**		5 mol% **3-Co**	
		Yield (%)[a]	Time (h)	Yield (%)[a]	Time (h)	Yield (%)[a]	Time (h)
1		>99, >99[b] (73)	1	95	1	59	1
2		97, 83[b] (>99)	4	97	4	98	4
3		64	4	13	4	27	4
4		>99 (75)	24	65	24	39	24
5		93 (60)	4	96	4	45	4
6		96 (92)	6	80[j]	1	22	4
7		90, 95[b] (85)	4	76	4	25	1
8		60[c]	24	-	-	-	-
9		30[c]	24	-	-	-	-

[a] Yield of product (average of two runs at 80 °C, unless otherwise stated) determined by use of gas chromatography against an internal standard (dodecane); in the case of incomplete reactions, the mass balance corresponds primarily to unreacted starting material. Numbers in parentheses are isolated yields following flash chromatography. [b] 5 mol% **2**, RT, 24 h. [c] 10 mol% **2**, 110 °C, toluene, 24 h.

Overall, these results reveal that while pre-catalysts **2** and **3-Fe** are both generally effective in the reduction of tertiary amides with $PhSiH_3$ under relatively mild conditions, **2** outperforms the alkyl derivative **3-Fe** in a number of instances, and is more broadly effective in such transformations. In an effort to further probe the efficacy of pre-catalyst **2**, we also evaluated its reactivity under room temperature conditions. Such room temperature reactivity is exceedingly rare for the reduction of tertiary amides by use of 3*d* transition-metal catalysts.[10, 11b, 12c] Indeed, at a loading of 5 mol% **2**, the efficient reduction of a number of amide substrates was observed over the course of 24 h at room temperature (Table 1, Entries 1-4; Table 2, Entries 1, 2, and 7). The sterically demanding substrate *N,N*-diisopropylbenzamide proved challenging to reduce under such room temperature conditions (Table 1, Entry 5), which is not surprising given that heating at 80 °C for 24 h was shown to be necessary in order to achieve high conversion to product with a 5 mol% loading of **2**. The hydrosilylation of secondary amide substrates was also challenging for pre-catalyst **2**. The reduction of *N*-methylbenzamide and *N*-benzylbenzamide with $PhSiH_3$ were each attempted under more forcing conditions, increasing the reaction temperatures to 110 °C and doubling the pre-catalyst loading to 10 mol%. Despite these changes, only 60% conversion to the corresponding secondary amine was observed for *N*-methylbenzamide (Table 2, Entry 8) and 30% conversion was obtained for *N*-benzylbenzamide (Table 2, Entry 9), highlighting the difficulty of this transformation; under similar conditions (5 - 10 mol % **2**, 80 °C, 24 h), complex reactivity leading to multiple unidentified products was observed in the attempted reduction of the primary amides benzamide and nicotinamide. Although isolated reports on the Fe-catalyzed hydrosilylation of such secondary amide substrates have appeared in the literature previously,[5a, 6b, 7] Fe-based catalysts for the hydrosilylative reduction of primary and secondary amides are not well established.[28]

While a direct comparison of the amide hydrosilylation catalysis reported herein with previously reported Fe catalysts (where useful substrate scope is established) is difficult due to slight differences in reaction conditions and choice of hydrosilane, the reactivity observed for **2** with respect to tertiary amides is certainly on par with the best of such catalysts. Particularly noteworthy is the ability of **2** to mediate amide hydrosilylation under room temperature conditions. To the best of our knowledge, this is the first example of an Fe-based catalyst to do this in the absence of photochemical activation. Also of note is the efficient reduction of *N,N*-diisopropylbenzamide using **2**. While pre-catalyst **2** requires heating at 80 °C to achieve high conversion to product for this substrate (Table 1, Entry 5), the hydrosilylation of amides that feature 2° alkyl substituents at nitrogen is a considerable synthetic challenge, with most Fe catalysts restricted to 1° alkyl substitution at this position. Limited examples of hydrosilylation of *N,N*-diisopropylbenzamide (or structurally related species that feature 2° alkyl substituents at nitrogen) by an Fe-based catalyst have been reported previously. Beller and co-workers[5a] reported a 59% isolated yield of *N,N*-diisopropylbenzylamine using an $Fe_3(CO)_{12}$ pre-catalyst (30 mol % Fe loading) and polymethylhydrosiloxane (PMHS, 8 equiv.) as the reductant after heating at 100 °C for 24 h. Sortais and Darcel[7] also evaluated the reduction of this substrate using the *N*-heterocyclic carbene complex $[CpFe(CO)_2(IMes)]I$ (5 mol %) as a pre-catalyst and two equiv. of $PhSiH_3$. An isolated yield of 73% *N,N*-diisopropylbenzylamine was reported following heating at 100 °C for 24 h under photolysis conditions. We have also previously reported on the hydrosilylation of *N,N*-diisopropylbenzamide using an *N*-phosphinoamidinate Fe hexamethyldisilazide complex that is structurally related to **2**.[12c] In the latter example, the use of 5 mol % Fe loading and two equiv. $PhSiH_3$ relative to amide led to 56% conversion to *N,N*-diisopropylbenzylamine following heating at 75 °C for 18 h. The results reported herein thus represent a notable improvement for Fe catalysis with respect to both catalyst loading and relatively mild reaction conditions.

While Fe-based catalysts are advantageous due to the ready availability of this inexpensive transition metal, examples of highly competitive 3*d* transition metal catalysis for amide hydrosilylation have also been reported. With respect to room temperature reactivity involving a demonstrated substrate scope, our recently reported *N*-phosphinoamidinate Mn pre-catalyst[10] was among the first examples of such hydrosilylative reduction of tertiary amides, achieving >90% conversion to the amine product for N,N-dimethyl- and N,N-dibenzylbenzamide, as well as 1-benzoylpiperidine under comparable conditions (2 mol% Mn, one equiv. $PhSiH_3$, 18 h) to those reported herein. Impressive Co-catalyzed room temperature amide hydrosilylation has also recently been reported by Khalimon and co-workers,[11b] who achieved high conversion for the reduction of substrates such as *N,N*-dimethylacetamide, *N,N*-dibenzylacetamide, and *N*-methyl-2-pyrrolidinone using 5 mol% $Co(acac)_2$ in combination with 5.5 mol% dpephos (bis[(2-diphenylphosphino)phenyl] ether) and 1.5 equiv. $PhSiH_3$. The room temperature hydrosilylation of *N,N*-diisopropylbenzamide was also achieved under these conditions, affording a 93% isolated yield of the amine product after 17 h. We also recently reported a Ni-catalyzed example of hydrosilylation of *N,N*-diisopropylbenzamide under ambient conditions using two equiv. of $PhSiH_3$ (5 mol% Ni, 18 h, >95% conversion to *N,N*-diisopropylbenzylamine).[12c] Such catalysts, specifically Co and Ni examples, have also shown some aptitude for the hydrosilylation of secondary amide substrates, although such reactivity typically requires more forcing conditions.[28]

Conclusions

The synthesis of new low-coordinate Fe(II) and Co(II) complexes supported by a bidentate, monoanionic, anilido phosphine ligand featuring bulky cyclohexyl substituents at phosphorus and 2,6-$^i Pr_2C_6H_3$ substitution at nitrogen has been described. A three-coordinate (P,N)Fe-hexamethyldisilazide (**2**) complex, and four-coordinate (P,N)Fe- (**3-Fe**) and (P,N)Co-alkyl (**3-Co**) complexes were structurally characterized and were evaluated as pre-catalysts for the hydrosilylative reduction of amides with $PhSiH_3$. In general, the Fe-based catalysts outperformed the Co-based

catalyst **3-Co** for the reduction of a variety of tertiary amide substrates under analogous reaction conditions (5 mol% catalyst, 80 °C, 1-24 h). Between the two Fe-based catalysts, the Fe hexamethyldisilazide complex (**2**) appeared to be more broadly effective in such reactions, and was shown to mediate the reduction of *N*,*N*-dibenzylbenzamide at a reduced loading of 1 mol% to achieve near quantitative formation of tribenzylamine in 1 h (80 °C). Most importantly, complex **2** also proved effective for the hydrosilylation of tertiary amides under ambient conditions (5 mol%, 24 h), which is a unique example of room temperature amide hydrosilylation mediated by an Fe catalyst without the need for photochemical activation. While some evidence for the hydrosilylation of *secondary* amides was also observed, the challenging nature of such reactions resulted in relatively low conversion to the corresponding secondary amines, even under forcing conditions (10 mol% Fe, 110 °C, 24 h).

The reactivity of the Fe-based pre-catalyst **2** in tertiary amide hydrosilylation is generally comparable to that of the best previously reported Fe catalysts with respect to substrate scope. In addition, while the large majority of previously reported 3*d* transition metal catalysts require reaction temperatures on the order of 100 °C and/or photochemical activation, the efficacy of **2** under room temperature conditions offers a significant advance in the development of efficient Fe-based catalysts that operate under mild conditions. Given that amides are among the most challenging carbonyl species to reduce, as well the widespread use of amide reduction protocols in the synthesis of pharmaceuticals, agrochemicals, and fine chemicals, the development of efficient, Fe-based catalysts for this application is highly relevant. Although the Fe pre-catalyst (**2**) reported herein is not without limitations, specifically in the hydrosilylation of secondary amide substrates, our future efforts will focus on applying a ligand design strategy to optimize the reactivity of such Fe catalysts for increasingly challenging amide reductions.

Experimental Section

General Considerations. All experiments were conducted under nitrogen in a glovebox or using standard Schlenk techniques. Tetrahydrofuran and diethyl ether were distilled from Na/benzophenone ketyl. Benzene, toluene, and pentane were first sparged with nitrogen and subsequently dried by passage through a double-column (one activated alumina column and one column packed with activated Q-5) solvent purification system. All purified solvents were stored over 4 Å molecular sieves. Benzene-d_6 was degassed via three freeze-pump-thaw cycles and stored over 4 Å molecular sieves. *N*-(2-Bromophenyl)-2,6-diisopropylaniline was prepared by use of previously reported methods.[29] Amide substrates were prepared from the corresponding acyl chlorides by using previously reported conditions.[10] All other reagents were purchased from Strem or Aldrich and used without further purification. Unless otherwise stated, ^{1}H, ^{13}C, and ^{31}P characterization data were collected at 300K, with chemical shifts reported in parts per million downfield of $SiMe_4$ (for ^{1}H and ^{13}C) or 85% H_3PO_4 in D_2O (for ^{31}P). ^{1}H and ^{13}C NMR chemical shift assignments are based on data obtained from ^{13}C{^{1}H}, ^{13}C-DEPTQ, ^{1}H-^{1}H COSY, ^{1}H-^{13}C HSQC, and ^{1}H-^{13}C HMBC NMR experiments. Solution magnetic moments were determined by use of the Evans method.[21]

***N*-(2-dicyclohexylphosphinophenyl)-2,6-diisopropylaniline (1).** Following a modified literature procedure,[30] $Pd(OAc)_2$ (0.19 g, 0.85 mmol) and 1,1'-diphenylphosphinoferrocene (0.42 g, 1.01 mmol) were combined with 10 mL toluene in a 250 mL Teflon-sealed reaction vessel and stirred for 5 min at room temperature. Subsequently, NaO^{t}Bu (2.28 g, 23.7 mmol) and $HPCy_2$ (3.71 mL, 16.9 mmol) were added to the reaction mixture. 5.62 g (0.0169 mol) *N*-(2-bromophenyl)-2,6-diisopropylamine (prepared according to literature procedure[29]) was also added to the reaction mixture and toluene was added to bring the total reaction volume to approximately 40 mL. The mixture was stirred at 110 °C for 18 hours after which time volatiles were removed *in vacuo* and the resulting residue was triturated with 3 × 10 mL pentane. The residue was extracted into 50 mL of a ca. 1 : 20 mixture of Et_2O in hexanes and filtered through a Celite and silica gel plug to yield a dark red filtrate. The solvent was removed from the filtrate in vacuo, and the residue was triturated with 3 × 5 mL pentane before being extracted with ca. 30 mL hexanes and filtered once again through a plug of Celite and silica gel. The filtrate was concentrated in vacuo and cooled to −35 °C yielding **1** as a beige crystalline material which was washed with 3 × 1 mL cold pentane. Additional **1** could isolated through serial crystallization from hexanes and washing the resulting crystals with cold pentane yielding 4.94 g **1** overall as a beige solid (11.0 mmol, 65% yield). Single crystals suitable for X-ray diffraction were isolated from a concentrated pentane solution of **1** at room temperature; additional crystallographic detail is available in the Supporting Information and the deposited CIF (CCDC 1905151). ^{1}H NMR (500 MHz, benzene-d_6): δ 7.34 – 7.19 (overlapping resonances, 3 H, H_{arom} + N*H*), 6.97 (t, 1 H, J_{HH} = 7 Hz, H_{arom}), 6.69 (t, 1 H, J_{HH} = 7 Hz, H_{arom}), 6.32 (m, 1 H, H_{arom}), 3.40 (sept, 2 H, $^3J_{HH}$ = 7 Hz, C*H*Me$_2$), 2.00 (m, 4 H, P*Cy*), 1.77 (m, 4 H, P*Cy*), 1.65 (m, 2H, P*Cy*), 1.58 (m, 2H, P*Cy*), 1.45 – 1.09 (overlapping resonances, 22 H, P*Cy* + CH*Me$_2$*; the CH*Me$_2$* resonances were identified as doublets at 1.23 and 1.15 ppm, $^3J_{HH}$ = 7 Hz). ^{13}C{^{1}H} NMR (125.8 MHz, benzene-d_6): δ 154.3 (d, $^1J_{PC}$ = 20 Hz, C_{arom}), 147.9 (C_{arom}), 136.9 (C_{arom}), 133.5 (CH_{arom}), 130.6 (CH_{arom}), 127.6 (CH_{arom}), 124.2 (CH_{arom}), 117.4 (CH_{arom}), 116.1 (d, $^2J_{PC}$ = 14 Hz, C_{arom}), 111.6 (CH_{arom}), 33.6 (d, *J* = 10 Hz, P*Cy*), 30.9 (d, *J* = 16 Hz, P*Cy*), 29.2 (d, *J* = 6 Hz, P*Cy*), 29.0 (*C*HMe$_2$), 27.5 (d, *J* = 13 Hz, P*Cy*), 27.3 (d, *J* = 8 Hz, P*Cy*), 26.8 (P*Cy*), 25.0 (CH*Me$_2$*), 23.0 (CH*Me$_2$*). ^{31}P{^{1}H} NMR (202.5 MHz, benzene-d_6): δ -27.2. Anal. Calcd for $C_{30}H_{44}N_1P_1$: C, 80.13; H, 9.86; N, 3.12. Found: C, 80.08; H, 10.12; N, 3.10.

(P,N)FeN(SiMe$_3$)$_2$ (2). A solution of $LiN(SiMe_3)_2$ (0.22 g, 1.33 mmol) in *ca.* 5 mL Et_2O was added dropwise to a suspension of $FeBr_2$ (0.14 g, 0.67 mmol) in *ca.* 5 mL Et_2O. The resulting mixture was then stirred for 30 min. at room temperature. Subsequently, a solution of **1** (0.30 g, 0.67 mmol) in *ca.* 5 mL Et_2O was added dropwise to the stirring reaction mixture. A color change to yellow-orange was observed as the mixture was stirred for 2 h at room temperature. The volatile components of the reaction mixture were removed *in vacuo* and the remaining residue was extracted with *ca.* 5 mL of benzene. The benzene extracts were filtered through Celite. The filtrate solution was collected and the benzene was removed *in vacuo.* The remaining orange-yellow solid was washed with 3 × 0.5 mL cold (-35 °C) pentane to afford **2** (0.35 g, 0.53 mmol, 79%) as a yellow solid. X-Ray quality crystals of **2** were grown from a concentrated pentane solution at -35 °C; additional crystallographic detail is available in the Supporting Information and the deposited CIF (CCDC 1905152). μ_{eff} (benzene-d_6): 5.2 μ_B (S = 2). ^{1}H NMR (300 MHz, benzene-d_6): 80.24, 64.86, 32.51, 31.44, 29.17, -11.87, -12.73, -15.12, -15.60, -19.68, -20.45, -32.86, -41.63, -43.96, -47.34, -75.87, -80.65. Anal. Calcd. for $C_{36}H_{61}N_2PSi_2Fe$: C, 65.03; H, 9.25; N, 4.21. Found: C, 64.79; H, 9.21; N, 4.18.

(P,N)Fe(py)CH$_2$SiMe$_3$ (3-Fe). A solution of $LiCH_2SiMe_3$ (0.021 g, 0.22 mmol) in *ca.* 5 mL Et_2O was added dropwise to a precooled (-35 °C) stirring suspension of py_4FeCl_2 (0.049 g, 0.11 mmol) in *ca.* 5 mL Et_2O. A

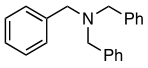
color change from bright yellow to dark red was observed over the course of 1-2 min. After *ca*. 15 min. of stirring at room temperature, the reaction mixture was again cooled to -35 °C and a solution of **1** (0.050 g, 0.11 mmol) in *ca*. 5 mL Et_2O was added dropwise to the reaction mixture. The resulting mixture was allowed to stir at room temperature for 18 h during which time the colour lightened to bright red. The volatile components of the reaction mixture were removed *in vacuo* and the remaining residue was triturated with 3 × 2 mL of pentane and then extracted with *ca*. 5 mL of benzene. The benzene extracts were filtered through Celite, and the filtrate solution was collected. The benzene solvent was removed *in vacuo* and the remaining residue was triturated with 3 × 2 mL pentane and washed with 3 × 0.5 mL of cold (-35 °C) pentane to afford **3-Fe** (0.067 g, 0.10 mmol, 90%) as a bright red solid. X-Ray quality crystals of **3-Fe** were obtained from a concentrated Et_2O solution -35 °C; additional crystallographic detail is available in the Supporting Information and the deposited CIF (CCDC 1905153). μ_{eff} (benzene-d_6): 5.2 μ_B (S = 2). ^{1}H NMR (300 MHz, benzene-d_6): δ 49.88, 37.72, 30.47, 28.60, 20.69, 20.03, 9.24, 3.91, 2.00, -1.02, -3.24, -9.22, -31.35, -38.38. Anal. Calcd. for $C_{39}H_{59}N_2PSiFe$: C, 69.83; H, 8.87; N, 4.18. Found: C, 69.61; H, 8.95; N, 4.46.

(P,N)Co(py)CH_2SiMe_3 (3-Co). A solution of $LiCH_2SiMe_3$ (0.13 g, 1.35 mmol) in *ca*. 5 mL of pentane was added dropwise to a precooled (-35 °C) stirring suspension of py_4CoCl_2 (0.30 g, 0.67 mmol) in *ca.* 7 mL of pentane. A color change from blue to dark red-brown was observed during the addition. After *ca*. 15 minutes of stirring at room temperature, the reaction mixture was cooled again to -35 °C and a solution of **1** (0.30 g, 0.67 mmol) in *ca*. 7 mL of pentane was added dropwise. The reaction mixture was allowed to stir at room temperature for 18 h. The volatile components of the reaction mixture were then removed *in vacuo*. The resulting red residue was triturated with 3 × 2 mL of pentane and then extracted with *ca*. 10 mL benzene. The benzene extracts were filtered through Celite. The filtrate solution was collected and the solvent was removed *in vacuo*. The remaining residue was triturated with 3 × 2 mL of pentane and washed with 3 × 2 mL cold (-35 °C) pentane to afford **3-Co** (0.37 g, 0.55 mmol, 82%) as a red solid. X-Ray quality crystals of **3-Co** were obtained from a concentrated Et_2O solution at -35 °C; additional crystallographic detail is available in the Supporting Information. μ_{eff} (benzene-d_6): 2.3 μ_B (S = ½). ^{1}H NMR (300 MHz, benzene-d_6): δ 30.30, 25.71, 14.59, 13.60, 11.43, 7.40, 5.30, 2.91. 1.94, 0.61, 0.28, -3.45, -6.53, -30.68. Anal. Calcd. for $C_{39}H_{59}N_2PSiCo$: C, 69.51; H, 8.82; N, 4.16. Found: C, 69.22; H, 8.64; N, 4.10.

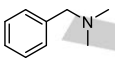
General Procedure for the Reduction of Amide Substrates. Amide (0.2 mmol) and $PhSiH_3$ (0.2 mmol) were combined in an oven-dried one dram vial equipped with a magnetic stirbar. The pre-catalyst (**2**, **3-Fe**, or **3-Co**) was then added as a stock solution (64 mM) in benzene (313 μL for 10 mol% runs, 156 μL for 5 mol% runs, 31 μL for 1 mol% runs), as well as an additional 300 μL of benzene. The vial was sealed with a PTFE-lined cap, removed from the glovebox, and heated to 80 °C or 110 °C for the specified reaction time. The reaction mixture was then exposed to air, diluted with 1 mL of dichloromethane, and filtered through a Celite plug. The filtrate solution was then analyzed by use of gas chromatography against a dodecane internal standard to measure conversion of the amide to the corresponding amine.

General Procedure for the Isolation of Tertiary Amines. Amide reductions were conducted on either a 0.4 mmol or 0.6 mmol scale for the purpose of isolation. The amide substrate (0.4 mmol or 0.6 mmol) and $PhSiH_3$ (0.4 mmol or 0.6 mmol, respectively) were combined in an oven-dried one dram vial equipped with a magnetic stirbar. The pre-catalyst **2** was then added as 312 μL (or 468 μL) of a 64 mM benzene stock solution, as was an additional 600μL (or 900 μL) of benzene. The vial was sealed with a PTFE-lined cap, removed from the glovebox, and heated to 80 °C for the specified reaction time. The reaction mixture was then exposed to air and the volatile components removed under vacuum. The crude residue was then purified by flash column chromatography employing silica gel or neutral alumina as the stationary phase. The combined fractions were concentrated under reduced pressure to afford the corresponding amine.

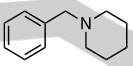
Characterization data for isolated amine products.



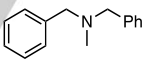
Tribenzylamine. Purified by silica gel column chromatography (ethyl acetate/hexanes, 1:4), 74% yield (0.13 g, 0.44 mmol). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.40 (m, 6 H, H_{arom}), 7.30 (m, 6 H, H_{arom}), 7.22 (m, 3 H, H_{arom}), 3.55 (s, 6 H, CH_2). ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$): δ 139.9 (C_{arom}), 128.9 (CH_{arom}), 128.4 (CH_{arom}), 127.1 (CH_{arom}), 58.1 (CH_2). Spectral data are in close agreement with previously reported ^{1}H and ^{13}C{^{1}H} NMR characterization data for the title compound.[5a]



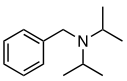
***N,N*-Dimethylbenzylamine.** Purified by silica gel column chromatography (ethyl acetate/hexanes, 1:50), 57% yield (0.046 g, 0.34 mmol). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.33 – 7.29 (overlapping resonances, 4 H, H_{arom}), 7.25 (m, 1 H, H_{arom}), 3.41 (s, 2 H, CH_2), 2.23 (s, 6 H, NMe_2). ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$): δ 139.1 (C_{arom}), 129.3 (CH_{arom}), 128.4 (CH_{arom}), 127.2 (CH_{arom}), 64.7 (CH_2), 45.6 (NMe_2). Spectral data are in close agreement with previously reported ^{1}H and ^{13}C{^{1}H} NMR characterization data for the title compound.[8]



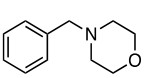
1-Benzylpiperidine. Purified by neutral alumina column chromatography (ethyl acetate/hexanes, 1:10), 74% yield (0.078 g, 0.45 mmol). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.32 – 7.18 (overlapping resonances, 5 H, H_{arom}), 3.46 (s, 2 H, CH_2), 2.36 (m, 4 H, CH_2), 1.56 (m, 4 H, CH_2), 1.42 (m, 2 H, CH_2). ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$): δ 138.9 (C_{arom}), 129.4 (CH_{arom}), 128.3 (CH_{arom}), 127.0 (CH_{arom}), 64.1 (PhCH_2), 54.7 (CH_2), 26.2 (CH_2), 24.6 (CH_2). Spectral data are in close agreement with previously reported ^{1}H and ^{13}C{^{1}H} NMR characterization data for the title compound.[5a]



***N*-Methyldibenzylamine.** Purified by silica gel column chromatography (ethyl acetate/hexanes, 1:4), 72% yield (0.091 g, 0.43 mmol). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.27 (m, 4 H, H_{arom}), 7.22 (m, 4 H, H_{arom}), 7.14 (m, 2 H, H_{arom}), 3.43 (s, 4 H, CH_2), 2.09 (s, 3 H, NMe). ^{13}C{^{1}H} NMR (125.8 MHz, $CDCl_3$): δ 139.6 (C_{arom}), 129.1 (CH_{arom}), 128.4 (CH_{arom}), 127.1 (CH_{arom}), 62.1 (CH_2), 42.5 (CH_3). Spectral data are in close agreement with previously reported ^{1}H and ^{13}C{^{1}H} NMR characterization data for the title compound.[7]

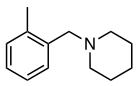


***N,N*-Diisopropylbenzylamine.** Purified by silica gel column chromatography (ethyl acetate/hexanes, 17:100), 78% yield (0.089 g, 0.47 mmol). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.40 (m, 2 H, H_{arom}), 7.30 (m, 2 H, H_{arom}), 7.21 (m, 1 H, H_{arom}), 3.67 (s, 2 H, CH_2), 3.04 (sept, 2 H, $^3J_{HH}$ = 7 Hz, CHMe$_2$), 1.04 (d, 12 H, $^3J_{HH}$ = 7 Hz, CHMe_2). ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$): δ 143.5 (C_{arom}), 128.2 (CH_{arom}), 128.0 (CH_{arom}), 126.3 (CH_{arom}), 49.1 (CH_2), 48.0 (CHMe$_2$), 21.0 (CHMe_2). Spectral data are in close agreement with previously reported ^{1}H and ^{13}C{^{1}H} NMR characterization data for the title compound.[5a]

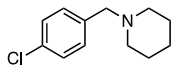


***4*-Benzylmorpholine.** Purified by neutral alumina column chromatography (ethyl acetate/hexanes, 1:10), 78% yield (0.083 g, 0.47 mmol). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34 – 7.28 (overlapping resonances, 4 H, H_{arom}), 7.25 (m, 1

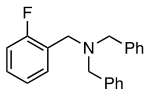
*H*arom), 3.70 (m, 4 H, C*H*$_2$), 3.49 (s, 2 H, C*H*$_2$), 2.43 (m, 4 H, C*H*$_2$). ^{13}C{^{1}H} NMR (125.8 MHz, $CDCl_3$): δ 138.0 (*C*arom), 129.4 (*CH*arom), 128.4 (*CH*arom), 127.3 (*CH*arom), 67.2 (*CH*$_2$), 63.7 (Ph*CH*$_2$), 53.8 (*CH*$_2$). Spectral data are in close agreement with previously reported ^{1}H and ^{13}C{^{1}H} NMR characterization data for the title compound.[5a]



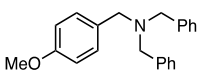
1-[(2-Methylphenyl)methyl]piperidine. Purified by neutral alumina column chromatography (ethyl acetate/hexanes, 1:20), 73% yield (0.083 g, 0.44 mmol). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39 (m, 1 H, *H*arom), 7.26 – 7.25 (overlapping resonances, 3 H, *H*arom), 3.52 (s, 2 H, C*H*$_2$), 2.49 – 2.47 (overlapping resonances, 7 H, C*H*$_2$ + *Me*), 1.67 (m, 4 H, C*H*$_2$), 1.55 (m, 2 H, C*H*$_2$). ^{13}C{^{1}H} NMR (125.8 MHz, $CDCl_3$): δ 137.6 (*C*arom), 137.3 (*C*arom), 130.3 (*CH*arom), 129.9 (*CH*arom), 126.9 (*CH*arom), 125.5 (*CH*arom), 61.7 (Ar-*CH*$_2$), 54.9 (*CH*$_2$), 26.3 (*CH*$_2$), 24.8 (*CH*$_2$), 19.4 (*CH*$_3$). Spectral data are in close agreement with previously reported ^{1}H and ^{13}C{^{1}H} NMR characterization data for the title compound.[31]



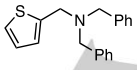
1-[(4-Chlorophenyl)methyl]piperidine. Purified by neutral alumina column chromatography (ethyl acetate/hexanes, 1:10), >99% yield (0.084 g, 0.40 mmol). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30 – 7.24 (overlapping resonances, 4 H, *H*arom), 3.43 (s, 2 H, C*H*$_2$), 2.36 (broad s, 4 H, C*H*$_2$), 1.57 (m, 4 H, 2 C*H*$_2$), 1.44 (m, 2 H, C*H*$_2$). ^{13}C{^{1}H} NMR (125.8 MHz, $CDCl_3$): δ 137.5 (*C*arom), 132.7 (*C*arom), 130.6 (*CH*arom), 128.4 (*CH*arom), 63.3 (*CH*$_2$), 54.7 (*CH*$_2$), 26.2 (*CH*$_2$), 24.6 (*CH*$_2$). Spectral data are in close agreement with previously reported ^{1}H and ^{13}C{^{1}H} NMR characterization data for the title compound.[31]



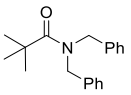
***N,N*-Dibenzyl-2-fluorobenzenemethanamine.** Purified by silica gel column chromatography (ethyl acetate/hexanes, 1:10), 75% yield, (0.092 g, 0.30 mmol). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.52 (m, 1 H, *H*arom), 7.38 (m, 4 H, *H*arom), 7.28 (m, 4 H, *H*arom), 7.21 – 7.14 (overlapping resonances, 3 H, *H*arom), 7.08 (m, 1 H, *H*arom), 6.97 (m, 1 H, *H*arom), 3.62 (s, 2 H, C*H*$_2$), 3.56 (s, 4 H, C*H*$_2$). ^{13}C{^{1}H} NMR (125.8 MHz, $CDCl_3$): δ 161.6 (d, *C*arom, $^1J_{CF}$ = 245 Hz), 139.7 (*CH*arom), 131.2 (d, *CH*arom, J_{CF} = 4 Hz), 128.9 (*CH*arom), 128.5 (d, *CH*arom, J_{CF} = 8 Hz), 128.4 (*CH*arom), 127.1 (*CH*arom), 126.4 (d, *C*arom, J_{CF} = 14 Hz), 124.1 (d, *CH*arom, J_{CF} = 3 Hz), 115.3 (d, *CH*arom, J_{CF} = 22 Hz), 58.3 (*CH*$_2$), 50.6 (*CH*$_2$). ^{19}F{^{1}H} NMR (470.5 MHz, $CDCl_3$): δ −118.2 (s). Spectral data are in close agreement with previously reported ^{1}H and ^{13}C{^{1}H} NMR characterization data for the title compound.[32]



***N,N*-Dibenzyl-4-methoxybenzenemethanamine.** Purified by silica gel column chromatography (ethyl acetate/hexanes, 3:20), 60% yield (0.076 g, 0.24 mmol). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.47 (m, 4 H, *H*arom), 7.39 – 7.34 (overlapping resonances, 6 H, *H*arom), 7.30 (m, 1 H, *H*arom), 7.27 (m, 1 H, *H*arom), 6.95 (m, 2 H, *H*arom), 3.84 (s, 3 H, O*Me*), 3.61 (s, 4 H, C*H*$_2$), 3.56 (s, 2 H, C*H*$_2$). ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$): δ 158.8 (*C*arom), 139.9 (*C*Harom), 131.8 (*C*arom), 130.1 (*CH*arom), 128.9 (*CH*arom), 128.4 (*CH*arom), 127.0 (*CH*arom), 113.8 (*CH*arom), 58.0 (O*Me*), 57.4 (*CH*$_2$), 55.4 (*CH*$_2$). Spectral data are in close agreement with previously reported ^{1}H and ^{13}C{^{1}H} NMR characterization data for the title compound.[5a]



***N,N*-Dibenzyl-2-thiophenemethanamine.** Purified by neutral alumina column chromatography (ethyl acetate/hexanes, 1:50), 92% yield (0.11 g, 0.37 mmol). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31 (m, 4 H, *H*arom), 7.19 (m, 4 H, *H*arom), 7.12 - 7.09 (overlapping resonances, 3 H, *H*arom), 6.82 – 6.78 (overlapping resonances, 2 H, *H*arom), 3.65 (s, 2 H, C*H*$_2$), 3.49 (s, 4 H, C*H*$_2$). ^{13}C{^{1}H} NMR (125.8 MHz, $CDCl_3$): δ 143.5 (*C*arom), 139.5 (*C*arom), 128.5 (*CH*arom), 128.3 (*CH*arom), 127.1 (*CH*arom), 126.6 (*CH*arom), 125.7 (*CH*arom), 124.9 (*CH*arom), 57.8 (*CH*$_2$), 52.4 (*CH*$_2$). Spectral data are in close agreement with previously reported ^{1}H and ^{13}C{^{1}H} NMR characterization data for the title compound.[5a]



Dibenzyl(2,2-dimethylpropyl)amine. Purified by silica gel column chromatography (ethyl acetate/hexanes, 3:20), 85% yield (0.091 g, 0.34 mmol). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.43 (m, 4 H, *H*arom), 7.36 (m, 4 H, *H*arom), 7.28 (m, 2 H, *H*arom), 3.66 (s, 4 H, C*H*$_2$), 2.40 (s, 2 H, C*H*$_2$), 0.87 (s, 9 H, C*Me*$_3$). ^{13}C{^{1}H} NMR (125.8 MHz, $CDCl_3$): δ 140.4 (*C*arom), 129.4 (*CH*arom), 128.3 (*CH*arom), 127.0 (*CH*arom), 66.1 (*CH*$_2$), 61.0 (Ph*CH*$_2$), 33.3 (*C*Me$_3$), 28.7 (C*Me*$_3$). Spectral data are in close agreement with previously reported ^{1}H and ^{13}C{^{1}H} NMR characterization data for the title compound.[5a]

Acknowledgements

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Keywords: iron • cobalt • amide • reduction • hydrosilylation

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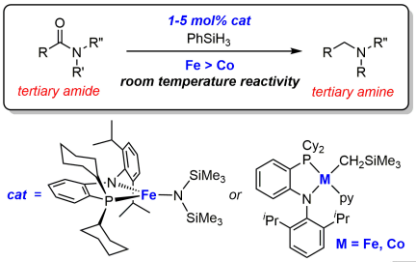
FULL PAPER

Low-coordinate Fe(II) and Co(II) complexes supported by a monoanionic P,N-ligand are described. A 3-coordinate (P,N)Fe-amido pre-catalyst proved particularly effective for the hydrosilylation of a variety of tertiary amides, including examples of room temperature transformations that are unprecedented for Fe.



*Dylan J. Hale, Luke J. Murphy, Robert McDonald, Michael J. Ferguson, and Laura Turculet**

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Hydrosilylative Reduction of Tertiary Amides to Amines Catalyzed by *N*-(Phosphinoaryl)anilido Complexes of Iron and Cobalt