Heavier Group 2 Element Catalyzed Hydrophosphination of Carbodiimides

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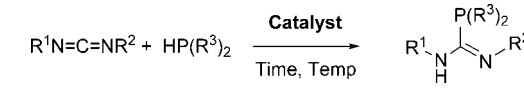
Summary: Amides of the heavier group 2 elements Ca, Sr, and Ba are effective precatalysts for the atom-efficient addition of phosphine P−H bonds to carbodiimides. A number of intermediates within the catalytic cycle have been identified by in situ NMR methods and by stoichiometric synthesis.

Over the past few years a number of well-defined heavier group 2 complexes have been reported for the catalytic heterofunctionalization or polymerization of substrates containing unsaturated carbon−carbon bonds.[1–3] Despite this advance, the understanding of such catalytic systems remains in its infancy. Although these heterofunctionalization processes are presumed to proceed via the insertion of the unsaturated substrate (alkene or alkyne) into the metal−heteroatom bond of an intermediate group 2 organometallic complex, isolation and characterization of the insertion products, group 2 alkyl complexes, are complicated by their highly reactive nature. As such, investigations into the general catalytic cycle postulated for heavier group 2 catalyzed heterofunctionalization reactions remains limited. In particular, the effects of acid–base equilibria, metal–ligand bond ionicity, and cation polarizability upon reactivity are yet to be understood.

Recent studies on the application of group 1 organometallic compounds to the hydrophosphination, hydroamination, and hydroacetylation of carbodiimides[4,5] have demonstrated not only the competence of group 1 bis(trimethylsilyl)amides, [MN(SiMe$_3$)$_2$] (M = Li, K), for the catalytic heterofunctionalization of carbodiimides but also the ease of isolation of reaction intermediates, group 1 amidinate/guanidinate complexes, through stoichiometric reactions between the precatalyst and reaction substrates. In addition, a number of well-defined organolanthanide catalysts have been reported for the heterofunctionalization of carbodiimides.[6] As part of a study toward the understanding of group 2 catalytic systems, we now present our initial findings on the intermolecular hydrophosphination of carbodiimides (Scheme 1).

Scheme 1. Intermolecular Hydrophosphination of Carbodiimides



An initial NMR experiment was conducted with diphenylphosphine, 1,3-diisopropylcarbodiimide, and 1.5 mol % of the β-diketiminato calcium amide [{ArNC(Me)CHC(Me)NAr}Ca{N(SiMe$_3$)$_2$}(THF)] (**1**; Ar = 2,6-diisopropylphenyl), in C_6D_6. Analysis of the reaction by ^{1}H and ^{31}P NMR showed 90% conversion to the phosphaguanidine product within 1 h at room temperature, a yield that rose to 99% after 6 h. A preparative-scale experiment allowed the isolation and characterization of the phosphaguanidine [Ph$_2$PC{NH^{i}Pr}{N^{i}Pr}].[7] A similar background reaction conducted without the catalyst showed no reaction after 2 weeks at room temperature. On the basis of this observation a series of heavier alkaline earth-based catalysts, including the heteroleptic calcium amide **1** and the homoleptic alkaline earth amides [Ca{N(SiMe$_3$)$_2$}$_2$] (**2**), [Ca{N(SiMe$_3$)$_2$}$_2$(THF)$_2$] (**3**), [Sr{N(SiMe$_3$)$_2$}$_2$(THF)$_2$] (**4**), and [Ba{N(SiMe$_3$)$_2$}$_2$(THF)$_2$] (**5**), were applied to the hydrophosphination of carbodiimides with diphenylphosphine, di-*p*-tolylphosphine, and dicyclohexylphosphine. The results of this study are presented in Table 1.

The hydrophosphination of a number of symmetric and unsymmetric carbodiimides was achieved at room temperature using catalyst loadings as low as 1.5 mol %. While **1** was found

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Table 1. Intermolecular Hydrophosphination of Carbodiimides

entry	R^1	R^2	R^3	cat. (amt (mol %))	T(C)	t(h)	yield (%)[a]
1	Cy	Cy	Ph	**1**(1.5)	25	28	85
2				**3** (3)	25	4	>95
3				**2** (2)	25	2	>95
4				**4** (2)	25	0.5	>99
5				**5** (2)	25	0.5	>95
7	i-Pr	i-Pr	Ph	**1**(1.5)	25	6	>99
8				**2** (2)	25	1	>95
9				**4** (2)	25	0.5	>99
10	t-Bu	t-Bu	Ph	**4** (5)	60	16	0
11	t-Bu	Et	Ph	**4** (2)	25	0.25	>95
12	p-tol	p-tol	Ph	**4** (2)	25	12	68
13	i-Pr	i-Pr	p-tol	**4** (10)	25	0.25	>95
14	i-Pr	i-Pr	Cy	**4** (5)	60	16	0

[a] Measured by integration against $(Me_3Si)_4Si$ as an internal standard. The yield is based on the limiting reagent.

to catalyze this reaction, the simpler homoleptic alkaline-earth amides **2**–**5** proved more active. The hydrophosphination of carbodiimides with dicyclohexylphosphine could not be achieved with either the homoleptic or heteroleptic alkaline earth-based catalysts, and it is postulated that in these cases catalyst activation did not occur, due to the decreased acidity of the dicyclohexylphosphine relative to diphenylphosphine. Support for this hypothesis was provided by the addition of $HPCy_2$ to **1**; monitoring the reaction mixture by ^{31}P NMR showed no signs of protonolysis to form the corresponding phosphide complex (vide infra). Additionally, the hydrophosphination of sterically demanding carbodiimides such as 1,3-di-*tert*-butylcarbodiimide with group 2 amides was not observed. This is most likely a reflection of the increased steric hindrance at nitrogen preventing the coordination of the carbodiimide to the alkaline earth-metal center (vide infra) and thus inhibiting the reaction. Indeed, a stoichiometric reaction between [{ArNC(Me)CHC(Me)-NAr}Ca{PPh_2}(THF)] (**6**) and 1,3-di-*tert*-butylcarbodiimide showed no sign of insertion of the carbodiimide into the Ca−P bond even after 2 h at 60 °C.[1b] Further evidence for this steric effect was provided by the ready hydrophosphination of 1-ethyl-3-*tert*-butylcarbodiimide (Table 1, entries 10 and 11).

Although the results in Table 1 suggest that both the strontium- and barium-based catalysts are more effective than the calcium analogue (entries 1–5), initial attempts to quantify this effect by kinetic analysis using ^1H NMR spectroscopy were complicated by the fast rates of the reactions. Turnover frequencies reflect the apparent effect of the cation radius and, for the hydrophosphination of 1,3-diisopropylcarbodiimide with Ph_2PH, exceed 250 h^{-1} for **4** but only reach 50 h^{-1} for **2**.

We have recently demonstrated that **3**–**5** react with diphenylphosphine to yield group 2 diphenylphosphido complexes of the form $[M(PPh_2)_2(L)_n]$ (M = Ca, Sr, Ba; L = THF, 18-crown-6).[8] These compounds display negligible solubility in hydrocarbon solvents, and thus it seems unlikely that coordinatively unsaturated homoleptic heavier alkaline earth phosphides are long-lived intermediates in the catalytic hydrophosphination of carbodiimides conducted in C_6D_6. The individual reaction steps for the reaction of diphenylphosphine with 1,3-diisopropylcarbodiimide catalyzed by **1** were, therefore, followed by ^{31}P NMR spectroscopy. The stoichiometric reaction of **1** with 1,3-diisopropylcarbodiimide yielded no insertion products, even after extended periods at elevated temperatures (12 h at 60 °C). Therefore, it is likely that the catalytic reaction is initiated by the reaction of diphenylphosphine ($\delta_{31}P$ −40.1 ppm) with **1** to form the previously characterized calcium phosphide **6** ($\delta^{31}P$ −21.3 ppm).[1b] This latter species, however, is only a transient intermediate which, following coordination of the carbodiimide to the metal center, undergoes an insertion reaction with the carbodiimide to form the phosphaguanidinate **7** ($\delta^{31}P$ −21.1 ppm).

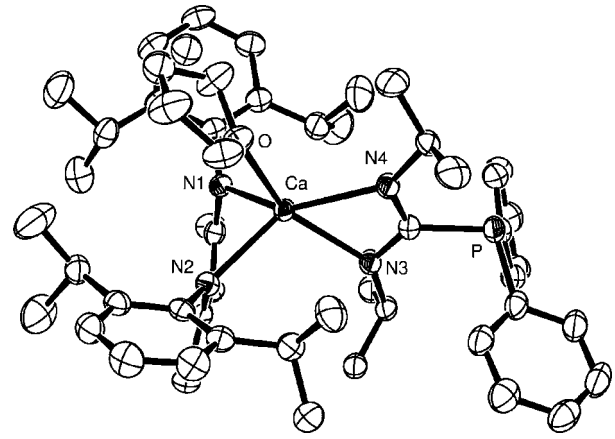

Figure 1. Ortep representation of **7**. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and bond angles (deg): Ca−N(2) = 2.3733(15), Ca−O = 2.3832(13), Ca−N(1) = 2.3876(14), Ca−N(3) = 2.3934(15), Ca−N(4) = 2.4410(15); N(2)−Ca−N(1) = 79.88(5), N(4)−Ca−N(3) = 55.83(5).

Synthesis of **7**, from the stoichiometric reaction of **6** with 1,3-diisopropylcarbodiimide, and crystallization from a hexane solution at −21 °C allowed the isolation of crystals suitable for X-ray diffraction analysis (Figure 1). This study revealed a mononuclear five-coordinate calcium complex in which the phosphaguanidinate ligand binds via a symmetric NCN chelate with auxiliary coordination at calcium provided by the β-diketiminate spectator ligand and a single molecule of THF. Consistent with previous studies on the coordination chemistry of phosphaguanidine ligands,[7c,e,f,g] the phosphorus lone pair is not delocalized across the amidinate moiety and there is a significant degree of pyramidalization at phosphorus. A pulsed gradient spin–echo NMR study demonstrated that **7** retains this monomeric constitution in C_6D_6 solutions (see the Supporting Information).

Surprisingly, the addition of diphenylphosphine to the isolated complex **7** did not result in quantitative formation of the phosphide complex **6**. Rather, no reaction was apparent after 24 h at room temperature and both diphenylphosphine and the heteroleptic calcium phosphaguanidinate **7** could be observed by ^{31}P NMR spectroscopy (Figure 2, spectrum d). Upon addition of the carbodiimide, however, catalytic turnover was observed and the diphenylphosphine was converted to the phosphaguanidine ($\delta_{31}P$ −18.6 ppm). This observation may be explained by considering an equilibrium between **7** and $HPPh_2$, and the phosphide **6** and phosphaguanidine product in solution. Complex **6** is formed in low concentration but readily reacts with the carbodiimide to re-form **7**, achieving catalytic turnover (Figure 2 spectrum e).

In addition to the resting state catalyst **7**, diphenylphosphine, and the phosphaguanidine, a further broad peak could be observed, albeit at very low intensity, at −22.8 ppm in the ^{31}P spectrum from the reaction of **7** with $HPPh_2$ and i-PrN═C═N-i-Pr. Addition of the carbodiimide to **7** confirmed this minor product to be the adduct between the two, **8**, presumably formed by displacement of THF from the coordination sphere. The two heteroleptic calcium compounds are in equilibrium, and although

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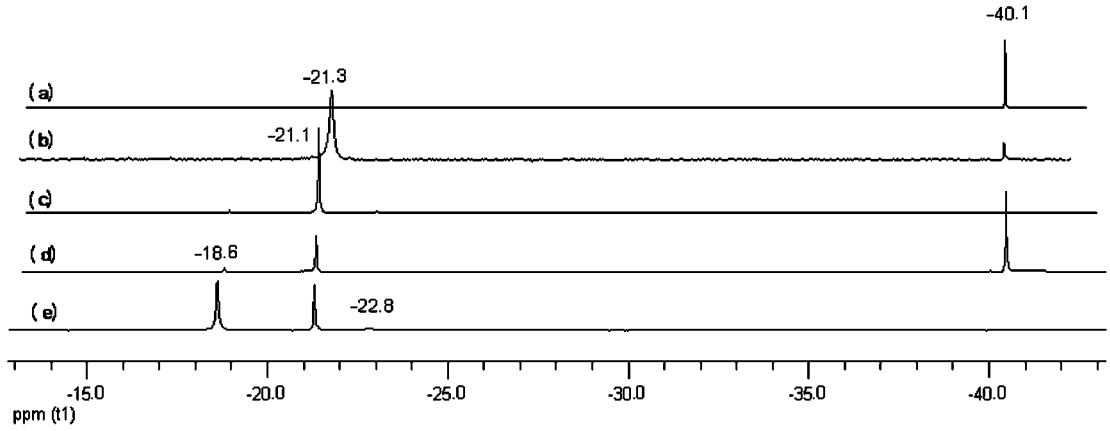
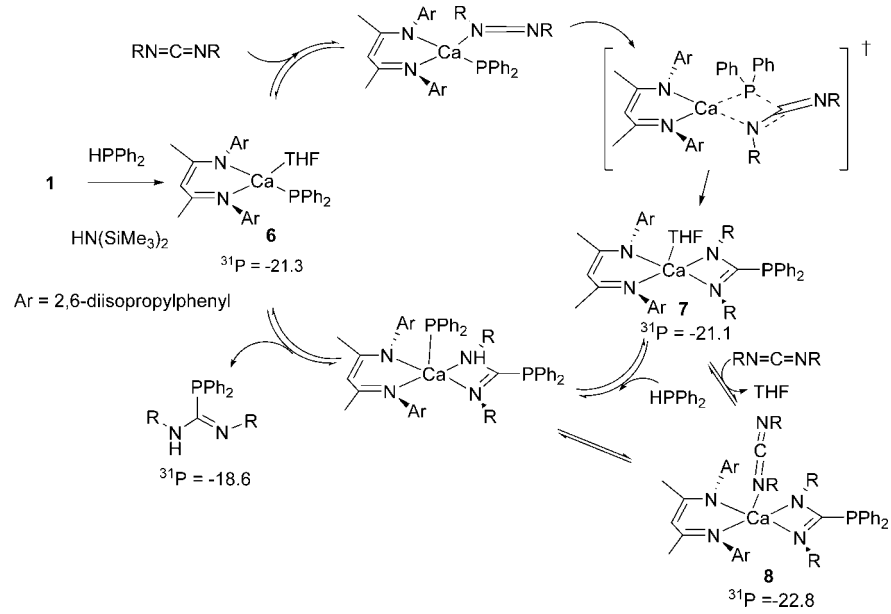


Figure 2. $^{31}P\{^{1}H\}$ NMR stack plot (C_6D_6) of the stoichiometric reactions (a) $HPPh_2$, (b) **1** + $HPPh_2$, (c) **6** + i-PrN=C=N-i-Pr, (d) **7** + $HPPh_2$, and (e) **7** + $HPPh_2$ + i-PrN=C=N-i-Pr.

Scheme 2. Proposed Catalytic Cycle[a]



[a] Chemical shift values are quoted in ppm for R = i-Pr.

variable temperature ^{31}P NMR spectroscopy showed a change in the position of the equilibrium with temperature, $K_c(d_8\text{-tol}, 293\ K) = 6.3 \times 10^{-3}$ and $K_c(d_8\text{-tol}, 253\ K) = 2.7 \times 10^{-2}$, the equilibrium lies predominantly toward the THF adduct **7** (see Figure S2 in the Supporting Information).

In conclusion, both heteroleptic and homoleptic group 2 amides may catalyze the reaction of secondary arylphosphines with carbodiimides to form phosphaguanidines. For **1** the catalyst resting state is a phosphaguanidinate calcium complex, which readily undergoes exchange of both neutral and monoanionic ligands through both Lewis-acid/Lewis-base and Brønsted-acid/Brønsted-base equilibria. (Scheme 2).

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Supporting Information Available: Text, tables, and figures giving full experimental details and a CIF file giving crystallographic data for **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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