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Articles

Isolation of an Intermediate in the Catalytic Trimerization of Isocyanates by a Monomeric Calcium Carbene with Chelating Iminophosphorane Substituents

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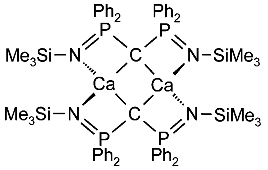
Twofold deprotonation of the bis-iminophosphorano ligand (DIPP−N=$(Ph_2)P)_2CH_2$ (DIPP = 2,6-diisopropylphenyl) by (*para*-*t*Bu-benzyl)$_2$Ca·(THF)$_4$ gave clean conversion to the monomeric THF adduct (DIPP−N=$(Ph_2)P)_2$CCa·(THF)$_2$ (**2**). This monomeric calcium carbene showed the same sluggish reactivity toward unsaturated electrophiles as the dimeric calcium carbene [(Me$_3$Si−N=(Ph_2)P)CCa]$_2$. No reaction was observed with 1-adamantyl cyanide, and with benzophenone a coordination complex was isolated: (DIPP−N=$(Ph_2)P)_2$CCa·(THF)·(O=CPh$_2$) (**4**). Reaction with a slight excess of cyclohexyl isocyanate gave the double-insertion product [(DIPP−N=PPh$_2$)$_2$C−C(O)−N(Cy)−C(O)−N(Cy)$^{2-}$][Ca^{2+}· (THF)$_{0.5}$] (**5**). The monomeric calcium carbene **2** is a very slow catalyst for the trimerization of cyclohexyl isocyanate but a much faster catalyst for the trimerization of phenyl isocyanate. Crystal structures for **2**, **4**, and **5** are presented.

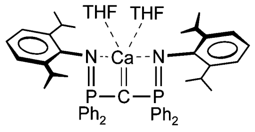
Introduction

Carbene complexes of the alkaline-earth metals, defined as Ae=CR$_2$ (Ae = alkaline-earth metal),[1] are extremely rare. The lighter members in the series, Be=CH$_2$ and Mg=CH$_2$, have been observed only trapped in a matrix at low temperature[2] or as very reactive ill-defined intermediates.[3] On account of the rather ionic nature of the Ae−C bond, which is especially distinctive for the heavier metals (Ca, Sr, and Ba),[4] alkaline-earth metal carbenes should be depicted as $H_2C^{2-}Ae^{2+}$. This explains the potentially high reactivity and complete lack of data for the heavier carbene complexes (Ae = Ca, Sr, and Ba).

Very recently we reported on the first molecular calcium carbene complex that crystallized as a C_2-symmetric dimer (**1**).[5] The bis-iminophosphorano ligand framework in this complex has been frequently used in the isolation of unusual metal−carbene complexes.[6] Although it has been argued that the π-electron density on the calcium carbene is considerably delocalized via resonance (Scheme 1), calculations on **1** (and also on its dilithio analogue) convincingly show that there is a rather high negative charge on the carbene carbon (ca. −1.78 in dimer **1**).[5,7] The charge distribution in the ligand compares well to the dipolar resonance form (**3**; Scheme 1), in which the carbene carbon is electrostatically stabilized by adjoining phosphonium centers.



1



2

The dimeric calcium carbene **1** exhibits rather tamed reactivity toward ketones and cyanides, as is evident from the isolation of its coordination complexes **1**·O=CPh$_2$ and **1**·(N≡C-adamantyl)$_2$.[5] Since this might be due to the dimeric nature of the complex, we set out to prepare a monomeric calcium carbene. It was reasoned that an increase of bulk of the substituents at the nitrogen atoms might prevent dimerization for steric reasons. Here we describe the syntheses and reactivity of a monomeric calcium carbene complex with sterically demanding 2,6-diisopropylphenyl substituents at the nitrogen atoms and a formal double bond between calcium and the carbene carbon (**2**).

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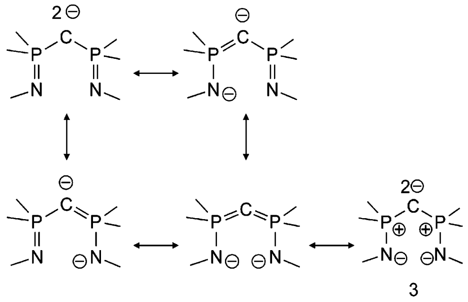
Scheme 1



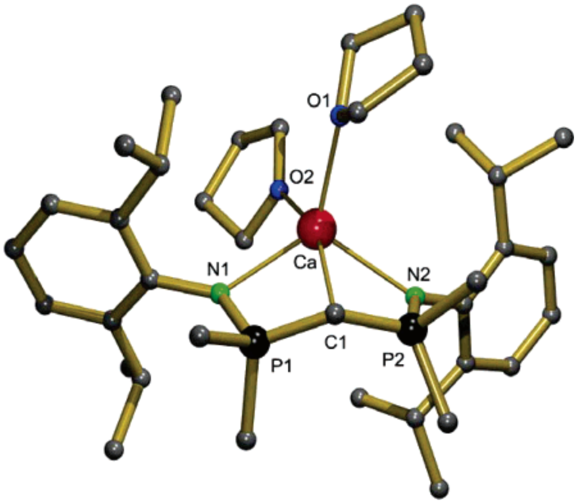


Figure 1. Crystal structure of **2**. For clarity all hydrogen atoms and phenyl substituents (except C_{ipso}) have been omitted. Selected bond distances and angles are given in Table 1.

Results and Discussion

Double deprotonation of (DIPP−N═(Ph$_2$)P)$_2$CH$_2$ (DIPP = 2,6-diisopropylphenyl) by (*para*-*t*Bu-benzyl)$_2$Ca·(THF)$_4$ gave a clean conversion to **2**, which could be isolated in 90% yield and was further purified by crystallization from a benzene/hexane mixture.

The crystal structure of **2** (Figure 1, Table 1) shows a monomeric calcium carbene with chelating iminophosphorano substituents and two additional THF ligands. The coordination geometry for Ca^{2+} can be described as square pyramidal with C1, N1, N2, and O2 in basal positions and O1 in apical position. The basal plane, however, is severely distorted from tetragonal symmetry due to the chelating nature of the three-coordinate ligand: the N1−Ca−N2 bite angle of 114.99(4)° differs substantially from linearity. The bis-iminophosphorano ligand in **2** displays an "open book" conformation that is typical for such monomeric carbene complexes and was also calculated for the monomeric model system (HN═PH$_2$)$_2$C═Ca.[5] The dihedral angle between the Ca−C−P−N planes of 45.4(1)° lies outside the 0−37.7° range observed in comparable Ti, Zr, Hf, and Sm complexes,[5a] however corresponds well to the value of 49.6° calculated for the model system. The Ca−C bond of 2.548(2) Å is very much comparable to that in the dimeric calcium carbene **1** (2.551(3) Å).[5] It is significantly longer than the Sm−C contact of 2.467(4) Å in a comparable Sm^{III}−carbene complex:[10] the difference of 0.081 Å is larger than the 0.042 Å difference in their ionic radii.[11] Interestingly, the N−Ca contacts in **2** have an average value of 2.359(1) Å and are considerably shorter than the Sm−N bonds (2.429(4) Å) in the comparable Sm^{III}−carbene complex. Apparently, the ratio of the metal−N and metal−C bond lengths increases with increasing covalency of the ligand−metal bond, a trend that has been observed not only in dimeric metal−carbene complexes[5] but also in a series of metal complexes containing the C,N-ligand (2-pyridyl)(Me$_3$Si)$_2$C$^-$.[12]

Table 1. Selected Bond Distances (Å) and Angles (degrees) for 2, 4, and 5

2					
Ca−N1	2.347(1)	P1−N1	1.636(1)	N1−Ca−N2	114.99(4)
Ca−N2	2.371(1)	P2−N2	1.636(1)	C1−Ca−N1	66.77(5)
Ca−C1	2.548(2)	P1−C1	1.660(2)	C1−Ca−N2	66.87(4)
Ca−O1	2.367(2)	P2−C1	1.657(2)	O1−Ca−O2	98.26(5)
Ca−O2	2.358(2)			C1−Ca−O1	100.59(5)
				C1−Ca−O2	159.57(5)
4					
Ca−N1	2.362(2)	P1−N1	1.639(2)	N1−Ca−N2	113.36(6)
Ca−N2	2.357(2)	P2−N2	1.627(4)	C1−Ca−N1	67.36(6)
Ca−C1	2.528(2)	P1−C1	1.669(2)	C1−Ca−N2	66.97(6)
Ca−O1	2.359(2)	P2−C1	1.674(2)	O1−Ca−O2	85.97(7)
Ca−O2	2.326(2)			C1−Ca−O1	110.26(6)
				C1−Ca−O2	163.39(7)
5					
Ca1−O1	2.278(2)	Ca2−O3	2.281(3)	O4−Ca1−N8	53.83(9)
Ca1−O2	2.417(2)	Ca2−O4	2.282(2)	O1−Ca1−N2	71.87(9)
Ca1−N2	2.426(3)	Ca2−N6	2.365(3)	O1−Ca1−O2	70.94(8)
Ca1−N8	2.501(3)	Ca2−O2	2.369(2)	O2−Ca1−O4	75.20(8)
Ca1−O4	2.436(2)	Ca2−N4	2.459(3)	O5−Ca1−O4	76.41(8)
Ca1−O5	2.401(2)			O2−Ca2−N4	55.48(9)
				O3−Ca2−N6	71.77(9)
				O3−Ca2−O4	73.29(9)
				O2−Ca2−O4	79.07(8)

Addition of adamantyl cyanide to a solution of **2** in benzene did not result in significant changes in the ^{1}H NMR spectrum, also not after prolonged heating to 60 °C. No adducts nor reaction products could be isolated or identified.

Addition of benzophenone to a solution of **2** in benzene resulted in the immediate appearance of a dark red color; however, no significant changes in the ^{1}H NMR spectrum were observed. Attempted crystallization from a concentrated benzene solution merely gave colorless crystals of **2**. Cooling a red toluene solution of **2** and benzophenone to −30 °C, however, yielded rose-red crystals of a complex with stoichiometry (DIPP−N═(Ph$_2$)P)$_2$CCa·(THF)·(benzophenone), **4**. A crystal structure determination revealed that the basal THF ligand in **2** has been replaced by a benzophenone ligand (Figure 2, Table 1). The latter substitution hardly affects the coordination geometry around the Ca^{2+} ion: all bonding distances and angles are rather similar. The C═O bond in the coordinated benzophenone ligand of 1.242(3) Å is only slightly elongated with respect to the C═O bond in free benzophenone (1.23(1) Å), which implies that the C═O bond is not significantly activated by coordination to Ca^{2+}. The red color, which persists in solution as well as in the solid state, likely arises from charge transfer to the benzophenone ligand. However, extensive ketyl character, like in the intensively blue calcium ketyl complex Ca^{2+}-(Ph$_2$CO$^{\bullet-}$)$_2$, is excluded: the calcium ketyl complex shows a

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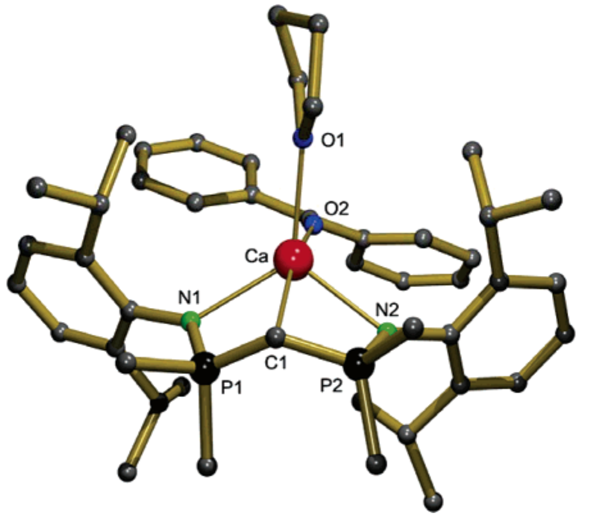


Figure 2. Crystal structure of **4**. For clarity all hydrogen atoms and phenyl substituents (except C_{ipso}) have been omitted. Selected bond distances and angles are given in Table 1.

much longer C−O bond length of 1.31(1) Å.[13] A similar observation has been recently described for another Ca^{2+}−benzophenone adduct.[14]

Addition of ca. 50% excess of highly electrophilic cyclohexyl isocyanate to a solution of **2** in benzene gave immediate reaction, and large colorless crystals suitable for a single-crystal X-ray diffraction study could be obtained. The crystal structure (Figure 3, Table 1) revealed an unexpected product (**5**) that is proposed to be formed by the reaction in Scheme 2. The [2+2]-cycloaddition of the Ca═C bond and the C═N bond gives an intermediate. This proposed monoinsertion product has been isolated in the reaction of the dimeric calcium carbene **1** with an isocyanate.[5] Reaction of its electron-rich imine functionality with a second isocyanate gives the double-insertion product **5**, a complex that can be envisioned as an intermediate in the anionic polymerization of isocyanates.[15]

The product crystallizes as a dimer in which the Ca^{2+} ions are bridged by two oxygen atoms (O2 and O4). The approximate C_i symmetry of this dimer is broken by coordination of a THF ligand (O5) to Ca1, whereas Ca2 remains unsolvated. Consequently, all bond distances to Ca1 are ca. 2−3% longer than the comparable bond distances to Ca2. On the other hand, bond distances and angles within the dianionic $[(DIPP{-}N{=}PPh_2)_2C{-}C(O){-}N(Cy){-}C(O){-}N(Cy)]^{2-}$ ligands are remarkably similar. Analysis of the ligand geometry (Figure 3b) allows conclusions regarding the charge distribution.

The average C1−C50 bond length of 1.448(5) Å is between that of a typical C−C single bond (1.53 Å) and a C═C double bond (1.32 Å).[16] This indicates extensive delocalization of electron density from C1 to O1. This enolate structure is confirmed by the elongated C50−O1 bond of 1.271(4) Å (the average C═O bond in amides is 1.23 Å)[16] and explains the lack of a C1−Ca contact in the present structure.

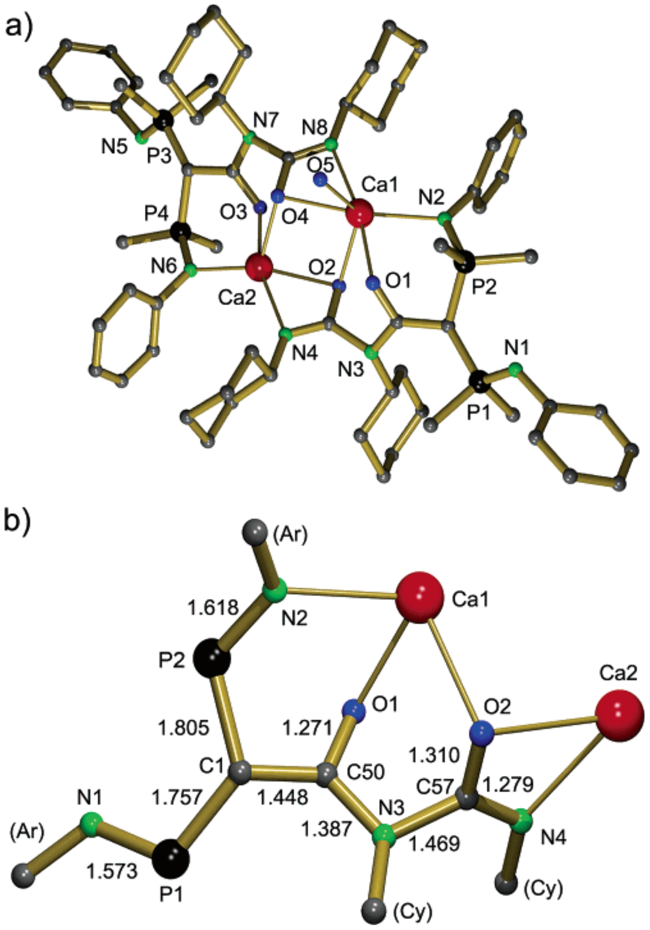
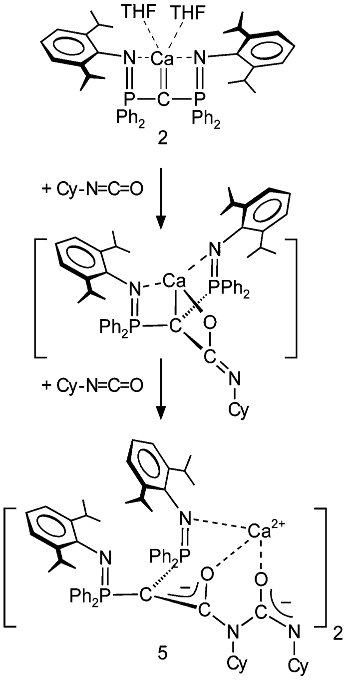


Figure 3. (a) Crystal structure of **5**; selected bond distances and angles are given in Table 1. For clarity all hydrogens, all phenyl atoms (except C_{ipso}), the *i*Pr substituents, and the carbons of THF have been omitted. (b) Partial structure of the ligand backbone with bond lengths (average values of the two ligands) indicated in Å.

Scheme 2



All three C−N bonds are of different length. The C50−N3 distance of 1.387(4) Å is somewhat longer than the average bond in an amide (1.35 Å),[16] whereas N3−C57 of 1.469(4) Å is considerably longer and C57−N4 of 1.279(4) Å substantially shorter. The latter short bond is comparable to the C═N double bond in imines (1.28 Å)[16] and should be explained by significant

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charge delocalization from the amide chain end N4 to O2, as confirmed by the long C57−O2 bond of 1.310(4) Å. This charge delocalization is enhanced by the fact that O2 bridges two positively charged Ca^{2+} ions. Less extreme delocalization was observed in the crystal structure of a Li−azaenolate, in which the C−N and C−O bond lengths measured 1.311(2) and 1.274(2) Å, respectively. The rather long N3−C57 bond of 1.469(4) Å can be explained by the orientation of the C50−N3−C_{Cy} plane with respect to the azaenolate plane (O2−C57−N4). The nearly perpendicular orientation (dihedral angle = 79.0(5)°) shuts off delocalization of the N3 p-lone pair with the azaenolate unit O2−C57−N4, whereas the coplanar arrangement of the C50−N3−C_{Cy} plane with the enolate plane C1−C50−O1 (dihedral angle = 13.3(5)°) allows conjugation of the N3 lone pair with the enolate system C1−C50−O1. Delocalization into a negatively charged enolate system is expected to be somewhat inhibited with respect to that in a ketone, which explains the slightly longer N3−C50 bond of 1.387(4) Å.

It should be noted that the torsion in the $(P_2)C-C(O)-N(Cy)-C(O)-N(Cy)$ chain is reminiscent of that in polyisocyanates, which form typical 8_3-helices.[17] The origin of such helical structures is O···O repulsion, which results in a twist between subsequent planar −[(R)N−C(O)]− units.[15]

The crystallization of **5** from a solution of **2** and cyclohexyl isocyanate is reproducible, and crystals can be obtained in 21% yield. Complex **5** represents a model for a growing chain during anionic polymerization of isocyanates with an organocalcium initiator. Its formation suggests a possible application of the calcium carbene as a polymerization catalyst for a secondary alkyl isocyanate, a monomer that due to its steric bulk cannot be polymerized.[18] Low-temperature (−80 °C) polymerization experiments, however, showed no reactivity of carbene **2** toward cyclohexyl isocyanate. At room temperature clean formation of cyclic trimers was observed. The formation of trimers at higher temperatures is typical and is due to back-biting in a growing polymer chain.[18b] Trimerization of cyclohexyl isocyanate with **2** is extremely slow: ca. 80% conversion is observed after one week at 5 mol % catalyst concentration. This is much slower than the catalytic trimerization of cyclohexylisocyanate with the recently introduced Arduengo carbene catalysts (99% conversion after 1 h; 1 mol % cat.).[19] However, smooth conversion is observed in the trimerization of phenylisocyanate with **2** (ca. 90% conversion after 3 h; 1 mol % cat.).

Intermediate **5**, which can be seen as an intermediate in the trimerization of cyclohexyl isocyanate, is not stable in solution and partially degrades into the monoinsertion product and Cy−NCO that trimerized under these conditions. The double-insertion product, however, is clearly shown by ESI-TOF-MS studies (see Experimental Section). The reversibility of isocyanate polymerization is well-established.[20]

Conclusions

The nuclearity of calcium carbene complexes can be controlled by the steric bulk of the ligands. Introduction of large substituents on the terminal nitrogen atoms in the bis-iminophosphorane ligand enabled isolation of monomeric calcium carbene complex **2**.

Monomeric calcium carbene **2** exhibits the same sluggish reaction behavior as the dimeric calcium carbene **1**, which allows isolation of coordination complexes such as **2**·O=CPh_2. Therefore, there is no clear dependence between the reactivity of the calcium carbene and its nuclearity.

The sluggishness of **2** as a catalyst in the trimerization of cyclohexyl isocyanate is probably the decisive factor that enabled the reproducible isolation of a well-defined intermediate in this process.

Experimental Section

All experiments were carried out using standard Schlenk techniques and freshly dried solvents. The calcium bis(iminophosphorano)methandiide **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 the literature: $H_2C(Ph_2P{=}N(DIPP))_2$[21] and bis[*p*-*t*Bu-benzyl]calcium·$(THF)_4$.[22] NMR spectra were measured on a Bruker DPX300 or DRX500 spectrometer. Crystals were measured on a Siemens Smart diffractometer with APEXII area detector system. ESI-TOF-MS studies have been performed with a Bruker BioTOF III spectrometer.

Synthesis of (DIPP−N=(Ph$_2$)P)$_2$CCa (2). $H_2C(Ph_2P{=}N(DIPP))_2$ (0.47 g, 0.64 mmol; DIPP = 2,6-diisopropylphenyl) and (*para*-*t*Bu-benzyl)$_2$Ca·$(THF)_4$[22] (0.44 g, 0.71 mmol) were dissolved in 6 mL of benzene. After stirring the orange solution for 1 h at room temperature all solvents were removed under vacuum. The resulting yellow foam was dried under vacuum (50 °C, 1 Torr, 20 min), washed three times with 4 mL portions of pentane, and again dried under vacuum (50 °C, 1 Torr, 20 min). The raw product, a light yellow powder (0.53 g, 90%), is essentially pure. Crystallization from a benzene/hexane mixture gave colorless blocks suitable for X-ray diffraction. Anal. Calcd for $C_{57}H_{70}CaN_2O_2P_2$ ($M = 917.23$): C, 74.64; H, 7.69. Found: C, 74.17; H, 7.75. Mp: 288−289 °C (dec). ^{1}H NMR (300 MHz, C_6D_6) δ: 0.94 (d, 12H, $^{3}J_{H-H} = 6.7$ Hz, CH*Me*$_2$), 1.09 (d, 12H, $^{3}J_{H-H} = 6.7$ Hz, CH*Me*$_2$), 3.96 (sept, $^{3}J_{H-H} = 6.7$ Hz, 4H, C*H*Me$_2$), 6.91−6.95 (m br, 12H, *m*-, *p*-Ph), 7.11 (t, $^{3}J_{H-H} = 7.5$ Hz, 4H, *m*-DIPP), 7.23 (d, $^{3}J_{H-H} = 7.5$ Hz, 2H, *p*-DIPP), 7.91 (dd, $^{3}J_{H-H} = 7.3$ Hz, $^{3}J_{P-H} = 12.5$ Hz, 8H, *o*-Ph). ^{13}C NMR (75 MHz, C_6D_6) δ: 26.6 (*i*Pr), 28.7 (*i*Pr), 120.9 (s, *p*-DIPP), 123.4 (s, *m*-DIPP), 126.9 (t, $^{3}J_{P-C} = 5.4$ Hz, *m*-Ph), 127.7 (s, *p*-Ph), 132.7 (t, $^{2}J_{P-C} = 4.6$ Hz, *o*-Ph), 142.9 (m, AXX′-spin system, *ipso*-Ph), 144.8 (t, $^{3}J_{P-C} = 3.0$ Hz, *o*-DIPP), 148.6 (t, $^{2}J_{P-C} = 5.6$ Hz, *ipso*-DIPP). The signal for the carbene carbon is not visible in the ^{13}C NMR spectrum (as for analogue carbenes complexes).[10,23]

Synthesis of (DIPP−N=(Ph$_2$)P)$_2$CCa·(THF)·(O=CPh$_2$) (4). Calcium carbene **2** (40.6 mg, 44.3 μmol) was dissolved in 0.5 mL of toluene to give an orange solution. Addition of benzophenone (8.0 mg, 43.9 μmol) resulted immediately in a color change to red. Reducing the volume to a fifth of the original volume and cooling the red solution to −30 °C gave crystals in the form of red blocks (39.0 mg, 87%). Anal. Calcd for $C_{66}H_{72}CaN_2O_2P_2$ ($M = 1027.35$): C, 77.16; H, 7.06. Found: C, 77.00; H, 7.36. ^{1}H NMR (300 MHz, C_6D_6) δ: 0.90 (br, 12H, CH*Me*$_2$), 0.95 (br, 12H, CH*Me*$_2$), 4.05 (br, 4H, C*H*Me$_2$), 6.88−6.96 (br, 16H, *m*- and *p*-Ph, *m*-benzophe-

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none), 7.06 (t, $^3J_{H-H}$ = 7.1 Hz, 2H, *p*-benzophenone), 7.17 (br, 4H, *p*-DIPP), 7.25 (d, $^3J_{H-H}$ = 7.2 Hz, 4H, *m*-DIPP), 7.36 (br, 4H, *o*-benzophenone), 7.99 (br, 8H, *o*-Ph). ^{13}C NMR (75 MHz, C_6D_6) δ: 26.5 (*i*Pr), 28.6 (*i*Pr), 120.6 (s, *p*-DIPP), 123.4 (s, *m*-DIPP), 126.8 (t, $^3J_{P-C}$ = 5.4 Hz, *m*-Ph), 127.7 (s, *p*-Ph), 128.5 (s, *m*-benzophenone), 131.6 (s, *o*-benzophenone), 132.7 (br s, *o*-Ph), 134.2 (s, *p*-benzophenone), 143.0 (m, AXX′-spin system, *ipso*-Ph), 144.5 (s, *ipso*-benzophenone), 144.8 (d, $^2J_{P-C}$ = 2.5 Hz, *o*-DIPP), 148.8 (br s, *ipso*-DIPP), 202.9 (s, CO). The signal for the carbene carbon is not visible in the ^{13}C NMR spectrum (as for analogue carbene complexes).[10,23]

Synthesis of [(DIPP−N═PPh$_2$)$_2$C−C(O)−N(Cy)−C(O)−N(Cy)$^{2-}$][Ca^{2+}·(THF)$_{0.5}$] (5). Calcium carbene **2** (0.15 g, 0.16 mmol) was dissolved in 3 mL of benzene, and cyclohexyl isocyanate (39.4 mg, 0.31 mmol) was added. After stirring the orange solution for 30 min the solvent was removed under vacuum. The resulting light orange powder was washed twice with 3 mL portions of pentane and dried in vacuum (20 °C, 1 Torr, 15 min). Layering a benzene solution of the raw product with hexane gave well-defined colorless crystals of **5** (35 mg, 21%). Anal. Calcd for $C_{65}H_{80}CaN_4O_{2,5P2}$ (M = 1059.38): C, 73.69; H, 7.61. Found: C, 74.03; H, 7.53. Mp: 169−170 °C (dec).

NMR analyses of the crystalline product **5** gave uninterpretable spectra of several unidentified species. ESI-TOF-MS studies on hydrolyzed crystals gave signals for the double insertion product (DIPP−N═PPh$_2$)$_2$CH−C(O)−N(Cy)−C(O)−N(Cy)H (exact mass (M + H$^+$) 985.5680; calcd 985.5678, Δ = 0.0002), the mono-insertion product (DIPP−N═PPh$_2$)$_2$CH−C(O)−N(Cy)H (exact mass (M + H$^+$) 860.4843; calcd 860.4838, Δ = 0.0005), and the hydrolyzed ligand (DIPP−N═PPh$_2$)$_2$CH$_2$ (exact mass (M + H$^+$) 735.3999; calcd 735.3997, Δ = 0.0002). In some cases also the trimerization product was detected. These data suggest that **5** degrades in solution into the monoinsertion product and isocyanate monomer, which under these conditions trimerizes. ESI-TOF-MS studies on the raw product of trimerization (*vide infra*) also show the double-insertion product (DIPP−N═PPh$_2$)$_2$CH−C(O)−N(Cy)−C(O)−N(Cy)H: exact mass (M + H$^+$) 985.5721; calcd 985.5678, Δ = 0.0043.

Trimerisation of Isocyanates. Trimerization experiments were performed analogously to those described before.[19] Trimerization of cyclohexyl isocyanate was performed at 50 °C without solvent (catalyst **2**: 1 or 5 mol %). Conversion of the isocyanate was followed by ^{1}H NMR spectroscopy. The observed deviation from first-order behavior (see Supporting Information) can be explained by the high viscosity of the reaction mixture in the later stages of the reaction. Trimerization of phenyl isocyanate was performed at room temperature in THF-d_8 (catalyst **2**: 1 mol %). Conversion of the isocyanate was followed by ^{1}H NMR spectroscopy. Since the trimer is rather insoluble in THF and precipitated in the course of the reaction, cyclohexane was added as an internal standard. The reaction follows first-order kinetics with $k = 0.011(1)$ L·mol^{-1}·s^{-1}.

Crystal Structure Determinations. Crystal structures have been solved by direct methods (SHELXS-97)[24] and were refined with SHELXL-97.[25] All geometry calculations and graphics have been performed with PLATON.[26] Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 632799−632801. 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 2: $C_{57}H_{70}CaN_2O_2P_2$, M_r = 917.17, monoclinic, space group $P2_1/n$, a = 11.2645(2) Å, b = 24.1967(6) Å, c = 19.0740(4) Å, β = 103.787(1)°, V = 5049.1(2) Å^3, Z = 4, ρ_{calcd} = 1.207 Mg m^{-3}, $F(000)$ = 1968, μ(Mo Kα) = 0.231 mm^{-1}. The data were collected on a Siemens SMART CCD diffractometer at −70 °C. Of the 210 551 measured reflections, 14 655 were independent (R_{int} = 0.077) and 11 098 observed ($I > 2\sigma(I)$). The final refinement converged to R_1 = 0.048 for $I > 2\sigma(I)$, wR_2 = 0.121, and GOF = 1.02 for all data. The final difference Fourier synthesis gave a min./max. residual electron density of −0.38/+0.53 e·Å^{-3}. All hydrogen atoms have been placed on calculated positions and were refined in a riding mode. One of the THF rings was refined with a disorder model (ratio 0.75/0.25).

Crystal data for 4: $C_{66}H_{72}CaN_2O_2P_2\cdot(C_7H_8)_3$, M_r = 1304.25, monoclinic, space group $P2_1/c$, a = 12.8306(5) Å, b = 25.8906(9) Å, c = 22.1311(7) Å, β = 93.049(2)°, V = 7341.4(4) Å^3, Z = 4, ρ_{calcd} = 1.178 Mg m^{-3}, $F(000)$ = 2792, μ(Mo Kα) = 0.174 mm^{-1}. The data were collected on a Siemens SMART CCD diffractometer at −70 °C. Of the 206 914 measured reflections, 13 444 were independent (R_{int} = 0.077) and 11 243 observed ($I > 2\sigma(I)$). The final refinement converged to R_1 = 0.053 for $I > 2\sigma(I)$, wR_2 = 0.144, and GOF = 1.10 for all data. The final difference Fourier synthesis gave a min./max. residual electron density of −0.37/+0.54 e·Å^{-3}. All hydrogen atoms have been placed on calculated positions and were refined in a riding mode. Two slightly disordered toluene solvent molecules could be located and were refined with large anisotropic displacement parameters. Disorder of the third toluene molecule could not be resolved and was treated with the SQUEEZE procedure.[27]

Crystal data for 5: $C_{130}H_{160}Ca_2N_8O_5P_4$, M_r = 2118.71, monoclinic, space group Cc, a = 33.0555(9) Å, b = 18.3600(5) Å, c = 22.3436(6) Å, β = 101.466(2)°, V = 13289.7(6) Å^3, Z = 4, ρ_{calcd} = 1.059 Mg m^{-3}, $F(000)$ = 4544, μ(Mo Kα) = 0.185 mm^{-1}. The data were collected on a Siemens SMART CCD diffractometer at −70 °C. Of the 139 360 measured reflections, 13 740 were independent (R_{int} = 0.066) and 13 044 observed ($I > 2\sigma(I)$). The final refinement converged to R_1 = 0.038 for $I > 2\sigma(I)$, wR_2 = 0.106, and GOF = 1.09 for all data. The final difference Fourier synthesis gave a min./max. residual electron density of −0.25/+0.23 e·Å^{-3}. All hydrogen atoms have been placed on calculated positions and were refined in a riding mode. In the chiral space group Cc, the Flack parameter did not converge for both possible enantiomers and the crystal was treated as a racemic twin; the batch scale factor refined to 0.43.

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Supporting Information Available: Crystal data (cif) and ORTEP plots for **2**, **4**, and **5** and conversion-time plots for the trimerization experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

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