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# Formation of Phosphino-Substituted Isocyanate by Reaction of $CO_2$ with Group 2 Complexes Based on the $(Me_3Si)(i\text{-}Pr_2P)NH$ Ligand

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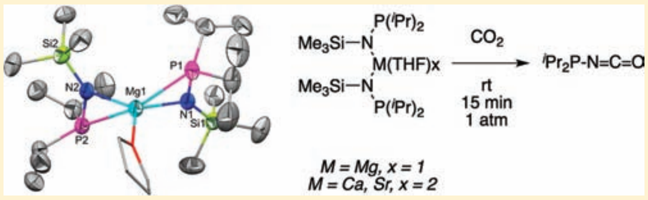
Ⓢ *Supporting Information*

**ABSTRACT:** The group 2 complexes $[(Me_3Si)(i\text{-}Pr_2P)N]_2M(THF)_x$ (M = Mg, $x = 1$; M = Ca/Sr, $x = 2$) as well as an unusual dimagnesium complex $\{[(Me_3Si)(i\text{-}Pr_2P)N]_3Mg\}Mg(n\text{-}C_4H_9)$ have been prepared and characterized by multinuclear NMR spectroscopy and single crystal X-ray diffraction. Each complex was shown to react with $CO_2$ under extremely mild conditions (15 min, 1 atm, room temperature) to give the isocyanate $(i\text{-}Pr)_2P{-}N{=}C{=}O$. The independent syntheses of $(i\text{-}Pr)_2P{-}N{=}C{=}O$ and the carbodiimide dimer $[(i\text{-}Pr)_2PNCNP(i\text{-}Pr)_2]_2$ are also reported.



## INTRODUCTION

Research into non-natural chemical systems that can transform $CO_2$ has increased dramatically in recent years because carbon dioxide is a cheap, abundant and nontoxic raw material that is currently being produced at rates higher than what can be used by natural biological and geological systems.[1] While sequestration systems to capture and store $CO_2$ are an important short-term answer, a true long-term solution will require that the $CO_2$ be recycled into new carbon-containing products. The bulk of research efforts into the activation and transformation of $CO_2$, whether for fuels (e.g., methanol),[2] polymers[3] or other products,[4] have historically been centered on transition-metal complexes, but more recently main-group complexes have also been investigated.[5] Such activating complexes have been required because $CO_2$ tends to be relatively inert under most conditions. While this is advantageous for certain applications, such as its use as a solvent under supercritical conditions, it is a challenge for those who seek to exploit $CO_2$ as a $C_1$ building block for new organic molecules.

One reaction that $CO_2$ does readily undergo is insertion into M−N bonds of main-group amido complexes (Scheme 1). We[6] and others[7] have shown that when R = alkyl or aryl, simple insertion occurs to form a carbamate **A**. In contrast, if one or both of the substituents are replaced with a silyl group, elimination of an isocyanate **B** is driven by the formation of a strong Si−O bond.[8] The remaining M−N bond may react with either a second molecule of $CO_2$ to form more isocyanate or with the isocyanate itself to form a carbodiimide **C**.

Recently, we have begun studying the reactivity of *phosphino*-substituted main-group amido complexes with $CO_2$. These ambidentate ligands have several possible coordination modes (Figure 1), and their complexes react in interesting and unexpected ways with $CO_2$. The group 2 series $M[N(PPh_2)_2]_2(THF)_x$ (M = Mg, $x = 2$; M = Ca/Sr, $x = 3$) binds as type **II**, analogous to the alkyl, aryl and silyl derivatives that inspired this work. The Ca and Sr complexes were found to react with $CO_2$ to form an unexpected hexanuclear species $M_6[O_2CN(PPh_2)_2]_6[N(CO_2)_3]_2(THF)_7$.[9] This hexanuclear species fixes 12 mol of $CO_2$: six as the novel carbamate $[{-}O_2CN(PPh_2)_2]^-$ and six as the unprecedented trianion $[N(CO_2)_3]^{3-}$. Moving across the periodic table to group 14, the complex $[(i\text{-}Pr_2P)_2N]_2Sn$ coordinates as type **I**, and reacts reversibly with $CO_2$ to form the adduct $Sn[O_2CP(i\text{-}Pr)_2NP(i\text{-}Pr)_2]_2$.[10] While we are still exploring the questions opened up by the products of those reactions, we have also returned to a ligand that more closely resembles the initial starting point, namely, $(Me_3Si)(i\text{-}Pr_2P)NH$ **1**. Herein, we present the synthesis and characterization of its group 2 complexes and the reactivity of those complexes with $CO_2$.

## RESULTS AND DISCUSSION

**Preparation and Characterization of Group 2 Complexes.** The ligand $(Me_3Si)(i\text{-}Pr_2P)NH$ **1** is readily prepared from the reaction of $HN(SiMe_3)_2$ with one equivalent of $i\text{-}Pr_2PCl$ in toluene (Scheme 2). Following removal of the solvent and $ClSiMe_3$ coproduct, the colorless liquid **1** is separated from small amounts of the disubstituted byproduct $(i\text{-}Pr_2P)_2NH$ by vacuum distillation. The $^1H$ and $^{13}C$ NMR spectra were consistent with the presence of two isopropyl groups and one trimethylsilyl group. The amine H was not observed in the $^1H$ NMR spectrum, but the N−H stretch did exhibit a strong absorbance at 3346 $cm^{-1}$ in the IR spectrum. The $^{31}P$ NMR signal for **1** appeared at 49 ppm.

The potassium salt of **1** was prepared by reaction of **1** with a slight excess of KH in THF solution. After stirring overnight at rt, the mixture was filtered to remove the remaining KH, and then the solution was added to a suspension of either $SrI_2$ or

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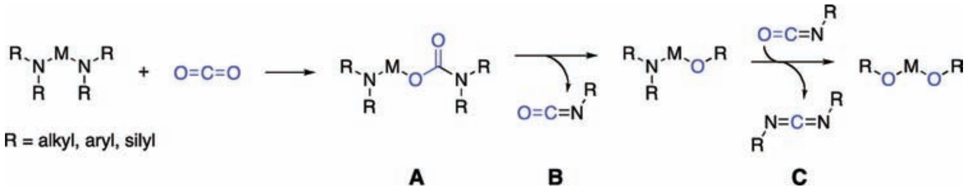
### Scheme 1. General Reaction of Divalent Main-Group Amido Complexes with $CO_2$



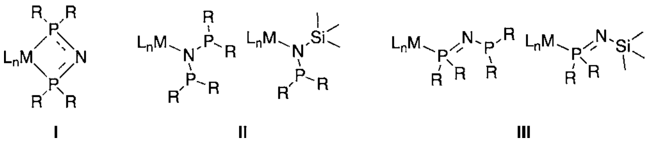
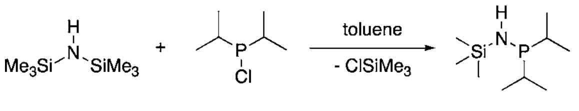


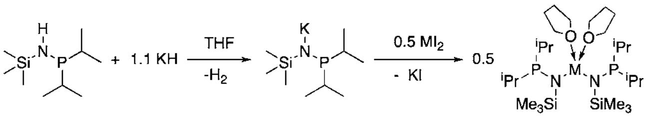
**Figure 1.** Possible coordination modes of ambidentate $[(R_2P)_2N]^-$ and $[(R_2P)(Me_3Si)N]^-$ ligands.

### Scheme 2. Synthesis of 1



1

### Scheme 3. Syntheses of Complexes 2 and 3



1

2 (M = Sr)
3 (M = Ca)

$CaI_2$ in THF to give **2** or **3**, respectively (Scheme 3). The isolated yields are somewhat low due to the high solubility of the compounds during recrystallization, but $^{31}P\{^1H\}$ NMR spectra of the crude reaction mixtures show complete conversion. The $^1H$ NMR spectra for both **2** and **3** indicated the presence of two molecules of coordinated THF in addition to the expected signals for the ligand. The $^{31}P$ NMR spectra of the complexes showed single resonances at 68 ppm for **2** and 67 ppm for **3**.

Because **1** is potentially a ditopic ligand, capable of coordinating though either N or P, single crystal X-ray diffraction studies (Table 1) were performed on **2** and **3** to ascertain the precise binding mode of the ligand. A series of papers by Foss and Veits and co-workers[11] proposed that complexes of **1** with group 14 and 15 elements (M = $SiR_3$, $GeR_3$, $SnR_3$, $PR_2$, $AsR_2$) were in equilibrium between two tautomeric forms: amido complexes with M bound to N (Figure 1, type **II**), and imido complexes with M bound to $P^v$ (type **III**). This assessment was based entirely on the $^{31}P$ NMR data with no structural verification.

As shown in Figures 2 and 3, both **2** and **3** crystallize with two distinct molecules in the asymmetric unit. The ligands are covalently bound through nitrogen to the metal center (type **II**). Two molecules of THF are also present, consistent with the $^1H$ NMR data. In the solid state, the metal coordination sphere is completed by dative interactions with the phosphorus atom of each ligand, although $^{31}P$ NMR studies on related molecules suggest that this interaction does not persist in solution at room temperature.[12] The N–M–P angles are extremely acute, averaging 32.2° in **2** and 35.0° in **3**. Therefore, despite being formally hexacoordinate, the geometry at either Sr or Ca is best described as a distorted tetrahedron. The N–P bonds are very similar in length, varying from 1.640(3) to 1.655(3) Å. Although these values fall within the ranges of both P═N (mean =1.586 Å) and P–N (mean =1.659 Å) bonds in the CSD,[13] it is clear that the bonds in **2** and **3** are best

### Table 1. Crystallographic Data for 2–5 and 6

| | **2** | **3** | **4** | **5** | **6a** |
|---|---|---|---|---|---|
| empirical formula | $C_{26}H_{62}N_2O_2P_2Si_2Sr$ | $C_{26}H_{62}CaN_2O_2P_2Si_2$ | $C_{22}H_{54}MgN_2OP_2Si_2$ | $C_{31}H_{78}Mg_2N_3P_3Si_3$ | $C_{13}H_{28}N_2P_2$ |
| FW | 640.52 | 592.98 | 505.10 | 718.76 | 274.31 |
| $T$ (K) | 228(2) | 228(2) | 228(2) | 173(2) | 223(2) |
| cryst syst | monoclinic | monoclinic | monoclinic | orthorhombic | triclinic |
| space group | $P2(1)/c$ | $P2(1)/c$ | $P2(1)/n$ | $P2(1)2(1)2(1)$ | $P\bar{1}$ |
| $a$, Å | 19.5246(14) | 19.4397(6) | 12.6163(6) | 11.8848(5) | 8.3294(3) |
| $b$, Å | 20.3746(14) | 20.1683(6) | 21.4649(11) | 18.5826(9) | 8.4283(3) |
| $c$, Å | 20.7825(15) | 20.6361(6) | 12.6163(6) | 20.5032(9) | 11.9681(4) |
| $\alpha$, deg | | | | | 74.085(2) |
| $\beta$, deg | 114.544(4) | 114.947(2) | 106.29 | | 89.399(2) |
| $\gamma$, deg | | | | | 89.489(2) |
| vol, Å$^3$ | 7520.4(9) | 7335.8(4) | 3279.4(3) | 4528.1(4) | 807.93(5) |
| $Z$ | 8 | 8 | 4 | 4 | 2 |
| calcd density (g/cm$^3$) | 1.131 | 1.074 | 1.023 | 1.054 | 1.128 |
| $\mu$, mm$^{-1}$ | 1.604 | 0.346 | 0.239 | 0.261 | 0.254 |
| cryst size (mm$^3$) | 0.41 × 0.34 × 0.23 | 0.50 × 0.49 × 0.25 | 0.34 × 0.16 × 0.09 | 0.53 × 0.32 × 0.30 | 0.18 × 0.17 × 0.11 |
| $R1[I > 2\sigma(I)]^a$ | 0.0412 | 0.0468 | 0.0463 | 0.0347 | 0.0394 |
| $wR2[I > 2\sigma(I)]^b$ | 0.1025 | 0.1274 | 0.1285 | 0.0844 | 0.1063 |

$^a R1 = [\sum||F_o| - |F_c||]/[\sum|F_o|]$. $^b wR2 = \{[\sum w(F_o^2 - F_c^2)^2]/[\sum w(F_o^2)^2]\}^{1/2}$.

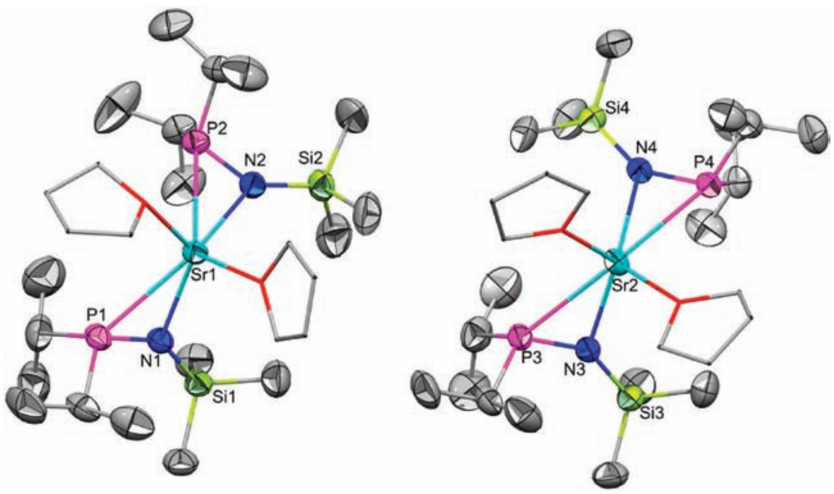


**Figure 2.** Structure of **2**. Thermal ellipsoids are shown at 50% probability. For clarity, hydrogen atoms have been removed and the THF molecules are shown as sticks.

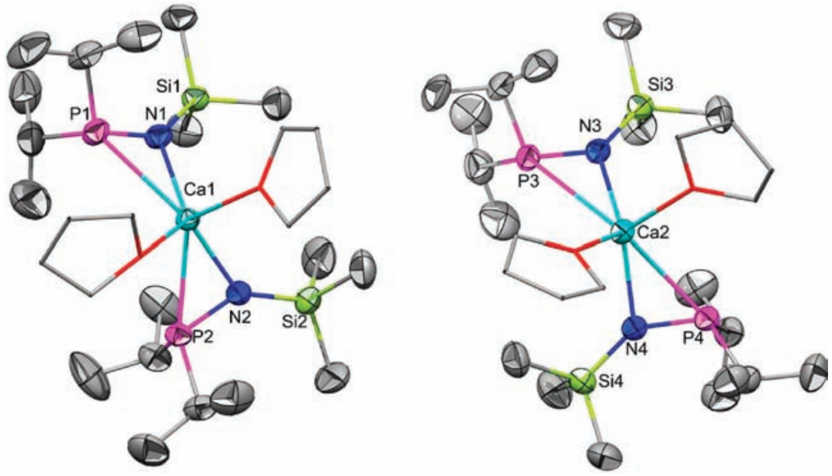


**Figure 3.** Structure of **3**. Thermal ellipsoids are shown at 50% probability. For clarity, hydrogen atoms have been removed and the THF molecules are shown as sticks.

described as single and that the molecules are amido rather than imido complexes.

The difference between the two crystallographically distinct molecules in both **2** and **3** is the relative orientation of the M−P bonds to one another within the molecule. If a plane is drawn through the N−M−N bonds, in one conformer the M−P bonds are on the same side of this plane, and in the other conformer they are on opposite sides. In Figures 2 and 3, these correspond to the left and right pictures, respectively. The most noticeable consequence of this bonding change is a difference of approximately 20° between the P1−M1−P2 angle and the P3−M2−P4 angle. Also noteworthy is the observation that these dative interactions are quite short, particularly for the Sr complex **2**. These range in length from 2.9767(8) to 3.0245(9) Å for **2** and 2.8414(7) to 2.9024(7) Å for **3** (Table 2). For comparison, a survey using the Cambridge Structural Database (CSD)[13] shows that previously reported Sr−P bonds range from 2.974 to 3.278 Å with a mean distance of 3.106 Å. For Ca−P bonds, the range is 2.824 to 3.145 Å and the mean distance is 2.954 Å.

Synthesis of the lightest congener in this series, the magnesium complex, can be accomplished via a salt metathesis route similar to that shown in Scheme 3. However, the availability of a convenient organometallic starting material $Mg(n\text{-}C_4H_9)_2$ led us to pursue a cleaner alkane elimination route. Reaction of 2 equiv of **1** with $Mg(n\text{-}C_4H_9)_2$ in THF solution led directly to the formation of **4** (Scheme 4). The $^1H$ and $^{13}C$ NMR spectra were unremarkable, indicating a single molecule of coordinated THF along with two ligands. The fact that **4** has a lower coordination number than **2** or **3** is not surprising given the much smaller size of the Mg center relative to Ca and Sr. The $^{31}P$ NMR spectrum showed a peak at 71 ppm, slightly downfield from the corresponding signals for **2** or **3**.

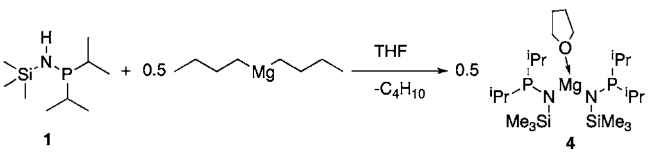
Single crystals of **4** suitable for X-ray diffraction experiments were grown from a concentrated solution in pentane. As with **2** and **3**, **4** crystallized in the *P*2(1)/*c* space group, but unlike the heavier congeners only a single molecule with the "opposite side" conformation was present in the asymmetric unit (Figure 4). One molecule of coordinated THF was present, consistent with the NMR data. The dative Mg−P bond lengths are unremarkable at 2.6095(9) and 2.6100(9) Å (CSD indicated the mean Mg−P distance = 2.602 Å, range 2.45 to 2.985 Å).[13] At 154.07(4)° the P1−Mg1−P2 angle is significantly wider in **4** than in the corresponding conformations of **2** or **3** [140.19(3) and 140.52(2)°, respectively]. The N1−Mg1−N2 angle has

**Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complexes 2−5**

| | **2** (M = Sr) | **3** (M = Ca) | **4** (M = Mg) | **5** (M = Mg) |
|---|---|---|---|---|
| M1−N1 | 2.486(3) | 2.3421(18) | 2.0067(19) | 2.0289(16) |
| M1−N2 | 2.482(3) | 2.3439(18) | 2.0017(19) | 2.0381(17) |
| M2−N3 | 2.474(3) | 2.3339(19) | | 2.0354(16)[a] |
| M2−N4 | 2.486(3) | 2.3455(19) | | |
| M1−P1 | 3.0142(9) | 2.8951(7) | 2.6095(9) | 2.7170(8)[b] |
| M1−P2 | 2.9767(8) | 2.8414(7) | 2.6100(9) | 2.6956(8)[b] |
| M2−P3 | 2.9809(9) | 2.8578(7) | | 2.7462(8) |
| M2−P4 | 3.0245(9) | 2.9024(7) | | |
| P1−N1 | 1.640(3) | 1.6494(18) | 1.6654(19) | 1.6612(16) |
| P2−N2 | 1.655(3) | 1.6536(18) | 1.6653(19) | 1.6540(17) |
| P3−N3 | 1.643(3) | 1.6474(17) | | 1.6554(15) |
| P4−N4 | 1.647(3) | 1.6477(18) | | |
| Si1−N1 | 1.687(3) | 1.6943(18) | 1.701(2) | 1.7148(16) |
| Si2−N2 | 1.689(3) | 1.7023(18) | 1.700(2) | 1.7205(17) |
| Si3−N3 | 1.686(3) | 1.6956(18) | | 1.7191(16) |
| Si4−N4 | 1.684(3) | 1.6973(19) | | |
| P1−M1−P2 | 120.28(3) | 121.50(2) | 154.07(4) | |
| P3−M2−P4 | 140.19(3) | 140.52(2) | | |
| N1-M1−N2 | 115.89(9) | 115.87(7) | 139.28(9) | |
| N3-M2−N4 | 121.99(9) | 123.08(7) | | |
| P1−M1−N1 | 32.96(6) | 34.72(4) | 39.66(6) | |
| P2−M1−N2 | 33.78(6) | 35.58(4) | 39.65(5) | |
| P3−M2−N3 | 33.46(6) | 35.20(4) | | |
| P4−M2−N4 | 32.97(6) | 34.58(4) | | |
| P1−N1−Si1 | 141.35(17) | 138.90(12) | 138.68(12) | 132.81(10) |
| P2−N2−Si2 | 137.32(16) | 135.30(12) | 138.02(11) | 133.50(10) |
| P3−N3−Si3 | 141.43(17) | 138.68(12) | | 132.43(9) |
| P4−N4−Si4 | 142.34(17) | 139.73(12) | | |

[a] Refers to Mg1. [b] Refers to Mg2.

**Scheme 4. Synthesis of 4**



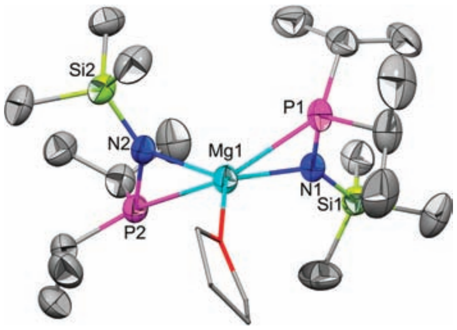
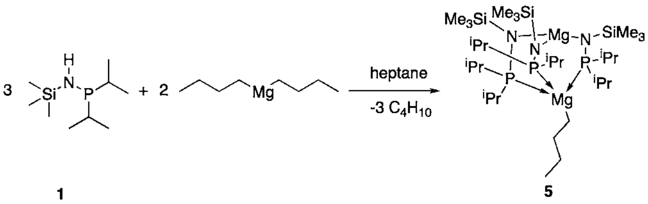


**Figure 4.** Structure of **4**. Thermal ellipsoids are shown at 50% probability. For clarity, hydrogen atoms have been removed and the coordinated THF molecule is shown as sticks.

also opened up significantly to 139.28(9)°, compared to 121.99(9) and 123.08(7)° for **2** and **3**. This increase is likely due to the decreased steric pressure caused by the lower coordination number at magnesium. Just as the hexacoordinate Sr and Ca complexes **2** and **3** were best considered distorted tetrahedral, the pentacoordinate Mg is best described as trigonal planar due to the extremely acute N−M−P angles.

During the salt metathesis synthetic route to **2** and **3**, use of the coordinating solvent THF ensured the solubility of the reactants. For consistency, the same solvent was initially used in the synthesis of **4**. However, since Mg($n$-$C_4H_9$)$_2$ was purchased as a 1.0 M solution in heptane, and **1** is miscible with nonpolar solvents, it was of interest to see if a magnesium complex without a coordinating solvent molecule could be prepared. As such, the Mg($n$-$C_4H_9$)$_2$ solution was added to neat **1** in an initial 1:2 molar ratio and the solution was stirred at rt for 2 h before being cooled to −25 °C, producing crystals of **5**. After the product was definitively identified, however, the stoichiometry for optimal preparation of **5** was adjusted to that shown in Scheme 5. Following standard workup, the $^1$H NMR spectrum of **5** was obtained and it showed a 3:1 ratio of peaks assignable to the ligand and to an $n$-butyl group. The presence of an $n$-butyl group was somewhat surprising, as excess unreacted **1** was detected in the supernatant solution. Even when the reaction time was extended to several days, the final butyl group did not react. The $^{31}$P NMR spectrum of **5** consisted of a single peak at 60 ppm. As the NMR spectra of **5** did not provide a definitive skeletal assignment, it was necessary to perform an X-ray structural analysis.

**Scheme 5. Synthesis of 5**



Single crystals were grown from a concentrated solution of **5** in heptane, and the structure is shown in Figure 5. Complex **5** is best described as a contact ion pair. The anion is the tricoordinate {[(Me$_3$Si)($i$-Pr$_2$P)N]$_3$Mg}$^-$ species, with the ligand bound to Mg through N. The cation is [Mg($n$-$C_4H_9$)]$^+$, stabilized by dative interactions with each of the

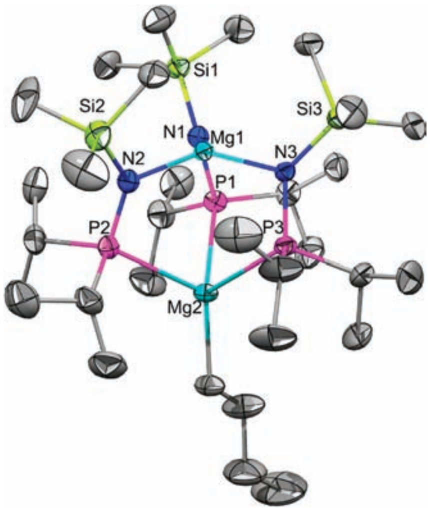


**Figure 5.** Structure of **5**. Thermal ellipsoids are shown at 50% probability. For clarity, hydrogen atoms have been removed.

three phosphorus atoms of the anion. The tricoordinate Mg1 has roughly trigonal planar geometry ($\sum_{\text{bond angles}}$ Mg1 = 354°), while Mg2 is tetrahedral. The Mg−N bond lengths in **5** range from 2.0289(16) to 2.0381(17) Å, only slightly longer than those seen in **4** at 2.0017(19) and 2.0067(19) Å. There is a greater difference between the Mg−P bond lengths in the two complexes, with **5** being significantly longer at 2.6956(8) to 2.7462(8) vs 2.6095(9) to 2.6100(9) in **4**. In **5**, unlike the other complexes, it is not possible to draw a reasonable resonance structure containing P═N double bonds. Since the P−N bond lengths in **5** are not substantially longer than those in **2**−**4**, our description of these molecules as amido complexes rather than imido complexes is supported (vide supra). The Flack parameter for **5** is −0.01(7).

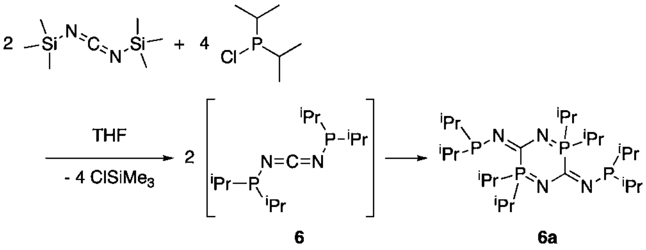
**Reactions of Group 2 Complexes with $CO_2$.** As was described in the Introduction, we had previously prepared the related group 2 complexes $M[N(PPh_2)_2]_2(THF)_x$ (M = Mg, $x = 2$; M = Ca/Sr, $x = 3$) and had reacted each with $CO_2$ under similar conditions. The Ca and Sr derivatives were found to give the same product, the unusual hexanuclear complex $M_6[O_2CN(PPh_2)_2]_6[N(CO_2)_3]_2(THF)_7$ (M = Ca, Sr).[9] The Mg complex did not follow the same reactivity trend, and the only P-containing product that was observed following reaction with $CO_2$ was $Ph_2P{-}P(Ph_2){=}N{-}PPh_2$.[14] Given the similarities between that series and complexes **2**−**4**, namely, coordination through N, dative M−P interactions, and one fewer molecules of THF coordinated to Mg than to Ca and Sr, it was not immediately clear whether **4** would behave analogously to **2** and **3**. Nor was it clear exactly what products would be formed despite our hypothesis that reactions would lead to the phosphino-substituted carbodiimide $(i\text{-Pr})_2P{-}N{=}C{=}N{-}P(i\text{-Pr})_2$ **6** and/or the isocyanate $(i\text{-Pr})_2P{-}N{=}C{=}O$ **7**. For **5**, the question was even more open due to the presence of the *n*-butyl group.

Complexes **2**−**5** were each dissolved in pentane, and $CO_2$ was bubbled through the colorless solutions for approximately 15 min. No color change nor precipitate was noted during this time for any of the reactions. Each solution was then analyzed by NMR and IR spectroscopy and mass spectrometry. Each technique gave virtually identical results for each solution. The $^{31}P\{^1H\}$ NMR spectra of the four $CO_2$ reaction products each showed a singlet at 89 ppm, significantly downfield from each of the starting complexes **2**−**5**. The IR spectrum of the reaction of **2** with $CO_2$ showed a very strong absorbance at 2256 $cm^{-1}$. For **3**−**5** with $CO_2$, the corresponding absorbances were at 2257 $cm^{-1}$, identical within error to that using **2**. Those signals are in the range of typical cumulene stretches for both isocyanates and carbodiimides, suggesting that elimination had indeed occurred and not simple insertion of $CO_2$ into the M−N bonds to give carbamates (Scheme 1). Finally, the GC−MS of each solution was run, and the mass spectrum of each showed fragments with $m/z$ = 159 and 117. As **7** has a molecular weight of 159 amu, it seemed likely that it was the product that had been formed exclusively in the reactions of **2**−**5** with $CO_2$. It was also possible, however, that that mass corresponded to a product derived from the fragmentation of **6**. The $m/z$ = 117 fragment can be confidently assigned to an $[i\text{-Pr}_2P]^+$ species, which would be expected in either **6** or **7**.

While the isocyanate **7** has been reported in the literature,[15] no NMR or IR data were given. The related compound[16] $(t\text{-Bu})_2P{-}N{=}C{=}O$ appears in the $^{31}P\{^1H\}$ NMR spectrum at 103 ppm and shows an absorbance in the IR spectrum at 2280 $cm^{-1}$. Neither **6** nor other dialkylphosphinocarbodiimides have been reported. The most closely related species, $[(i\text{-Pr})_2N]_2P{-}N{=}C{=}N{-}P[N(i\text{-Pr})_2]_2$, was reported[17] to have a $^{31}P\{^1H\}$ NMR chemical shift of 84 ppm and an IR stretch of 2126 $cm^{-1}$. Given that the data from the reactions of **2**−**5** with $CO_2$ are quite close to both the reported isocyanate and carbodiimide, independent syntheses of both **6** and **7** were undertaken.

**Carbodiimide and Isocyanate Syntheses.** Following a procedure similar to that used to prepare **1**, *i*-$Pr_2PCl$ was added to a solution of $Me_3Si{-}N{=}C{=}N{-}SiMe_3$ in THF in an attempt to produce **6** (Scheme 6). Heating of the reaction mixture to reflux overnight followed by slow evaporation of the solvent and removal of the $ClSiMe_3$ coproduct afforded a crystalline yellow solid as the sole product. However, the NMR and IR spectroscopic data immediately indicated that the product was not **6**. Instead of exhibiting stretches in the cumulene region, the IR spectrum showed a strong absorbance at 1536 $cm^{-1}$, characteristic of an isolated C═N bond. The $^1H$ and $^{13}C\{^1H\}$ NMR spectra were complicated, with overlapping signals for multiple inequivalent isopropyl groups. Two virtual triplets at 15 and 64 ppm ($^3J_{P-P}$ = 9.3 Hz) were seen in the $^{31}P\{^1H\}$ NMR spectrum.

**Scheme 6. Synthesis of 6**



Single crystal X-ray diffraction confirmed that the product was not **6** but instead the dimeric molecule **6a** (Figure 6) formed by an unusual [3 + 3] homoleptic cycloaddition through the nucleophilic P atom and the electrophilic carbodiimide C atom. The six-membered C−N−P heterocycle is planar. The exocyclic P1 remains in its original trivalent state and gives rise to the downfield $^{31}P$ NMR signal, while P2 has been formally oxidized to $P^v$ and is associated with the upfield NMR signal. The formal double bond between P2 and N2 measures 1.6012(15) Å, while the single bond P1−N1 outside the ring is 1.7336(15) Å. The dimer-forming P2−C13 bond measures 1.8386(18) Å, only slightly longer than the $P2{-}C_{i\text{-Pr}}$ bonds of 1.8144(19) and 1.825(2) Å, and longer than the $P1{-}C_{i\text{-Pr}}$ bonds at 1.855(2) and 1.860(2) Å. The C−N single bond length within the ring is much longer [N2−C13 = 1.351(2) Å]

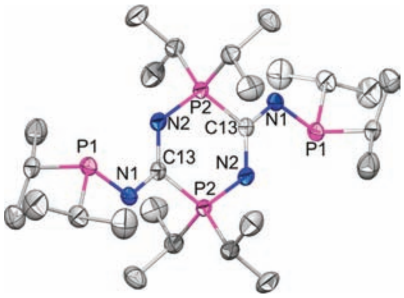


**Figure 6.** Structure of **6a**. Thermal ellipsoids are shown at 50% probability. For clarity, hydrogen atoms have been removed.

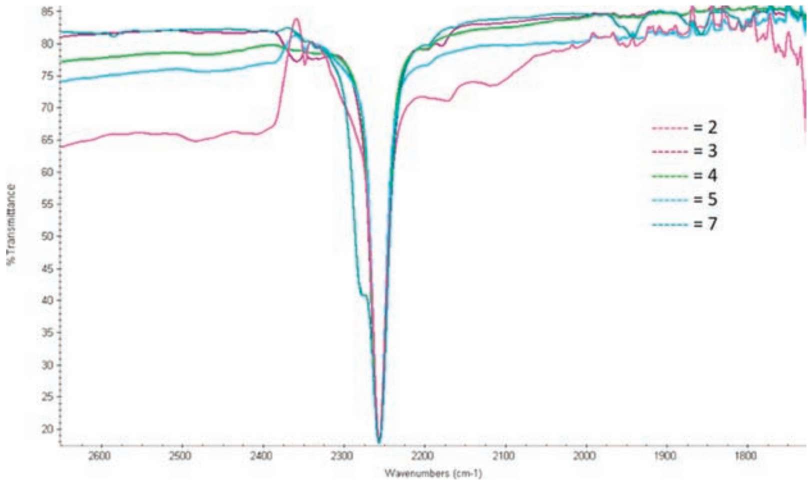


**Figure 7.** IR spectrum of **7** overlaid with the IR spectra of the products of the reaction of **2**−**5** with $CO_2$.

than the exocyclic C═N bond length [N1−C13 = 1.292(2) Å], and the presence of distinct C−N and C═N bonds is consistent with the IR data.

To synthesize **7**, a solution of $Me_3Si$−N═C═O and *i*-$Pr_2PCl$ in toluene was prepared and the progress of the reaction was monitored by $^{31}P\{^1H\}$ NMR spectroscopy. A single new P-containing compound with a peak at 90 ppm was observed after the reaction had been stirred overnight at rt, but a large amount of the starting *i*-$Pr_2PCl$ remained. The NMR chemical shift was consistent with what had been observed in the reactions of **2**−**5** with $CO_2$ (i.e., 89 ppm in pentane). In an attempt to force the reaction to completion, the solution was heated to reflux for four days, but the effects of both the increased time and temperature were negligible and did not lead to higher conversions.

We were unable to isolate **7** in a pure state, and so subsequent characterization studies were done on the partially converted solution. The IR spectrum of the crude reaction mixture showed a very strong absorbance at 2256 $cm^{-1}$, again consistent with the reactions of **2**−**5** with $CO_2$ (Figure 7). The shoulder at 2281 $cm^{-1}$ is due to the unreacted $Me_3Si$−N═C═O. Final confirmation that **7** was indeed the product of the reactions of **2**−**5** with $CO_2$ was provided by mass spectrometry (Figure 8). All five solutions show the same splitting pattern of a molecular ion peak ($m/z$ = 159) and a fragment assigned to $[i\text{-}Pr_2P]^+$ ($m/z$ = 117).

## ■ CONCLUSIONS

The group 2 complexes $[(Me_3Si)(i\text{-}Pr_2P)N]_2M(THF)_x$ (M = Mg, $x$ = 1; M = Ca/Sr, $x$ = 2) **2**−**4** and $\{[(Me_3Si)(i\text{-}Pr_2P)N]_3Mg\}MgC_4H_9$ **5** have been prepared. Characterization by multinuclear NMR spectroscopy and X-ray crystallography determined that the primary metal−ligand interaction in **2**−**4** is a covalent bond through nitrogen, with dative M−P interactions. Complex **5** was found to be a contact ion pair with three ligands bound covalently through N to one Mg and datively through Mg to the other, which is also bound to a butyl group. Each of these complexes reacts with $CO_2$ quickly (~15 min) under extremely mild conditions (1 atm, rt) to produce exclusively the isocyanate $(i\text{-}Pr)_2P$−N═C═O **7**. The formation of this product was confirmed by the independent synthesis of **7** from $Me_3Si$−N═C═O. An attempt to synthesize the carbodiimide $(i\text{-}Pr)_2P$−N═C═N−$P(i\text{-}Pr)_2$ **6** resulted instead in the isolation of the [3 + 3] homodimer **6a**.

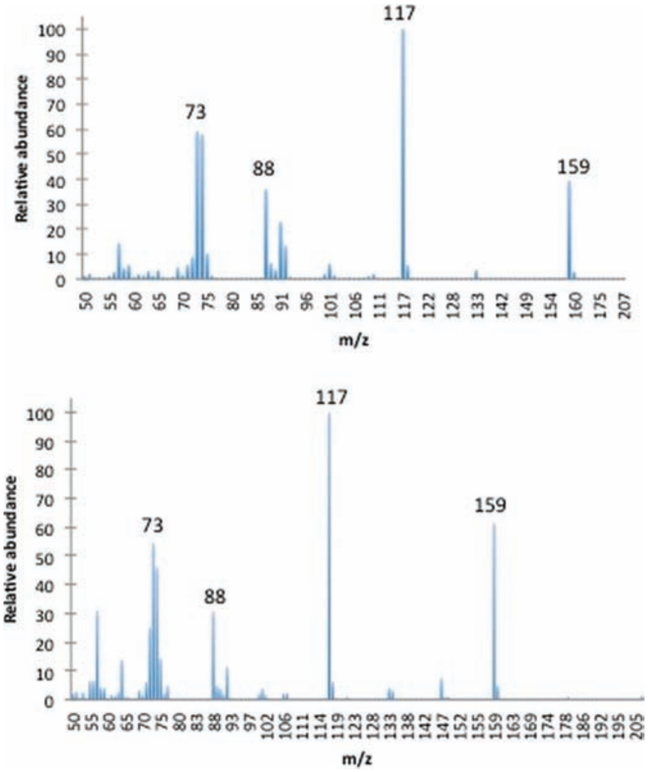


**Figure 8.** Mass spectrum of **7** (upper) and **3** + $CO_2$ (lower).

## ■ EXPERIMENTAL SECTION

**General Experimental.** All manipulations were carried out in an argon-filled glovebox or by using standard Schlenk techniques. Anhydrous solvents were purchased from Aldrich or Alfa Aesar and used as received, or obtained from an LC Technology Solutions solvent purification system, after which they were stored in the glovebox over 4 Å molecular sieves. Carbon dioxide was obtained from Matheson Tri-Gas. Other reagents were obtained from commercial sources such as Aldrich, Acros or Alfa Aesar and used without further purification. $^1H$, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were obtained on Bruker Avance 500 or Bruker Avance III 300 spectrometers. $^1H$ and $^{13}C\{^1H\}$ spectra were referenced to residual solvent downfield of TMS. $^{31}P\{^1H\}$ spectra were referenced to external 85% $H_3PO_4$. IR spectra were recorded on a Nicolet 6700 Ft-IR spectrometer on KBr windows. GC−MS data were collected on a Hewlett-Packard 5972 mass spectrometer coupled to an HP 5890 series II gas chromatograph with an Ultra I (cross-linked methyl silicone gum) column (50 m × 0.2 mm × 0.33 μm) with an Agilent 6980 Injector. Melting points are not reported due to desolvation and decomposition upon heating. Elemental analyses were performed by Columbia Analytical Services, Inc. of Tucson, AZ. We note that it is difficult to obtain accurate elemental analyses of these molecules due to both their solvation and the known tendencies of Si and P to interfere in combustion analysis.

**Synthesis of 1.** A solution of chlorodiisopropylphosphine (15.0 g, 98 mmol) in ca. 20 mL of toluene was added dropwise to a solution of hexamethyldisilazane in ca. 40 mL of toluene. The colorless solution was stirred overnight, and then the solvent and chlorotrimethylsilane coproduct were removed under vacuum. HN(SiMe$_3$)(P*i*-Pr$_2$) **1** was separated by vacuum distillation (20 μmHg, 27−32 °C) from the disubstituted byproduct HN(P*i*-Pr$_2$)$_2$. Yield = 8.45 g (42%). $^{1}$H NMR (C$_6$D$_6$, 300 MHz): δ 0.16 (s, 9H, Si(C*H*$_3$)$_3$), 0.89 (d, $^{3}J_{\mathrm{H-H}}$ = 6.9 Hz, 3H, CH(C*H*$_3$)$_2$), 0.93 (d, $^{3}J_{\mathrm{H-H}}$ = 6.9 Hz, 3H, CH(C*H*$_3$)$_2$), 0.96 (d, $^{3}J_{\mathrm{H-H}}$ = 6.9 Hz, 3H, CH(C*H*$_3$)$_2$), 1.01 (d, $^{3}J_{\mathrm{H-H}}$ = 6.9 Hz, 3H, CH(C*H*$_3$)$_2$), 1.34 (sept of d, $^{2}J_{\mathrm{P-H}}$ = 1.8 Hz, $^{3}J_{\mathrm{H-H}}$ = 6.9 Hz, 2H, C*H*(CH$_3$)$_2$). $^{13}$C{$^{1}$H} (C$_6$D$_6$, 75 MHz): δ 1.7 (d, $^{3}J_{\mathrm{P-C}}$ = 5 Hz, Si(CH$_3$)$_3$), 16.7 (d, $^{2}J_{\mathrm{P-C}}$ = 7 Hz, CH(CH$_3$)$_2$), 19.2 (d, $^{2}J_{\mathrm{P-C}}$ = 21 Hz, CH(CH$_3$)$_2$), 27.0 (d, $^{1}J_{\mathrm{P-C}}$ = 15 Hz, CH(CH$_3$)$_2$) ppm. $^{31}$P{$^{1}$H} (C$_6$D$_6$, 121 MHz): δ 49 (lit. 47.5)[11c] ppm. Anal. Calcd for C$_9$H$_{24}$NPSi: C, 52.64; H, 11.78; N, 6.82. Found, C, 53.20; H, 11.20; N, 6.73.

**Synthesis of 2.** Potassium hydride (0.18 g, 4.55 mmol) was added to a solution of **1** (0.85 g, 4.14 mmol) in ca. 10 mL of THF. After stirring overnight, the yellow suspension was filtered to remove excess KH and added to a suspension of SrI$_2$ (0.71 g, 2.07 mmol) in ca. 10 mL of THF. The cloudy mixture was stirred at rt for 1.5 h, and then the solvent was removed under vacuum. The residue was suspended in ca. 15 mL of toluene and then filtered to remove KI. The toluene was removed under vacuum, and the residue was recrystallized from pentane (ca. 5 mL) at −25 °C. Yield = 0.47 g (35%). $^{1}$H (C$_6$D$_6$, 500 MHz): δ 0.41 (s, 18H, Si(C*H*$_3$)$_3$), 1.8 (d, $^{3}J_{\mathrm{H-H}}$ = 7.0 Hz, 6H, CH(C*H*$_3$)$_2$), 1.21 (d, $^{3}J_{\mathrm{H-H}}$ = 7.0 Hz, 6H, CH(C*H*$_3$)$_2$), 1.28 (d, $^{3}J_{\mathrm{H-H}}$ = 7.0 Hz, 6H, CH(C*H*$_3$)$_2$), 1.31 (d, $^{3}J_{\mathrm{H-H}}$ = 7.0 Hz, 6H, CH(C*H*$_3$)$_2$), 1.32 (m, 8H, THF), 1.96 (sept of d, $^{2}J_{\mathrm{P-H}}$ = 3.5 Hz, $^{3}J_{\mathrm{H-H}}$ = 7.0 Hz, 4H, C*H*(CH$_3$)$_2$), 3.64 (m, 8H, THF) ppm. $^{13}$C{$^{1}$H} (C$_6$D$_6$, 75 MHz): δ 6.3 (s, Si(CH$_3$)$_3$), 19.7 (s, CH(CH$_3$)$_2$), 19.8 (s, CH(CH$_3$)$_2$), 19.9 (s, CH(CH$_3$)$_2$), 20.2 (s, CH(CH$_3$)$_2$), 25.2 (s, THF), 28.6 (d, $^{1}J_{\mathrm{P-C}}$ = 19 Hz, CH(CH$_3$)$_2$), 69.4 (s, THF) ppm. $^{31}$P{$^{1}$H} (C$_6$D$_6$, 121 MHz): δ 68 ppm. Anal. Calcd for C$_{26}$H$_{62}$N$_2$O$_2$P$_4$Si$_2$Sr: C, 48.75; H, 9.76; N, 4.37. Found: C, 47.61; H, 9.11; N, 4.21. (Calcd for 1.5 THFs per metal: C, 47.69; H, 9.67; N, 4.63.)

**Synthesis of 3.** The same procedure was followed as for **2**, beginning with 0.95 g (4.63 mmol) of **1**. Yield = 0.74 g (54%). $^{1}$H (C$_6$D$_6$, 500 MHz): δ 0.39 (s, 18H, Si(C*H*$_3$)$_3$), 1.19 (d, $^{3}J_{\mathrm{H-H}}$ = 7.0 Hz, 6H, CH(C*H*$_3$)$_2$), 1.21 (d, $^{3}J_{\mathrm{H-H}}$ = 7.0 Hz, 6H, CH(C*H*$_3$)$_2$), 1.30 (d, $^{3}J_{\mathrm{H-H}}$ = 7.0 Hz, 6H, CH(C*H*$_3$)$_2$), 1.32 (d, $^{3}J_{\mathrm{H-H}}$ = 7.0 Hz, 6H, CH(C*H*$_3$)$_2$), 1.34 (m, 8H, THF), 1.99 (sept of d, $^{2}J_{\mathrm{P-H}}$ = 2.5 Hz, $^{3}J_{\mathrm{H-H}}$ = 7.0 Hz, 4H, C*H*(CH$_3$)$_2$), 3.69 (m, 8H, THF) ppm. $^{13}$C{$^{1}$H} (C$_6$D$_6$, 75 MHz): δ 6.4 (s, Si(CH$_3$)$_3$), 19.9 (s, CH(CH$_3$)$_2$), 20.2 (s, CH(CH$_3$)$_2$), 20.3 (s, CH(CH$_3$)$_2$), 20.4 (s, CH(CH$_3$)$_2$), 25.2 (s, THF), 29.2 (d, $^{1}J_{\mathrm{P-C}}$ = 19 Hz, CH(CH$_3$)$_2$), 69.7 (s, THF) ppm. $^{31}$P{$^{1}$H} (C$_6$D$_6$, 121 MHz): δ 67 ppm. Anal. Calcd for C$_{26}$H$_{62}$CaN$_2$O$_2$P$_4$Si$_2$: C, 52.66; H, 10.54; N, 4.72. Found: C, 51.44; H, 10.35; N, 4.55. (Calcd for 1.5 THFs per metal: C, 51.76; H, 10.50; N, 5.03.)

**Synthesis of 4.** Di-*n*-butylmagnesium (1.8 mL, 1.0 M in heptane) was added dropwise to a solution of **1** (0.75 g, 3.65 mmol) in ca. 10 mL of THF. After stirring overnight, the solvent was removed under vacuum and the residue was recrystallized from ca. 5 mL of pentane at −25 °C. Yield = 0.41 g (44%). $^{1}$H (C$_6$D$_6$, 500 MHz): δ 0.35 (s, 18H, Si(C*H*$_3$)$_3$), 1.13 (d, $^{3}J_{\mathrm{H-H}}$ = 7.0 Hz, 6H, CH(C*H*$_3$)$_2$), 1.16 (d, $^{3}J_{\mathrm{H-H}}$ = 7.0 Hz, 6H, CH(C*H*$_3$)$_2$), 1.21 (d, $^{3}J_{\mathrm{H-H}}$ = 7.0 Hz, 6H, CH(C*H*$_3$)$_2$), 1.22 (m, 4H, THF), 1.23 (d, $^{3}J_{\mathrm{H-H}}$ = 7.0 Hz, 6H, CH(C*H*$_3$)$_2$), 1.90 (sept of d, $^{2}J_{\mathrm{P-H}}$ = not resolved, $^{3}J_{\mathrm{H-H}}$ = 7.0 Hz, 4H, C*H*(CH$_3$)$_2$), 3.72 (m, 4H, THF) ppm. $^{13}$C{$^{1}$H} (C$_6$D$_6$, 75 MHz): δ 6.1 (s, Si(CH$_3$)$_3$), 19.5 (s, CH(CH$_3$)$_2$), 19.6 (s, CH(CH$_3$)$_2$), 19.7 (s, CH(CH$_3$)$_2$), 19.8 (s, CH(CH$_3$)$_2$), 25.2 (s, THF), 29.3 (d, $^{1}J_{\mathrm{P-C}}$ = 17 Hz, CH(CH$_3$)$_2$), 70.3 (s, THF) ppm. $^{31}$P{$^{1}$H} (C$_6$D$_6$, 121 MHz): δ 72 ppm. Anal. Calcd for C$_{22}$H$_{54}$MgN$_2$OP$_4$Si$_2$: C, 52.31; H, 10.78; N, 5.55. Found: C, 50.08; H, 10.18; N, 5.29. (Calcd for no THF: C, 49.93; H, 10.71; N, 6.47.)

**Synthesis of 5.** Di-*n*-butylmagnesium (2.4 mL, 1.0 M in heptane) was added dropwise to neat **1** (0.75 g, 3.65 mmol). The solution was stirred at rt for 2 h and then cooled to −25 °C until crystals formed. Yield = 0.40 g (46%). $^{1}$H (C$_6$D$_6$, 300 MHz): δ 0.02−0.03 (m, 2H, MgC*H*$_2$), 0.29 (s, 27 H, Si(C*H*$_3$)$_3$, 1.10−1.20 (m, 21H, CH(C*H*$_3$)$_2$) and Mg(C$_3$H$_6$C*H*$_3$)), 1.30−1.37 (m, 18H, CH(C*H*$_3$)$_2$), 1.66−1.73 (m, 2H, Mg(CH$_2$C*H*$_2$C$_2$H$_5$)), 1.79−1.85 (m, 2H, Mg(C$_2$H$_4$C*H*$_2$CH$_3$), 2.24−2.26 (m, 6H, C*H*(CH$_3$)$_2$). $^{13}$C{$^{1}$H} (C$_6$D$_6$, 75 MHz): δ 1.4 (s, MgCH$_2$), 5.9 (s, Si(CH$_3$)$_3$), 18.5 (s), 21.7 (s), 30.1 (s), 32.7 (d, $^{1}J_{\mathrm{P-C}}$ = 59 Hz, CH(CH$_3$)$_2$) ppm. $^{31}$P{$^{1}$H} (C$_6$D$_6$, 121 MHz): δ 60 ppm. Anal. Calcd for C$_{31}$H$_{78}$Mg$_2$N$_3$P$_3$Si$_3$: C, 51.80; H, 10.94; N, 5.85. Found: C, 51.07; H, 10.05; N, 5.74.

**Reactions of 2−5 with CO$_2$.** The metal complex (**2** = 175 mg; **3** = 350 mg; **4** = 150 mg; **5** = 125 mg) was dissolved in ca. 10 mL of pentane. Carbon dioxide was bubbled through each colorless solution for 15 min. No precipitation or color change was observed. $^{31}$P{$^{1}$H} (pentane, 121 MHz) (all reactions): δ 89 ppm. IR (film on KBr): ν (**2** + CO$_2$) 2256 cm$^{-1}$; (**3**−**5** + CO$_2$) 2257 cm$^{-1}$. GC−MS *m*/*z* (relative intensity, ion): (**2** + CO$_2$) 159 (64.0%, M$^+$), 117 (100%, M$^+$ − NCO); (**3** + CO$_2$) 159 (61.7%, M$^+$), 117 (100%, M$^+$ − NCO); (**4** + CO$_2$) 159 (61.4%, M$^+$), 117 (100%, M$^+$ − NCO); (**5** + CO$_2$) 159 (63.5%, M$^+$), 117 (100%, M$^+$ − NCO).

**Synthesis of 6.** Chlorodiisopropylphosphine (2.38 g, 15.6 mmol) and bis(trimethylsilyl)carbodiimide (1.45 g, 7.8 mmol) were dissolved in ca. 10 mL of THF. The colorless solution was heated to reflux overnight under argon to give a yellow solution. Slow evaporation of the reaction mixture gave yellow crystals of **6**. Yield = 1.97 g (92%). $^{1}$H NMR (C$_6$D$_6$, 300 MHz): δ 0.91−1.17 (overlapping doublets, 3H, PCH(C*H*$_3$)$_2$), 1.27−1.35 (overlapping doublets, 3H, PCH(C*H*$_3$)$_2$), 1.99−2.12 (overlapping sept, 1H, PC*H*(CH$_3$)$_2$) ppm. $^{13}$C{$^{1}$H} NMR (C$_6$D$_6$, 125 MHz): δ 15.4 (s), 16.4 (s), 17.4 (d, $J_{\mathrm{CP}}$ = 7.8 Hz), 18.2 (d, $J_{\mathrm{CP}}$ = 21 Hz), 19.3 (d, $J_{\mathrm{CP}}$ = 8.9 Hz), 20.3 (d, $J_{\mathrm{CP}}$ = 20 Hz), 26.1 (overlapping doublets), 27.1 (d, $J_{\mathrm{CP}}$ = 16 Hz), 27.4 (d, $J_{\mathrm{CP}}$ = 16.5 Hz), 157.3 (overlapping doublets, PC═N) ppm. $^{31}$P{$^{1}$H} (C$_6$D$_6$, 121 MHz): δ 15.3 (virtual t, $J_{\mathrm{PP}}$ = 9.9 Hz, N═P(*i*-Pr)$_2$), 63.5 (virtual t, $J_{\mathrm{PP}}$ = 9.3 Hz, N−P(*i*-Pr)$_2$) ppm. IR (Nujol): ν 1536 (s), 1322 (m) cm$^{-1}$. Anal. Calcd for C$_{26}$H$_{56}$N$_4$P$_4$: C, 56.92; H, 10.29; N, 10.21. Found: C, 56.88; H, 10.24; N, 10.10.

**Synthesis of 7.** A solution of chlorodiisopropylphosphine (1.32 g, 8.7 mmol) in ca. 10 mL of toluene was added to neat trimethylsilylisocyanate (1.0 g, 8.7 mmol). The colorless solution was allowed to stir overnight at rt and was then heated to reflux under argon for four days. An aliquot removed for analysis showed partial conversion to **7**. $^{31}$P{$^{1}$H} (toluene, 121 MHz): δ 90 ppm. IR (film on KBr): ν 2256 cm$^{-1}$. GC−MS *m*/*z* (relative intensity, ion): 159 (39.4%, M$^+$), 117 (100%, M$^+$ - NCO).

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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