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Practical Access to Amines by Platinum-Catalyzed Reduction of Carboxamides with Hydrosilanes: Synergy of Dual Si−H Groups Leads to High Efficiency and Selectivity

Shiori Hanada, Emi Tsutsumi, Yukihiro Motoyama, and Hideo Nagashima*

Graduate School of Engineering Sciences, Institute for Materials Chemistry and Engineering, Kyushu University, Kasuga, Fukuoka 816-8580, Japan

Received July 6, 2009; E-mail: nagasima@cm.kyushu-u.ac.jp

Abstract: The synergetic effect of two Si−H groups leads to efficient reduction of carboxamides to amines by platinum catalysts under mild conditions. The rate of the reaction is dependent on the distance of two Si−H groups; 1,1,3,3-tetramethyldisiloxane (TMDS) and 1,2-bis(dimethylsilyl)benzene are found to be an effective reducing reagent. The reduction of amides having other reducible functional groups such as NO_2, CO_2R, CN, C=C, Cl, and Br moieties proceeds with these groups remaining intact, providing a reliable method for the access to functionalized amine derivatives. The platinum-catalyzed reduction of amides with polymethylhydrosiloxane (PMHS) also proceeds under mild conditions. The reaction is accompanied by automatic removal of both platinum and silicon wastes as insoluble silicone resin, and the product is obtained by simple extraction. A mechanism involving double oxidative addition of TMDS to a platinum center is discussed.

1. Introduction

Hydrosilylation is a term which describes the addition reaction of organosilicon compounds having one or more Si−H bonds to unsaturated organic molecules. It is well-known that certain transition metal salts and complexes effectively catalyze hydrosilylation. In particular, platinum-catalyzed hydrosilylation reactions of alkenes and alkynes is one of the most powerful methods of producing a variety of organosilicon compounds on both laboratory and industrial scales.[1] Several platinum compounds are easily available from commercial sources, and reactions rapidly proceed with only a small amount of the catalyst, being highly tolerant to various functional groups.[2] In contrast to numerous papers and patents reporting that platinum-catalyzed hydrosilylation successfully occurs to carbon−carbon multiple bonds, there is a surprisingly small number of papers which refer to the catalysis of hydrosilylation of carbon−oxygen double bonds by platinum compounds.[3] This is in sharp contrast to the fact that hydrosilylation of ketones with trialkyl- or diarylsilanes is efficiently catalyzed by rhodium, cobalt, ruthenium, and iridium complexes.[4] In particular, rhodium-catalyzed hydrosilylation has now become a standard methodology for the reduction of ketones in organic synthesis including asymmetric production of alcohols. In this context, we found it curious when we began the research described here that platinum catalysts do not work well to reduce carbonyl compounds, though some Rh, Co, Ru, and Ir compounds are useful for hydrosilylation of both the C=O and C=C bonds.[4]

Among carbonyl compounds, it is well-known that carboxamides are hardly reducible with alumino- or borohydrides.[5] In this sense, application of the metal-promoted reduction of amides to amines with hydrosilanes under mild conditions is a challenge to be solved. The first successful example was reported by Buchwald et al. who found the reduction of tertiary amides to aldehydes with Ph_2SiH_2 using a stoichiometric amount of $(i\text{-PrO})_4Ti$.[6] Stimulated by this, further efforts were made to achieve catalytic reduction with hydrosilanes. Harrod et al. reported the Cp_2TiF_2-catalyzed reduction of tertiary amides to tertiary amines with $PhMeSiH_2$;[7] Ito and Ohta et al. showed that rhodium-triphenylphosphine complexes are also effective catalysts for the reduction of tertiary- and secondary amides

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(3) (a) Yamamoto, K.; Hayashi, T.; Kumada, M. *J. Organomet. Chem.* **1972**, *46*, C65–C67. (b) Hayashi, T.; Yamamoto, K.; Kumada, M. *J. Organomet. Chem.* **1976**, *112*, 253–262. (c) Barlow, A. P.; Boag, N. M.; Stone, F. G. A. *J. Organomet. Chem.* **1980**, *191*, 39–47. (d) Cullen, W. R.; Evans, S. V.; Han, N.-F.; Trotter, J. *Inorg. Chem.* **1987**, *26*, 514–519. (e) Zuev, V. V.; de Vekki, D. A. *Phosphorus, Sulfur, Silicon Relat. Elem.* **2005**, *180*, 2071–2083.

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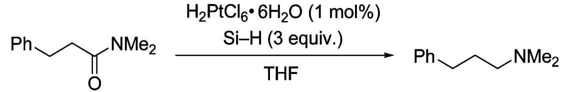
10.1021/ja9055307 CCC: $40.75

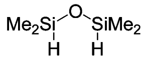
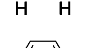
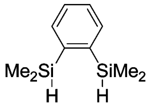
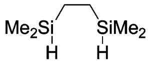
using Ph_2SiH_2 as a reducing agent.[8] Reduction of tertiary and secondary amides with $PhSiH_3$ was accomplished by catalysis of MoO_2Cl_2.[9] Our research group showed that a triruthenium cluster, ($\mu_3,\eta^2:\eta^3:\eta^5$-acenaphthylene)$Ru_3(CO)_7$, efficiently catalyzes the reduction of tertiary amides with hydrosilanes.[10] The reaction is exothermic, giving the corresponding tertiary amines in high yields under mild conditions. There are three notable features for this reduction: The first is the possible use of trialkylsilanes, which are more easily handled than $PhSiH_3$ and Ph_2SiH_2. Fuchikami et al. reported that several metal complexes of groups 8−10 catalyzed the reduction of amides with Et_3SiH.[11] However, these reactions require application of high temperature in the presence of cocatalysts such as haloalkanes and/or amines. The second feature is a significant rate enhancement using hydrosilanes having dual Si−H groups, which made possible the reduction of secondary amides to secondary amines, a result not achievable with common monohydrosilanes under mild conditions.[10d] The third feature is the automatic removal of the catalyst species, which was first achieved when polymethylhydrosiloxane (PMHS) was used as the hydrosilane.[10c] Entrainment of the catalyst species in the silicone resin formed occurs during the reduction of amides to amines. In a typical example, reduction of certain amides with PMHS proceeds at room temperature and 99.75% of the charged ruthenium was retained by the insoluble silicone resin formed. The desired amine containing only 15 ppm of Ru was isolated by simple extraction of the silicone resin by ether.

Success of the catalytic reduction of amides by combination of the ruthenium catalyst **1** and judicious choice of hydrosilanes, particularly those having dual proximate Si−H moieties in the molecule, prompted us to reconsider use of platinum catalysts for the reduction of carboxamides with hydrosilanes under mild conditions. The target of the improvement was the reaction conditions, following up on a brief comment by Fuchikami and co-workers that *N*-acetylpiperidine was reduced to *N*-ethylpiperidine using Et_3SiH at 100 °C for 16 h in the presence of $PtCl_2$ (1 mol %) and Et_2NH as a cocatalyst (5 mol %).[11] Our efforts to reduce the reaction temperature and reaction time were crowned with success by using the "dual Si−H effect" previously experienced in the ruthenium-catalyzed reduction of amides.[10d] Use of hydrosilanes containing two proximate Si−H groups in a molecule such as 1,1,3,3-tetramethyldisiloxane (TMDS) and 1,2-bis(dimethylsilyl)benzene made the reduction of amides possible in the presence of commercially available platinum compounds such as chloroplatinic acid[12] and Karstedt's catalyst.[13] Reaction proceeds under mild conditions, showing high amido-group selectivity in the presence of other reducible functional groups. Furthermore, extension of the two proximate Si−H group effects to polyproximate Si−H moieties results in both reduction of amides under mild conditions and facile separation of the amine product from the silicon and platinum residues by self-entrainment of the catalyst species into the insoluble silicone resin. A preliminary account has appeared in an earlier communication,[14] and we report here the scope of this reaction mainly from the standpoint of practical organic synthesis. The utility of this reaction is unequivocally supported by scale-up of the experiments.

Table 1. Structural Effect of Hydrosilanes[a]



1a **2a**

entry	hydrosilane	yield (%)[b]
1	$PhMe_2SiH$	<1
2	$EtMe_2SiH$	<1
3	$(EtO)_3SiH$	<1
4	Me_3SiOSi Me_2H	<1
5	Ph_2SiH_2	<1
6	 $Me_2\underset{H}{Si}{-}O{-}\underset{H}{Si}Me_2$	>98 (90)[c]
7[d]	 $(Me_3SiO)Me\underset{H}{Si}{-}O{-}\underset{H}{Si}Me(OSiMe_3)$	>98 (63)[c]
8[e,f]		>98
9[f]	 $Me_2\underset{H}{Si}{-}CH_2CH_2{-}\underset{H}{Si}Me_2$	<1

[a] All reactions were carried out with **1a** (1 mmol), $H_2PtCl_6 \cdot 6H_2O$ (0.01 mmol), and hydrosilane (Si−H = 3 equivalent) in THF (0.5 mL) at 50 °C for 3 h. [b] Determined by ^1H NMR analysis with ferrocene as an internal standard. [c] Isolated yield after alumina column chromatography. [d] For 10 h. [e] For 8 h. [f] 4 equiv of Si−H was used.

2. Results and Discussion

2.1. Two Proximate Si−H Effects from Structural Variation of Hydrosilanes. The "dual Si−H effect" in the platinum-catalyzed reduction of amides was monitored by the reduction of *N,N*-dimethyl-3-phenylpropionamide (**1a**) with several hydrosilanes (Si−H = 3 equivalent to **1a**) using $H_2PtCl_6 \cdot 6H_2O$ (1 mol %) as a catalyst in THF at 50 °C (Table 1). No reaction took place with hydrosilanes containing one Si−H group in the molecule, $PhMe_2SiH$, $EtMe_2SiH$, $(EtO)_3SiH$, or $Me_3SiOSiMe_2H$, as shown in entries 1−4. Although Ph_2SiH_2 is known to be a powerful reducing reagent for a number of transition metal-catalyzed reductions of carbonyl compounds, only starting amide was recovered quantitatively under these conditions (entry 5). In sharp contrast, reactions using hydrosilanes containing two proximate Si−H groups in the molecule afforded the *N,N*-dimethyl-3-phenylpropylamine (**2a**) in good to high yields. In typical examples, treatment of **1a** with 1,1,3,3-tetramethyldisiloxane (TMDS) in the presence of $H_2PtCl_6 \cdot 6H_2O$ at 50 °C for

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(10) (a) Matsubara, K.; Iura, T.; Maki, T.; Nagashima, H. *J. Org. Chem.* **2002**, *67*, 4985–4988. (b) Motoyama, Y.; Itonaga, C.; Ishida, T.; Takasaki, M.; Nagashima, H. *Org. Synth.* **2005**, *82*, 188–195. (c) Motoyama, Y.; Mitsui, K.; Ishida, T.; Nagashima, H. *J. Am. Chem. Soc.* **2005**, *127*, 13150–13151. (d) Hanada, S.; Ishida, T.; Motoyama, Y.; Nagashima, H. *J. Org. Chem.* **2007**, *72*, 7551–7559. (e) Sasakuma, H.; Motoyama, Y.; Nagashima, H. *Chem. Commun.* **2007**, 4916–4918.

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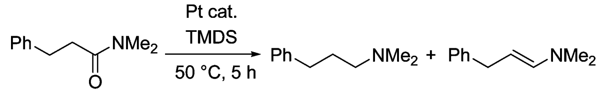
Table 2. Reduction of **1a** with TMDS by Various Pt Catalysts[a]



1a **2a** **3a**

entry	Pt catalyst (mol %)	solvent	conv (%)[b]	yield (%)[b] 2a	yield (%)[b] 3a
1	$H_2PtCl_6 \cdot 6H_2O$ (1.0)	THF	>98	>98	<2
2	$H_2PtCl_6 \cdot 6H_2O$ (0.1)	THF	>98	92	7
3	$H_2PtCl_6 \cdot 6H_2O$ (0.1)	THP	>98	>98	<2
4	$H_2PtCl_6 \cdot 6H_2O$ (0.1)	DME	>98	>98	<2
5	$H_2PtCl_6 \cdot 6H_2O$ (0.1)	toluene	>98	>98	<2
6[c,d]	$H_2PtCl_6 \cdot 6H_2O$ (0.1)	toluene	>98	87	13
7	$H_2PtCl_6 \cdot 6H_2O$ (0.05)	toluene	>98	92	8
8	Karstedt's cat. (0.1)	toluene	95	69	14
9	$Pt(dba)_2$ (0.1)	toluene	90	76	8
10	$PtCl_2$(cod) (0.1)	toluene	>95	88	7
11[d]	Pt/C (1.0)[e]	toluene	89	76	13

[a] All reactions were carried out with **1a** (1 mmol), Pt catalyst (0.05−1 mol %), and TMDS (2.5 mmol, Si−H = 5 equivalent) in solvent (0.5 mL) at 50 °C for 5 h. [b] Determined by ^{1}H NMR analysis with ferrocene as an internal standard. [c] At 25 °C. [d] For 24 h. [e] Purchased from Aldrich (5 wt % Pt).

3 h resulted in formation of **2a** quantitatively, and the product was obtained in 90% yield after alumina column chromatography (entry 6). 1,1,1,3,5,7,7,7-Octamethyltetrasiloxane, which has a structure similar to that of TMDS, was also an effective reducing reagent for the platinum-catalyzed reaction of **1a** (entry 7). The reaction with 1,2-bis(dimethylsilyl)benzene also proceeded smoothly to afford **2a** in quantitative yield (entry 8). The reactivity vs structure of the hydrosilane is much different from our findings previously reported in $RhCl(PPh_3)_3$-catalyzed hydrosilylation of ketones[15] and the Ru_3 cluster-catalyzed hydrosilylation of carbonyl compounds[16] in that $Me_2HSi(CH_2)_2SiHMe_2$, which was generally a reactive hydrosilane in the previous cases, was not effective for the platinum-catalyzed reduction of amides (entry 9). This may imply that "the dual Si−H effect" in the platinum-catalyzed reduction may be more sensitive to the distance between two Si−H groups than Rh- or Ru_3-catalyzed reactions.

2.2. Optimal Conditions of the Reaction with TMDS. Commercially available and inexpensive TMDS is a practically useful reductant. Optimization of the reaction conditions was carried out using *N,N*-dimethyl-3-phenylpropionamide (**1a**), TMDS, and several Pt compounds as the amide, the hydrosilane, and the catalyst, respectively (Table 2). With all of the platinum catalysts including heterogeneous Pt/C, conversion of the amide reached over 89% after 5 h. One problem is a side reaction to produce enamine (**3a**). For instance, the reaction with 1.0 mol % of $H_2PtCl_6 \cdot 6H_2O$ in THF afforded **2a** exclusively, whereas lowering the catalyst concentration to 0.1 mol % caused formation of a small amount of enamine **3a** (7%) as a byproduct (entries 1 and 2). When 0.1 mol % of $H_2PtCl_6 \cdot 6H_2O$ was used, appropriate selection of the solvent was important for the selective formation of **2a**; tetrahydropyran (THP), 1,2-dimethoxyethane (DME), and toluene effectively suppressed the formation of **3a** (entries 3−5). Formation of **3a** was observed in the reaction at room temperature (entry 6) and when 0.05 mol % of the catalyst was used (entry 7). Other platinum compounds such as Karstedt's catalyst, $Pt(dba)_2$, $PtCl_2$(cod), and Pt/C also act as a catalysts for the reduction of amides under mild conditions (entries 8−11). In all cases, the amide **1a** was consumed smoothly, but a small amount of enamine **3a** was formed as the byproduct.

2.3. Reduction of Various Tertiary Amides with TMDS. In Tables 3 and 4 are summarized the results obtained for the reduction of various tertiary amides **1a**−**r** with TMDS (Si−H = 5 equivalent to **1**) in toluene. In the presence of H_2PtCl_6 (0.1 mol %) at 50 °C, the corresponding amine **2a** was produced in 85% isolated yield after 5 h (Table 3, entry 1). Lactams **1e** and **1f** were reduced even at room temperature to form the corresponding cyclic amines **2e** and **2f** in high yields (entries 7 and 8). In contrast, reduction of an aromatic amide **1g** required somewhat higher temperature (75 °C) as shown in entry 9. Formation of enamine was observed when there were crowded steric circumstances of the amide oxygen in the substrate. The amide **1b** is an example of such substrate having a bulky substituent on the nitrogen atom, whereas **1c** is a substrate having a bulky cyclohexyl group adjacent to the carbonyl group. Although significant amounts of enamine were concomitantly formed with H_2PtCl_6 (entries 2 and 4), use of Karstedt's catalyst effectively suppressed the production of enamine in these cases (entries 3 and 5). The reaction of *N*-benzyl-*N*-methylpivaloylamide (**2d**) was slow due to the steric circumstances around the carbonyl group; however, no enamine formation was observed with Karstedt's catalyst.

Chemoselective reduction of amides with other functional groups remaining intact is a challenge to be developed in the organic synthesis of multifunctional molecules. In Table 4, entries 1−8 summarize the reduction of a series of para-substituted benzamides. The first two benzamides having OMe and NMe_2 group were reduced to the corresponding amines in high yields as we expected (entries 1 and 2). The next six substrates have a functional group which potentially reacts with hydrosilanes. Reductive dehalogenation was not seen in the reactions of chloro- or bromobenzamides as shown in entries 3 and 4, whereas there was no reduction of the NO_2, CN, and CO_2R groups in the substrates shown in entries 5−7. In these cases, the corresponding amines were isolated in over 80% yields as a single product. In the reaction of keto amide **1o**, reduction of the amide function was competitive with that of the keto group to give a mixture of products. With the higher catalyst loading (2 mol %) and addition of larger amounts of hydrosilane, both the keto- and amide functions were completely reduced to give the corresponding amino alcohol in good yield (entry 8). The reaction of α-phenoxyacetamide **1p** proceeded smoothly to afford 2-*N,N*-dimethylaminoethyl phenyl ether (**2p**) in 79% yield (entry 9); this is a good entry to production of *β*-amino alcohol derivatives. It is known that H_2PtCl_6 is a powerful catalyst for hydrosilylation of C═C bonds; the rate was decreased in the order, monosubstituted > disubstituted > trisubstituted alkenes. Hydrosilylation of α,*β*-unsaturated carbonyl compounds proceeds in the manner of 1,4-addition. As shown in entries 10 and 11, the amide bearing a 1,2-disubstituted or 1,1,2-trisubstituted C═C bond underwent the reaction of TMDS to give the corresponding amine with the C═C bond remaining intact. In contrast, complicated mixtures of products were formed in the reaction of amides with terminal alkenes and α,*β*-unsaturated amides.

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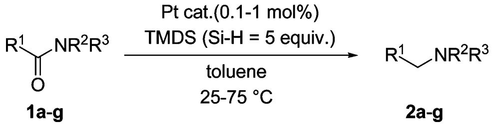
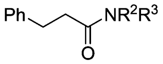
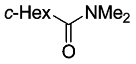
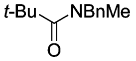
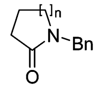
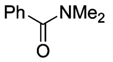
(16) Nagashima, H.; Suzuki, A.; Iura, T.; Ryu, K.; Matsubara, K. *Organometallics* **2000**, *19*, 3579–3590.

Table 3. Reduction of Various Tertiary Amides[a]

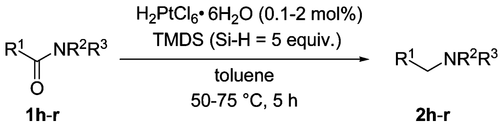


1a-g **2a-g**

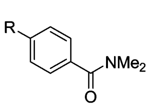
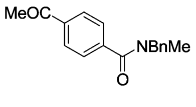
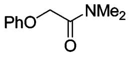
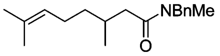
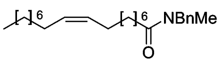
entry	amide		Pt cat.[b] (mol%)	temp. (°C)	time (h)	yield (%)
1		**1a:** $R^2 = R^3 = Me$	**A** (0.1)	50	5	85
2		**1b:** $R^2 = Et$, $R^3 = PMP$	**A** (0.1)	50	5	69 (31)[c]
3			**B** (0.1)	50	5	82
4		**1c**	**A** (0.1)	50	5	70 (30)[c]
5			**B** (0.1)	50	5	95[c]
6		**1d**	**B** (1.0)	70	54	91
7		**1e:** n = 1	**A** (0.1)	25	3	90
8		**1f:** n = 3	**A** (0.1)	25	3	86
9		**1g**	**A** (1.0)	75	5	88

[a] All reactions were carried out with **1** (1 mmol), Pt catalyst (0.1−1 mol %), and TMDS (2.5 mmol, Si−H = 5 equivalent) in toluene (0.5 mL). [b] **A**: $H_2PtCl_6 \cdot 6H_2O$, **B:** Karstedt's catalyst. [c] Determined by ^1H NMR analysis with ferrocene as an internal standard. The yield in parentheses was the yield of enamine.

Table 4. Reduction of Functionalized Tertiary Amides[a]



1h-r **2h-r**

entry	amide		catalyst (mol%)	temp (°C)	yield (%)
1		**1h:** R = OMe	1	75	95
2		**1i:** $R = NMe_2$	1	75	89
3		**1j:** R = Cl	1	75	82
4[b]		**1k:** R = Br	1	75	91
5		**1l:** $R = NO_2$	1	75	93
6		**1m:** R = CN	1	75	82
7		**1n:** $R = CO_2Me$	1	75	96
8[c]		**1o**	2	50	76[d]
9		**1p**	1	50	79
10		**1q**	0.1	50	76
11[e]		**1r**	0.1	50	93

[a] All reactions were carried out with **1** (1 mmol), $H_2PtCl_6 \cdot 6H_2O$ (0.01 mmol), and TMDS (2.5 mmol, Si−H = 5 equivalent) in toluene (0.5 mL). [b] For 3 h. [c] TMDS (5 mmol, Si−H = 10 equivalent to **1k**) was used. [d] Amino alcohol was obtained as a product. [e] Karstedt's catalyst was used.

2.4. Reduction of Secondary and Primary Amides with TMDS. It is known that the hydride reduction of secondary amides is generally more difficult than that of tertiary amides. Catalytic reduction of secondary amides with hydrosilanes has the same problem; no reaction took place in some cases,[8a] whereas high reaction temperature was required in other cases.[9,11] In our ruthenium cluster-catalyzed reduction of amides, reduction of secondary amides did not take place under the same conditions as those for the reaction of tertiary amides. We have solved this problem by combining the "dual Si−H effect" and application of higher concentration of the catalyst (3 mol %) at slightly higher temperature.[10d] A similar approach was effective for the platinum-catalyzed reduction of secondary amides as shown in Table 5; three amides **4a**, **4c**, and **4d** were converted to the corresponding amines in good yields by the reactions using 3 mol % of H_2PtCl_6 and TMDS (Si−H = 10 equivalent to **4**) at 75 °C. Similar to the reduction of tertiary amides, the lactam **4d** was easily reducible, whereas benzamide **4c** required longer reaction time. A bulky amide **4b** reacted with TMDS much more slowly than the others to give the amine in moderate yield. The secondary amine was isolated as the ammonium salt by treatment of the reaction mixture with conc. HCl. Attempted Pt-catalyzed reduction of primary amides such as decanamide and *p*-toluamide with TMDS led to vigorous hydrogen gas evolution, but aqueous workup resulted in quantitative recovery of the starting materials. Neither reduction nor dehydration took place.

2.5. Multigram-Scale Synthesis of Tertiary Amines. General procedures for the reduction of carboxamides by alumino- and borohydrides have safety problems due to their air- and moisture

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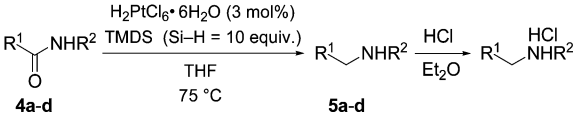
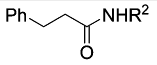
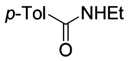
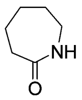
(17) (a) Hudlicky, M. *Reductions in Organic Chemistry*; Wiley: New York, 1984. (b) Trost, B. M., Fleming, I., Eds. *Comprehensive Organic Synthesis*; Pergamon: Oxford, 1992; Vol. 8. (c) Seyden-Penne, J. *Reductions by the Alumino- and Borohydrides in Organic Synthesis*, 2nd ed.; Wiley: New York, 1997.

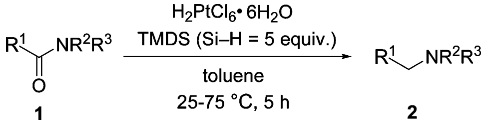
Table 5. Reduction of Secondary Amides[a]

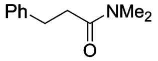
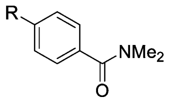
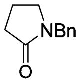


entry	amide		time (h)	yield (%)[b]
1		**4a:** R^2 = Bn	8	79
2		**4b:** R^2 = PMP	72	56
3		**4c**	15	81
4[c]		**4d**	3	84

[a] All reactions were carried out with **4** (1 mmol), $H_2PtCl_6 \cdot 6H_2O$ (0.03 mmol), and TMDS (Si−H = 10 equivalent) in THF (3 mL) at 75 °C. [b] Product was obtained as an ammonium salt by treatment of secondary amine **5** with HCl/Et_2O. [c] At 40 °C.

Table 6. Multigram-Scale Synthesis of Tertiary Amines[a]



entry	amide		cat. (mol%)	temp. (°C)	yield (%)
1		**1a**	0.1	50	81
2		**1g:** R = H	1	75	83
3		**1l:** R = NO_2	1	75	85[b]
4		**1e**	0.1	25	63

[a] All reactions were carried out with amide (5 g), $H_2PtCl_6 \cdot 6H_2O$ (0.1 or 1 mol %), and TMDS (Si−H = 5 equivalent) in toluene (13−17 mL) at 25−75 °C. Product was isolated by distillation. [b] Isolated by alumina column chromatography.

sensitivity.[17] Separation of the product from aluminum or boron wastes is often problematic. Since hydrosilanes are more advantageous than the conventional hydride reagents due to their ease of handling, the present platinum-catalyzed reduction of amides with hydrosilanes deserves further attention, especially when the reaction can be adaptable to production of amines in large quantity. In Table 6 are summarized results of four reactions in a scale where 5 g of the carboxamides was used as the substrate. In all of these reactions, the desired amine is formed quantitatively. Removal of the siloxanes concomitantly produced is easily achieved by treatment of the reaction mixture by strong acid to convert the amine to the corresponding ammonium salt soluble to water. The ammonium salt without contamination of the siloxane waste is extracted to the aqueous phase, from which the desired amine is isolated by treatment with base. In a typical example, amide **1a** (5 g, 28.2 mmol) and TMDS (Si−H = 5 equivalent to **1a**) were treated with $H_2PtCl_6 \cdot 6H_2O$ (0.1 mol %) in toluene at 50 °C. The starting material was consumed within 5 h. Addition of 6 N HCl aq to the reaction mixture gave a biphasic mixture; ^1H NMR spectra of both of the phases suggested that the aqueous phase contained the ammonium salt of **2a** as a single organic component, while the siloxane residue was in the organic phase. The aqueous phase was separated and treated with potassium hydroxide. Extraction with ether followed by concentration gave crude amine, of which distillation under reduced pressure gave **2a** in 81% (3.7 g) (entry 1). Similarly, reactions of benzamide **1g** and lactam **1e** afforded the corresponding amines **2g** and **2e** in 83% (3.8 g) and 63% (2.9 g) yields, respectively (entries 2 and 4). In the reaction of *N,N*-dimethyl-*p*-nitrobenzamide (**1L**), the product **2L** was isolated by alumina column chromatography in 85% yield (3.9 g) (entry 3).

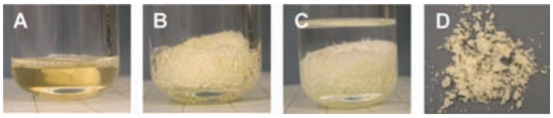
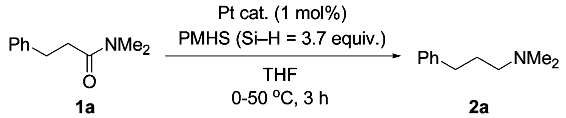


Figure 1. Photos of the Pt/PMHS system. (A) Initial homogeneous solution, (B) after the reaction (gel), (C) extraction with ether, (D) insoluble silicone resin containing platinum residue.

2.6. Reduction of Amides with PMHS: Automatic Removal of Silicone and Platinum Wastes. Recently, removal of metal catalysts and reactant residues from products has been recognized as a problem to be solved from an environmental point of view. Our previous papers provide one of the clear solutions for this problem: a triruthenium cluster-catalyzed reduction of carboxamides with PMHS giving the desired amine in good yield is accompanied by formation of insoluble silicone resin, into which almost all of the metal species (>99.7%) are soaked.[10c] Thus, both ruthenium and silicon wastes are automatically removed from the reaction mixture as a Ru-containing siloxane resin, and the product is obtained in high purity by simple filtration. Similar automatic removal of the catalyst and silicon wastes can also be achieved in the present Pt-catalyzed deoxygenative reduction of carboxamides. In a typical example, the reaction of *N,N*-dimethyl-3-phenylpropionamide (**1a**) (1 mmol) with PMHS [$n = 25.6$ (average), Si−H = 4 equivalent to **1a**], and $H_2PtCl_6 \cdot 6H_2O$ (1 mol %) was carried out using THF as the solvent (0.6 mL) at 50 °C. After the reaction mixture was stirred for 30 min, the initial homogeneous solution set to gel (Figure 1, A→B). After 3 h, washing the gel with ether gave a clear, colorless solution containing the amine **3a** and a light-yellow solid (Figure 1, C→D). ICP mass analysis revealed that the extracted amine contained approximately 138 ppm of platinum species. In other words, over 98.9% of the charged platinum species was removed by this simple purification procedure. The product was obtained from the extract in 88% yield after a short-path alumina column with less than 1 ppm of platinum content (Table 7, entry 1). It is noteworthy that the encapsulated platinum species is still active in the silicone resin and is reusable; the recovered platinum-containing resin (0.01 mmol of Pt species) catalyzed the reduction of **1a** (1 mmol) with PMHS (Si−H = 3.7 equivalent to **1a**) to afford the desired amine **2a**, although the conversion of amide was somewhat decreased (first: 100%, second: 84%, third: 76%).

Reduction of **1a** with PMHS also proceeded smoothly with Pt(II)Cl_2(cod) and a Pt(0)−vinylsiloxane complex (Karstedt's catalyst) to afford **2a** in good yields along with the formation of the Pt-encapsulating gel (entries 2 and 3). In these reactions, >99% of the charged platinum species was also absorbed by the silicon resin formed. It is noteworthy that the activity of the platinum catalysts increased in the order H_2PtCl_6 < $PtCl_2$(cod) < Karstedt's catalyst; lower-valent platinum species

Table 7. Pt-Catalyzed Reduction of **1a** with PMHS[a]



entry	Pt catalyst	temp (°C)	Pt amount in crude **2a** (ppm)[b]	Pt amount in crude **2a** (%)[c]	yield (%)[d]
1	$H_2PtCl_6 \cdot 6H_2O$	50	138	1.1	84
2	$PtCl_2$(cod)	40	106	0.9	77
3	Karstedt's cat.	0	36	0.3	86

[a] All reactions were carried out with **1a** (1 mmol), $H_2PtCl_6 \cdot 6H_2O$ (0.01 mmol), and PMHS (Si−H = 3.7 equivalent) in THF (0.6 mL) at 0−50 °C for 3 h. [b] Determined by ICP-mass analysis. [c] Calculated by the charged Pt species. [d] Purified by short-pass alumina column.

showed higher catalytic activity, and the reaction using Karstedt's catalyst proceeded even at 0 °C.

Table 8 summarizes the reactions of various tertiary amides (**1a**−**u**) and secondary amides (**4e**−**h**) with PMHS in THF using $H_2PtCl_6 \cdot 6H_2O$ as the catalyst. Gel formation occurred in all cases, and the corresponding amines were obtained in good to high yields. Similar to the results obtained by the reactions with TMDS, both aliphatic and aromatic tertiary amides underwent the reduction below 80 °C within a few hours. As shown in entries 7−11, the reaction is tolerant to several reducible functional groups, Cl, Br, NO_2, CN, and CO_2Me. Amides containing a di- or trisubstituted C═C bond underwent the reduction with the C═C bond remaining intact (entries 12 and 13). In all cases, extraction of the reaction mixture with ether gave a solution containing the desired amine as a single product. In the reaction of **1s** with PMHS, no organic product was detected in the extracts due to hydrosilylation of a terminal C═C bond. The hydrosilylation leads to immobilization of the product derived from **1s** in the insoluble silicone resin; this is supported by ^{29}Si solid state NMR of the silicone resin formed.[18] Secondary amides having bulky *N-i*-Pr and *N-t*-Bu groups underwent the reduction at somewhat elevated temperatures. Extraction of the silicone resin that formed gave the corresponding secondary amine in good yields. In contrast, no organic product was extractable from the gel formed by the reaction of secondary amides having a less bulky *N*-Me or *N*-Et group. As reported previously, the secondary amine formed by the reduction of secondary amides with PMHS is potentially linkable to the silicone resin through a Si−N bond.[10d] It is likely that bulky substituents on the nitrogen atom would disturb the Si−N bond formation; this is the reason why the amine products from **4g** or **4h** were extractable, whereas those from **4e** and **4f** were not.[19]

2.7. Mechanistic Consideration. As described in the Introduction, platinum compounds are excellent catalysts for hydrosilylation of alkenes, but not for reduction of carbonyl compounds. Our discovery is the use of hydrosilanes such as 1,2-bis(dimethylsilyl)benzene, 1,1,1,3,5,7,7,7-octamethyltetrasiloxane, and 1,1,3,3-tetramethyldisiloxane (TMDS) as shown in Table 1 to be a clue to achieving the platinum-catalyzed reduction of amides efficiently. Three hydrosilanes having two Si−H groups located close together reacted with amides under mild conditions where the reaction with other hydrosilanes listed in Table 1 did not occur. The enormous acceleration of the reaction rate by synergy of two proximate Si−H groups was first reported in the $RhCl(PPh_3)_3$-catalyzed hydrosilylation of ketones, in which the rate of the reaction of acetone with $Me_2HSi(CH_2)_2SiHMe_2$ is 50 times faster than that with $EtMe_2SiH$, leading to selective conversion of one Si−H group to the corresponding *i*-PrO−Si group, with the other Si−H moiety remaining intact.[15] The effect is sensitive to the distance of two Si−H moieties; for instance, $EtMe_2SiH = Me_2HSiCH_2SiHMe_2 = Me_2HSi(CH_2)_4SiHMe_2 \ll Me_2HSi(CH_2)_2SiHMe_2 < Me_2HSi(CH_2)_3SiHMe_2$. Effects of hydrosilanes, which cannot be explained by conventional consideration on the basis of the electronic structure of hydrosilanes or steric circumstances around the Si−H groups, were later investigated in detail by studies on the oxidative addition of 1,2-bis(dimethylsilyl)benzene with $RhCl(PPh_3)_3$ in which catalytic cycles involving disilametallacyclic intermediates were proposed.[20] Thus, double oxidative addition of 1,2-bis(dimethylsilyl)benzene to $RhCl(PPh_3)_3$ is accompanied by replacement of the chloride by hydride to form the Rh(V)−trihydride disilarhodacyclic complex (Scheme 1, **E**). The species **E** is stable in solution under hydrogen atmosphere, and loses H_2 upon removal of the solvent under reduced pressure to form the Rh(III) monohydride species **F**. The reaction of $RhCl(PPh_3)_3$ with two equivalents of 1,2-bis(dimethylsilyl)benzene forms **G**.

It seems plausible to assume that similar double oxidative addition of 1,2-bis(dimethylsilyl)benzene to Pt(0) species proceeds. In fact, it is known that double oxidative addition of 1,2-bis(dimethylsilyl)benzene to certain Pt(0) precursors followed by elimination of H_2 results in the formation of disilaplatinacyclopentane;[21,22] the reaction pathway is analogous to the double oxidative addition to form the platinum analogue of **E** followed by H_2 elimination to give the platinum analogue of **F**. It is important that the disilaplatinacyclopentanes previously reported are synthesized by the double oxidative addition of 1,2-bis(dimethylsilyl)benzene and 1,1,3,3-tetramethyldisiloxane. Tanaka reported that reaction of platinum(0) complex and *o*-disilylbenzene derivatives resulted in the formation of disilaplatinapentane through multiple oxidative additions of Si−H groups.[21] Curtis et al. and Milstein et al. reported that oxadisilaplatinacyclobutanes are synthesized by reaction of platinum(0) species and 1,3-dihydrodisiloxane derivatives.[22] This is in accord with the results summarized in Table 1, in which platinum-catalyzed reduction of amides took place with 1,2-bis(dimethylsilyl)benzene and 1,1,3,3-tetramethyldisiloxane. These results strongly support the mechanisms involving interaction of two proximate Si−H groups located to the platinum center.

Although our efforts to capture the silylplatinum intermediates in the actual catalytic system have thus far been unsuccessful,

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(18) It is known that ^{29}Si resonances due to−$OSi(R)_2O$−moieties are generally seen around δ−20 ppm. ^{29}Si CP-MAS NMR spectrum of the siloxane resin showed a broad signal at δ−19.8 ppm. See: Engelhardt, G.; Jancke, H. *J. Organomet. Chem.* **1981**, *210*, 295–301.

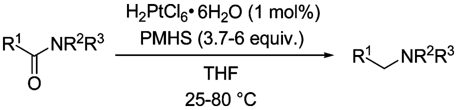
(19) Since the Si−O−Si linkage of polysiloxanes is cleaved under strongly basic conditions, it was confirmed from ^1H NMR spectrum that treatment of polysiloxane gels entrapping a secondary amine, **4e** or **4f**, with NaOH/MeOH actually released the amine. Attempted separation of **4e** or **4f** from a complicated mixture of siloxane and silanols has thus far been unsuccessful.

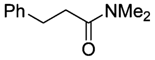
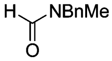
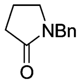
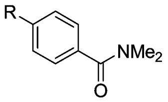
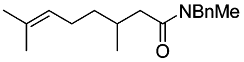
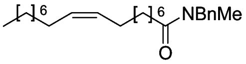
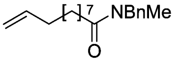
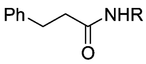
(20) Sunada, Y.; Fujimura, Y.; Nagashima, H. *Organometallics* **2008**, *27*, 3502–3513.

(21) (a) Shimada, S.; Tanaka, M.; Honda, K. *J. Am. Chem. Soc.* **1995**, *117*, 8289–8290. (b) Shiamada, S.; Tanaka, M. *Coord. Chem. Rev.* **2006**, *250*, 991–1011, and references therein.

(22) (a) Eaborn, C.; Metham, T. N.; Pidcock, A. *J. Organomet. Chem.* **1973**, *54*, C3–C4. (b) Curtis, M. D.; Greene, J. *J. Am. Chem. Soc.* **1978**, *100*, 6362–6367. (c) Greene, J.; Curtis, M. D. *J. Am. Chem. Soc.* **1977**, *99*, 5176–5177. (d) Curtis, M. D.; Greene, J.; Butler, W. M. *J. Organomet. Chem.* **1979**, *164*, 371–380. (e) Golkhman, R.; Karakuz, T.; Shimon, L. J. W.; Leitus, G.; Milstein, D. *Can. J. Chem.* **2005**, *83*, 786–792.

Table 8. Reduction of Various Amides by the $H_2PtCl_6 \cdot 6H_2O$/PMHS System[a]



entry	amide		Si-H (equiv.)	temp. (°C)	time (h)	yield (%)
1		**1a**	3.7	50	3	84
2		**1t**	3.7	50	3	72
3		**1e**	3.7	25	3	92
4		**1g:** R= H	3.7	60	3	75
5		**1h:** R= OMe	3.7	60	3	88
6[b]		**1i:** R= NMe_2	3.7	80	3	89
7		**1j:** R= Cl	3.7	60	3	94
8		**1k:** R= Br	4	70	4	86
9		**1l:** R= NO_2	4	70	4	52[c]
10		**1m:** R= CN	4	70	4	83
11		**1n:** R= CO_2Me	4	70	4	89
12		**1q**	3.7	50	3	95
13		**1r**	3.7	50	3	80[d]
14		**1s**	3.7	50	3	trace
15[e]		**4e:** R= Me	6	50	24	<1
16[e]		**4f:** R= Et	6	50	24	<1
17[e]		**4g:** R= *i*-Pr	6	70	24	73
18[e]		**4h:** R= *t*-Bu	6	70	24	75

[a] All reactions were carried out with amide (1 mmol), $H_2PtCl_6 \cdot 6H_2O$ (0.01 mmol), and PMHS (Si−H = 3.7−6 equivalent) in THF (0.5 mL) at 25−70 °C for 3−24 h. The amine product was purified by short-pass alumina column. [b] In DME. [c] 36% of **1 L** was recovered. [d] Purified by short-pass silica gel column. [e] 3.0 mL of THF and 3.0 mol % of catalyst were used.

mechanisms analogous to those proposed for the rate enhancement that occurred in the $RhCl(PPh_3)_3$-catalyzed hydrosilylation of acetone with 1,2-bis(dimethylsilyl)benzene seem to have been adopted for the explanation of platinum-catalyzed reduction of amides with 1,1,3,3-tetramethyldisiloxane or 1,2-bis(dimethylsilyl)benzene. In the mechanism involving Pt(IV) intermediates shown in the left-hand side in Scheme 2, double oxidative addition of proximate Si−H groups affords $Pt(IV)H_2Si_2$ species, which is followed by the reaction of amides in retaining the disilaplatinacyclopentane structures until the final step. In contrast, the right-hand side in Scheme 2 shows a mechanism involving redox between Pt(0) and Pt(II), in which the Pt(IV) species may form in the reaction medium, but act as a precursor reversibly generating Pt(II)H*Si* species. The rate acceleration in the Pt(II) cycle occurs in the reductive elimination of the product, which is triggered by intramolecular oxidative addition of the second Si−H bond to the platinum center. These mechanisms can be adapted to explain the reduction of amides with PMHS.

A well-known proposal related to the mechanisms of platinum-catalyzed hydrosilylation by Lewis et al. is that the colloidal platinum(0) species are often formed during platinum-catalyzed hydrosilylation of alkenes and alkynes.[23] It seems worthwhile to discuss the possibility that platinum nanoparticles may be involved in the catalytic cycle. While the colloidal platinum species by Lewis is reported to be dark brown, the platinum-catalyzed reduction of amides with TMDS is homogeneous and retains a clear, pale-yellow color solution throughout the reaction. In the reaction with PMHS, all of the platinum species is soaked up to insoluble silicone resin formed during the reaction, and the color of the resin is also pale-yellow. High-resolution TEM analysis of the siloxane resin, by which metal particles 1−2 nm in size are detectable, did not show any platinum nanoparticles. These results indicate that the net

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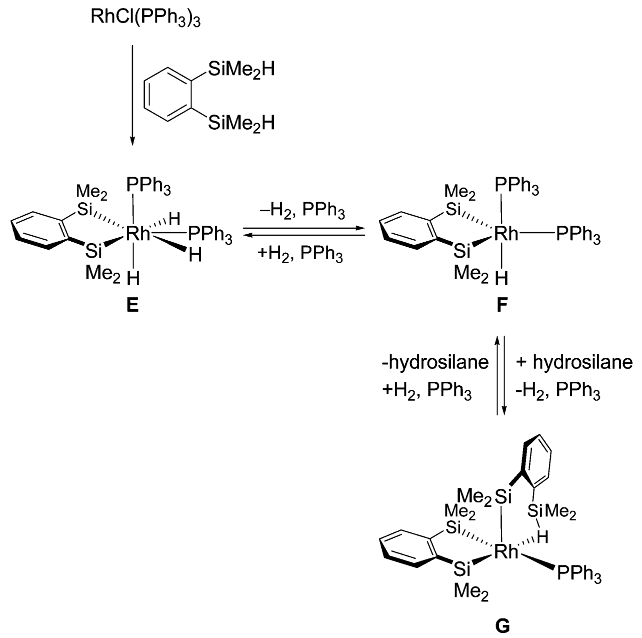
(23) (a) Lewis, L. N.; Lewis, N. *J. Am. Chem. Soc.* **1986**, *108*, 7228–7231. (b) Lewis, L. N. *J. Am. Chem. Soc.* **1990**, *112*, 5998–6004.

Scheme 1. Disilametallacycle Formation by Reaction of Wilkinson's Complex and 1,2-Bis(dimethylsilyl)benzene



catalyst species in our reaction would be molecular platinum species and not colloidal platinum(0) species.

3. Conclusion

As described in the Introduction, platinum catalysts are very useful for the hydrosilylation of alkenes but usually not for reduction of carbonyl compounds. A key discovery that the reduction of amides to amines proceeds under mild conditions was the "dual Si−H effect", in which two proximate Si−H groups cooperatively accelerate the reaction. In particular, it is of practical importance that inexpensive TMDS can be used as the reductant, whereas use of PMHS is accompanied by automatic removal of the silicone and platinum species from the product. It is known that conventional hydride reduction of amide with $LiAlH_4$ is useful for reduction of amides in laboratory-scale experiments; however, the reagent is sensitive to oxygen and moisture, and separation of aluminum wastes from the product is often problematic. Stable hydrosilanes are advantageous for handling, and the reduction reported here is tolerant to several reducible functional groups such as NO_2, CN, esters, and halides. Compared with the ruthenium cluster (μ_3,η^2:η^3:η^5-acenaphthylene)$Ru_3(CO)_7$ previously reported by our research group, the present platinum-catalyzed reactions require somewhat higher reaction temperatures; however, they have an advantage that commercially available platinum compounds, typically H_2PtCl_6, can be used as the catalyst. We believe that the present results accelerate the practical use of metal-catalyzed silane reduction of amides for the synthesis of various amines, and studies including experiments to elucidate the mechanisms are underway.

4. Experimental Section

Typical experimental procedures and representative spectroscopic data of the products are described. Further experimental details and the compound data are summarized in the Supporting Information.

General Procedure for the Reduction of Tertiary Amides with TMDS. To a solution of amide **1** (1 mmol) and 1,1,3,3-tetramethyldisiloxane (TMDS: 2.5 mmol, 5 equivalent Si−H to **1**) in toluene (0.5 mL) was added a THF solution of $H_2PtCl_6\cdot 6H_2O$ (0.1−1 mol % based on the amide). The solution was stirred at 25−75 °C for 3−54 h. After complete consumption of **1** was confirmed by TLC analysis, the reaction mixture was passed through a Florisil column with Celite putting on the head. After removal of the solvent, purification of the residue by alumina column chromatography gave the amine **2**.

***N*-Ethyl-*N*-(*p*-methoxyphenyl)-3-phenylpropylamine (2b):** IR (neat) ν 3025, 2934, 2830, 1509, 1453, 1371, 1243, 1180, 1040, 813, 748, 700 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.12 (t, J = 7.0 Hz, 3H), 1.92 (tt, J = 7.8, 7.4 Hz, 2H), 2.69 (t, J = 7.8 Hz, 2H), 3.24 (t, J = 7.4 Hz, 2H), 3.30 (q, J = 7.0 Hz, 2H), 3.79 (s, 3H), 6.70 (d, J = 9.0 Hz, 2H), 6.85 (d, J = 9.0 Hz, 2H), 7.18−7.36 (m, 5H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 29.1, 33.5, 46.1, 50.9, 55.9, 114.9, 115.3, 125.9, 128.39, 128.42, 142.0, 143.0, 151.6; HRMS (EI) calcd for $C_{18}H_{23}NO$ 269.1780, found 269.1778.

General Procedure for the Reduction of Secondary Amides with TMDS. To a stirred solution of secondary amide **4** (1 mmol) and $H_2PtCl_6\cdot 6H_2O$ (3 mol % based on the amide) in toluene was added TMDS (5.0 mmol, 910 μL, 10 equivalent Si−H to **4**) at 40−75 °C. After the reaction was complete, the resulting mixture was passed through a Florisil column with Celite putting on the head. After removal of the volatiles, the residue was dissolved in Et_2O. Hydrochloric acid (1.0 M Et_2O, 2.0 mL) was added to the solution. The ammonium chloride precipitated was separated, washed with Et_2O, and dried under reduced pressure. The corresponding amine from the ammonium salt was reported earlier.[10d]

Azepane Hydrochloride (5d·HCl): [10d] IR (KBr) ν 2957, 2819, 2761, 1601, 1462, 1105 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.63−1.79 (m, 4H), 1.85−2.01 (m, 4H), 3.12−3.30 (m, 4H), 9.54 (bs, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 25.2, 26.8, 45.8.

General Procedure for the Reduction of Tertiary Amides with PMHS. A solution of amide **1** (1 mmol) and PMHS (3.7−4.0 equivalent Si−H to **1**) was treated with a THF solution of $H_2PtCl_6\cdot 6H_2O$ (1 mol % based on the amide) at 25−80 °C. The homogeneous solution became gradually viscous, and set to gel. After it was allowed to stand for 3−4 h, the reaction mixture was extracted with Et_2O. The extracts were passed through a pad of cotton to remove the fine resins. After removal of ether, purification of residue by alumina column chromatography gave the amine **2**.

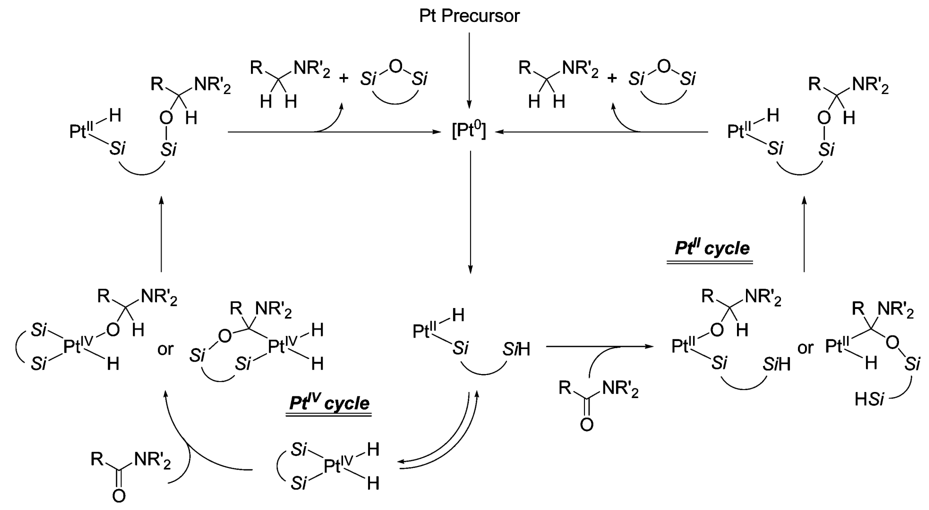
(*p*-Dimethylaminomethyl)bromobenzene (2k): IR (neat) ν 2941, 2815, 1487, 1361, 1259, 1173, 1070, 1011, 856, 796 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 2.22 (s, 6H), 3.36 (s, 2H), 7.18 (d, J = 8.4 Hz, 2H), 7.44 (d, J = 8.4 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 45.4, 63.7, 120.9, 130.7, 131.4, 138.1; HRMS (EI) calcd for $C_9H_{12}NBr$ 213.0153, found 213.0157.

General Procedure for the Reduction of Secondary Amides with PMHS. To a stirred solution of amide **4** (1 mmol) and PMHS (400 μL, 6 equivalent Si−H to **4**) in THF (2.7 mL) was added a THF solution of $H_2PtCl_6\cdot 6H_2O$ (0.1 *N*, 300 μL, 3 mol % based on the amide) at 75 °C. The homogeneous solution became gradually viscous, and set to gel. After it was allowed to stand for 24 h, the reaction mixture was extracted ten times with Et_2O (20 mL in total). The extracts contained fine siloxane resins, which were filtered off by passing through a pad of cotton. After removal of ether, purification of the residue by alumina column chromatography gave the desired amine.

***N*-*tert*-Butyl-3-phenylpropylamine (5h):**[10d] ^1H NMR (396 MHz, $CDCl_3$) δ 1.11 (s, 9H), 1.83 (tt, J = 7.9, 7.6 Hz, 2H), 2.61 (t, J = 7.6 Hz, 2H), 2.66 (t, J = 7.9 Hz, 2H), 7.14−7.30 (m, 5H); ^{13}C NMR (99.5 MHz, $CDCl_3$) δ 28.9, 32.4, 33.8, 42.1, 50.7, 125.8, 128.3, 128.4, 142.1.

A Procedure for Gram-Scale Production of Amines. *As a representative experimental procedure, that shown in Table 6*, entry 1 is described. To a stirred solution of *N,N*-dimethyl-3-phenylpropionamide (**1a**) (5.0 g, 28.2 mmol) and TMDS (12.8 mL, 70.5 mmol) in toluene (14 mL) was added a THF solution of $H_2PtCl_6\cdot 6H_2O$ (0.01 *N*, 2.82 mL, 0.1 mol % based on the amide) at 50 °C. After 5 h, the resultant mixture was filtered through a

Scheme 2. Plausible Reaction Mechanisms



pad of Celite and Florisil. The solvents were removed under reduced pressure, and the residue was dissolved in Et_2O. The solution was washed three times with conc. HCl (totally 30 mL), and the combined aqueous layers were treated with KOH (~40 g). The mixture was extracted three times with ether (30 mL in total). The combined extracts were dried over $MgSO_4$, and concentrated. Distillation (52−53 °C/3.0 Torr) of the residue gave *N*,*N*-dimethyl-3-phenylpropylamine (**2a**) in 81% yield (3.70 g).

***N*,*N*-Dimethyl-3-phenylpropylamine (2a):**[24] IR (neat) ν 3062, 3026, 2942, 2764, 1603, 1496, 1454, 1265, 1030 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.81 (tt, J = 7.8, 7.5 Hz, 2H), 2.24 (s, 6H), 2.31 (t, J = 7.5 Hz, 2H), 2.65 (t, J = 7.8 Hz, 2H), 7.19 (t, J = 7.6 Hz, 1H), 7.20 (d, J = 7.1 Hz, 2H), 7.29 (dd, J = 7.6, 7.1 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 29.5, 33.7, 45.5, 59.3, 125.7, 128.3, 128.4, 142.3.

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Supporting Information Available: Detailed experimental procedures, characterization data of both the substrates and the products. This material is available free of charge via the Internet at http://pubs.acs.org.

JA9055307

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[24] Bhattacharyya, S. *J. Org. Chem.* **1995**, *60*, 4928. See also ref 10b.