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# HSiCl$_3$-Mediated Reduction of Nitro-Derivatives to Amines: Is Tertiary Amine-Stabilized SiCl$_2$ the Actual Reducing Species?

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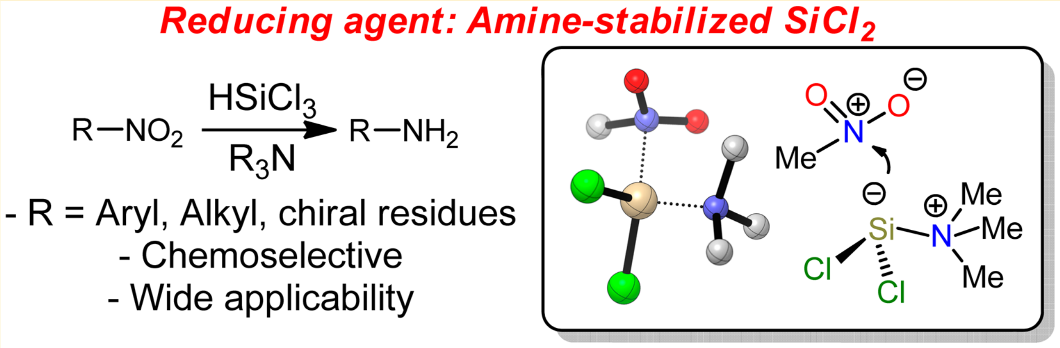
S Supporting Information

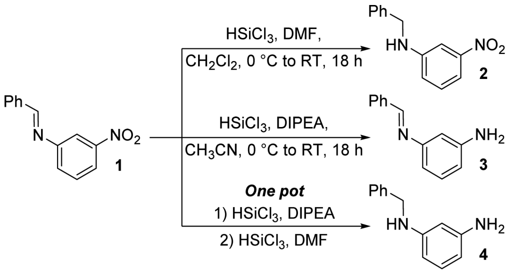


**ABSTRACT:** The mechanism of a recently reported, highly chemoselective metal-free protocol of wide general applicability for the reduction of aromatic and aliphatic nitro-derivatives to amines has been investigated. The reaction is supposed to occur through the generation of a Si(II) reducing species; quantum mechanical calculations, and spectroscopic and experimental data strongly suggest the tertiary amine-stabilized dichlorosilylene to be the most probable reducing agent.

A very convenient, metal-free, HSiCl$_3$-mediated reduction of both aromatic and aliphatic nitro-groups to amines has been recently reported.[1] The very simple experimental procedure that involves the use of extremely inexpensive and not hazardous chemicals, together with its wide general applicability, is a distinctive feature of this attractive protocol. One of the fundamental transformations in organic synthesis, the nitro group reduction,[2] is performed in high yields under very mild conditions, with a method that is tolerant of many functional groups and respectful of the stereochemical integrity of stereocenters.[3]

While studying the chemoselectivity of the methodology, we performed (inter alia) the reactions of Scheme 1, which show that by combining trichlorosilane with a Lewis base[4] or with a tertiary amine, the specific reduction of an imine[5] or of a nitro group may be accomplished, respectively. For instance, when *N*-benzal 3-nitro aniline **1** was reacted with HSiCl$_3$ in the presence of *N*,*N*-dimethylformamide (DMF), 3-nitro-*N*-benzylaniline **2** was isolated in 90% yield, whereas by using trichlorosilane in combination with *N*,*N*-diisopropylethylamine (DIPEA) the transformation of the nitro group to amine **3** was exclusively observed, without any concomitant imine reduction. Remarkably, a two step, one pot reduction of both imine and nitro groups of the same substrate afforded 3-amino-*N*-benzyl aniline **4** in 80% overall yield.

**Scheme 1. Chemoselectivity in Trichlorosilane-Mediated Reductions**



In an attempt to explain this chemoselective behavior and to get some insights in to the nitro reduction mechanism, we considered the HSAB (hard and soft bases and acids) theory. In this context, soft Lewis bases, such as DMF, are expected to preferentially interact with the soft oxophilic silicon atom giving a hypervalent silicon species,[6] known to reduce imines. However, hard Brønsted bases, such as tertiary amines, prefer to interact with the hard acidic site in the molecule, the proton, leading to proton abstraction and formation of the R$_3$NH$^+$/$^-$SiCl$_3$ adduct (Scheme 2).[7]

Noteworthy, calculations performed using different computational methods[8] within the HSAB theory correctly confirmed the dichotomic behavior of HSiCl$_3$: DMF was found to interact stronger with the silicon atom, while trimethylamine preferentially reacted with the hydrogen atom (see SI).

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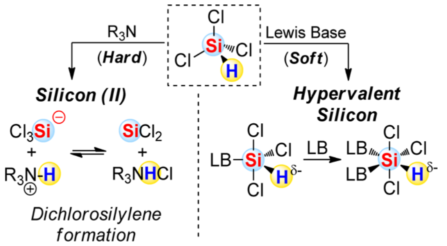
Scheme 2. Peculiar Behavior of $HSiCl_3$ with Lewis or Brønsted Bases



Even if the formation of the $R_3NH^+/^-SiCl_3$ species from the reaction of trichlorosilane with a tertiary amine was postulated 30 years ago,[9] more recently[10] it was proposed that a dichlorosilylene species ($SiCl_2$) could also be generated (Scheme 2).[11] Considering that both $SiCl_3^-$ or $SiCl_2$ might be the effective nitro reducing agent, a first essential step toward the understanding of the mechanism of the nitro reduction is the evaluation of the reducing ability of these two species.

Therefore, experiments were performed, aiming at the formation of $SiCl_2$ from sources which do not allow that of $SiCl_3^-$. Dichlorosilylene was generated from $SiCl_4$ and Mg,[12] with or without DIPEA, in the presence of 4-nitrotoluene **5** as a benchmark substrate for the reduction. The same reduction was studied also by using a mixture of $Si_2Cl_6$ and TEA or DIPEA, according to Lerner's method for dichlorosilylene formation.[13]

The data of Table 1 show that $SiCl_2$ is indeed able to reduce the nitro group to amine and that the presence of a base notably improves the reactivity of the reducing agent.[14] Although the involvement of $SiCl_3^-$ cannot be ruled out, the reported experiments suggest dichlorosilylene is the more likely reducing agent. Unfortunately, due to the instability and to the intrinsic coexistence of the two species in the equilibrium of Scheme 2, the unambiguous identification of the effective reducing species required further work. Hence, we decided to perform other experiments and calculations.

Table 1. Different Methods to Generate Dichlorosilylene and Their Efficiency in the Reduction

| entry | red. agent | base | solvent | conv. (%) |
|---|---|---|---|---|
| 1 | $SiCl_4$, Mg | | THF | 20 |
| 2 | $SiCl_4$, Mg | DIPEA | THF | 64 |
| 3 | $Si_2Cl_6$ | DIPEA | $CH_3CN$ | 27 |
| 4 | $Si_2Cl_6$ | TEA | $CH_3CN$ | 60 |
| 5 | $Si_2Cl_6$ | TEA | $CH_2Cl_2$ | 9 |

By using NMR to monitor the reduction of nitrotoluene in $CDCl_3$, the only detectable species were the starting material and the N-silylated aniline product (that upon aqueous workup afforded the expected amine), while no traces of the nitroso intermediate could be detected. Since it is very likely that the nitroso compound is the first reduction product of the reaction, this observation suggested the nitro to nitroso reduction as the rate-determining step of the process (for NMR spectra, see SI).[15] The TSs of the reaction of nitromethane as a model substrate were calculated (Figure 1), considering different possible reducing species such as electrophilic $SiCl_2$, nucleophilic $SiCl_3^-$, and the adduct $Me_3N$-$SiCl_2$.[14]

The structures (Figure 1)[16] are related to four different mechanisms. Structure A illustrates the $SiCl_2$ insertion in a N═O bond of the nitro group. Indeed, $SiCl_2$ can be regarded as a carbene analogue and in structure A is simultaneously donating electron density from the HOMO to nitromethane's $\pi$*LUMO and accepting electrons from the nitromethane's $\pi$HOMO into its LUMO. In panel B, the simple addition of $SiCl_3^-$ to the electrophilic nitrogen of the nitro group is shown, while in TS C the same addition is considered in the presence of the H-bond coordination of the nitro by $Me_3NH^+$. Finally, TS D involves the addition of $NMe_3$-stabilized $SiCl_2$ that behaves as a nucleophile due to the formal negative charge deriving from the amine coordination. The Gibbs free energies of activation calculated for the four mechanisms are reported in Table 2. Notably, with the exception of the B3LYP method, all of the DFT computational setups indicate mechanism **D** as the preferred one.

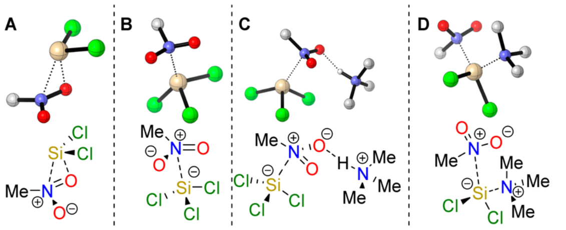


Figure 1. M06-2X geometries of the TSs for the reaction of nitromethane with different reducing species.

Table 2. Calculated Activation Gibbs Free Energies in kcal/mol for TSs A−D

| theory level | A | B | C | D |
|---|---|---|---|---|
| B3LYP[a] | 27.0 | 33.5 | 44.6 | 33.5 |
| M06-2X[a] | 22.5 | 30.6 | 38.3 | 15.8 |
| wB97XD[a] | 26.2 | 32.7 | 43.1 | 23.0 |
| MP2[b] | 28.0 | 28.1 | | 18.0 |
| MP2[c] | 26.6 | 26.8 | | 15.6 |
| MP2[d] | 26.6 | 27.1 | | 16.8 |

[a] Basis set: 6-311++G(3df,3pd); PCM-chloroform. [b] Calculated on the B3LYP/6-311++G(3df,3pd)[PCM] geometries basis set MP2/6-311+G(2d,2p). [c] Calculated on the M06-2X/6-311++G(3df,3pd)-[PCM] geometries basis set MP2/6-311+G(2d,2p). [d] Calculated on the wB97XD/6-311++G(3df,3pd)[PCM] geometries basis set MP2/6-311+G(2d,2p).

Since $SiCl_3^-$ and $Me_3N$-$SiCl_2$ behave as nucleophiles, mechanisms B and D should be favored if the reduction is carried out on electron-poor nitroderivatives. Therefore, in order to corroborate the computational results, some competition experiments were performed. Equimolar mixtures of nitrobenzene and differently substituted nitroarenes were mixed, and the reduction was carried out in the presence of the amount of $HSiCl_3$ necessary for the reduction of only 1 equiv of nitrocompound. The crude reaction mixtures were analyzed by $^1H$ NMR. Since the observed selectivities are related to the ratio between the rate constants ($k_X/k_H$ where $k_X$ is the rate constant for the reduction of the nitroarene with X substituent), the activation energy difference between the two competing processes ($\Delta\Delta G^\ddagger$) may be obtained.

The correlation between $\Delta\Delta G^\ddagger$ and the $\sigma_H$ Hammett constants[17] of the different nitrobenzenes is reported in Table 3. It is clear that electron-poor nitro groups were reduced faster, thus suggesting a nucleophilic species as the active reducing agent, in agreement with the computational observation that

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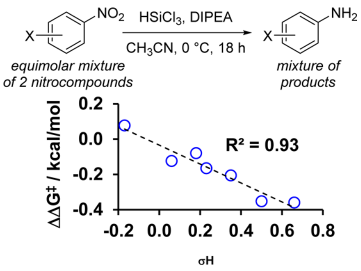
**Table 3. Correlation between Experimental $\Delta\Delta G^{\ddagger}$ (kcal/mol) and the Hammett $\sigma_H$ Constants in the Reduction of Different Nitrobenzenes**

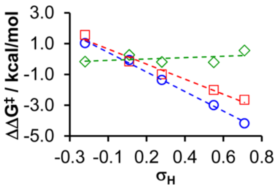


| X | $\sigma_H$ | $k_X/k_H$ | $\Delta\Delta G^{\ddagger}$ (kcal/mol) |
|---|---|---|---|
| 4-$OCH_3$ | −0.27 | <0.01 | >3.0 |
| 4-Me | −0.17 | 0.74 | 0.08 |
| 4-F | 0.06 | 1.62 | −0.12 |
| 4-I | 0.18 | 1.36 | −0.08 |
| 4-Cl | 0.23 | 1.90 | −0.17 |
| 3-I | 0.35 | 2.22 | −0.21 |
| 4-$COCH_3$ | 0.50 | 3.94 | −0.35 |
| 4-CN | 0.66 | 4.05 | −0.36 |

indicated that a nucleophile ($Me_3N$-$SiCl_2$) was involved in the mechanism with lower activation energy.

To further prove this point, we calculated the energy barriers for the reduction of five compounds among the substituted nitroarenes of Table 3, within mechanisms A, B, and D. The energy difference between the calculated activation energies ($\Delta\Delta G^{\ddagger}$) were then correlated to $\sigma_H$ values (Table 4 for M06-2X-based calculations; see SI). Because of the increased number of atoms, the computational optimizations have been performed with the 6-311+G(2d,2p) basis set, and electronic energies have been refined at the 6-311++G(3df,3pd) level with the PCM model for acetonitrile. The reported $\Delta\Delta G^{\ddagger}$ values in kcal/mol refer to the reduction of nitrobenzene.

**Table 4. Comparison of the Calculated $\Delta\Delta G^{\ddagger}$ (kcal/mol) Values of the Three Proposed Reduction Mechanisms[a] of 4-Substituted Nitroarenes**



| X | $\sigma_H$ | A | B | D |
|---|---|---|---|---|
| 4-Me | −0.17 | −0.17 | 1.03 | 1.56 |
| 4-F | 0.06 | 0.27 | −0.07 | −0.15 |
| 4-Cl | 0.23 | −0.19 | −1.36 | −0.99 |
| 4-$COCH_3$ | 0.50 | −0.21 | −3.00 | −2.01 |
| 4-CN | 0.66 | 0.56 | −4.18 | −2.65 |

[a] Mechanism A, green; B, blue; D, red.

Despite the fact that conclusive evidence has not been obtained, the present study strongly suggests an amine stabilized $SiCl_2$ species to be the main one responsible for the reducing activity of the $HSiCl_3/R_3N$ system toward nitro groups.

The whole reaction mechanism for the three reduction steps mediated by $Me_3N$-$SiCl_2$ was then calculated. The Gibbs free energies have been obtained with the M06-2X/6-311++G-(3df,3pd)[PCM = $CHCl_3$] computational setup.

The generation of the $Me_3N$-$SiCl_2$ species is highly favored (−20.6 kcal/mol).[13] The addition of such a reducing species to nitromethane occurs with an energy barrier of 15.8 kcal/mol, where zero energy is set for the separated reagents (Figure 2).

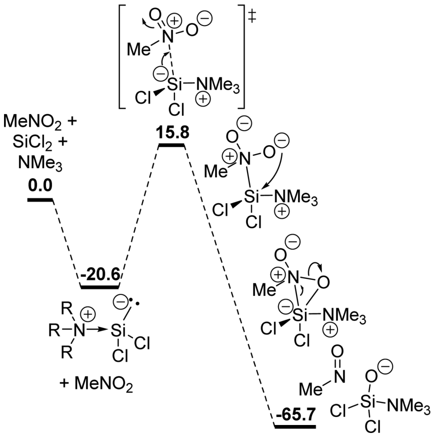


**Figure 2.** MP2/6-311+G(d,p)//M06-2X/6-311++G(3df,3pd)[PCM] Gibbs free energy profile for the first step: from nitro to nitroso derivative. The energies are in kcal/mol.

The transition state involves the addition of the negatively charged Si atom to the positively charged nitro group's nitrogen. Once the Si−N bond is formed, the mechanism leads to a transient three-membered ring that evolves to nitrosomethane and $Me_3N$−Si(O)$Cl_2$. The reaction Gibbs free energy associated with this step is −65.7 kcal/mol. $Me_3N$−Si(O)$Cl_2$ may be seen as a $Me_3N$-stabilized silicon analogue of phosgene; the addition of HCl from the hydrochloride salt of a tertiary amine (DIPEA for instance) would lead to the formation of trichlorosilanol ($Cl_3SiOH$).

In the second step, $Me_3N$-$SiCl_2$ attacks the N atom of the nitroso group, affording as intermediate a Si−N−O three-membered ring **7**, evolving into **8**, with the same oxidation state as hydroxylamine (Figure 3).

Finally, in the third and last step a nucleophilic ring opening of **8** by $Me_3N$-$SiCl_2$ occurs, breaking the N−O bond. The process was calculated to be spontaneous and leads to the formation of the silylated amine **9** that is converted to the final product by the aqueous workup (Figure 4).[18]

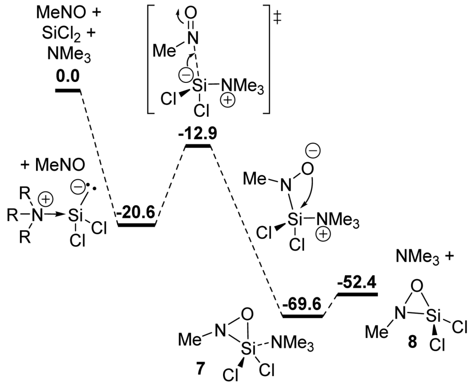


**Figure 3.** Gibbs free energy profile for the second step: from nitroso to cyclic hydroxylamine analogue **8**. The energies are in kcal/mol.

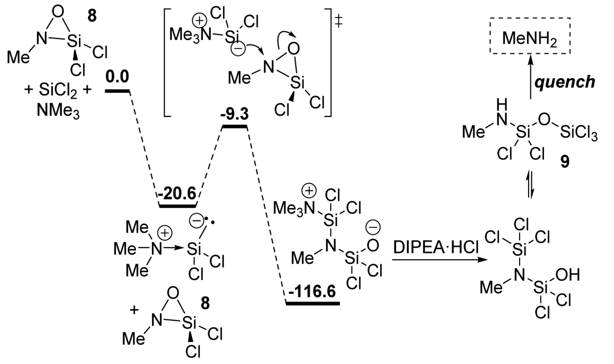


**Figure 4.** Gibbs free energy profile for the third step: from silylated cyclic hydroxylamine **8** to silylated amine **9**. (Energies are given in kcal/mol.)

In summary, the mechanism of a convenient and metal-free protocol for the reduction of nitrocompounds to amine by trichlorosilane and a tertiary amine[1] has been elucidated. The reaction is supposed to occur through the generation of a reducing Si(II) species. Experimental studies demonstrated that dichlorosilylene's ability to reduce the $NO_2$ group is considerably increased in the presence of a tertiary amine. Considering the known instability of $SiCl_2$ at temperatures above −50 °C, the computational studies and competition experiments hereby presented strongly suggest the amine-stabilized dichlorosilylene to be the most probable reducing agent, although it is not possible to exclude a priori the involvement of $SiCl_3^-$.

The reaction path in the presence of $Me_3N$-$SiCl_2$ was fully characterized by calculations. The first reduction step (from nitro to nitroso) was found to be rate-determining (in agreement with the experimental observations) and to present a low energy barrier.

In conclusion, the present study allowed us to shed new light on to the mechanism of trichlorosilane-mediated nitro group reduction, highlighting the role and the nature of the in situ generated dichlorosilylene species as the actual reducing agent. In view of the possible industrial application of the methodology, a clear understanding of the reaction mechanism is a tool of great importance in the setup of optimized process conditions.

## ■ EXPERIMENTAL SECTION

**General Information.** Dry solvents were purchased and stored under nitrogen over molecular sieves (bottles with crown caps). Reactions were monitored by analytical thin-layer chromatography (TLC) using silica gel 60 F254 precoated glass plates (0.25 mm thickness) and visualized using UV light. Flash chromatography was carried out on silica gel (230−400 mesh). $^1H$ NMR spectra were recorded on spectrometers operating at 300 MHz. $^{29}Si$ NMR spectra were recorded on a spectrometer operating at 99.4 MHz. Proton and Silicon chemical shifts are reported in ppm ($\delta$) with the solvent reference relative to tetramethylsilane (TMS) employed as the internal standard ($CDCl_3$ $\delta(^1H) = 7.26$ ppm; $\delta(29Si) = 0$ ppm).

**Experimental Procedure for the Reduction of Compound 1.** *Reduction to Compound 2.* In a round bottomed flask were charged nitro-imine **1** (100 mg, 0.43 mmol) and dichloromethane (2.2 mL) under nitrogen atmosphere. The solution was cooled to 0 °C, and DMF (0.33 mL) was added. After 5 min, 3.2 mL of a 1 M solution (in DCM) of freshly distilled $HSiCl_3$ was added dropwise, and the resulting mixture was allowed to warm to room temperature overnight. Five milliliters of $NaHCO_3$ ss was added slowly. The phases were separated, and the organic layer was washed twice with water (5 mL). The crude product was purified through flash column chromatography (Hex/AcOEt) yielding compound **2** as a pale yellow solid (78 mg, 80%). $^1H$ NMR ($CDCl_3$, 300 MHz): 7.51 (d, $J = 6.0$ Hz, 1H), 7.49 (m, 1H), 7.40−7.25 (m, 6H), 6.92 (d, $J = 6.0$ Hz, 1H), 4.41 (s, 2H).[19]

*Reduction to Compound 3.* In a round bottomed flask, the nitro-imine **1** (100 mg, 0.43 mmol) and DIPEA (408 uL, 2.34 mmol) were dissolved into dry DCM (2.2 mL) under magnetic stirring and nitrogen atmosphere. A solution of freshly distilled $HSiCl_3$ (1.5 mmol) in 1.5 mL of dry solvent was prepared separately, and it was added dropwise to the first solution over 10 min at 0 °C. After stirring the reaction mixture for 18 h, 5 mL of a saturated solution of $NaHCO_3$ was added dropwise, and the biphasic mixture was allowed to stir for 30 min. The crude mixture was extracted with ethyl acetate, dried over $Na_2SO_4$, filtered, and then dried under reduced pressure to afford the crude product **3**. The product was found to be unstable over silica gel, and part of the product hydrolyzes during the aqueous workup. However, from the spectrum of the crude product the absence of starting material and the absence of benzylic signals can be seen.[20]

*One Pot Reduction to Compound 4.* In a round bottomed flask, nitro-imine **1** (100 mg, 0.43 mmol) and DIPEA (408 uL, 2.34 mmol) were dissolved into dry DCM (2.2 mL) under magnetic stirring and nitrogen atmosphere. A solution of freshly distilled $HSiCl_3$ (1.5 mmol) in 1.5 mL of dry solvent was prepared separately, and it was added dropwise to the first solution over 10 min at 0 °C. After stirring the reaction mixture for 18 h, the mixture was cooled to 0 °C, and 0.33 mL of DMF was added. After 5 min, 3.2 mL of a 1 M solution (in DCM) of freshly distilled $HSiCl_3$ was added dropwise, and the resulting mixture was allowed to warm to room temperature overnight. Ten milliliters of $NaHCO_3$ ss was added slowly, the phases were separated, and the organic layer was washed twice with water (5 mL). The crude product was purified through flash column chromatography (Hex/AcOEt) yielding compound **4** as a pale yellow solid (75 mg, 88%). $^1H$ NMR ($CDCl_3$, 300 MHz): 7.40−7.30 (m, 5H), 7.01 (t, $J = 5.9$ Hz, 1H), 6.13 (d, $J = 5.9$ Hz, 2H), 6.02 (s, 1H), 4.32 (s, 2H), 3.51 (bs, 2H).[21]

**Generation of $SiCl_2$ from Other Sources.** *Method A.* 4-Nitrotoluene (400 mg, 2.91 mmol), magnesium (638 mg, 26.25 mmol), and DIPEA (2.6 mL, 14.55 mmol) were added to 10 mL of THF under nitrogen atmosphere. The mixture was cooled to −78 °C before the addition of $SiCl_4$ (1.06 mL, 8.75 mmol) was performed dropwise. The reaction was then allowed to warm to room temperature and stirred for 18 h, then the reaction was cautiously quenched with $NaHCO_3$ ss and extracted with $CH_2Cl_2$. The organic layer was dried over $Na_2SO_4$ and concentrated to give the crude product that was analyzed by $^1H$ NMR to evaluate the reaction conversion.

*Method B.* In a round bottomed flask, the nitro-compound (0.7 mmol) and the tertiary amine (3.5 mmol) were dissolved into the dry solvent (5 mL) under magnetic stirring and nitrogen atmosphere. Hexachlorodisilane was added dropwise to the first solution over 10 min at 0 °C. After stirring the reaction mixture for 18 h, 5 mL of a saturated solution of $NaHCO_3$ was added dropwise, and the biphasic mixture was allowed to stir for 30 min. The crude mixture was extracted with ethyl acetate, dried over $Na_2SO_4$, filtered, and then dried under reduced pressure to afford the crude product. The crude product was analyzed by $^1H$ NMR to evaluate the reaction conversion.

**Competition Experiments.** Nitroarene X-$PhNO_2$ (0.73 mmol), nitrobenzene (75 $\mu$L, 0.73 mmol), and DIPEA (0.64 mL, 3.65 mmol) were charged in a 25 mL flask containing 7.3 mL of dry acetonitrile under nitrogen atmosphere. The mixture was cooled to 0 °C, and $HSiCl_3$ (0.22 mL, 2.19 mmol) was added dropwise to the solution. The reaction was stirred for 18 h, then the reaction was cautiously quenched with $NaHCO_3$ ss and extracted with $CH_2Cl_2$. The organic layer was dried over $Na_2SO_4$ and concentrated to give the crude product that was analyzed by $^1H$ NMR to evaluate reaction selectivity. The observed selectivities are reported in Table S3.

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## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b00191.

> Spectroscopic data for the reduction of compound **1**, HSAB theory details, NMR spectra for $SiCl_2$ generation methods from other sources, Table S3 for competition experiments, in silico competition experiments, and geometries of TSs A–D (PDF)

## ■ AUTHOR INFORMATION

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### Notes

The authors declare no competing financial interest.

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## ■ REFERENCES

(1) Orlandi, M.; Tosi, F.; Bonsignore, M.; Benaglia, M. *Org. Lett.* **2015**, *17*, 3941 The methodology is described in a patent: International Patent Application: Bonsignore, M.; Benaglia, M. PCT/EP/2013/0683 (Università degli Studi di Milano, Milano, Italy), now owned by DexLeChem GmbH (Berlin, Germany)..

(2) (a) Downing, R. S.; Kunkeler, P. J.; van Bekkum, H. *Catal. Today* **1997**, *37*, 121. (b) Ono, N., Ed. *The Nitro Group in Organic Synthesis*; Wiley-VCH: New York, 2001. (c) For a review on selective hydrogenation of nitroarenes, see: Blaser, H. U.; Steiner, H.; Studer, M. *ChemCatChem* **2009**, *1*, 210.

(3) For the use of the method in the synthesis of a chiral pharmaceutical product, see: Rossi, S.; Benaglia, M.; Porta, R.; Cotarca, L.; Maragni, P.; Verzini, M. *Eur. J. Org. Chem.* **2015**, *2015*, 2531.

(4) Reviews: (a) Guizzetti, S.; Benaglia, M. *Eur. J. Org. Chem.* **2010**, *2010*, 5529. (b) Jones, S.; Warner, C. J. A. *Org. Biomol. Chem.* **2012**, *10*, 2189.

(5) For the most recent contributions of our group in the field see: (a) Genoni, A.; Benaglia, M.; Massolo, E.; Rossi, S. *Chem. Commun.* **2013**, *49*, 8365. (b) Barrulas, P. C.; Genoni, A.; Benaglia, M.; Burke, A. *Eur. J. Org. Chem.* **2014**, *2014*, 7339.

(6) Review: (a) Rossi, S.; Benaglia, M.; Genoni, A. *Tetrahedron* **2014**, *70*, 2065. For a review on Lewis base-catalyzed reactions: (b) Denmark, S. E.; Beutner, G. L. *Angew. Chem., Int. Ed.* **2008**, *47*, 1560. (c) Beutner, G. L.; Denmark, S. E. *Angew. Chem., Int. Ed.* **2013**, *52*, 9086.

(7) As evidence that the H atom in $HSiCl_3$ seems to be a proton rather than a hydride, unless activated by Lewis bases, the $^1$H NMR chemical shift of $HSiCl_3$ in $CDCl_3$ shows a singlet at 6.1 ppm, a value too high to be assigned to a hydride.

(8) Geerlings, P.; De Proft, F.; Langenaeker, W. *Chem. Rev.* **2003**, *103*, 1793 See the Supporting Information for further details..

(9) (a) Bernstein, C. S. *J. Am. Chem. Soc.* **1970**, *92*, 699. (b) Benkeser, R. A.; Smith, W. E. *J. Am. Chem. Soc.* **1969**, *91*, 1556. (c) Benkeser, R. A.; Smith, W. E. *J. Am. Chem. Soc.* **1968**, *90*, 5307. (d) Benkeser, R. A.; Gaul, J. M.; Smith, W. E. *J. Am. Chem. Soc.* **1969**, *91*, 3666. (e) Benkeser, R. A.; Foley, K. M.; Gaul, J. M.; Li, G. S.; Smith, W. E. *J. Am. Chem. Soc.* **1969**, *91*, 4578.

(10) Karsch, H. H.; Schlüter, P. A.; Bienlein, F.; Herker, M.; Witt, E.; Sladek, A.; Heckel, M. *Z. Anorg. Allg. Chem.* **1998**, *624*, 295.

(11) (a) Ghadwal, R. S.; Roesky, H. W.; Merkel, S.; Henn, J.; Stalke, D. *Angew. Chem., Int. Ed.* **2009**, *48*, 5683. (b) Roy, S.; Stollberg, P.; Irmer, R. H.; Stalke, D.; Andrada, D. M.; Frenking, G.; Roesky, H. W. *J. Am. Chem. Soc.* **2015**, *137*, 150. (c) Roy, S.; Stückl, A. C.; Demeshko, S.; Dittrich, B.; Meyer, J.; Maity, B.; Koley, D.; Schwederski, B.; Kaim, W.; Roesky, H. W. *J. Am. Chem. Soc.* **2015**, *137*, 4670.

(12) Belzner, J.; Dehnert, U.; Ihmels, H.; Hübner, M.; Müller, P.; Usón, I. *Chem. - Eur. J.* **1998**, *4*, 852.

(13) Meyer-Wegner, F.; Nadj, A.; Bolte, M.; Auner, N.; Wagner, M.; Holthausen, M. C.; Lerner, H.-W. *Chem. - Eur. J.* **2011**, *17*, 4715.

(14) A further evidence of the importance of the amine molecule in the reduction process comes from our optimized protocol that typically requires 5 mol/equiv of base for 3 mol/equiv of HSiCl3, where 1 equiv is used to deprotonate trichlorosilane and the excess may be hypothesized to stabilize the resulting reducing species. For the ability of amines to stabilize $SiCl_2$, see refs 13 and 11.

(15) (a) Uhlig, F.; Marsmann, H. C. In *$^{29}$Si NMR, Some Practical Aspects, from Gelest Catalog: Silicon Compounds, Silanes & Silicones*, 2nd ed.; Arkles, B.; Larson, G., Eds.; Gelest Inc.: Morrisville, PA, 2008; pp 208–222; www.pascal-man.com/periodic-table/29Si.pdf. (b) Frenzel, A.; Buffy, J. J.; Powell, D. R.; West, R.; Müller, T. *Chem. Ber.* **1997**, *130*, 1579.

(16) The TSs were calculated with the B3LYP, M06-2X, and wB97XD functionals using the 6-311++G(3df,3pd) basis set and PCM model for the inclusion of chloroform as the solvent (the same used also in the NMR experiments). Finer single point energy values have also been calculated at the post-Hartree–Fock MP2/6-311+G(2d,2p) level of theory.

(17) (a) Anslyn, E. V.; Dougherty, D. A. In *Modern Physical Organic Chemistry*; University Science Books: Herndon, VA, 2006. (b) Hansh, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165.

(18) It is worth mentioning that, by monitoring the reaction via $^{29}$Si NMR, some peaks at ca. −45, −55, and −65 ppm have been detected, typical of species which present Si atoms directly bound to one, two, or three O and/or N and Cl atoms. See ref 15.

(19) (a) King, F. D.; Caddick, S. *Tetrahedron* **2013**, *69*, 8592. (b) Reddy, M. M.; Kumar, M. A.; Swamy, P.; Naresh, M.; Srujana, K.; Satyanarayana, L.; Venugopal, A.; Narender, N. *Green Chem.* **2013**, *15*, 3474.

(20) Kumar, D.; Sonawane, M.; Pujala, B.; Jain, V. K.; Nhagat, S.; Chakraborti, A. K. *Green Chem.* **2013**, *15*, 2872.

(21) (a) See ref 18; see also (b) Zhou, W.; Fan, M.; Yin, J.; Jiang, Y.; Ma, D. *J. Am. Chem. Soc.* **2015**, *137*, 11942.