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Tris(oxazolinyl)boratomagnesium-Catalyzed Cross-Dehydrocoupling of Organosilanes with Amines, Hydrazine, and Ammonia

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Abstract
We report magnesium-catalyzed cross-dehydrocoupling of Si–H and N–H bonds to give Si–N bonds and H2. A number of silazanes are accessible using this method, as well as silylamines from NH3 and silylhydrazines from N2H4. Kinetic studies of the overall catalytic cycle and a stoichiometric Si–N bond-forming reaction suggest nucleophilic attack by a magnesium amide as the turnover-limiting step.

Keywords
Bond-forming reactions, Catalytic cycles, kinetic study, nucleophilic attack, organosilanes, si-N bonds, silazanes, magnesium, silicon, ammonia, hydrogen, magnesium derivative, nitrogen, tris(oxazolinyl)boratomagnesium, chemical binding, cross coupling reaction, nucleophilicity, stoichiometry

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Tris(oxazoliny)-boratormagnesium-Catalyzed Cross-Dehydrocoupling of Organosilanes with Amines, Hydrazine, and Ammonia

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ABSTRACT: We report magnesium-catalyzed cross-dehydrocoupling of Si–H and N–H bonds to give Si–N bonds and H2. A number of silazanes are accessible using this method, as well as silylamines from NH3 and silylhydrazines from N2H4. Kinetic studies of the overall catalytic cycle and a stoichiometric Si–N bond-forming reaction suggest nucleophilic attack by a magnesium amide as the turnover-limiting step.

Compounds containing Si–N bonds have important applications in synthetic chemistry as bases, silylating agents, ligands for metal centers, and polymeric precursors for ceramic materials. Amines are often protected with tertiary silanes as silazanes, and amines serve as useful protecting groups in silicon chemistry for the selective conversion of chlorosilanes because the Si–N bond forms readily and is easily transformed into Si–X species (X = halide, alkoxide). However, the HCl produced by (SiHMe2)2 reacts at 135°C. Dimethyltinocene catalyzes the coupling of silanes with primary amines. Finally, a number of amine and hydrazine, while cuprous chloride catalyzes the aminolysis of optically active tertiary naphthylphenylmethylsilane with inversion of the silicon stereocenter, while Pd/C gives the racemic product. Ammonia and the tertiary silazane HN-(SiHMe2)2 react at 135°C in the presence of Ru2CO12 to give polysilazanes and H2, while rhodium dimers give mixtures of oligosilazanes from amines and organosilanes. A chromium catalyst provides Ph3HSi-NHPPh from Ph3SiH and aniline. Dimethyltinocene catalyzes the coupling of silanes with ammonia and hydrazine, while cuprous chloride catalyzes the coupling of silanes and primary amines. Finally, a number of silazanes have been prepared using [U(NMe2)3][BPh4] as a catalyst. These few examples show the general challenge of controlling the selectivity, and in addition, there have been few opportunities for direct investigation of the silicon–nitrogen bond-forming steps of these catalytic reactions.

Some of these issues are addressed by the catalytic behavior of the four-coordinate magnesium complex ToMgMe ([ToM = tris(4,4-dimethyl-2-oxazoliny)phenylborate]), which we now report to be an effective precatalyst for the cross-dehydrocoupling of Si–H bonds in organosilanes and N–H bonds in amines to give Si–N bonds and H2 (eq 1).

\[
R_3\text{Si}-H + R'-\text{NR}_2 \xrightarrow{\text{ToMg-NR}_2\text{catalyst}} R_3\text{Si}-\text{NR}_2 + H_2 \quad (1)
\]

With this catalyst system, a range of silazanes can be prepared in high conversion and high yield, as shown in Table 1.

The catalytic reaction rates and product identities are noticeably affected by the steric bulk of the organosilane and amine reactants. For example, 3.5 equiv of n-PrNH2 and PhSiH3 provide the tris(amide)silane (n-PrHNN)3SiPh within 15 min (Table 1, entry 1) with ToMgMe as the catalyst, while i-PrNH2 and PhSiH3 form only the bis(amido) ([i-PrHN]3SiPh) after 45 min at room temperature. Use of excess i-PrNH2 and heating at 100°C does not afford ([i-PrHN]3SiPh), while heating at 60°C. The more hindered secondary amine Ph2NH and PhSiH3 give a 10% yield of Ph2SiH2Ph after 72 h at 110°C, and i-Pr2NH does not form detectable silazane products in the presence of ToMgMe after 5 days at 100°C. The low reactivity of secondary amines likely inhibits polysilazane formation, which would require coupling of disubstituted R'HNSiR3. Additionally, only starting materials are observed from mixtures of tertiary BnMe2SiH and Et2SiH (Bn = CH2Ph) with primary amines (PhNH2, t-BuNH2, i-PrNH2, n-PrNH2) under catalytic conditions at 110°C after 72 h. The interaction between the tris(oxazoliny)-borate ancillary ligand and the magnesium(II) center is not disrupted in the presence of excess primary amine. For example, ToMgNHPh-Bu is robust in the presence of 10 equiv of t-BuNH2 (although amine–amide exchange occurs). Therefore, we decided to investigate the reductive silylation of hydrazine as a multiple

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(C₃H₅)Me₂SiH reacts quantitatively over 7 h, giving (C₃H₅)Me₂Si⁻ with Et₃SiH, (C₃H₅)Me₂SiH, or BnMe₂SiH (eq 2).

- **Dehydrogenative silylations.** Remarkably, monosilylhydrazines are NH-containing compounds that could undergo one or more dehydrogenative silylations. Monosilylhydrazines are accessible from the ToM MgxMgMe-catalyzed reactions of N₂H₄ with Et₃SiH, (C₃H₅)Me₂SiH, or BnMe₂SiH (eq 2).

\[
\text{N}_2\text{H}_4 + 10 \text{ mol}\% \text{ToM MgxMgMe} \rightarrow \text{Et}_3\text{SiH} + (\text{C}_3\text{H}_5)\text{Me}_2\text{SiH} + \text{H}_2
\]

(C₃H₅)Me₂SiH reacts quantitatively over 7 h, giving (C₃H₅)Me₂Si⁻ and benzene, which proceed only to 50% yield after 12 h. The magnesium species (κ²-ToM)₂Mg was observed in ¹H NMR spectra of micromolar-scale reactions in benzene-d₆ and this species appears to form from the transient intermediate ToM MgxMgNH₂ as the catalyst decomposition pathway. This intermediate, ToM MgxMgNH₂, forms upon reaction of ToM MgxMgMe and N₂H₄ but attempts to isolate it by evaporation of volatiles afforded mixtures of H₂[ToM] and ToM MgxMgMe, respectively, all of which are obtained. Moreover, the monosilylation of hydrazine highlights the impressive selectivity available in these magnesium-catalyzed reactions.

Selective conversion of ammonia is also challenging. The N—H bond is strong (104 kcal/mol) and nonacidic (pKₐ = 41 in DMSO). Silylation of ammonia increases the acidity of the remaining NH moieties, potentially increasing their reactivity and making monosilylation difficult. Furthermore, ammonia is a good ligand for metal centers and can shield the (typically Lewis acidic) catalytic site from interactions with other substrates. While this can also be a problem with amines, bulky ancillary ligands sterically inhibit coordination of substituted amines. This strategy is not effective with ammonia because of its small size.

The successful reductive silylation of hydrazine and the apparent coordinative saturation of ToM MgNH₃ suggested that the coordination of ammonia would not be an issue. Controlling the extent of silylation might remain a problem, as a monosilylamine is significantly more acidic than ammonia and might be expected to be more reactive. To test our magnesium catalyst for ammonolysis of silanes, excess ammonia was condensed into a storage flask containing BnMe₂SiH, benzene, and 5 mol % ToM MgMe, and the reaction provided BnMe₂SiNH₂ as the sole product after 15 h. BnMe₂SiNH₂ was isolated by Kugelrohr distillation (175 °C, 150 mmHg). In the presence of catalytic ToM MgMe, (C₃H₅)Me₂SiH reacts more rapidly with ammonia than BnMe₂SiH, and quantitative formation of (C₃H₅)Me₂SiNH₂ was observed after 5 h in micromolar-scale experiments monitored by ¹H NMR spectroscopy (eq 3).

\[
\text{N}_2\text{H}_4 + 10 \text{ mol}\% \text{ToM MgxMgMe} \rightarrow \text{Et}_3\text{SiH} + (\text{C}_3\text{H}_5)\text{Me}_2\text{SiH} + \text{H}_2
\]

ToM MgxMgMe (relative to the silane), and the reaction provided BnMe₂SiNH₂ as the sole product after 15 h. BnMe₂SiNH₂ was isolated by Kugelrohr distillation (175 °C, 150 mmHg). In the presence of catalytic ToM MgxMgMe, (C₃H₅)Me₂SiH reacts more rapidly with ammonia than BnMe₂SiH, and quantitative formation of (C₃H₅)Me₂SiNH₂ was observed after 5 h in micromolar-scale experiments monitored by ¹H NMR spectroscopy (eq 3).

**Figure 1.** ORTEP diagram of ToM MgNH₂-Bu. Ellipsoids are plotted at 50% probability, and only the H atom bonded to N4 is shown.

ToM MgMe, however, requires 15 h for quantitative formation (5 mol % ToM MgMe, benzene, room temperature). Disilazanes such as (Et₃Si)₂NH are not detected by ¹H NMR spectroscopy, in contrast to the case of transition-metal-catalyzed dehydrogenative silylations of ammonia.

Attempts to isolate ToM MgNH₂H₂ or ToM MgNH₂ as possible intermediates by treatment of ToM MgMe with N₂H₄ or NH₃ provided the ligand redistribution product ToM Mg and unidentifiable species. Therefore, we focused our mechanistic studies on catalytic aminolysis reactions that are conveniently monitored by ¹H NMR spectroscopy. Spectra of reaction mixtures revealed that H₂ is formed as the dehydrocoupling reactions proceed and that the catalyst resting state is a tris(oxazolinyl)borate magnesium amide. No other resonances that could be attributed to a ToM Mg species were observed in the reaction mixture. These ToM MgNH₂H₂ species (R = Pr, i-Pr, Ph) see below and the Supporting Information for synthesis and characterization) are formed rapidly upon addition of RNH₂ to ToM MgMe. Over 2 h, ToM MgNH₃Pr and ToM MgNH₃Pr precipitate from benzene. During independent synthesis, ToM MgMe and i-BuNH₂ were heated in benzene at 75 °C for 18 h to ensure quantitative formation of ToM MgNH₂Bu. In this compound, all three oxazoline donors coordinate to magnesium (II) in the ground state [¹N NMR: −158.4 (N-oxazoline) and −117.8 (NHR-Bu); νCN = 1590 cm⁻¹]; an ORTEP diagram is shown in Figure 1.

In the solid state, ToM MgNH₂Bu contains a planar amido group [Mg1—N2—C22, 137.2(4)°; Mg1—N4—H4, 113.6(6)°; C22—N4—H4, 107.6(5)°; Σ(X—N—X) = 357°] and a four-coordinate magnesium center. Solid-angle analysis revealed that the ToM (7.38 sr) and NH₂-Bu (2.81 sr) ligands occupy
Scheme 1. Catalytic Cycle for Organosilane Aminolysis

Scheme 2. Proposed Mechanism for ToMg-Mediated Si–N Bond Formation

58.8 and 22.4% of the space surrounding the magnesium center, respectively.19

In catalytic reactions, the consumption of organosilane and the formation of the silazane product are evident from the SiH resonances, which shift downfield as the hydrides are replaced with amides. Additionally, the 3J_HH coupling constants (≈ 3 Hz) between the SiH and NH groups give rise to doublet SiH resonances in RH2SiNH2 and triplets in RH2Si(NH2)2, and therefore, the SiH signal assists in product identification. Furthermore, all of the silazane products in Table 1 are isomeric. The in situ concentrations of TO^4MgNH2-Bu, t-BuNH2, and PhMeSiH2 in catalytic reactions were monitored by 1H NMR spectroscopy, and under conditions of excess t-BuNH2 (17–43 equiv vs PhMeSiH2) and 20–50 mol % TO^4MgNH2-Bu at 335 K, the rate law was found to be

\[
\frac{d[PhMeSiH2]}{dt} = k[t^4MgNH2-Bu]^{1/2}[PhMeSiH2]^{1/2}[t-BuNH2]^0, \quad \text{with } k' = 0.060(4) \text{ M}^{-1/2} \text{s}^{-1}.
\]

This rate law indicates that the turnover-limiting step involves an interaction of the catalyst and PhMeSiH2 t-BuNH2 is not present in that transition state. As noted above, 1H NMR spectra of the catalytic reaction mixture suggest that TO^4MgNH2-Bu is the catalyst resting state. These observations are consistent with the general mechanism shown in Scheme 1, where both steps are irreversible and the interaction of TO^4MgNH2 and the organosilane is turnover-limiting.

Under stoichiometric conditions, isolated TO^4MgNH2-Bu reacts with hydroxides, and this step models Si–N bond formation under catalytic conditions. For example, TO^4MgNH2-Bu and PhMeSiH2 (1.4 equiv, −20 to 80 °C) react quantitatively to give t-BuHNSiHMePh. A black precipitate forms as the reaction proceeds, and this material is presumed to be the decomposition product from a putative TO^4MgH species. Linear second-order integrated rate law plots of ln \([\text{PhMeSiH2/TO}^4\text{MgNH2-Bu}]\) versus time provided a rate law of

\[
\frac{d[To^4MgNH2-Bu]}{dt} = k_\beta[To^4MgNH2-Bu][PhMeSiH2], \quad \text{with } k_\beta = (3.9 ± 0.3) \times 10^{-3} \text{ M}^{-1} \text{s}^{-1}.
\]

The curve obtained from linear regression analysis of a plot of ln \([k/T] \) versus 1/T was used to calculate the second-order rate constant \(k_\beta = 0.04 \text{ M}^{-1} \text{s}^{-1}\), which is in reasonable agreement with the rate constant obtained from the catalytic experiments [0.060(4) M\(^{-1}\) s\(^{-1}\)].

The activation parameters calculated from a plot of ln \([k/T] \) versus 1/T from −20 to 80 °C are \(\Delta H^\text{f} = 5.9(2) \text{ kcal mol}^{-1} \) and \(\Delta S^\text{f} = -46.5(8) \text{ cal mol}^{-1} \text{ K}^{-1}\), suggesting a highly ordered transition state. A primary kinetic isotope effect of \(k_\beta/k_\beta = 1.0(2)\) at 0 °C was measured for the reaction of TO^4MgNH2-Bu and PhMeSiD2. This small primary isotope effect was essentially temperature-independent from −20 to 80 °C, and activation parameters identical to those for PhMeSiH2 were obtained for PhMeSiD2 (\(\Delta H^\text{f} = 5.7(2) \text{ kcal mol}^{-1} \) and \(\Delta S^\text{f} = -46.1(8) \text{ cal mol}^{-1} \text{ K}^{-1}\)). For comparison, kinetic studies of Si–C bond formations mediated by early transition metals and rare-earth elements, which are proposed to involve concerted, four-center transition states (i.e., \(\sigma\)-bond metathesis), have primary isotope effects for Si–C bond formation of ca. 1.1,21 highly negative \(\Delta S^\text{f}\) values, and small \(\Delta H^\text{f}\) values that are similar to those for the magnesium-mediated Si–N bond formation.

A few studies probing electronic effects in \(\sigma\)-bond metathesis have shown small changes in rate with electron-donating or electron-withdrawing groups, consistent with small polarization in the transition state.22 Similarly small electronic effects were observed in the [2σ + 2τ] four-center transition state of styrene insertion into Zr–H bonds \([\rho = 0.46(1)\)] , whereas \(\beta\)-elimination provides a large negative \(\rho\) value of −1.8(5) and large KIEs \((k_\beta/k_\beta = 3.9–4.5)\). The aryl group is pendent from the \(\beta\)-position of the four-center transition state in both of these transformations.

Second-order rate constants were determined for the reactions of TO^4MgHt-Bu and several Ph(aryl)SiH2 (aryl = Ph, p-C6H4F, p-C6H4Me, p-C6H4OMe, p-C6H4CF3). The organosilanes with electron-withdrawing groups react more rapidly than those with electron-donating groups. A Hammett plot of \(log(k_\beta/k_\beta)\) versus \(\sigma\) provides a positive slope \((\rho = 1.4)\). Thus, the activation barrier is decreased with electron-withdrawing substituents on silicon. This effect is consistent with a reaction pathway involving a five-coordinate silicon species TO^4MgHt-Bu–SiPh(aryl)H2 that is stabilized by electron-withdrawing groups. However, the magnitude of the inductive electronic effect is inconsistent with a concerted bond-breaking and bond-forming process; electron-withdrawing groups are expected to have counteracting effects on bond formation and bond cleavage by simultaneously increasing the barrier for hydride transfer to magnesium while stabilizing the five-coordinate silicon center. The temperature-independent primary isotope effect of unity further supports little Si–H bond cleavage in the transition state.

Considering these points, we suggest that these reactions involve nucleophilic attack of the amide on silicon to form a five-coordinate silicon center in the rate-determining step, which is followed by rapid hydrogen transfer to magnesium in a step reminiscent of \(\beta\)-elimination (Scheme 2). Two additional observations suggest that this mechanism is more reasonable than the concerted four-centered transition-state-like pathway. First, the reaction rate is decreased with the less nucleophilic anilide versus the aliphatic amide, which is consistent with nucleophilic attack playing an important role in the rate-limiting step. Second, a zeroth-order amine concentration dependence was observed in the catalytic rate law even at very high concentrations without evidence of inhibition by amine coordination. Thus, these reactions may be performed even in liquid NH3. In contrast, intermolecular \(\sigma\)-bond metathesis reactions require coordinative unsaturation and are inhibited by ...
coordinating groups. Our hydroamination studies suggest that amines coordinate to the magnesium center in ToMgNH compounds, either to give a five-coordinate magnesium or substitute an oxazoline. Thus, the zeroth-order amine dependence (rather than an inverse dependence) suggests that an open coordination site is not important in the current Si–N bond formation.

Notably, the nature of nucleophilic substitution at silicon and the role of electrophilic assistance have long been debated, primarily by assessing retention or inversion of stereochemistry in chiral silicon centers. In fact, n-Bu4NF catalyzed silane amination is proposed to involve five-coordinate silicon centers without electrophilic assistance. Despite the importance of Si–E bond formations (E = C, Si, O, N) in catalytic chemistry, experimental investigations of electronic effects in d0- and f-d-metal-mediated Si–E bond formations are scarce. Thus, we are currently examining the kinetic features of other d0- and f-d-metal-mediated Si–E bond formations to identify the features (coordinate unsaturation, bond polarity, steric constraints, and related effects of ancillary ligands) that influence the mechanism of these types of reactions in order to develop new catalysis.

ASSOCIATED CONTENT

Supporting Information. Experimental procedures, data from kinetic measurements, and crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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REFERENCES

(18) Three νC=N bands in the IR spectra suggest To4MgNHPr and To4MgNHnPr are not monomeric as solids (see the Supporting Information), although the 1H NMR spectra of species generated in situ suggest monomeric structures. Precipitated To4MgNHPr and To4MgNHnPr are sufficiently insoluble that solution NMR data were not obtained.
(24) Rate constants used in the Hammett plot were determined from second-order integrated rate law plots of ln([Pd(PhC6H4)SiH2]/[To4MgNHPr-Bu]) vs Δν (X = OMe, Me, H, F) for reactions at 313 K; for X = CF3, the rate constant was calculated from an Eyring plot for reactions measured over the range 245–313 K because the rate at 313 K was sufficiently high to require verification.