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Mechanochemically directed metathesis in Group 2 chemistry: Calcium amide formation without solvent

Isaiah R. Speight [a], Stephen C. Chmely [a], Timothy P. Hanusa*[a], and Arnold. L. Rheingold[b]

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Ball milling CaI_2 and $[KN(SiMe_3)_2]$ in a 1:1 ratio without solvent, and then extracting the ground material with toluene, yields the synthetically valuable neutral amide $[Ca(N(SiMe_3)_2)_2]$ in good yield, without the contamination by calciate species that complicates solution metathesis routes. The effects on yield of grinding time, milling frequency, and calcium halide identity are also examined.

Mechanochemically enabled synthesis, specifically that promoted by grinding or milling when no or a minimal amount of solvent is present, can provide access to chemistry different from that observed with solvent-based reactions.[1] The benefits extend across organic,[2] organometallic,[3] and coordination chemistry,[4] and have helped stimulate an upsurge in mechanochemical research in the last decade.[5] Owing to the myriad roles that solvents play in reactions (e.g., facilitating mixing, dispersing heat, altering the polarity of reaction environments, and shifting equilibria, among others), predicting how a given reaction will respond to the removal of solvent(s) is not straightforward. This is particularly true with compounds of the s-block metals, where highly polar bonding is combined with increased ligand lability.[6] Solvent effects play a major role in setting the position of equilibrium in these systems (e.g., Schlenk redistribution in Grignard reagents ($2\,RMgX \rightleftarrows R_2Mg + MgX_2$) is strongly influenced by the polarity of the solvent),[7] and coordinated solvent can affect structure and bonding.[8] We report here that, by avoiding the use of a solvent during its formation, ball milling can materially improve the halide metathetical synthesis of the synthetically valuable calcium amido complex $[Ca(N(SiMe_3)_2)_2]$ (Figure 1a). These results also suggest that mechanochemistry could offer analogous benefits to other metathetical Group 2 syntheses.

Calcium amides $[Ca(NR_2)_2]$ are versatile synthetic reagents, as depending on the R group they can serve as hydrocarbon-soluble sources of Ca^{2+} ions for organometallic synthesis,[9] and as non-nucleophilic bases for enolization reactions.[10] More recently, they have found use as hydrogenation catalysts that can be employed under mild conditions.[11] They also catalyse the ring opening polymerization of lactide, and when paired with coordinating chiral ligands, can influence the stereochemistry of the polymer.[12] These traits are exemplified in the bis(trimethylsilyl)amido derivative, $[Ca(N(TMS)_2)_2]$, one of the most commonly used calcium amido complexes.[13] Multiple synthetic routes have been developed for this compound, often involving redox transmetallation/ligand exchange with elemental calcium.[14] Several of these syntheses involve toxic mercury[15] or tin[16] reagents, and hence metathetical preparations employing calcium sulfonates,[17] alkoxides,[18] or iodide (e.g., $[KN(TMS)_2]$ (Figure 1b)[19] and CaI_2 in diethyl ether[9a,10a,20] or toluene[21]) have been employed as well.

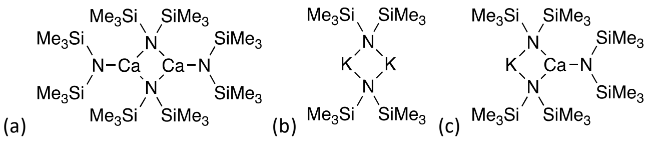

Figure 1. (a) The calcium bis(amido) complex $[Ca(N(TMS)_2)_2]_2$, (b) the potassium amide $[KN(TMS)_2]_2$, and (c) the potassium calciate $[KCa(N(TMS)_2)_3]$. Both $[Ca(N(TMS)_2)_2]_2$[13b] and $[KN(TMS)_2]_2$[19] crystallize as dimers.

These solvent-based syntheses are marked by relatively long reaction times (ranging from 3 hours to 5 days),[15b] the frequent formation of solvated species (with THF, DME, or Et_2O), and most seriously with the salt metathesis methods, the concomitant generation of calciate species, $[MCa(N(TMS)_2)_3]$ (M = Li, K, Figure 1c)), regardless of the stoichiometry of the starting reagents.[22] The formation of unintended calciates is not unique to the bis(trimethylsilylamido) group, but has been observed during the metathesis formation of calcium complexes containing $[N(Ph)R']^-$ (R' = Me, ^{i}Pr) ligands as well.[23]

The generally faster reactions and relative freedom from solvent interactions provided by mechanochemical activation made its use an attractive alternative route for the synthesis of $[Ca(N(TMS)_2)_2]$. In initial experiments, a typical solution protocol was followed by using stoichiometric amounts of CaI_2 and the potassium amido reagent,

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[a] Department of Chemistry, Vanderbilt University, Nashville, Tennessee, 37235, USA. E-mail: t.hanusa@vanderbilt.edub

[b] Department of Chemistry and Biochemistry, University of California, San Diego, La Jolla, California 92093, USA.

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Table 1. Effect of molar equivalents on product distributions[a]

Entry	Molar equiv. ($CaI_2 : KNR_2$)	Time (min)	Yield (%)[b]	Ratio[c] ($Ca(NR_2)_2 : KCa(NR_2)_3$)
1	1 : 2	10	—	1 : 2.5
2	1 : 2	30	—	1 : 1
3	1 : 2	60	—	1.2 : 1
4	1 : 1	10	68	1 : 0
5	1 : 0.5	10	63	1 : 0

[a] Reactions were performed under N_2 on 0.5 mmol scale (CaI_2) and milled at 30 Hz with two 8 mm SS ball bearings (3.5 g ball^{-1}) in a Retsch MM400 mill. [b] Typical yield of isolated $[Ca(NR_2)_2]$ with respect to limiting reagent $[KNR_2]$. [c] R = TMS.

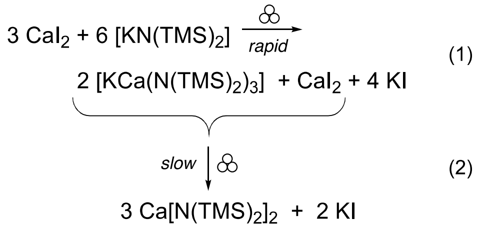
i.e., a 1:2 ratio of CaI_2 and $[KN(TMS)_2]$. Grinding the two solids for 10 min at 30 Hz in a mixer mill left a white powder that displayed the peaks characteristic of KI in its powder X-ray diffraction spectrum; other products presumably had insufficient crystallinity to be observed. The powder was then extracted with toluene, the extract filtered, and solvent removed from the filtrate. NMR (^1H) analysis indicated that a mixture of the amide $[Ca(N(TMS)_2)_2]$ and the calciate $[KCa(N(TMS)_2)_3]$ was present (Table 1, entry 1). Prolonging the reaction to 30 min (entry 2) and then 60 min (entry 3) decreased the amount of $[KCa(N(TMS)_2)_3]$ relative to $[Ca(N(TMS)_2)_2]$, but the calciate still comprised nearly half of the mixture, suggesting that its conversion to the neutral amido complex is slow. After adjusting the starting ratio of CaI_2 to $[KN(TMS)_2]$ to 1 : 1, the neutral amido product was isolated in good yield with no evidence for the calciate species (Table 1, entry 4); the use of an even higher ratio of CaI_2 to $[KN(TMS)_2]$ (entry 5) led to a similar yield. Larger scale reactions provided comparable results; i.e., the reactions reported in Table 1, typically conducted with 0.15 g of CaI_2 and 0.1–0.2 g of $[KN(TMS)_2]$, and yielding 60 mg of $[Ca(N(TMS)_2)_2]$, could be readily scaled up to yield ca. 0.45 g of $[Ca(N(TMS)_2)_2]$ from a total of 1.3 g of reagents. A sample from the largest of the scaled-up grinds was found by elemental analysis to be essentially free of potassium (<1%), supporting the NMR results.

The results from entries 4 and 5 in Table 1 are distinctly different from solution synthesis in aromatics. In particular, there is no evidence that the reaction of CaI_2 and $[KN(TMS)_2]$ in toluene ever yields pure $[Ca(N(TMS)_2)_2]$, regardless of the initially used reagent ratio.[22] This is fundamentally a consequence of the different solubilities of CaI_2 and $[KN(TMS)_2]$ in aromatic solvents; the very low solubility of CaI_2 and the high solubility of $[KN(TMS)_2]$ ensures that the latter will always be in a large excess in solution, thus promoting calciate formation. Under mechanochemical conditions, such solubility differences are less important, and the use of CaI_2 in excess of the stoichiometrically required ratio effectively serves to suppress the formation of $[KCa(N(TMS)_2)_3]$.

Table 2. Effect of milling environment on product distribution[a]

Entry	Mill type	Freq (Hz)	Ratio[c] ($Ca(NR_2)_2 : KCa(NR_2)_3 : K(NR_2)_2$)
1	mixer	10	0 : 1 : 4.5
2	mixer	20	1 : 2 : 0
3	mixer	25	1 : 0 : 0
4	mixer	30	1 : 0 : 0
5[b]	planetary	10 (600 rpm)	0 : 1 : 6.8
6[c]	planetary	10 (600 rpm)	1 : 0 : 0

[a] Reaction conditions: N_2 atm, 0.5 mmol (CaI_2) scale, 1:1 molar ratio of CaI_2 : $K(NR_2)_2$, mixer mill (Retsch MM400), two 8 mm stainless steel (SS) ball bearings (3.5 g ball^{-1}), 10 min. [b] Reaction in Retsch PM 100 at 600 rpm with two 8 mm SS ball bearings (3.5 g ball^{-1}). [c] Reaction in Retsch PM 100 at 600 RPM with fifty 4.8 mm ball bearings (0.44 g ball^{-1}). [c] R = TMS.



Scheme 1. Proposed formation of $[Ca(N(TMS)_2)_2]$ from CaI_2 and $[KN(TMS)_2]$ in a 1:2 molar ratio. The initial step produces only the calciate $[KCa(N(TMS)_2)_3]$, which is slowly converted into the neutral amido complex $[Ca(N(TMS)_2)_2]$ in a second step.

The effect of milling frequency and mill type on product formation was also investigated with a 1:1 ratio of CaI_2 to $[KN(TMS)_2]$ (Table 2). In a mixer mill at 10 Hz, a 10 min grind (entry 1) leaves a considerable amount of $[KN(TMS)_2]$ unreacted, but somewhat unexpectantly, yields only the calciate $[KCa(N(TMS)_2)_3]$ rather than any of the neutral amido complex $[Ca(N(TMS)_2)_2]$, consistent with the former's being the kinetic product of the reaction. Increasing the frequency to 20 Hz (entry 2) consumes all the potassium amide, but still leaves twice the molar amount of calciate compared to the neutral amide. At 25 Hz, the calciate is no longer present, and the result is the same as was previously found at 30 Hz (Table 1, entry 3). When the mill type was changed from a mixer mill to a planetary version, but with the use of only two large ball bearings, milling at 600 rpm (~10 Hz) left proportionally more $[KN(TMS)_2]$ than did the mixer mill (entry 5). Using a larger number of smaller ball bearings to increase the rate of collisions produced results at 600 rpm similar to those from the 30 Hz mixer mill conditions (entry 6).[24] With the exception of the evidently incomplete reactions conducted at 10 Hz, the results in Tables 1 and 2 can be summarized in two steps (Scheme 1): with a 1:2 ratio of CaI_2 to $[KN(TMS)_2]$, the first represents the rapid formation of the kinetic product $[KCa(N(TMS)_2)_3]$ (eq 1); the second is the slower reaction between $[KCa(N(TMS)_2)_3]$ and the remaining CaI_2 (eq 2). The effectiveness of the use of larger amounts of CaI_2 (e.g., in the 1:1 reactions) can then be seen as the result of its being a source of additional iodide that scavenges K^+, converting it into KI and preventing the formation of the potassium calciate.

A characteristic feature of mechanochemical synthesis is that it can lift restrictions on the solubility requirements for suitable reagents. Calcium iodide is commonly used in halide displacement reactions as it is the most soluble of the dihalides in ethers (a saturated solution in THF is 42 mmol L^{-1}).[25] Of course, the crystal lattice must be disrupted during the reaction whether by solvent or milling, and the greater lattice energy of CaF_2 compared to CaI_2 (U_0 of -626 and -476 kcal mol^{-1}, respectively),[26] for example, would disfavour the fluoride as a source regardless of the reaction

Table 3. Effect of halide identity on product distribution[a]

Halide	Time (min)	Ratio ($Ca(NR_2)_2$: $KCa(NR_2)_3$: $K(NR_2)_2$)	Yield (%)[b] ($Ca(NR_2)_2$)
CaI_2	10	1 : 0 : 0	68
	30	1 : 0 : 0	84
	60	1 : 0 : 0	65
$CaBr_2$	10	0 : 5 : 4	–
	30	1 : 10 : 0	9.5
	60	19 : 1 : 0	68
$CaCl_2$	10	0 : 0 : 1	–
	30	0 : 2 : 3	–
	60	0 : 7 : 2	–
CaF_2	10	0 : 0 : 1	–
	30	0 : 0 : 1	–
	60	0 : trace : 1	–

[a]Reactions performed on 0.5 mmol scale of CaX_2 salt at 30 Hz in a Retsch MM 400 mill with two 8 mm SS ball bearings (3.5 g ball^{-1}). [b]Spectroscopic yield of $[Ca(NR_2)_2]$ determined from ^1H NMR data. R = TMS.

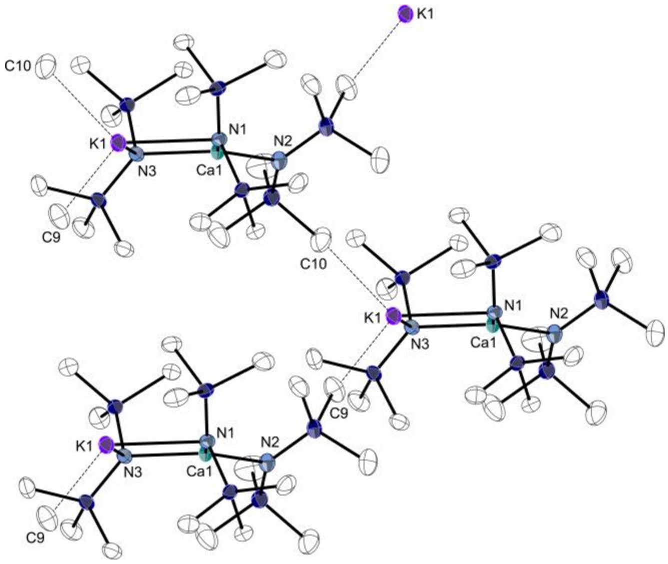


Figure 2. Thermal ellipsoid plot (50% level) of a portion of the crystal lattice of $[KCa(N(TMS)_2)_3]$. For clarity, hydrogens have been removed. Selected bond distances (Å) and angles (deg): K1–N1 = 2.882(2); K1–N3 = 2.943(2); Ca1–N2 = 2.325(2); Ca1–N1 = 2.386(2); Ca1–N3 = 2.376(2); K1···C9 = 3.235(3); K1···C10 = 3.185(3); N1–K1–N3: 79.96(5); N1–Ca1–N3: 103.60(6); N1–Ca1–N2: 126.17(7); N2–Ca1–N3: 130.19(7).

environment. To examine this point further, 1:1 mixtures of CaX_2 with $[KN(TMS)_2]$ were ground for various times, and Table 3 displays relative amounts of $[Ca(N(TMS)_2)_2]$ and $[KCa(N(TMS)_2)_3]$ as a function of the calcium salt and milling time. An inverse correlation can be observed between the amount of $[Ca(N(TMS)_2)_2]$ and/or $[KCa(N(TMS)_2)_3]$ and lattice energy (U_0, kcal mol^{-1}); i.e., CaF_2 (trace, -626) < $CaCl_2$ (-535) < $CaBr_2$ (-515) < CaI_2 (-476).[26] Generally the calcium product(s) increase with the milling time, although calcium fluoride does not show any signs of product formation until the one-hour mark, at which point a trace amount ($\lesssim$1%) of $[KCa(N(TMS)_2)_3]$ was detectible (^1H NMR). $CaCl_2$ provides only slightly more reactivity, with a 3.5:1 ratio of $[KCa(N(TMS)_2)_3]$: $[KN(TMS)_2]$ after 60 minutes of grinding, but no evidence for the neutral $[Ca(N(TMS)_2)_2]$. $CaBr_2$ generates the most complete evidence for the shift from $[KCa(N(TMS)_2)_3]$ to $[Ca(N(TMS)_2)_2]$ with increased grinding time: considerable starting material is left after 10 min, and after 30 min, the ratio of $[Ca(N(TMS)_2)_2]$: $[KCa(N(TMS)_2)_3]$ is 1:10. After an hour, however, the sample is 95% of $[Ca(N(TMS)_2)_2]$. The recovered weight puts the yield of $[Ca(N(TMS)_2)_2]$ at 68%, although it was not isolated. Finally, the yield from CaI_2 increased from the 68% observed at 10 min (Table 1, entry 4) to 84% at 30 min. Interestingly, the yield decreases to 65% at one hour of milling. A decrease in yield has been observed before with long grinding times (e.g., in the mechanochemical synthesis of ferrocene),[27] and may reflect decomposition assisted by the reaction between the products and by-products that all exist in a single phase, a critical difference from solution-based metathesis, where the alkali metal halide is removed from the reaction environment by precipitation.

The rapid formation of the calciate $[KCa(N(TMS)_2)_3]$ in preference to the neutral bis(amide) $[Ca(N(TMS)_2)_2]$ prompted a closer look at the molecule. The X-ray crystal structure of the THF-solvated species $[(thf)KCa(N(TMS)_2)_3]$ has been published,[10a] but we were able to grow crystals of the base-free material from hexanes and obtain its structure (Figure 3). As with the THF-solvated version, the molecule comprises a four-membered CaNKN′ ring, with the calcium also bound by a terminal $-N(TMS)_2$ group. The coordination environment of the potassium consists of two amido groups at distances of 2.882(2) and 2.943(2) Å, and intermolecular K···C(Me) interactions to amido groups at 3.19 and 3.24 Å. There are longer intramolecular contacts (ca. 3.3–3.5 Å) to methyl groups on the bridging amido ligands that help to fill the coordination sphere of the potassium. In the THF-solvated analogue, a chain is formed in the solid state by virtue of a single intermolecular K···C(Me) interaction (3.37 Å).[10a] In $[KCa(N(TMS)_2)_3]$, the absence of THF permits the existence of multiple, shorter K···C(Me) interactions, which together allow the molecule to form a sheet-like structure. With the exchange of Mg for Ca, and Li for K, the structure of $[KCa(N(TMS)_2)_3]$ is also related to that of $[LiMg(N(TMS)_2)_3]$;[28] the magnesiate structure is strictly monomeric, with closest intermolecular Me···Me′ contacts > 3.8 Å. Although detailed information about the formation of $[KCa(N(TMS)_2)_3]$ is lacking, it is conceptually possible to replace one $[N(TMS)_2]^-$ group in the potassium amide dimer (Figure 1b) with the $[CaN(TMS)_2]^-$ fragment to form the calciate. The Ca–(μ-N) bonds found in the structure of $[KCa(N(TMS)_2)_3]$ (avg length of 2.36 Å) are 0.12 Å shorter, and hence presumably stronger, than the comparable distance found in the $[Ca(N(TMS)_2)_2]$ dimer (Figure 1a),[13b] which may correlate with the former's faster formation and the slowness of its conversion into the neutral bis(amido) complex.

In summary, we have employed mechanochemical methods to produce $[Ca(N(TMS)_2)_2]$ via halide metathesis without employing toxic reagents or coordinating solvents, or requiring the synthesis of intermediate organometallic compounds.[22] Not all the features associated with solvent-based reactions are avoided, i.e., calcium iodide is still the preferred halide, as its lattice is the most easily disrupted. There is no reason that the method could not be extended to other Group 2 metals or amido ligands.[29] The critical role that solvents play in directing product formation in s-block chemistry suggests that their removal during reactions by means of mechanochemical assistance may have a substantial impact on the synthesis of a broad range of complexes.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

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29. In preliminary experiments, we have found that grinding $MgBr_2$ with $[KN(TMS)_2]$ in a 1:1 ratio for 15 min, followed by workup similar to that used for the the calcium complex, yields the magnesium amide $[Mg(N(SiMe_3)_2)_2]$ in 87% yield (M. Westerhausen and W. Schwarz, *Z. Anorg. Allg. Chem*., 1992, **609**, 39-44).