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Synthesis, Structure, and Reactivity of a Stabilized Calcium Carbene: R_2CCa

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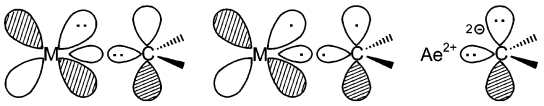
Abstract: Attempted 2-fold deprotonation of the bis(iminophosphorano)methane ligand, $H_2C(Ph_2P{=}NSiMe_3)_2$ (**4**−H_2), with a calcium amide led only to mono-deprotonation. The crystal structure of (**4**−H)$_2$Ca shows two tridentate ligands with short Ca−N and a rather long Ca−C bond. Reaction of **4**−H_2 with a dibenzylcalcium complex gave the desired 2-fold deprotonation and formation of **4**−Ca, which crystallized as a dimeric complex. Analysis of the calculated atomic and group charges in **4**−H_2, (**4**−H)$_2$Ca, and [**4**−Ca]$_2$ showed that the negative charge at the imine nitrogens only slightly increases upon successive deprotonation of **4**−H_2. The electron density at the central carbon, however, increases considerably: the charge on the carbene carbon in [**4**−Ca]$_2$ is ca. −1.8. The negative charge in $\mathbf{4}^{2-}$ is therefore mainly located on the carbon. Reaction of [**4**−Ca]$_2$ with benzophenone in benzene gave the remarkably stable adduct [**4**−Ca]$_2$·O=CPh$_2$, which was characterized by X-ray diffraction. Reaction of [**4**−Ca]$_2$ with adamantylcyanide gave exclusive formation of the adduct [**4**−Ca]$_2$·(N≡CR)$_2$, which did not react further, even at higher temperatures. Addition of cyclohexyl isocyanate to a benzene solution of [**4**−Ca]$_2$ gave immediate [2 + 2]-cycloaddition and formation of a dianionic tetradentate ligand that binds to Ca^{2+} through two nitrogens, the central carbon, and an oxygen. This product crystallized as a dimer with bridging oxygen atoms.

Introduction

The concept of metal−carbon multiple bonding is well-established in the organometallic chemistry of the transition metals.[1] Especially transition-metal carbenes have found widespread applications in organic syntheses and catalysis.[2] Such complexes can be classified either as Fischer carbenes based on a singlet carbene (**1**) or Schrock carbenes based on a triplet carbene (**2**). These modes of bonding, in which d-orbitals play an important role, largely determine their chemical reactivity.



1 2 3

Alkaline-earth-metal carbenes, defined as Ae=CR_2 (Ae = alkaline-earth metal),[3] are much less common and only the lighter members in the series have been studied. Be=CH_2 and Mg=CH_2 were characterized by IR in an argon matrix at low temperature.[4] Ziegler obtained Mg=CH_2 via α-elimination of methane from Me_2Mg and demonstrated its activity in ethylene polymerization.[5] Bickelhaupt et al. prepared Mg=CH_2 by disproportionation of the di-Grignard $CH_2(MgBr)_2$ and showed its potential as a building block in organometallic syntheses.[6] Apart from calculations on the simple carbene Ca=CH_2,[7] no data are available for the heavier alkaline-earth metal carbenes.

In contrast to transition-metal carbenes, such alkaline-earth-metal carbenes are highly ionic species with a considerable concentration of negative charge at the carbon (**3**). Therefore, they rather should be depicted as methandiides (H_2C^{2-} Ae^{2+}). Although the concept of double bonding is usually applied to covalent systems, the metal−carbon interaction in ionic **3** can also be regarded as a double bond: the electrostatic bond energy is proportional to the charge on the participitating ions.

Hitherto, there is a complete lack of structural information on any alkaline-earth-metal carbene. Similar to H_2CLi_2,[8] these higly ionic compounds are likely polymeric in the solid state. Recently, some stabilized molecular dilithiomethandiides have

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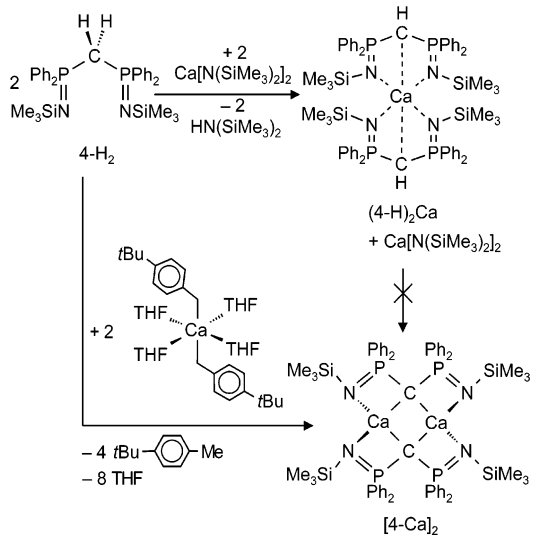
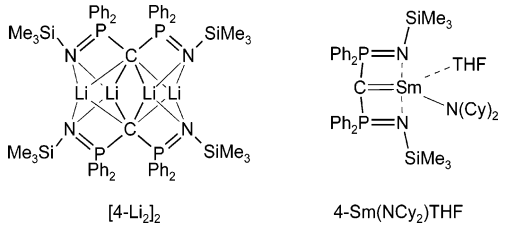
Scheme 1



been structurally characterized.[9−12] The use of the bis(iminophosphorano)methane ligand[13] in the syntheses of a well-defined dilithiomethandiide complex[10] [**4**−Li_2]$_2$, as well as in a rather polar lanthanide carbene complex **4**−Sm(NCy_2)·THF,[14] urged us to probe this ligand in the synthesis of a calcium carbene.



Here we describe the structure of its dimeric complex. In addition we report a computational analysis of the charge distribution in the ligand system and first studies on its reactivity.

Results and Discussion

Late main group metal carbenes such as **4**−Sn (or Pb) can conveniently be prepared by 2-fold deprotonation of ligand **4**−H_2 with a metal amide.[15] Reaction of a calcium amide with 1 equiv of **4**−H_2, however, only gave the mono-deprotonated product (**4**−H)$_2$Ca, even under forcing conditions (Scheme 1).

Complex (**4**−H)$_2$Ca crystallized as a pseudo-C_2 symmetric monomer (Figure 1). The Ca^{2+} ion is sandwiched between two $HC(Ph_2P{=}NSiMe_3)_2^-$ ions, which coordinate as η^3-(C,N,N′)-ligands. The Ca−C bond (average 2.765(1) Å) is rather long when compared with that in dibenzyl calcium complexes

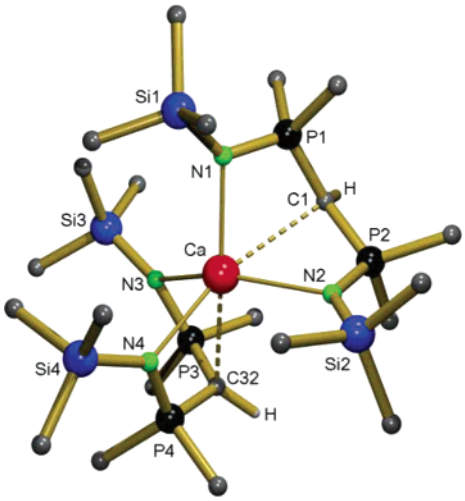


Figure 1. The crystal structure of (**4**−H)$_2$Ca; for clarity all hydrogens (except HCP_2) and all phenyl atoms (except C_{ipso}) have been omitted. Selected bond distances (Å) and angles (deg): Ca−C1, 2.724(1); Ca−C32, 2.805(1); Ca−N1, 2.4582(9); Ca−N2, 2.679(1); Ca−N3, 2.614(1); Ca−N4, 2.444(1); N1−Ca−N2, 86.43(3); N3−Ca−N4, 90.14(3); C1−Ca−C32, 109.39(3).

(range: 2.59−2.65 Å),[16] but compares well with that of 2.735(6) Å in the recently reported heteroleptic complex (**4**−H)CaI·(THF)$_2$.[17] Analogue Li, Na, and K complexes[18] generally show nonbonding contacts between the central carbon and the metal. The N−Ca distances in (**4**−H)$_2$Ca display a large discrepancy. Each ligand shows one short Ca−N bond [2.444(1) and 2.4582(9) Å] and a somewhat longer Ca−N bond [2.614(1) and 2.679(1) Å]. The shorter Ca−N bond distances compare well to those in (**4**−H)CaI·(THF)$_2$ (average 2.457 Å).[17] The longer Ca−N contacts must be due to the large steric bulk of two tridentate bis(iminophosphorane)methanide ligands coordinating at a common metal center (this is confirmed by calculations; vide infra)

Whereas reaction of **4**−H_2 with a calcium amide only led to mono-deprotonation, reaction with the more basic (*p*-*t*Bu-benzyl)$_2$Ca·(THF)$_4$ gave at elevated temperatures clean conversion to **4**−Ca (Scheme 1). This extremely air-sensitive calcium methandiide crystallized as a dimer with crystallograpic C_2-symmetry (Figure 2). The doubly deprotonated carbons bridge the Ca^{2+} ions symmetrically. Two additional chelating N−Ca bonds extend the total coordination number of Ca^{2+} to four. The rather wide N−Ca−N′ angle of 156.37(8)° causes a large void in the metal coordination sphere. This open space is shielded by the Me_3Si substituents, but no obvious agostic Me···Ca interactions are observed [the shortest Ca···H contact measures 3.00(4) Å]. The average Ca−C bond length of 2.551(3) Å is considerably shorter than that in (**4**−H)$_2$Ca and is in the lower range of Ca−C bond lengths observed in bridging benzylides (range 2.54−2.62 Å)[19] or acetylides [2.536(8) Å].[20] It is longer than the Ca−C bond of 2.459(9) Å in [(Me_3-

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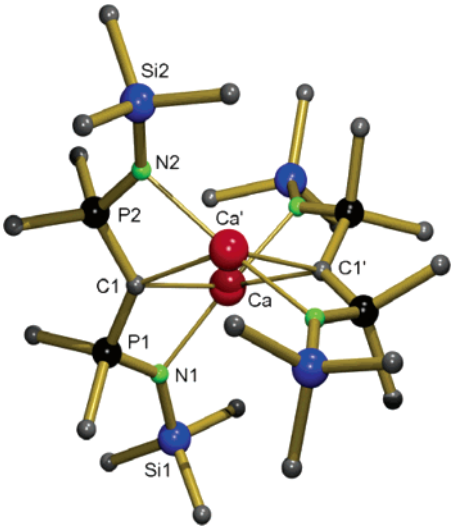


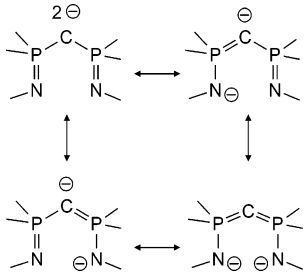
Figure 2. The crystal structure of [**4**−Ca]$_2$; for clarity all hydrogens and all phenyl atoms (except C_{ipso}) have been omitted. Selected bond distances (Å) and angles (deg): Ca−C1, 2.558(3); Ca−C1′, 2.543(2); Ca−N1, 2.304(2); Ca−N2, 2.307(2); C1···C1′, 3.853(3); Ca···Ca′, 3.323(2); C1−Ca−N1, 67;14(8); C1−Ca−N2, 66.62(7); C1−Ca−C1′, 98.11(8).

Si)$_3$C]$_2$Ca in which the Ca^{2+} is only two-coordinate.[21] The Ca−N bonds in [**4**−Ca]$_2$ (average 2.306(2) Å) are considerably shorter than the Ca−C bonds. A similar observation has been made in the analogue dilithium compound **4**−Li$_2$ (Table 1). This discrepancy between metal−N and metal−C distances decreases in an isostructural chromium complex [**4**−Cr]$_2$[22] and inverts for the analogue Pb^{II} dimer [**4**−Pb]$_2$.[15] The ratio of the metal−N and metal−C bond lengths apparently increases with increasing covalency of the ligand−metal bond: [**4**−Ca]$_2$ → [**4**−Cr]$_2$ → [**4**−Pb]$_2$. An analogue relationship has been observed in a series of metal complexes containing the C,N-ligand (2-pyridyl)(Me$_3$Si)$_2$C$^-$.[23]

Complex [**4**−Ca]$_2$ dissolves well in C_6D_6. The ^{13}C NMR chemical shifts for the central carbon is observed as a triplet at 47.7 ppm with $^1J_{P-C}$ = 78.0 Hz. Since this carbon seems to be NMR silent for the dimers [**4**−Li$_2$]$_2$, [**4**−Cr]$_2$, and [**4**−Pb]$_2$, no comparisons can be made. The phenyl groups in the Ph$_2$P unit are inequivalent in the solid-state structure, and also in solution two sets of signals are observed. Coalescence of the signals in the ^{1}H NMR spectrum occurs at 75 °C ($\Delta G^{\ddagger}$ = 16.9 kcal mol^{-1}). Exchange of both phenyl groups probably proceeds by a twist of the tridentate ligand in respect to the Ca···Ca axis. Stepwise addition of THF likewise results in line broadening; in pure THF, coalescence of the two sets of phenyl signals is observed already at room temperature. This is presumably due to exchange of the dimer [**4**−Ca]$_2$ with a THF-solvated monomer: **4**−Ca·(THF)$_2$. Attempts to crystallize this proposed monomeric calcium carbene failed on account of the very high solubility of **4**−Ca in the presence of THF.

The nature of the carbon−metal bond in complexes containing the dianionic ligand **4**$^{2-}$ has been the subject of debate. Description of the Sm−C contact in **4**−Sm(NCy$_2$)·THF as a double bond was disputed on the basis of bond length: the Sm−C bond distance falls well within the range for common

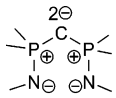
Scheme 2



Sm−C σ-bonds.[24] Likewise, the P−C and P−N bond distances within the ligand framework suggest extensive delocalization of π-electron density from the central carbon to the terminal nitrogen atoms (Scheme 2).

The Ca−C bond in [**4**−Ca]$_2$, which might be considered long for the unprecedented $R_2C^{2-}Ca^{2+}$ contact, as well as the short Ca−N bonds also indicate such charge delocalization in the dimeric calcium carbene. This observation is enforced by changes in the ligand geometry upon gradual deprotonation (Table 1): P−C bonds shorten and P−N bonds elongate gradually along the line **4**−H$_2$ → (**4**−H)$_2$Ca → [**4**−Ca]$_2$. The P−C distances in [**4**−Ca]$_2$ compare well with those in the analogue dilithium compound **4**−Li$_2$; however, the P−N bonds are somewhat shorter in the calcium complex. The ligand geometry in [**4**−Ca]$_2$ is remarkably similar to that in the chromium dimer [**4**−Cr]$_2$, but compares less well to that in the more covalent [**4**−Pb]$_2$ for which charge delocalization might play a lesser role.

Although the above data seem to converge to the conclusion that the negative charge on the central carbon in [**4**−Ca]$_2$ is significantly delocalized, we like to stress the point that classical multiple bond indicators, such as bond lengths and angles, have very limited meaning for multiple bonds in which elements of the higher periods are involved.[25] Especially electrostatic contributions are often neglected in bond length/bond order correlations.[26] For example, short P−C bonds in the Wittig reagent have always been an argument for the ylene resonance structure R$_3$P═CH$_2$,[27] whereas it could be explained just as well by electrostatic bond shortening in the ylide resonance form R$_3$P$^+$CH$_2^-$.[26] A recent experimental charge-density analysis on an isolobal iminophosphorane showed that the latter dipolar resonance form, R$_3$P$^+$N(R′)$^-$, is dominant.[28] It would therefore be appropriate to include ylide and amide resonance structures, for which **5** is an extreme case, in the discussion on the charge distribution in [**4**−Ca]$_2$.



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To analyze the charge distribution in the calcium complexes described here, a DFT-calculational study with a high-quality basis set (triple-ζ valence plus an extended set of polarization

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Table 1. Comparison of the Molecular Geometries for Selected Bis(iminophosphorano)methane Derivatives; Average Bond Distances (Å) and Angles (deg) Are Given

complex		M–C	M–N	P–C	P–N	P–C–P	C–P–N
4−H_2	exp[48]	−	−	1.825(1)	1.536(2)	124.9(2)	115.1(1)
	calc[a]			1.872	1.583	124.7	113.2
(**4**−H)$_2$Ca	exp	2.765(1)	2.451(1)/2.647(1)	1.739(1)	1.592(1)	125.40(7)	110.76(5)
	calc[a]	2.842	2.580/2.750	1.775	1.632	125.0	109.9
[**4**−Ca]$_2$	exp	2.551(3)	2.306(2)	1.706(2)	1.605(2)	128.7(1)	108.3(1)
	calc[a]	2.672	2.420	1.746	1.657	127.3	107.3
[**4**−Li_2]$_2$	exp[10]	2.395(7)	2.111(6)	1.694(5)	1.630(3)	132.6(3)	104.4(1)
[**4**−Cr]$_2$	exp[22]	2.141(5)	2.092(5)	1.713(6)	1.604(5)	132.0(3)	105.0(3)
[**4**−Pb]$_2$	exp[15]	2.477(7)	2.647(6)	1.753(5)	1.588(6)	129.0(4)	106.1(3)
6−H_2	calc[b]	−	−	1.822	1.567	111.8	107.7
(**6**−H)$_2$Ca	calc[b]	3.231	2.414	1.725	1.608	125.9	112.4
6−Ca	calc[b]	2.454	2.299	1.684	1.657	123.4	109.8
[**6**−Ca]$_2$	calc[b]	2.589	2.351	1.705	1.631	121.6	108.0

[a] B3LYP/TZVP. [b] B3LYP/TZVPP.

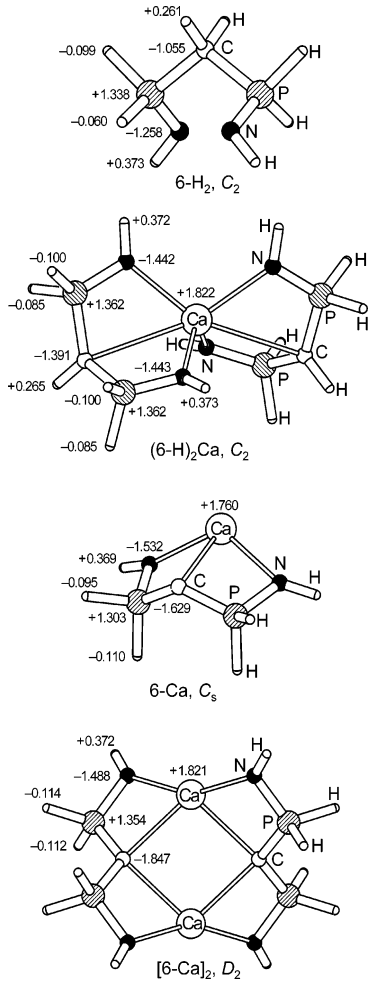


Figure 3. Ab initio structures (B3LYP/TZVPP) and NPA charges[29] of simple model systems.

functions) on simple model systems was employed. The optimized structures of **6**−H_2, (**6**−H)$_2$Ca, **6**−Ca, and [**6**−Ca]$_2$ are all true minima on the potential energy surface (Figure 3).

Comparison of the calculated simplified model systems with the crystal structures (Table 1) shows that the metal coordination geometry for [**4**−Ca]$_2$ is remarkably well reproduced by the simple model [**6**−Ca]$_2$ in which all substituents have been replaced by hydrogens. The calculated geometry for (**6**−H)$_2$Ca compares less well with the crystal structure of (**4**−H)$_2$Ca. Both N−Ca bonds are now of similar length (2.414 Å) and comparable to the shortest Ca−N bond in the crystal structure. The Ca−C contact in the calculated structure is significantly longer, likely on behalf of the two short Ca−N bonds. These discrepancies are likely due to loss of steric effects in the simple model system. The calculated geometries of the ligands itself compare well with those in the experimentally known complexes (apart for some of the bond angles which are much more sensitive to steric effects). More important, the same tendencies as in the crystal structures are observed (vide supra).

Calculated atomic and group charges (by natural population analysis, NPA)[29] are given in Figure 3 and Table 2, respectively.

Table 2. NPA Group Charges (i.e., the Charge of the Heavy Atom + That of the Attached Hydrogens)

complex	CH_x	PH_2	NH
6−H_2	−0.533	+1.179	−0.912
(**6**−H)$_2$Ca	−1.126	+1.177	−1.070
6−Ca	−1.629	+1.098	−1.163
[**6**−Ca]$_2$	−1.847	+1.128	−1.116

The following major conclusions can be drawn:

(i) As the charges on Ca vary between +1.760 and +1.822, the Ca-ligand bond is highly ionic.

(ii) Group charges on the PH_2 units (Table 2) are rather constant and highly positive; this suggests that stabilization by negative hyperconjugation in the anions **6**$^-$ and **6**$^{2-}$ only plays a minor role.

(iii) The ligand **6**−H_2 already shows a high electron density on the CH_2 group (−0.533) and particularly on the NH group (−0.912); this underscores the importance of the dipolar resonance form P^+N^-.

(iv) The negative charge on the carbon increases considerably upon stepwise deprotonation, whereas that on the NH group only slightly increases. Therefore, **6**−Ca can be considered a true methandiide with strong electrostatic Ca−C bonding. Stabilization of the high negative charge on the central carbon proceeds mainly through electrostatic interactions with the H_2P^+ units and to a much lesser extent through negative hyperconjugation or electron delocalization. The short P−C distances in **6**−Ca can also be explained by H_2P^+−C^{2-} attraction. Elongation

(29) Mulliken population analyses fail to give a useful and reliable characterization of the charge distribution in many cases, especially when highly ionic compounds and diffuse basis functions are involved. Charges calculated according to the Natural Population Analysis (NPA) do not show these deficiencies and are relatively basis set independent: (a) Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735. (b) Reed, A. E.; Curtis, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.

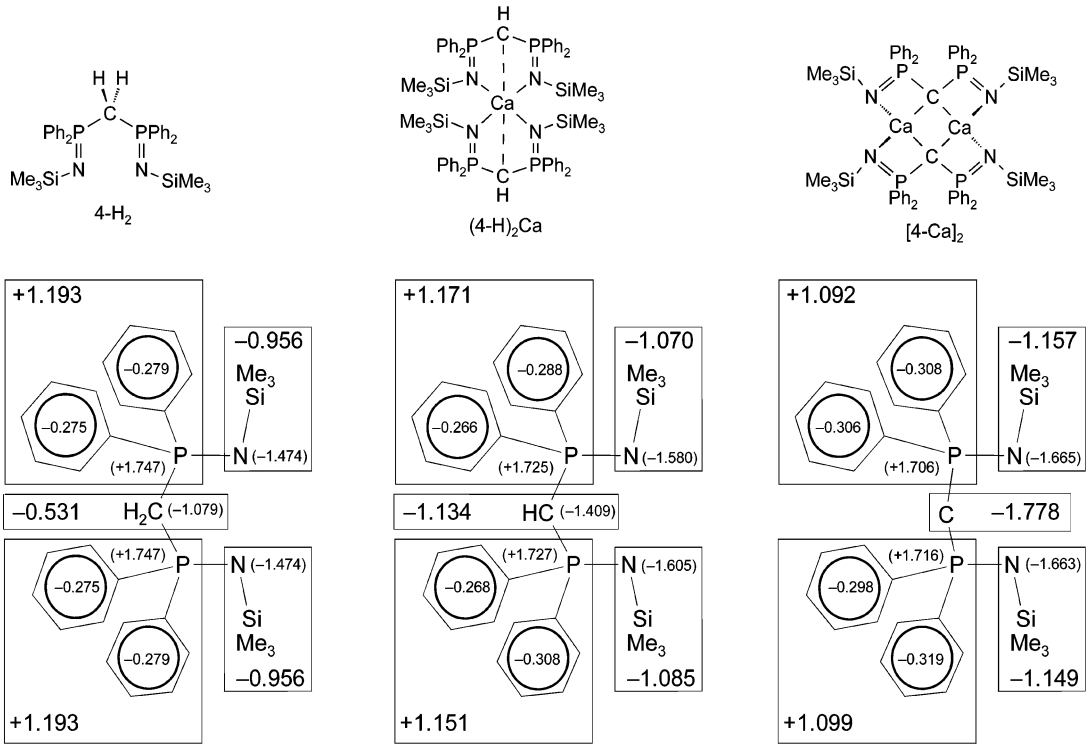


Figure 4. Calculated NPA charges[29] in the molecules **4**−H_2, (**4**−H)$_2$Ca, and [**4**−Ca]$_2$ systems (B3LYP/TZVP); heavy-atom charges in parentheses, Ph group charges in circles and group charges in frame corners.

of the P−N bonds along the row **6**−H_2, (**6**−H)$_2$Ca, and **6**−Ca can be explained by increased $N^{\delta-}\cdots C^{\delta-}$ repulsion in this series.

(v) Interestingly, formation of a dimer increases the negative charge on the bridging carbon from −1.629 to −1.847, whereas the electron density on the NH group decreases. Apparently, the contact of the bridging carbon with two positively charged Ca^{2+} ions results in localization of electron density on this atom. The opposite has been observed in an electron density analysis of [**4**−Li_2]$_2$: a charge of −1.79 was calculated for the central carbon in a monomeric model complex, whereas the electron density on carbon decreased considerably to −1.25 upon dimerization.[30] This discrepancy is likely due to different modes of bridging. The much shorter $(P)_2C^{2-}\cdots{}^{2-}C(P)_2$ distance in [**4**−Li_2]$_2$ (3.367 Å) compared to that in [**6**−Ca]$_2$ (3.803 Å) leads to repulsion and electron delocalization.

To strengthen these conclusions based on simplified model systems, the complete molecular structures of **4**−H_2, (**4**−H)$_2$Ca, and [**4**−Ca]$_2$ were optimized with a simplified basis set composed of essentially the same triple-ζ valence basis and a reduced set of polarization functions. Their fully optimized geometries, which are all true minima, compare well with the analogue crystal structures (Table 1) but show in general somewhat longer bond distances. The inequivalent Ca−N bonds and the relatively long Ca−C bonds in (**4**−H)$_2$Ca are well-reproduced by calculation. The calculated NPA charges (Figure 4) compare well with those calculated for the simpler model systems: a high negative charge of −1.778 has been calculated for the carbene carbon. The only difference between charges in the simple model systems and those in the complete molecules are the charges on the P atoms, which are much more positive in the fully calculated structures. The lower positive charge on P in the model systems is due too the lower electronegativity of the H substituents when compared to that of Ph rings. Group charges in model systems (Table 2), however, show a striking resemblance with those in the complete molecules (Figure 4).

Although several metal carbenes with ligand **4** have been prepared, reports on their reactivity are mainly limited to the transition-metal species. Early transition metal carbenes react similar to Schrock carbenes, i.e. possess a nucleophilic carbon center.[13] On the other hand, a platinum carbene complex containing **4** displayed rather unusual reaction behavior and showed nucleophilic nitrogen centers.[31] We here present initial studies on the reactions of the early main group metal carbene [**4**−Ca]$_2$ with several unsaturated substrates (Scheme 3).

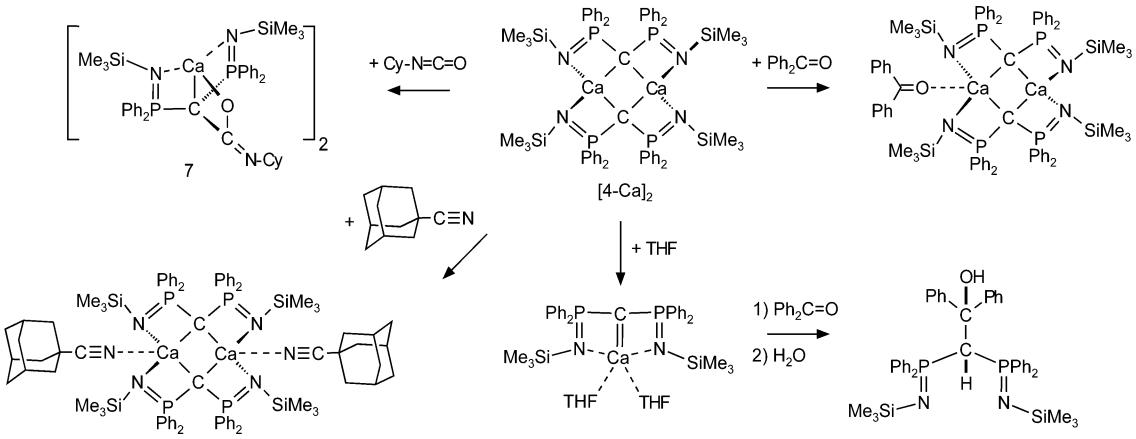
Addition of 2 equiv of benzophenone to a benzene solution of [**4**−Ca]$_2$ results in formation of colorless crystals, which were identified as the adduct [**4**−Ca]$_2$·O=C(Ph)$_2$. The crystal structure (Figure 5) shows a dimeric [**4**−Ca]$_2$ unit in which a benzophenone molecule fills the large void between the two nitrogen ligands, thus extending the coordination number for Ca1 to five. The coordination geometries for Ca1 and Ca2 can be described as distorted trigonal bipyrimidal and distorted tetrahedral, respectively. Coordination of benzophenone results in elongation of the Ca−C and Ca−N bonds involving Ca1; however, no activation of the C=O bond is observed.[32] Coordination of the benzophenone also gives rise to a tilting of the bisiminophosphorane ligands. This results in closing the void at Ca2: the rather large N−Ca−N′ angle in [**4**−Ca]$_2$ is

(30) Klobukowski, M.; Decker, S. A.; Lovallo, C. C.; Cavell, R. G. *J. Mol. Struct. (THEOCHEM)* **2001**, *536*, 189.

(31) Lin, G.; Jones, N. D.; Cossage, R. A.; McDonald, R.; Cavell, R. G. *Angew. Chem.* **2003**, *115*, 4188; *Angew. Chem., Int. Ed.* **2003**, *42*, 4054.

(32) The observed C=O bond length of 1.232(3) Å is comparable to its value of 1.23(1) Å in free benzophenone: Fleischer, E. B.; Sung, N.; Hawkinson, S. *J. Phys. Chem.* **1968**, *72*, 4311.

Scheme 3



decreased from 156.37(8)° to 147.54(6)° for Ca2 in [**4**−Ca]$_2$·O=C(Ph)$_2$. For that reason, benzophenone coordinates only to one of the two Ca^{2+} ions.

A benzene solution of the adduct [**4**−Ca]$_2$·O=C(Ph)$_2$ does not react further even under reflux conditions. Reaction of [**4**−Ca]$_2$ with benzophenone in THF at 60 °C, gave very slow conversion in several unidentified products. After aqueous workup, the alcohol $Ph_2C(OH)CH(Ph_2P{=}NSiMe_3)_2$ could be identified, i.e. the product of a [2 + 2]-cycloaddition. The final metathesis product, the alkene $Ph_2C{=}C(Ph_2P{=}NSiMe_3)_2$, was not observed in the reaction mixture. Apparently, the intermediate calcium alkoxide is rather stable against elimination of CaO. This is in contrast with the reactivity behavior of Schrock carbenes. Likewise, reaction of the comparable samarium bis-carbene $Sm[{=}C(Ph_2P{=}S)_2]_2^-$ with benzophenone gave after double [2 + 2]-addition a bicyclic intermediate, which already at room temperature reacted to give the expected alkene and samarium oxide.[33]

Reaction of [**4**−Ca]$_2$ with 2 equiv of adamantyl cyanide in benzene gave immediate precipitation of colorless crystals. The crystalline product was identified as the adduct [**4**−Ca]$_2$·(N≡C-adamantyl)$_2$ (Figure 6). This adduct consists of a dimeric unit, similar to that in reactant [**4**−Ca]$_2$, in which the coordination sphere of each calcium has been extended to five by coordination of adamantyl cyanide. The rather small spatial demand of the needlelike cyanide substituent allows for coordination of two Lewis base reactants at the carbene dimer. This cyanide adduct did not react further even under forcing reflux conditions in benzene or THF.

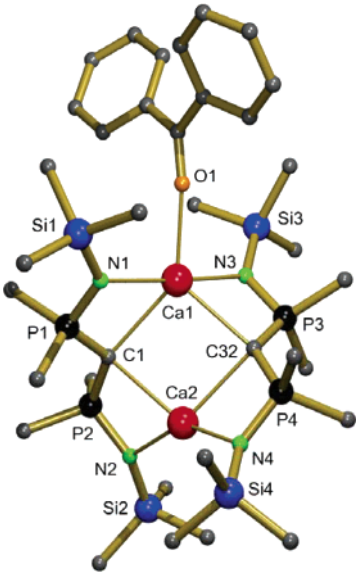


Figure 5. The crystal structure of [**4**−Ca]$_2$·O=C(Ph)$_2$; for clarity all hydrogens and all ring atoms in the Ph_2P units (except C_{ipso}) have been omitted. Selected bond distances (Å): Ca1−C1, 2.587(2); Ca1−C32, 2.566(2); Ca1−N1, 2.404(2); Ca1−N3, 2.392(2); Ca1−O1, 2.330(2); Ca2−C1, 2.552(2); Ca2−C32, 2.544(2); Ca2−N2, 2.325(2); Ca2−N4, 2.328(2); N1−Ca1−N3, 175.10(6); N2−Ca2−N4, 147.54(6).

The very sluggish reaction behavior of the dimeric calcium carbene [**4**−Ca]$_2$ prompted us to investigate its reaction with stronger unsaturated electrophiles. Addition of 2 equiv of cyclohexyl isocyanate to a benzene solution of [**4**−Ca]$_2$ at room temperature gave immediate precipitation of a colorless crystalline product. A single-crystal structure determination (Figure 7) revealed clean addition of the carbene to the isocyanate functionality (**7**). This results in a bowl-like dianionic tetradentate ligand that encapsulates the Ca^{2+} ion by bonding through both imine functionalities, the negatively charged central carbon, and oxygen. The complex crystallizes as a dimer with bridging oxygens.

In contrast, reaction of (**4**−H)ZnMe with an isocyanate gave after cycloaddition a monoanionic tridentate ligand in which the isocyanate nitrogen chelates the metal.[34] Also, cycloaddition of **4**−$ZrCl_2$ and **4**−$HfCl_2$ with isocyanates gave products with metal chelation via nitrogen.[35] Intramolecular coordination via oxygen in the present complex is likely due to the bridging nature of this least sterically encumbered atom. The $CyNC(R)O^-$ unit in **7** binds in a bidentate fashion to the neighboring Ca^{2+} ion. The hybridization at the central carbon is closer to sp^2 than sp^3 [the sum of the valence angles at C1 is 349.6(1)°]. Despite this near planarity, the Ca−C bond of 2.753(2) Å is rather long yet comparable to the formal Ca−C single bond in (**4**−H)$_2$Ca.

Conclusions

We present here the first molecular structure of an alkaline-earth-metal carbene complex. This calcium bis(iminophosphorano)methandiide chelate complex crystallizes as a dimer in which the carbene carbons bridge the metal centers. Calcula-

(33) Cantat, T.; Jaroschik, F.; Nief, F.; Ricard, L.; Mézailles, N.; Le Floch, P. *Chem. Commun.* **2005**, 5178.
(34) Kasani, A.; McDonald, R.; Cavell, R. G. *Organometallics* **1999**, *18*, 3775.
(35) Kamalesh Babu, R. P.; McDonald, R.; Cavell, R. G. *Organometallics* **2000**, *19*, 3462.

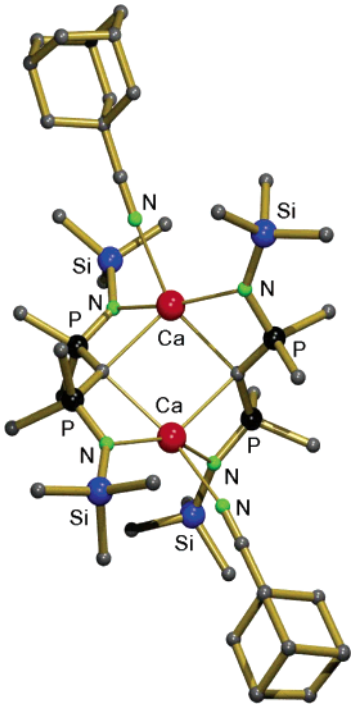


Figure 6. The crystal structure of [**4**−Ca]$_2$·(N≡C-adamantyl)$_2$; for clarity all hydrogens and all phenyl atoms (except C_{ipso}) have been omitted. Due to poor crystal quality, no detailed geometry is discussed. Average bond distances (Å): Ca−C, 2.58(2), Ca−N(ligand), 2.40(1); Ca−N(cyanide), 2.53(2).

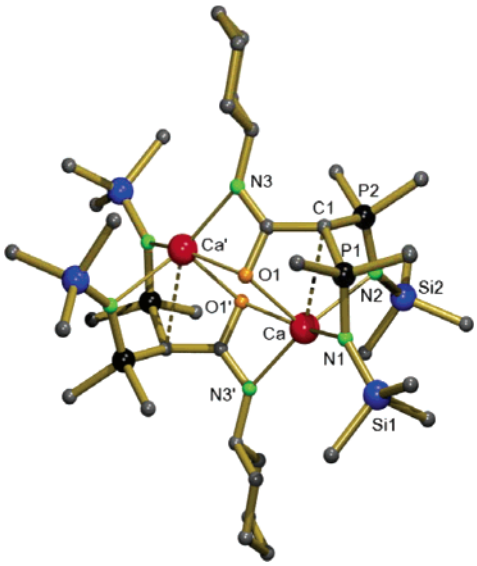


Figure 7. The crystal structure of the dimer [**7**]$_2$; for clarity all hydrogens and all phenyl atoms (except C_{ipso}) have been omitted. Selected bond distances (Å): Ca−O1, 2.347(1); Ca−N1, 2.427(2); Ca1−N2, 2.455(2); Ca1−C1, 2.753(2); Ca1−O1′, 2.366(2); Ca1−N3′, 2.434(2).

tional studies on simple model systems as well as on the complete molecules show that successive deprotonation of bis-(iminophosphorano)methane results mainly in an increase of negative charge on the carbene carbon, whereas the charges on the terminal nitrogens are much less affected. This indicates that charge delocalization from carbon to nitrogen is less important. The calcium carbene should therefore be described as a methandiide in which dipolar resonance structures such as **5** play an important role. Stabilization of the high negative charge on the central carbon proceeds through electrostatic interactions with the Ph_2P^+ units rather than through negative hyperconjugation or electron delocalization.

These stabilized calcium carbene complexes react poorly with ketones and cyanides. In fact, several stable intermediate coordination complexes of the dimeric calcium carbene and the reactants could be isolated and characterized. The nucleophilicity of the bis(iminophosphorano)methandiide dianion is apparently tamed by electrostatic interaction of the negatively charged carbene carbon with the two adjoining positively charged phosphonium centers. The rather poor accessibility of the carbene carbon in the dimer might also influence its reactivity. The dimeric calcium carbene reacted smoothly with the stronger electrophilic cyclohexyl isocyanate, yielding the [2 + 2]-cycloaddition product.

Experimental Section

All experiments were carried out using standard Schlenk techniques and freshly dried solvents. The calcium bis(iminophosphorano)-methandiide [**4**−Ca]$_2$ is extremely moisture sensitive and very reactive toward protic species. Therefore, solvents used for this compound were stored over Na/K alloy. The following compounds were prepared according to literature: bis(*N*-Me_3Si-imino-diphenylphosphorano)-methane (**4**−H_2),[36] bis[*p*-*t*Bu-benzyl]calcium·(THF)$_4$,[16c] and Ca-[N($SiMe_3$)$_2$]$_2$·(THF)$_2$.[37]

Synthesis of (4-H)$_2$Ca. Ca[N($SiMe_3$)$_2$]$_2$·(THF)$_2$ (404 mg, 0.80 mmol) and **4**−H_2 (813 mg, 1.45 mmol) were dissolved in 5 mL of benzene. The yellow solution was stirred for 2 h at 60 °C, after which all solvents were removed under vacuum. Drying the resulting colorless slime under vacuum (40 °C, 1 Torr, 15 min) gave a colorless foam. The foam was washed twice with 5-mL portions of hexane and was dried again under vacuum (40 °C, 1 Torr, 30 min). The resulting colorless powder (720 mg, 86%) is essentially pure product. Crystals for X-ray diffraction were obtained in the form of large blocks by reducing the original reaction mixture to half its volume and slowly cooling to 7 °C. Mp: 189 °C. Anal. Calcd for $C_{62}H_{78}CaN_4P_4Si_4$ (M = 1155.66): C, 64.44; H, 6.80. Found: C, 64.24; H 6.96. ^{1}H NMR (300 MHz, C_6D_6, 20 °C): δ 0.34 (s, 36 H, Me_3Si), 2.00 (s, 2 H, HCP_2), 6.93−6.95 (24 H, phenyl), 7.57−7.61 (16 H, phenyl). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 20 °C): δ 5.96 (s, Me_3Si), 23.4 (t, ^1J(P,C) = 108.5 Hz, PCP), 127.5 (t, $^3J_{P-C}$ = 5.9 Hz, *m*-Ph), 129.4 (s, *p*-Ph), 131.9 (t, $^2J_{P-C}$ = 5.1 Hz, *o*-Ph), 139.5 (dd, $^1J_{P-C}$ = 90.3 Hz, $^3J_{P-C}$ = 4.1 Hz, *ipso*-Ph).

Synthesis of [4-Ca]$_2$. An orange solution of bis-(*p*-*t*Bu-benzyl)-calcium·(THF)$_4$ (187 mg, 0.30 mmol) and **4**−H_2 (289 mg, 0.25 mmol) in 5 mL of benzene was stirred for 2 h at 60 °C. After removal of all solvents under vacuum, an orange foam resulted. This was dried under vacuum (50 °C, 1 Torr, 20 min), washed twice with 3-mL portions of pentane, and again dried under vacuum (50 °C, 1 Torr, 15 min). The resulting off-white powder (250 mg, 84%) is essentially pure product. Crystalization from hot hexane gave colorless blocks suitable for X-ray diffraction. Mp: 277 °C (dec). Anal. Calcd for $C_{62}H_{76}Ca_2N_4P_4Si_4$ (M = 1193.72): C, 62.38; H, 6.42. Found: C, 62.37; H, 6.71. ^{1}H NMR (500 MHz, C_6D_6, 20 °C): δ −0.03 (s, 18 H, Me_3Si), 6.89 (t, $^3J_{H-H}$ = 7.5 Hz, 4 H, *m*-Ph$_a$), 7.00 (t, $^3J_{H-H}$ = 7.5 Hz, 2 H, *p*-Ph$_a$), 7.18 (t, $^3J_{H-H}$ = 7.5 Hz, 2 H, *p*-Ph$_b$), 7.26 (t, $^3J_{H-H}$ = 7.5 Hz, 4 H, *m*-Ph$_b$), 7.33 (dd, $^3J_{H-H}$ = 6.5 Hz, $^3J_{P-H}$ = 11.3 Hz, 4 H, *o*-Ph$_a$), 7.59 (dd, $^3J_{H-H}$ = 6.5 Hz, $^3J_{P-H}$ = 11.3 Hz, 4 H, *o*-Ph$_b$). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6, 20 °C): δ 3.6 (s, Me_3Si), 47.7 (t, $^1J_{P-C}$ = 78 Hz, PCP), 127.6 (t, $^3J_{P-C}$ = 5.5 Hz, *m*-Ph), 128.0 (t, $^3J_{P-C}$ = 5.5 Hz, *m*-Ph), 129.0 (s, *p*-Ph), 129.1 (s, *p*-Ph), 130.9 (t, $^2J_{P-C}$ = 5.1 Hz, *o*-Ph), 132.0 (t, $^2J_{P-C}$ = 5.1 Hz, *o*-Ph), 141.2 (m, AXX′-spin system; *ipso*-Ph), 143.4 (m, AXX′-spin system; *ipso*-Ph). ^{31}P{^{1}H} NMR (202.3 MHz, C_6D_6, 20 °C): δ = 10.09 (s, PCP).

(36) Appel, R.; Ruppert, I. *Z. Allg. Anorg. Chem.* **1974**, *406*, 131.
(37) Westerhausen, M. *Inorg. Chem.* **1991**, *30*, 96.

Synthesis of [4-Ca]$_2$·O=C(Ph)$_2$. Addition of benzophenone (7.8 mg, 0.049 mmol) to a yellow solution of [**4**−Ca]$_2$ (29.2 mg, 0.024 mmol) in 0.5 mL of benzene gave an orange solution which was concentrated to 50% of its original volume. Large crystalline blocks formed overnight (13.0 mg, 38%). Mp: 145 °C (dec). Anal. Calcd for $C_{75}H_{86}Ca_2N_4OP_4Si_4$ (M = 1375.95): C, 65.47; H, 6.30. Found: C, 65.11; H, 6.13. ^{1}H NMR (300 MHz, C_6D_6, 20 °C): δ −0.12 (s, 18 H, Me_3Si), 6.98 (t, $^3J_{H-H}$ = 7.1 Hz, 4 H, *m*-Ph$_a$), 7.01−7.19 (m, 7 H, *p*-Ph$_a$, *p*-Ph$_b$, *m*,*p*-Ph of Ph_2CO), 7.23 (t, $^3J_{H-H}$ = 7.1 Hz, 4 H, *m*-Ph$_b$), 7.60 (dd, $^3J_{H-H}$ = 6.1 Hz, $^3J_{P-H}$ = 11.5 Hz, 4 H, *o*-Ph$_a$), 7.70 (d, $^3J_{H-H}$ = 7.4 Hz, 2H, *o*-Ph of Ph_2CO), 7.78 (dd, $^3J_{H-H}$ = 6.1 Hz, $^3J_{P-H}$ = 11.5 Hz, 4 H, *o*-Ph$_b$). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 20 °C): δ 4.3 (s, Me_3Si), 45.7 (t, $^1J_{P-C}$ = 75.0 Hz, PCP), 127.3 (t, $^3J_{P-C}$ = 5.0 Hz, *m*-Ph), 128.0 (t, $^3J_{P-C}$ = 5.5 Hz, *m*-Ph), 128.6 (br s, *p*-Ph and *m*-Ph of Ph_2-CO), 131.0 (s, *o*-Ph of Ph_2CO), 131.4 (t, $^2J_{P-C}$ = 4.8 Hz, *o*-Ph), 132.5 (t, $^2J_{P-C}$ = 4.8 Hz, *o*-Ph), 133.0 (s, *p*-Ph of Ph_2CO), 137.8 (s, *ipso*-Ph of Ph_2CO), 142.2 (m, AXX′-spin system; *ipso*-Ph), 144.1 (m, AXX′-spin system; *ipso*-Ph), 195.7 (s, Ph_2C=O).

Synthesis of [4-Ca]$_2$·(N≡C-adamantyl)$_2$. A solution of [**4**−Ca]$_2$ (185 mg, 0.16 mmol) and adamantyl cyanide (50 mg, 0.31 mmol) in 3 mL of benzene was stirred for 15 min. Removal of all solvent resulted in a white powder. This was washed once with 1 mL of pentane and dried under vacuum (50 °C, 1 Torr, 15 min). The resulting white powder (122 mg, 52%) is essentially pure product. Crystals for X-ray diffraction were obtained by slowly cooling a hot benzene solution of the product to room temperature. Mp: 210 °C. Anal. Calcd for $C_{84}H_{106}Ca_2N_6P_4Si_4$ (M = 1516.22): C, 66.54; H, 7.05. Found: C, 66.17; H, 7.04. ^{1}H NMR (300 MHz, C_6D_6, 20 °C): δ 0.08 (s, 18 H, Me_3Si), 1.27 (br, 6 H, adamantyl), 1.52 (br, 3 H, adamantyl), 1.80 (d, $^3J_{H-H}$ = 2.5 Hz, 6 H, adamantyl), 6.97 (t, $^3J_{H-H}$ = 7.1 Hz, 4 H, *m*-Ph$_a$), 7.07 (t, $^3J_{H-H}$ = 7.1 Hz, 2 H, *p*-Ph$_a$), 7.21 (t, $^3J_{H-H}$ = 7.1 Hz, 2 H, *p*-Ph$_b$), 7.34 (t, $^3J_{H-H}$ = 7.3 Hz, 4 H, *m*-Ph$_b$), 7.45 (dd, $^3J_{H-H}$ = 6.6 Hz, $^3J_{P-H}$ = 11.5 Hz, 4 H, *o*-Ph$_a$), 7.73 (dd, $^3J_{H-H}$ = 6.5 Hz, $^3J_{P-H}$ = 11.5 Hz, 4 H, *o*-Ph$_b$). ^{13}C-{^{1}H} NMR (75 MHz, C_6D_6, 20 °C): δ 4.5 (s, Me_3Si), 27.1 (s, adamantyl), 30.3 (s, adamantyl), 35.6 (s, adamantyl) 39.5 (s, adamantyl), 47.0 (t, $^1J_{P-C}$ = 78.0 Hz, PCP), 125.1 (s, C≡N), 127.3 (t, $^3J_{P-C}$ = 5.0 Hz, *m*-Ph), 127.7 (t, $^3J_{P-C}$ = 5.0 Hz, *m*-Ph), 128.2 (s, *p*-Ph), 128.3 (s, *p*-Ph), 131.5 (t, $^2J_{P-C}$ = 4.8 Hz, *o*-Ph), 132.6 (t, $^2J_{P-C}$ = 4.8 Hz, *o*-Ph), 143.1 (m, AXX′-spin system; *ipso*-Ph), 144.8 (m, AXX′-spin system; *ipso*-Ph).

Synthesis of 7. [**4**−Ca]$_2$ (79.6 mg, 0.067 mmol) and cyclohexyl isocyanate (16.7 mg, 0.13 mmol) were dissolved in 0.5 mL of benzene. Crystallization of the product started after half an hour at room temperature. After 16 h the crystalline product was isolated and dried in a vacuum (50 °C, 1 Torr, 15 min). The resulting white powder (60.0 mg, 63%) is essentially pure product. Crystals for X-ray diffraction were obtained by slow cooling of a saturated benzene solution to room temperature. Mp: 87 °C. Anal. Calcd for $C_{76}H_{98}Ca_2N_6O_2P_4Si_4$ (M = 1444.02): C, 63.21; H, 6.84. Found: C, 62.90; H, 7.12. ^{1}H NMR (300 MHz, C_6D_6/THF-d_8, 20 °C): δ −0.01 (s, 18 H, Me_3Si), 0.72−0.9 (m, 3 H, Cy), 0.94−1.10 (m, 3 H, Cy), 1.16−1.28 (m, 2 H, Cy), 1.45−1.59 (m, 2H, Cy), 3.04 (quintet, $^3J_{H-H}$ = 6.5 Hz, 1 H, Cy), 6.76−6.86 (m, 6 H, *m*-Ph$_a$, *p*-Ph$_a$), 7.22 (t, $^3J_{H-H}$ = 7.0 Hz, 2 H, *p*-Ph$_b$), 7.32 (t, $^3J_{H-H}$ = 7.3 Hz, 4 H, *m*-Ph$_b$), 7.63 (dd, $^3J_{H-H}$ = 6.8 Hz, $^3J_{P-H}$ = 12.5 Hz, 4 H, *o*-Ph$_a$), 7.91 (dd, $^3J_{H-H}$ = 6.8 Hz, $^3J_{P-H}$ = 12.5 Hz, 4 H, *o*-Ph$_b$).

Crystal Structure Determination. Single crystals have been measured on a Siemens SMART CCD diffractometer. Structures have been solved and refined using the programs SHELXS-97 and SHELXL-97, respectively.[38] All geometry calculations and graphics have been performed with PLATON.[39] Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 603303-603304 and 614002-614004. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK [fax: (+44)1223−336−033; E-mail: deposit@ccdc.cam.ac.uk].

Crystal Data for (4-H)$_2$Ca. Measurement at −90 °C, Mo Kα, $2\theta_{max}$ = 69.6°, 209 015 reflections measured, 28 072 independent reflections (R_{int} = 0.042), 20 002 reflections observed with $I > 2\sigma(I)$, triclinic, space group $P\bar{1}$, a = 11.9706(2) Å, b = 14.8783(3) Å, c = 21.3712(4) Å, α = 77.791(1)°, β = 87.505(1)°, γ = 68.785(1)°, V = 3465.8(1) Å^3, formula $C_{62}H_{78}CaN_4P_4Si_4$·$(C_6H_6)_{0.5}$, Z = 2, R = 0.0426, wR2 = 0.1241, GOF = 1.091, ρ_{max} = 0.43 e Å^{-3}, ρ_{min} = −0.31 e Å^{-3}. Some hydrogen atoms have been located and were isotropically refined, and others have been placed on calculated positions and were refined in a riding mode.

Crystal Data for [4-Ca]$_2$. Measurement at −70 °C, Mo Kα, $2\theta_{max}$ = 52.8°, 41 184 reflections measured, 6866 independent reflections (R_{int} = 0.052), 4941 reflections observed with $I > 2\sigma(I)$, monoclinic, space group $C2/c$, a = 23.2067(5) Å, b = 12.2438(3) Å, c = 27.0581-(5) Å, β = 118.744(1)°, V = 6740.9(3) Å^3, formula $C_{31}H_{38}CaN_2P_2Si_2$, Z = 8, R = 0.0430, wR2 = 0.1102, GOF = 1.06, ρ_{max} = 0.29 e Å^{-3}, ρ_{min} = −0.29 e Å^{-3}. All hydrogens have been located and were isotropically refined.

Crystal Data for [4-Ca]$_2$·O=C(Ph)$_2$. Measurement at −70 °C, Mo Kα, $2\theta_{max}$ = 47.4°, 158 090 reflections measured, 13 878 independent reflections (R_{int} = 0.050), 11 701 reflections observed with $I > 2\sigma(I)$, triclinic, space group $P\bar{1}$, a = 14.0694(4) Å, b = 16.2726(5) Å, c = 20.5634(7) Å, α = 90.391(2)°, β = 92.101(2)°, γ = 102.574(2)°, V = 4591.4(2) Å^3, formula $C_{75}H_{86}Ca_2N_4OP_4Si_4$·$(C_6H_6)$, Z = 2, R = 0.0380, wR2 = 0.1054, GOF = 1.02, ρ_{max} = 0.26 e Å^{-3}, ρ_{min} = −0.24 e Å^{-3}. All hydrogen atoms have been placed on calculated positions and were refined in a riding mode. The asymmetric contains three benzene solvent molecules of which one was ordered and refined, whereas the other two were disordered and treated with the SQUEEZE procedure incorporated in PLATON.[39]

Crystal Data for [4-Ca]$_2$·(N≡C-adamantyl)$_2$. Only very thin platelike crystals (0.4 × 0.4 × 0.05 mm^3) that showed poor diffraction power could be obtained. Therefore, only the heteroatoms were refined anisotropically. The resulting structure determination shows high standard deviations in the geometrical parameters and only allows for a rough comparison with the other complexes. Measurement at −70 °C, Mo Kα, $2\theta_{max}$ = 32.6°, 250 139 reflections measured, 9167 independent reflections (R_{int} = 0.090), 8389 reflections observed with $I > 2\sigma(I)$, monoclinic, space group $C2/c$, a = 91.647(3) Å, b = 19.2995-(7) Å, c = 20.5818(4) Å, β = 100.1630(16)°, V = 35833(2) Å^3, formula $C_{84}H_{106}Ca_2N_6P_4Si_4$·$C_6H_6$, Z = 16, R = 0.0991, wR2 = 0.2412, GOF = 1.09, ρ_{max} = 1.00 e Å^{-3}, ρ_{min} = −0.50 e Å^{-3}. The long a-axis in the face-centered ac-plane has been checked in different crystals from different crystallization experiments. In all cases no other cell settings or higher symmetry could be found. The hydrogen atoms have been placed on calculated positions and were refined in a riding mode. The asymmetric unit contains two ordered benzene molecules. The adamantyl substituents in one of the complexes show rotational disorder that was resolved.

Crystal Data for 7. Measurement at −70 °C, Mo Kα, $2\theta_{max}$ = 53.4°, 41 876 reflections measured, 9711 independent reflections (R_{int} = 0.059), 7107 reflections observed with $I > 2\sigma(I)$, monoclinic, space group $P2_1/n$, a = 13.8153(4) Å, b = 17.5149(5) Å, c = 18.9903(4) Å, β = 91.418(2)°, V = 4593.7(2) Å^3, formula $C_{76}H_{98}Ca_2N_6O_2P_4Si_4$·$(C_6H_6)_3$, Z = 2, R = 0.0442, wR2 = 0.1180, GOF = 1.03, ρ_{max} = 0.38 e Å^{-3}, ρ_{min} = −0.39 e Å^{-3}. All hydrogen atoms have been placed on calculated positions and were refined in a riding mode. The asymmetric unit contains one and a half ordered benzene molecules.

Ab initio Calculations. All geometries were fully optimized within the designated symmetry constraints (using tight criteria) at the density functional theory level. Geometries for the model systems **6**−H$_2$, (**6**−

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H)$_2$Ca, **6**−Ca, and [**6**−Ca]$_2$ have been optimized by employing the B3LYP functional[40] and the Gaussian-type function basis set termed TZVPP composed of a triple-ζ valence quality set[41] combined with the polarization functions of Dunning's cc-pVTZ set[42] for all atoms except for Ca, where a 2p1d polarization function set[43] has been used. Frequency analyses, making use of analytical second derivatives, showed that all model compounds are true minima on this level of theory. Charges have been calculated by the NPA method.[29] All calculations for the model compounds have been performed with the Gaussian 03 program.[44]

The complete molecules and complexes **4**−H$_2$, (**4**−H)$_2$Ca, and [**4**−Ca]$_2$ have been optimized using their respective crystal structures as starting geometries and employing the BP86 exchange-correlation functional.[40a−d,g] First, structures were calculated using a small split-valence plus polarization functions basis set termed SV(P),[45] followed by numerical calculations of the frequencies employing analytical gradients in a central differences formula to verify that the obtained structures are minima. These structures in turn served as starting structures for geometry optimizations at the BP86/TZVP level, followed by determination of NPA atomic charges at the same level of theory. The valence orbital part of the TZVP basis set[41] is essentially the same as that of the TZVPP basis set described above with, however, a smaller set of polarization functions (1p instead of 2p1d for H and Ca, 1d instead of 2d1f for the other atoms) and a slighly different contraction scheme for the Si and P atoms (6111 for the p functions in TZVP, 51111 for TZVPP). The computation of geometries and frequencies was carried out with the Turbomole V 5.7 program package[46] in the framework of the "resolution-of-the-identity" (RI) approximation using the appropriate SV(P) and TZVP auxiliary basis sets.[47] Essentially the same approximation, also called the "density-fitting" (DF) approximation, has been used in the calculation of the NPA charges with the Gausssian 03 program, again using the appropriate TZVP auxiliary basis set, but now due to program limitations in an uncontracted version.

Atom coordinates, energies and frequencies of all optimized geometries are included in the Supporting Information.

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Supporting Information Available: Detailed information on the crystal structure determinations (CIF files and ORTEP-plots) and on the calculations (coordinates, energies, and frequency listings) as well as the full ref 44. This material is available free of charge via the Internet at http://pubs.acs.org.

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