

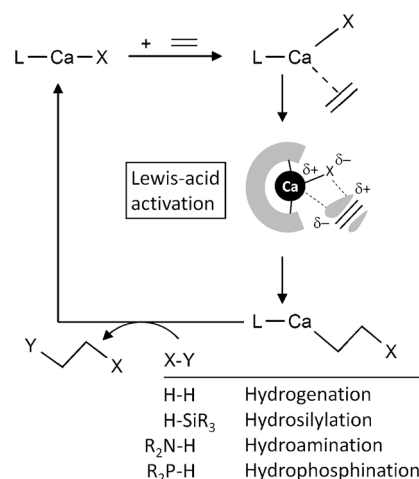
Hydroamination

Early Main Group Metal Catalysis: How Important is the Metal?*

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Abstract: Organocalcium compounds have been reported as efficient catalysts for various alkene transformations. In contrast to transition metal catalysis, the alkenes are not activated by metal–alkene orbital interactions. Instead it is proposed that alkene activation proceeds through an electrostatic interaction with a Lewis acidic Ca^{2+} . The role of the metal was evaluated by a study using the metal-free catalysts: $[\text{Ph}_2\text{N}^-][\text{Me}_4\text{N}^+]$ and $[\text{Ph}_3\text{C}^-][\text{Me}_4\text{N}^+]$. These “naked” amides and carbanions can act as catalysts in the conversion of activated double bonds ($\text{C}=\text{O}$ and $\text{C}=\text{N}$) in the hydroamination of $\text{Ar}-\text{N}=\text{C}=\text{O}$ and $\text{R}-\text{N}=\text{C}=\text{N}-\text{R}$ ($\text{R}=\text{alkyl}$) by Ph_2NH . For the intramolecular hydroamination of unactivated $\text{C}=\text{C}$ bonds in $\text{H}_2\text{C}=\text{CHCH}_2\text{CPh}_2\text{CH}_2\text{NH}_2$ the presence of a metal cation is crucial. A new type of hybrid catalyst consisting of a strong organic Schwesinger base and a simple metal salt can act as catalyst for the intramolecular alkene hydroamination. The influence of the cation in catalysis is further evaluated by a DFT study.

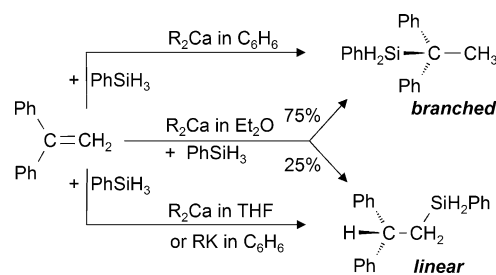
The field of early main group metal (EMGM) catalysis is rapidly growing.^[1] This is partially driven by the nontoxicity and low prices of the metals but also strongly stimulated by academic interest. In this context, organocalcium compounds have been reported as efficient precatalysts for catalytic conversions of alkenes by polymerization,^[2] hydroamination,^[3] hydrosilylation,^[4] hydrogenation,^[5] and hydrophosphination^[6] (Scheme 1). In contrast to transition metal (TM) catalysis, the alkenes are not activated by metal–alkene ($d \rightarrow \pi^*$) orbital interactions, i.e., backbonding according to Dewar–Chatt–Duncanson, but instead it is suggested that alkene activation proceeds through an electrostatic interaction with a Lewis acidic Ca^{2+} . This leads to vertical and



Scheme 1. Lewis acidic alkene activation by Ca^{2+} .

horizontal polarization of the π -electron density thus giving an incentive for nucleophilic attack (Scheme 1). Clark and co-workers showed already at an early stage that such electrostatic activation of double bonds by an EMGM cation like Li^+ drastically lowers activation energies for epoxidation or radical addition/polymerization.^[7] In fact, also TM activation of alkenes contains an electrostatic component which can be modeled by the Li^+ –alkene interaction. Electrostatic double bond activation decreases with Lewis acidity, that is, along the row $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Rb}^+ > \text{Cs}^+$.^[7c] Similar models of cation activation have been proposed for the stronger Lewis acid Ca^{2+} .^[8]

There is some experimental evidence for an important role of the metal in EMGM-catalyzed reactions. For example: the regioselectivity of alkene hydrosilylation can be controlled by metal or solvent choice (Scheme 2).^[4] Increasing the polarity of the system (metal: $\text{Ca} \rightarrow \text{K}$; solvent: $\text{C}_6\text{H}_6 \rightarrow \text{Et}_2\text{O} \rightarrow \text{THF}$) results in a regioselectivity switch, which is likely due to a change in mechanism in which the metal plays a crucial role.



Scheme 2. Polarity effects on product distribution in alkene hydrosilylation.

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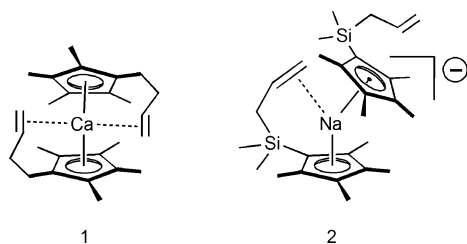
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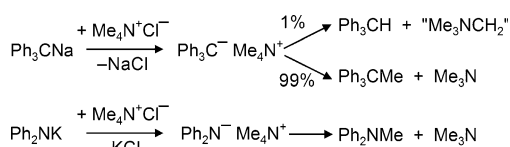
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Also in catalytic intramolecular hydroamination, metal cation charge densities can have major consequences for kinetics, selectivities, or side reactions.^[3b] Since the metal also strongly influences solubility and Schlenk equilibria, it is not always clear if such differences are related to EMGM–substrate interactions. Precedence for EMGM–alkene interactions is restricted to intramolecular examples (**1** and **2**) and such bonds are long and considered weak (average values: Ca...C 3.074(2) Å; Na...C 3.246(5) Å).^[9] This is especially the case for the heavier alkali metals (Na⁺, K⁺):^[9a] the CpNa...(η^2 -ethylene) interaction (7.9 kcal mol⁻¹, MP2/6-31 + G*) is half as strong as a CpNa...OH₂ interaction (15.2 kcal mol⁻¹) and also much weaker than biologically important Na⁺...(π -arene) interactions;^[10] for example CpNa...(η^6 -benzene) (14.0 kcal mol⁻¹).^[9a]



Given the weakness of the EMGM–alkene interaction, the question arises whether EMGM-mediated reactions should be considered organometallic catalysis (crucial role of metal cation) or organocatalysis (limited or no influence of metal cation). For further clarification, we replaced the EMGM cations for organic noncoordinating cations and tested “naked” anions as catalysts either in the intermolecular hydroamination of activated double bonds (C=O, C=N) or in the intramolecular hydroamination of unactivated double bonds (C=C).

Metal-free catalysts were prepared according to the early pioneering routes of Wilhelm Schlenk reported nearly a century ago (Scheme 3).^[11] Although Schlenk initially



Scheme 3. Schlenk's early syntheses of a “naked” carbanion and amide and their decomposition in THF solution (20 °C): $t_{1/2}$ = 5 h for [Ph₃C⁻][Me₄N⁺] and 3 days for [Ph₂N⁻][Me₄N⁺].

believed in the existence of pentavalent N, for example, Ph₃C–NMe₄, the ion pair character in [Ph₃C⁻][Me₄N⁺] is well-established.^[12] As [Ph₃C⁻][Me₄N⁺] shows limited stability,^[13] we also tested Schlenk's “naked” amide [Ph₂N⁻][Me₄N⁺] in catalysis. The latter is more stable against decomposition (Scheme 3).

Hydroamination of the highly activated C=N bond in carbodiimides giving guanidines can partially be achieved under uncatalyzed but harsh reaction conditions. The use of

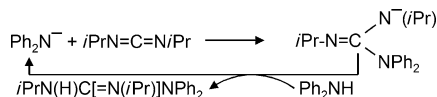
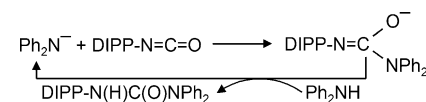
less nucleophilic amines (anilines or secondary amines), however, requires a catalytic protocol. Richeson and co-workers showed that simple metal amides MN(SiMe₃)₂·(THF)₂ (M = Li, Na, K) can catalyze this reaction.^[14] This was followed up by Hill and co-workers using similar Group 2 metal catalysts M[N(SiMe₃)₂]₂·(THF)₂ (M = Ca, Sr, Ba).^[15] Carrillo-Hermosilla and co-workers explored reactions mediated by MgBn₂·(THF)₂ or Mg_nBu₂.^[16] Similar, the hydroamination of the highly activated C=O bond in isocyanates yielding ureas can proceed under forced conditions without catalyst. However, less nucleophilic amines require a catalyst like M[N(SiMe₃)₂]₂·(THF)₂ (M = Ca, Sr, Ba)^[17] or LiN(SiMe₃)₂.^[1a]

In our hands, the sterically hindered isocyanate DIPP–N=C=O (DIPP = 2,6-*i*Pr₂-phenyl) does not react with Ph₂NH at 60 °C (Table 1, entry 1). Hydroamination is catalyzed by Ca[N(SiMe₃)₂]₂·(THF)₂ (entry 2). Interestingly, the metal-free catalyst [Ph₂N⁻][Me₄N⁺] gave a similar conversion, independent of temperature and solvent (entries 3–5).^[18] Incomplete conversion has earlier been explained by product inhibition: the urea product acts as a ligand for the catalytically active calcium species and hinders substrate coordination and activation at the metal.^[17] As incomplete conversion is also observed with a metal-free catalyst, it likely has to be explained by an acid–base equilibrium between the product anion O=C(NPh₂)–N(DIPP)⁻ and Ph₂NH.

Also *i*PrN=C=N*i*Pr does not react with Ph₂NH under forced conditions but this reaction can be catalyzed by Ca[N(SiMe₃)₂]₂·(THF)₂ (entries 6–7). The metal in the catalyst is not a necessity: catalytic quantities of [Ph₂N⁻][Me₄N⁺] gave similar results that are independent of temperature and solvent (entries 8–10).^[18] Changing the substrate to CyN=C=

Table 1: Catalytic hydroamination of isocyanate and carbodiimide substrates.

	Catalyst	mol %	Solvent	T [°C]	t [h]	Conv. [%] ^[a]
1	–	–	benzene or THF	60	48	0
2	Ca[N(SiMe ₃) ₂] ₂ ·THF ₂ ^[17]	6	benzene	60	3	62
3	[Ph ₂ N ⁻][Me ₄ N ⁺]	5	benzene	25	1	74
4	[Ph ₂ N ⁻][Me ₄ N ⁺]	5	THF	25	1	71
5	[Ph ₂ N ⁻][Me ₄ N ⁺]	5	THF	60	1	71

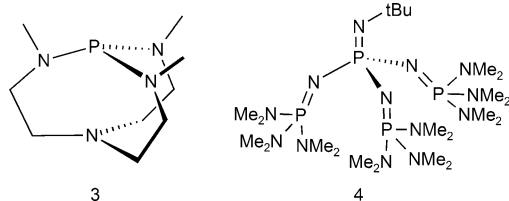


6	–	–	benzene or THF	60	72	0
7	Ca[N(SiMe ₃) ₂] ₂ ·THF ₂ ^[15]	2	benzene	25	1	74
8	[Ph ₂ N ⁻][Me ₄ N ⁺]	5	benzene	25	1	82
9	[Ph ₂ N ⁻][Me ₄ N ⁺]	5	THF	25	0.5	85
10	[Ph ₂ N ⁻][Me ₄ N ⁺]	5	THF	60	1	88

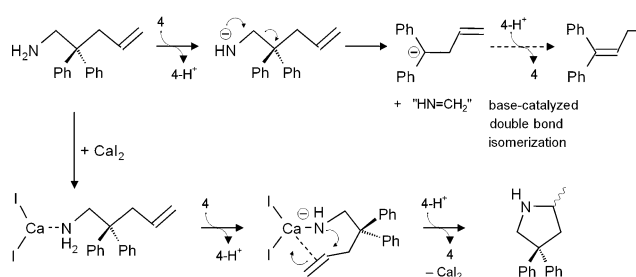
[a] Conversion determined by ¹H NMR spectroscopy.

NCy gave comparable results (see the Supporting Information, SI) but no conversion was found for $\text{ArN}=\text{C}=\text{NAr}$ ($\text{Ar} = \text{DIPP}$ or *p*-tolyl). Problematic catalytic hydroamination of $\text{ArN}=\text{C}=\text{NAr}$ is in agreement with the lack of examples for Group 2 metal-mediated reactions,^[15] which is likely caused by the high stability of the product anion $\text{ArN}=\text{C}(\text{NPh}_2)^-\text{N}(\text{Ar})^-$. This resonance-stabilized anion is less basic than an alkylated product anion like $i\text{PrN}=\text{C}(\text{NPh}_2)^-\text{N}(i\text{Pr})^-$, thus inhibiting the deprotonation of Ph_2NH . The acid–base equilibrium constant likely reflects the conversion reached in catalysis.

Encouraged by these examples of metal-free catalysis of strongly activated double bonds, we turned to probe the intramolecular hydroamination of unactivated C=C bonds.^[19] This cyclization reaction is catalyzed by a large variety of heteroleptic or also homoleptic Group 2 metal complexes.^[3] Testing several amino alkenes $\text{H}_2\text{C}=\text{CHCH}_2\text{CR}_2\text{CH}_2\text{NH}_2$ ($\text{CR}_2 = \text{CMe}_2$, Cy, or CPh_2) we found with 5 mol % of the catalyst $[\text{Ph}_2\text{N}^-][\text{Me}_4\text{N}^+]$ under no circumstances any indication for substrate conversion ($T = 25\text{--}80^\circ\text{C}$ in benzene or THF over 3–12 days). We reasoned that the anion $[\text{Ph}_2\text{N}^-]$ might not be basic enough ($\text{p}K_{\text{a}}(\text{Ph}_2\text{NH}) = 25.0$)^[20] to deprotonate a primary alkyl amine sufficiently (estimated $\text{p}K_{\text{a}}$ value > 35). Acid–base equilibria with the stronger basic “naked” anion $[\text{Ph}_3\text{C}^-]$ [$\text{p}K_{\text{a}}(\text{Ph}_3\text{CH}) = 30.6$]^[21] could be more favorable for catalysis. However, also $[\text{Ph}_3\text{C}^-][\text{Me}_4\text{N}^+]$ gave no conversion of various aminoalkene substrates at similar conditions. At this stage it was unclear whether this is due to: 1) catalyst decomposition (Scheme 3), 2) insufficient deprotonating abilities of the catalyst, or 3) the lack of a metal cation for C=C bond activation. To exclude catalyst decomposition and catalyst basicity, we tested two strong and robust organic Brønsted bases: the Verkade base (**3**, $\text{p}K_{\text{a}}$ value of $3\text{--H}^+ = 29.6$) and the Schwesinger P4 base (**4**, $\text{p}K_{\text{a}}$ value of $4\text{--H}^+ = 42$).^[22]



The Verkade base **3** did not react with $\text{H}_2\text{C}=\text{CHCH}_2\text{CR}_2\text{CH}_2\text{NH}_2$ even in stoichiometric ratio (C_6H_6 , 80°C , 5 days). Stoichiometric addition of the stronger Schwesinger P4-*t*Bu base **4**, however, gave only in the case of $\text{R} = \text{Ph}$ slow but full conversion (toluene, 90°C , 5 days, 98%), which could be accelerated in THF (55°C , 60 h, $> 99\%$). However, instead of the ring closure product we found clean formation of 1,1-diphenyl-2-ethylethene (Scheme 4). We propose deprotonation of the aminoalkene followed by decomposition to methanimine $\text{H}_2\text{C}=\text{NH}$ and a carbanion stabilized by resonance through Ph substituents. The final product is formed after double bond isomerization/protonation. Despite the deprotonation of the substrate, no ring closure is observed. This experiment suggests that in the case of unactivated C=C bonds the role of the metal is crucial for



Scheme 4. Metal salt effect in catalytic conversion of aminoalkenes by a strong organic Schwesinger base (**4**).

double bond activation. We tested this hypothesis by addition of a metal salt. Simple addition of catalytic quantities of **4** and CaI_2 (10 mol %) to $\text{H}_2\text{C}=\text{CHCH}_2\text{CPh}_2\text{CH}_2\text{NH}_2$ gave smooth ring closure to the anticipated five-membered ring (C_6H_6 , 25°C , 2 h, $> 99\%$) under mild conditions. Product formation is clean and favored by polar solvents (THF, 25°C , 0.5 h, $> 99\%$). This polar solvent effect could be explained by increased CaI_2 solubility or decreased CaI_2 aggregation. CaI_2 alone does not catalyze the intramolecular alkene hydroamination, nor does the CaI_2 /Verkade base combination. The activating ability of the CaI_2 /Schwesinger base combination may be related to bond activation by frustrated Lewis pairs.^[23] A potential route is proposed in Scheme 4: amine- CaI_2 coordination acidifies the NH_2 protons after which deprotonation by the base and cyclization can take place. The cycle is closed by protonation of the product anion either by $(\text{P4-}t\text{Bu})\text{H}^+$ or by the amine substrate.

Preliminary we conclude that for hydroamination of unactivated C=C bonds the metal plays an important role whereas for activated double bonds (C=N, C=O) metal-free catalysts with “naked” anions are sufficient. It is questionable, however, to what extent the amide anion in $[\text{Ph}_2\text{N}^-][\text{Me}_4\text{N}^+]$ is “naked”. The crystal structure of Schlenk’s early “free” carbanion, $[\text{Ph}_3\text{C}^-][\text{Me}_4\text{N}^+]$, already revealed a network of nonclassical C–H...C hydrogen bonds between $[\text{Me}_4\text{N}^+]$ (C–H donor) and $[\text{Ph}_3\text{C}^-]$ (C acceptor).^[12] Although $[\text{Ph}_2\text{N}^-][\text{Me}_4\text{N}^+]$ crystallized in thin needle-like crystals that are unsuitable for a crystal structure determination, the related $[p\text{-tolyl}_2\text{N}^-][\text{Me}_4\text{N}^+]$ crystallized as plates of which we determined a crystal structure (Figure 1). The crystal structure clearly shows bonding between anions and cations through short C–H...N contacts ($\text{H}\cdots\text{N}$ 2.33–2.46 Å; $\text{C–H}\cdots\text{N}$ $158^\circ\text{--}174^\circ$) resulting in a helix. This “metal-like” behavior of $[\text{Me}_4\text{N}^+]$ brings up the question whether it could fulfill an activating role in double bond hydroamination.

To evaluate the role of the Me_4N^+ cation in the reaction mechanism, we chose the hydroamination of $i\text{PrN}=\text{C}=\text{NiPr}$ as a model for a set of DFT calculations at the level B3PW91/6-311G** including solvent correction (THF) at the PCM level. The reaction of $i\text{PrN}=\text{C}=\text{NiPr}$ with the “naked” anion (Figure 2) proceeds through a transition state with a small barrier of $13.9\text{ kcal mol}^{-1}$ and is slightly endergonic (4.3 kcal mol^{-1}), however, the full reaction profile with subsequent H transfer from Ph_2NH to the product is nearly thermoneutral (see SI for more detailed reaction profiles and geometry information). The product anion shows a delocalized struc-

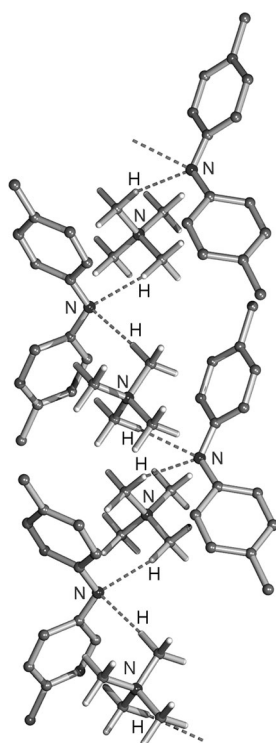


Figure 1. a) Crystal structure of $[p\text{-tolyl}_2\text{N}^-][\text{Me}_4\text{N}^+]$; only hydrogen atoms for $[\text{Me}_4\text{N}^+]$ are shown (short $\text{C}-\text{H}\cdots\text{N}$ contacts indicated by dashed lines).

ture with similar $\text{C}-\text{NiPr}$ distances. Hydroamination with Ph_2NLi starts from a carbodiimide $\cdots\text{LiNPh}_2$ complex, in which one of the $\text{C}=\text{N}$ bonds is activated by Li coordination. This gives rise to asymmetry in the $\text{N}=\text{C}=\text{N}$ skeleton: the activated bond is longer (1.238 Å), whereas the other bond is shorter (1.202 Å) than that in free $i\text{PrN}=\text{C}=\text{NiPr}$ (1.218 Å). Subsequent reaction over a cyclic transition state (16.8 kcal mol $^{-1}$) gives the product in which unequal $\text{C}-\text{NiPr}$ bonds indicate electron localization by the Li^+ ion. The reaction is even more endergonic (7.2 kcal mol $^{-1}$) which originates from the poor $\text{Ph}\cdots\text{Li}$ coordination (versus the $\text{N}\cdots\text{Li}$ coordination in the starting complex). Hydroamination with the ion pair $[\text{Ph}_2\text{N}^-][\text{Me}_4\text{N}^+]$ starts from a complex in which substrate and ion pair form a network of short nonclassical $\text{C}-\text{H}\cdots\text{N}$ bridges. This causes a similar but slightly less pronounced asymmetry in the $\text{N}=\text{C}=\text{N}$ skeleton as found in the carbodiimide $\cdots\text{LiNPh}_2$ complex. The reaction proceeds through a rather low-energy transition state (12.8 kcal mol $^{-1}$), in which the Me_4N^+ cation bridges those N atoms that show a decreasing negative charge (Ph_2N^-) or increasing negative charge (carbodiimide). The Me_4N^+ -anion interaction is still observed in the product ion pair and gives rise to unequal $\text{C}-\text{NiPr}$ bonds. Although this asymmetry is less pronounced than that in $i\text{PrN}=\text{C}(\text{NPh}_2)-\text{N}(\text{iPr})\text{Li}$, it reflects a similar charge localization. The resemblance between the function of Li^+ and Me_4N^+ is striking. The latter behaves as a very large cation which is bound to anion and substrate through bifurcating $\text{C}-\text{H}\cdots\text{N}$ bridges. The last pathway evaluates a possible reaction mechanism in which no cation is involved. Instead the Ph_2NH substrate fulfills the role of a bridge between Ph_2N^-

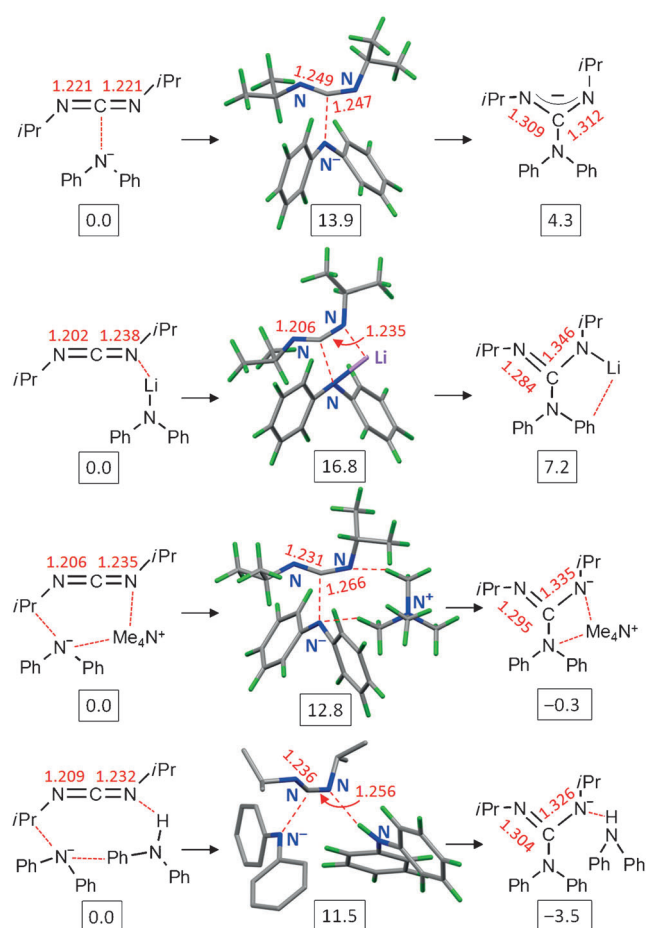


Figure 2. DFT calculations (B3PW91/6-311G**) for the hydroamination of $i\text{PrN}=\text{C}=\text{NiPr}$ by Ph_2N^- , Ph_2NLi , $[\text{Ph}_2\text{N}^-][\text{Me}_4\text{N}^+]$ or $\text{Ph}_2\text{N}^-\cdots\text{HNPh}_2$; transition states are shown in wireframe models (relative ΔG° (298 K) in kcal mol $^{-1}$).

and carbodiimide. Especially at the start of the reaction the reagent could be present as $[\text{Ph}_2\text{N}^-\cdots\text{HNPh}_2]$, an anion with a strong classical $\text{N}-\text{H}\cdots\text{N}$ bridge. The starting complex shows less asymmetry in the $\text{N}=\text{C}=\text{N}$ skeleton which means that the $\text{Ph}_2\text{NH}\cdots\text{carbodiimide}$ is less activating than the $\text{Me}_4\text{N}^+\cdots\text{carbodiimide}$ interaction. The product is formed through a low-energy transition state (11.5 kcal mol $^{-1}$) and the reaction is slightly exergonic (3.5 kcal mol $^{-1}$). The presence of the $\text{NH}\cdots\text{N}$ hydrogen bridge also causes asymmetry in the $\text{C}-\text{NiPr}$ bonds of the product anion but again, less pronounced than for interaction of this anion with Li^+ or Me_4N^+ . Route 4 in Figure 2 seems to be the most competitive pathway, however, it should be noticed that disrupting the ion pair $[\text{Ph}_2\text{N}^-][\text{Me}_4\text{N}^+]$ costs 68.0 kcal mol $^{-1}$ (gas phase). Although the anion-cation dissociation energy drops dramatically to 5.0 kcal mol $^{-1}$ when a solvent correction for THF solution is included (PCM), full energy profiles including solvent correction (Figure 3) show that route 4 is not feasible. In metal-free catalysis the “naked” anion (Ph_2N^-) or ion-pair routes ($[\text{Ph}_2\text{N}^-][\text{Me}_4\text{N}^+]$) are preferred.

Our combined experimental and calculation studies led us to conclude the following: 1) Intermolecular hydroamination of strongly activated double bonds ($\text{C}=\text{O}$ in isocyanates, $\text{C}=\text{N}$

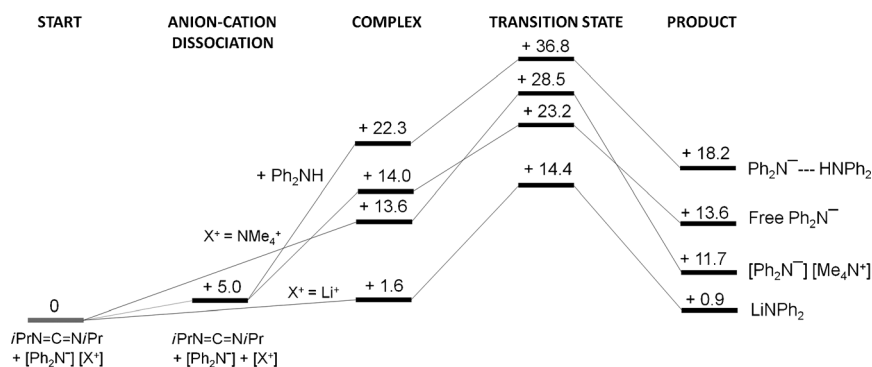


Figure 3. Full energy profiles for the hydroamination of $i\text{PrN}=\text{C}=\text{NiPr}$ by Ph_2N^- , Ph_2NLi , $[\text{Ph}_2\text{N}^-][\text{Me}_4\text{N}^+]$ or $\text{Ph}_2\text{N}---\text{HNPh}_2$; relative $\Delta G^\circ(298\text{ K})$ in kcal mol^{-1} with solvent correction at the PCM level (THF).

in carbodiimides) can also be accomplished by metal-free catalysts in which the anion is combined with a “noncoordinating” cation like Me_4N^+ . This could be defined as organo-catalysis. 2) The crystal structure of $[p\text{-tolyl}_2\text{N}^-][\text{Me}_4\text{N}^+]$ reveals numerous C—H...N bonds between cation and anion which suggests that the cation is weakly coordinating and behaves like a larger metal. 3) Calculations on the hydroamination of carbodiimides confirm this metal-like behavior of Me_4N^+ in the reaction mechanism. The C=N double bond in a carbodiimide is activated by interaction with Me_4N^+ . However, the extent of activation is less than that in the carbodiimide... Li^+ complex and under polar conditions cation-free routes might be feasible. 4) Most interestingly, intramolecular hydroamination of unactivated C=C double bonds needs a more Lewis acidic metal cation for substrate activation and should therefore be defined as organometallic catalysis.^[24] A simple hybrid catalyst consisting of a strong organic Schwesinger base and the salt CaI_2 gave smooth and quantitative conversion already at room temperature. We are currently exploring the validity of this concept by extending it to a variety of bases, metal complexes, and substrates.

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