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A Dialkyl Calcium Carbene Adduct: Synthesis, Structure and Catalytic Cross-Dehydrocoupling of Silanes with Amines

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Abstract: Eleven neutral ligands were investigated in promoting the calcium-catalyzed cross-dehydrocoupling reaction between phenylsilane and diisopropylamine. Among which, an *N*-heterocyclic carbene (NHC) ligand I^{i}Pr$_2$Me$_2$ displayed superior activity and selectivity. The first neutral NHC-supported alkyl calcium complex {(I^{i}Pr$_2$Me$_2$)$_2$Ca[CH(SiMe$_3$)$_2$]$_2$} **4** was subsequently synthesized and characterized by NMR and X-ray crystallography. Complex **4** displayed high activity and excellent chemoselectivity in the catalytic cross-dehydrocoupling reactions between bulky amines and silanes under mild conditions. The asymmetric version was also achieved by combining Ca[CH(SiMe$_3$)$_2$]$_2$ with a chiral NHC ligand, affording optically active silicon stereogenic silazane in 26% *ee*.

Introduction

Organocalcium chemistry is recently receiving more attention for the plentiful reserves and nontoxicity of calcium element. Further attractive features of calcium complexes comprise Lewis acidity of calcium(II) cation, basicity and nucleophilicity of the alkyl or amide anions. However, the low stability, low solubility and fast ligand exchange of organocalcium complexes plagued its blossom.[1] To conquer these disadvantages, great efforts have been made by using bulky and multidentate ligands such as β-diketiminate,[2] β-diketonate,[3] cyclopentadienyl,[4] tris(pyrazolyl)borate,[2a,c],[5] and functionalization NHCs[6] to tune the stability, solubility and reactivity. Some coordinating solvents including tetrahydrofuran, tetrahydropyran, 1,4-dioxane and pyridine were inventively employed in organocalcium chemistry not only as solvents but also as neutral ligands.[7] Very recently, using multidentate neutral Me$_4$TACD and PMDTA ligands, Okuda and Harder achieved the synthesis of calcium silyl, alkyl, amide and hydride complexes, and realized their catalytic hydrogenation reactions.[8] *N*-Heterocyclic carbenes (NHCs), as strong σ-donor and poor π-acceptor ligands, are widely used in both transition metal complexes and main group metal complexes. The first calcium-NHC adduct was synthesized by Arduengo with calcium metallocene and a carbene IMe$_4$ (tetramethylimidazol-2-ylidene).[6b] Schumann and co-workers later synthesized more adducts with calcium metallocenes and a steric bulkier carbene I^{i}Pr$_2$Me$_2$ (1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene).[6c] Barrett, Hill and co-workers synthesized the NHC adducts of calcium amide with carbenes IMes (1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene) and IDipp (1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene).[6e] Very recently, Westerhausen achieved the synthesis of calcium carbene adducts with a neutral, tridentate bis(carbene)-based ligand.[6i] Despite these advances, the synthesis of NHC adducts of alkyl calcium complexes is undeveloped and the catalytic application of calcium carbene adducts still remains limited.

The catalytic silane-amine dehydrogenative coupling reactions generally represent an efficient method for silazane synthesis. Various catalysts have been developed based on alkali metals,[9] alkaline-earth-metals,[10] early-transition-metals,[11] metal carbonyls[12] and other complexes.[13] The calcium catalysts were firstly investigated by Harder and co-workers,[10a] who disclosed that the addition of polar solvent HMPA (hexamethylphosphateamide) could significantly improve the conversion (from 1% to 48% and 49%) in the catalytic dehydrogenative silylation of aniline and 1-hexyne. Cui[11e], Sadow[11g] and Nembenna[10h] found that the neutral NHC ligands could accommodate the catalytic performances of ytterbium amide，ytterbium and samarium dialkyls, and magnesium amide complexes. Inspired by these fascinating experimental phenomena, herein we investigate the behaviors of a series of neutral ligands in the calcium-catalyzed cross-dehydrocoupling reactions between silanes and amines.

Results and Discussion

We commenced our investigation with the cross-dehydrocoupling reaction between phenylsilane **1a** and diisopropylamine **2a** in C$_6$D$_6$ at room temperature (Table 1). Considering the possible side reactions of calcium amides and also the better catalytic potential of alkyl calcium complexes, we preferred Ca[CH(SiMe$_3$)$_2$]$_2$(THF)$_2$ (5 mol%), a THF-coordinated dialkyl calcium complex, as catalyst. After 8 hours, the desired silazane product **3aa** was obtained in only 10% yield (entry 1). Considering the reported accelerating effect of HMPA and NHCs ligands, we tested a series of neutral ligands (10 mol%) in the calcium-catalyzed dehydrogenative coupling reaction. Neutral *O*-donor ligands DME (dimethoxyethane) and triphenylphosphine oxide, which are commonly used as stabilizers of alkaline-earth-metal complexes, gave even lower conversions and yields (entries 2-3). HMPA could improve the yield but not as efficiently as it worked in Harder's work (entry 4).[10a] Multidentate *O*-donor ligand 18-crown-6 completely converted phenylsilane but gave the desired product in 63% yield, suggesting that some side reactions took place (entry 5). We then further carried out the reaction with neutral *N*-donor ligands such as DMAP and TMEDA,

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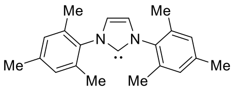
but failed to get better yields (9% and 33%, entries 6-7). Phosphonium ylide was subjected into the reaction as a neutral ligand, and the desired product was obtained in 63% yield, along with 72% conversion of phenylsilane (entry 8). Several neutral NHC ligands were subsequently tested in the reaction. *N*-Aryl NHCs IDipp and IMes gave the product in 19% and 35% yields (entries 9-10). To our delight, *N*-alkyl NHCs such as IMe_4 and $I^iPr_2Me_2$ displayed much better efficiency and selectivity (entries 11-12). In particular, 10 mol% of $I^iPr_2Me_2$ gave the product in a high yield up to 98%. Using 5 mol% or 15 mol% of $I^iPr_2Me_2$, however, led to lower yields of 90% (entries 13-14). Further increasing the amount of $I^iPr_2Me_2$ to 20 mol% resulted in a much reduced yield (40%, entry 15), suggesting that excess NHC ligand greatly inhibits the catalytic activity of calcium catalyst. Calcium amide $Ca(HMDS)_2$, which was used as catalyst in some silane-amine dehydrogenative coupling reactions[10c], failed to efficiently catalyze the reaction between phenylsilane and diisopropylamine even under elevated temperature (entries 16-17). This comparison demonstrated the unique catalytic activity of the combination of dialkyl calcium and the neutral NHC ligand.

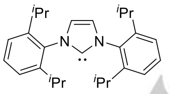
Table 1. Ligand screening[a]

$$\underset{\mathbf{1a}}{PhSiH_3} + \underset{\mathbf{2a}}{HN(iPr)_2} \xrightarrow[C_6D_6,\ 25\ °C,\ 8\ h]{Ca[CH(SiMe_3)_2]_2(THF)_2\ (5\ mol\%)\ \text{neutral ligand}} \underset{\mathbf{3aa}}{PhSiH_2N(iPr)_2} + H_2$$

Entry	Ligand (10 mol%)	Yield (%)[b]
1	--	10 (19)
2	DME (10 mol%)	<5 (8)
3	Ph_3PO (10 mol%)	<5 (10)
4	HMPA (10 mol%)	25 (34)
5	18-crown-6 (10 mol%)	63 (96)
6	DMAP (10 mol%)	9 (24)
7	TMEDA (10 mol%)	33 (40)
8	Ph_3PCH_2 (10 mol%)	63 (72)
9	IMes (10 mol%)	35 (39)
10	IDipp (10 mol%)	19 (28)
11	IMe_4 (10 mol%)	91 (97)
12	$I^iPr_2Me_2$ (10 mol%)	98 (100)[d]
13	$I^iPr_2Me_2$ (5 mol%)	90 (96)[d]
14	$I^iPr_2Me_2$ (15 mol%)	90 (100)[d]
15	$I^iPr_2Me_2$ (20 mol%)	40 (56)[d]
16[c]	--	10 (17)
17[c]	$I^iPr_2Me_2$ (10 mol%)	8 (19)

[a] Reaction conditions: phenylsilane **1a** (0.18 mmol), diisopropylamine **2a** (0.18 mmol), dialkyl calcium (5 mol%), neutral ligand (10 mol%), hexamethylbenzene (0.011 mmol), C_6D_6 (0.4 mL), 25 °C, 8 h. DME: dimethoxyethane; HMPA: hexamethyl phosphate amide; DMAP: 4-dimethylaminopyridine; TMEDA: tetramethylethylenediamine. [b] NMR yields (conversions in parentheses) based on phenylsilane were recorded using hexamethylbenzene as an internal standard. [c] $Ca(HMDS)_2$ (5 mol%) as catalyst, 80 °C. [d] Reaction time: 12 h.


IMes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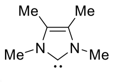
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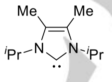
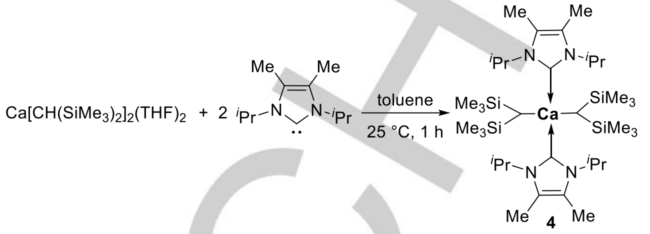

$I^iPr_2Me_2$

As the combination of $Ca[CH(SiMe_3)_2]_2$ with 2 equiv. of $I^iPr_2Me_2$ displayed the best catalytic activity, we further attempted to synthesize and isolate the NHC-coordinated dialkyl calcium complex. The ligand substitution reaction between $I^iPr_2Me_2$ and $Ca[CH(SiMe_3)_2]_2(THF)_2$ was carried out in toluene at room temperature (Scheme 1). After removing the solvent, we got a pale yellow solid (adduct **4**). Its ^1H NMR spectrum in C_6D_6 showed that there was no more THF left, instead of coordinated NHC.



Scheme 1. Preparation of dialkyl calcium NHC adduct **4**.

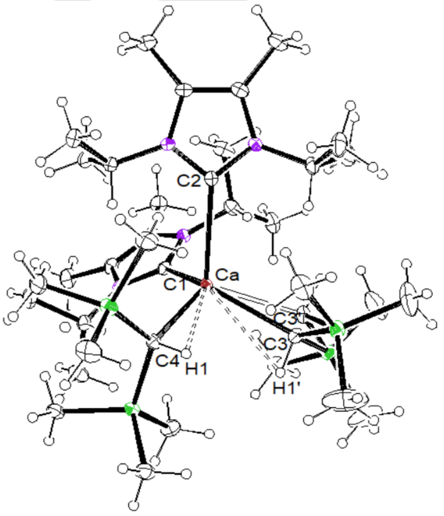
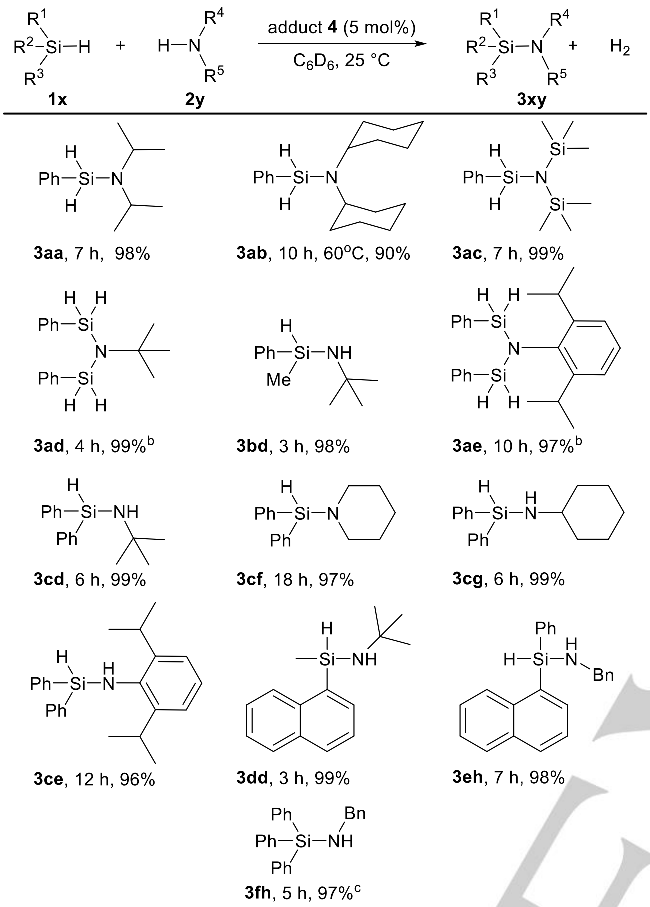


Figure 1. ORTEP drawing of **4** with 30% probability thermal ellipsoids. Selected bond lengths [Å]: Ca-C1 2.659(3), Ca-C2 2.650(3), Ca-C3' 2.484(2), Ca-C3 2.517(1), Ca-C4 2.528(3), Ca-H1 2.849(3), Ca-H1' 2.813(2).

Both signals of the methylene (δ -1.47 ppm) and methyl groups (δ 0.48 ppm) of the alkyl anions shift slightly downfield compared to that of the THF-coordinated complex $Ca[CH(SiMe_3)_2]_2(THF)_2$ (δ -1.62 ppm and 0.36 ppm)[7n]. The ^{13}C NMR signal of the carbene carbon shifts drastically upfield (δ 193.9 ppm) compared to that of the free carbene (δ 205.9 ppm). The Ca-NHC adduct **4** is extremely air- and moisture-sensitive. A colorless crystal suit for X-ray analysis was obtained by recrystallization from its solution in toluene/hexane (1:2) at -30 °C in a glovebox (Figure 1). The molecular structure of adduct **4** reveals a pseudo-tetrahedral complex containing two alkyl ligands and two NHC ligands. The Ca-C bond distances of the NHC ligands (2.65-2.66 Å) are in good agreement with results (2.60-2.67 Å) previously reported in NHC-calcocene adducts.[6c] The Ca-C bond distances of the alkyl anions (Ca-C3, Ca-C4, 2.48-2.53 Å) are slightly longer than those observed in the THF or dioxane-coordinated dialkyl calcium complexes (2.49 and 2.48 Å)[7a,n], mainly because of the larger steric hindrance of the carbene ligands. Another notable feature is the short interatomic distances of Ca−H1 and Ca−H1' (2.85 and 2.81 Å, respectively) and the small angles of Ca−C4−H1 and Ca−C3−H1' (98.89 and 97.17°, respectively), which suggests an agostic interaction between the calcium center and the C-H bond of the alkyl group. It is noteworthy that complex **4** is the first example of neutral NHC-supported dialkyl calcium complex.

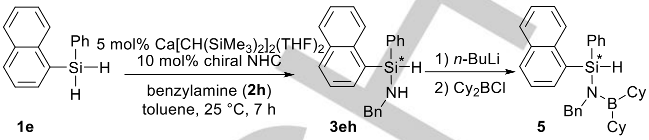
Table 2. Substrates scope[a]

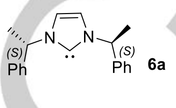
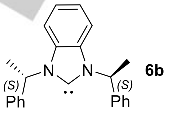


[a] Reaction conditions: silane **1** (0.26 mmol), amine **2** (0.26 mmol), adduct **4** (5 mol%), C_6D_6 (0.45 mL), 25 °C. Yields were recorded by ^1H NMR analysis using hexamethylbenzene as an internal standard. [b] Amine **2** (0.13 mmol). [c] $Ca[CH(SiMe_3)_2]_2(THF)_2$ was used as catalyst.

With dialkyl Ca-NHC adduct **4** in hand, we then tested its catalytic activity in silane-amine cross-dehydrocoupling reactions. In general, the adduct **4** is highly active for the reactions of $PhSiH_3$ with bulky amines such as $HN(i\mathrm{Pr})_2$, $HNCy_2$, $HN(SiMe_3)_2$, $H_2N(t\mathrm{Bu})$ and $DippNH_2$, giving the desired products (Table 2, **3aa**-**3ae**) in good yields (90-99%) under mild conditions. Moreover, the reactions of diphenylsilane (**1c**) with bulky primary or secondary amines were also applicable, and produced mono(amino)silanes (**3cd**-**3cg**) in nearly quantitative yields (96-99%). Gratifyingly, some other secondary silanes such as methylphenylsilane (**1b**), methyl(naphthalen-1-yl)silane (**1d**) and phenyl(naphthalen-1-yl)silane (**1e**) smoothly underwent the catalytic dehydrogenative coupling reactions with $H_2N(t\mathrm{Bu})$ or benzylamine, and afforded silazanes (**3bd**, **3dd**, **3eh**) in excellent yields (98-99%). The cross-dehydrocoupling reaction between sterically bulky triphenylsilane (**1f**) and benzylamine, which was achieved successfully with $Ca(HMDS)_2$ or $Ba(HMDS)_2$ catalysts [10c], failed to take place when using adduct **4** as catalyst. However, in the absent of NHC ligands, dialkyl calcium complex $Ca[CH(SiMe_3)_2]_2(THF)_2$ (5 mol%) itself as catalyst could smoothly drive on the reaction, and gave the desired product silazane **3fh** in 97% yield. These results suggested that the participation of NHC ligand could inhibit the reaction with steric bulky silanes, which could be the key reason for the nice selectivity of the NHC adduct catalyst.

Table 3. Synthesis and *ee* value determination of compound **5**



ligand 6		
5	**5**: 72% yield[a], 1.4% *ee*[b]	**5**: 70% yield[a], 26% *ee*[b]

[a] Isolated yields
[b] Determined by chiral HPLC analysis

Now that the neutral carbene ligands could well coordinate with dialkyl calcium complex and tune its activity and selectivity，we would like to further explore the possibility in controlling the stereoselectivity. Using chiral NHC **6a**[14] and **6b**[15] as ligands (Table 3), we carried out the calcium catalyzed cross-dehydrocoupling reactions between a prochiral silane phenyl(naphthalen-1-yl)silane (**1e**) and benzylamine. The reactions took place smoothly at room temperature, and 7 hour later the desired product **3eh** was obtained in high yields. The moisture sensitive silazane **3eh** was allowed to undergo the boronation reaction to give compound **5**, who is stable for the HPLC analysis.[11h] Using the more rigid chiral carbene **6b** as ligand, compound **5** was obtained in 70% yield with 26% *ee* value, which suggested that the chiral carbene ligand did endue the dialkyl calcium complex with stereoselectivity.

Conclusions

In summary, we systematically evaluated the behavior of a series of neutral ligands in a calcium-catalyzed cross-dehydrocoupling reaction between phenylsilane and diisopropylamine. We found that *N*-heterocyclic carbene $I^i Pr_2Me_2$ displayed the best activity and selectivity. Thus, we synthesized the first neutral NHC-coordinated alkyl calcium complex **4** and characterized its structure with NMR and X-ray crystallographic analysis. The dialkyl calcium NHC adduct showed nice catalytic activity in the cross-dehydrocoupling reactions between silanes and bulky amines under mild conditions. Furthermore, an asymmetric version was also realized in this catalytic system by combining dialkyl calcium catalyst with a chiral NHC ligand. These results suggested that NHCs could coordinate well with dialkyl calcium complex and successfully tune its activity, chemoselectivity and even stereoselectivity.

Experimental Section

In a glovebox, to a solution of $Ca[CH(SiMe_3)_2]_2(THF)_2$ (0.19 mmol, 0.10 g) in toluene (2 mL) was added a solution of 1,3-diisopropyl-4,5-dimethyl-imidazol-2-ylidene (0.38 mmol, 0.07 g, 2 equiv.) in toluene (3 mL). The mixture was stirred at room temperature for 1 h. After removing the volatiles, the resulting pale yellow solid was recrystallized in toluene/hexane (1:2) at -30 °C to give colorless crystals of Ca-NHC adduct **4** (0.09 g, 65%). ^{1}H NMR (400 MHz, C_6D_6) δ 4.37–4.18 (m, 4 H), 1.58 (s, 12 H), 1.28 (d, J = 6.8 Hz, 24 H), 0.48 (s, 36 H), -1.47 (s, 2 H); ^{13}C NMR (101 MHz, C_6D_6) δ 193.9, 124.1, 52.2, 23.3, 19.4, 9.8, 6.8; ^{29}Si NMR (79 MHz, C_6D_6) δ -7.9. CCDC 1811685 contains the supplementary crystallographic data for complex **4** and is available free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

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Keywords: calcium • carbene ligands • adduct • cross-dehydrocoupling • silazane

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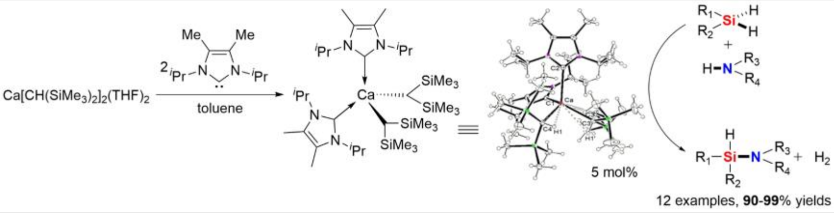

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A Dialkyl Calcium Carbene Adduct: Synthesis, Structure and Catalytic Cross-Dehydrocoupling of Silanes with Amines

The first neutral NHC-supported alkyl calcium complex {$(I^{i}Pr_2Me_2)_2Ca[CH(SiMe_3)_2]_2$} was synthesized and structurally characterized. Thanks to the neutral NHC ligand, the complex displayed excellent reactivity and chemoselectivity on catalytic cross-dehydrocoupling of silanes with amines under mild conditions.