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Frustrated Lewis Pairs

Activation of Carbon Dioxide by Silyl Triflate-Based Frustrated Lewis Pairs

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Abstract: Silyl triflates of the form $R_{4-n}Si(OTf)_n$ ($n=1$, 2; $OTf=OSO_3CF_3$) are shown to activate carbon dioxide when paired with bulky alkyl-substituted Group 15 bases. Combinations of silyl triflates and 2,2,6,6-tetramethylpiperidine react with CO_2 to afford silyl carbamates via a frustrated Lewis pair-type mechanism. With trialkylphosphines, the silyl triflates $R_3Si(OTf)$ reversibly bind CO_2 affording $[R'_3P(CO_2)SiR_3][OTf]$ whereas when $Ph_2Si(OTf)_2$ is used one or two molecules of CO_2 can be sequestered. The latter bis-CO_2 product is favoured at low temperatures and by excess phosphine.

Introduction

Nature delicately balances carbon dioxide levels through the processes of photosynthesis, cellular respiration, and organic decomposition. In the past two centuries, however, this global carbon cycle has been disrupted by human activities. Anthropogenic carbon dioxide emissions, most significantly from fossil fuel combustion, have resulted in increased atmospheric CO_2 concentrations and have been a strong contributor to global climate change.[1] As such, CO_2 is very attractive for use as a cheap, abundant, and environmentally-friendly C1 building block. The development of systems designed to sequester or chemically modify CO_2 to fuels or compounds of higher value has garnered significant attention.[2] Frustrated Lewis pairs (FLPs), combinations of sterically hindered Lewis acids and bases with unquenched reactivity, can capture CO_2 by simultaneous nucleophilic attack of the Lewis base at carbon and binding of the Lewis acid to oxygen (Figure 1). In 2009, we described the activation of CO_2 by boron Lewis acids in conjunction with phosphines.[3] Subsequent studies by Piers,[4] O'Hare,[5] Fontaine,[6] and ourselves[7] revealed that B/N, B/P, or Al/P based FLPs can effect the stoichiometric or catalytic reduction of the activated CO_2 moiety upon treatment with an appropriate reducing agent.

Main Group Lewis acids outside of Group 13 have also been employed in the activation of CO_2. In 2012, we[8] reported the insertion of CO_2 into the P–N bonds of strained amidophosphoranes. This reactivity was compared to a frustrated Lewis pair, as the amidophosphoranes contained both acidic and basic P,N functionalities. Efforts to apply silicon Lewis acids in CO_2 activation have focused on highly Lewis acidic silylium cations. Müller and co-workers[9] used silylium cations in conjunction with hydrosilanes to stoichiometrically reduce CO_2 to yield formic acid or methanol after an aqueous quench. The Müller[10] and Ashley[11] groups have also described CO_2 sequestration by silylium/phosphine Lewis pairs.

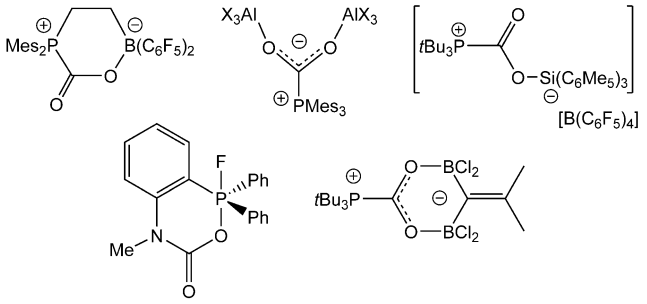

Figure 1. Selected examples of CO_2 activation by frustrated Lewis pairs.

The application of neutral four-coordinate silicon Lewis acids in the context of FLP chemistry has been quite limited, although Manners and co-workers[12] have described the reactions of Group 14 triflates/amine based FLPs with amine and phosphine–borane adducts. As electronically-saturated, four-coordinate silicon compounds can display Lewis acidic properties, they have been previously employed as Lewis acid catalysts for organic carbon–carbon bond forming reactions such as the Diels–Alder reaction,[13] Mukaiyama aldol,[14] and couplings of acetals or acetal-like compounds with nucleophiles.[15] Recently, Tilley and co-workers[16] have also reported catalytic aldehyde hydrosilylation by bis(perfluorocatecholato)silane.

Motivated by the above findings and targeting FLP chemistry beyond traditional Lewis acids, we have probed the use of electronically-saturated silicon Lewis acids, demonstrating that combinations of four-coordinate silyl triflates and amine or phosphine bases can be exploited in FLP/CO_2 chemistry.

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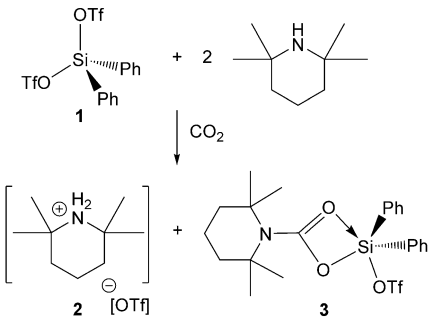
Results and Discussion

A CD_2Cl_2 solution of $Ph_2Si(OTf)_2$ (**1**) was added to one equivalent of 2,2,6,6-tetramethylpiperidine (TMP) in a J-Young NMR tube. The ^1H NMR spectrum of this mixture appeared unchanged from the starting materials, indicating that an adduct was not formed. The NMR tube was degassed and backfilled with carbon dioxide gas prompting precipitation of a white solid. Analysis of the CD_2Cl_2 soluble components by ^1H NMR spectroscopy revealed two sets of aromatic resonances in a 1:1 ratio, corresponding to a mixture of free **1** and a new compound containing phenyl substituents. The resonance attributable to the tetramethylpiperidine N-H proton was absent from the ^1H NMR spectrum, implying complete consumption of TMP. The presence of unreacted **1** suggested that the stoichiometry of this reaction was not 1:1 with respect to the Lewis acid and Lewis base. Adjusting the ratio of reagents to a 2:1 mixture of TMP and **1** followed by exposure to CO_2 yielded the same white precipitate. The precipitate was isolated by filtration and dissolved in CD_3CN. Proton NMR spectroscopy revealed a broad downfield 1:1:1 triplet at $\delta_H = 6.53$ ppm ($^1J_{HN} = 12$ Hz) and aliphatic proton signals, while the ^{19}F spectrum exhibited a single free triflate resonance at $\delta_F = -79.39$ ppm. These observations suggested the formulation of this species as [TMPH][OTf] (**2**). The $^{13}C\{^1H\}$ NMR spectrum of the CD_2Cl_2 soluble product displays a resonance at $\delta_C = 165.02$ ppm, attributable to a carbonyl carbon. Repeating this reaction again using $^{13}CO_2$ resulted in augmentation of this resonance, confirming the incorporation of carbon dioxide into this product. While the spectroscopic data was consistent with the formulation $C_9H_{18}NCO_2SiPh_2(OTf)$ (**3**) (Scheme 1), the identity of this species was ultimately confirmed by X-ray crystallographic studies (Figure 2). Compound **3** was isolated as a white solid in 88% yield.



Scheme 1. Synthesis of **3**.

The solid-state molecular structure of **3** reveals a five-coordinate silicon centre with a distorted trigonal bipyramidal geometry. Interestingly, the CO_2 moiety is bound to silicon in a κ^2 fashion. The Si1–O1 and Si1–O2 bond lengths are not equal in magnitude, with values of 1.747(3) and 1.938(3) Å, respectively. Additionally, the Si1–O3 bond length of 1.823(3) Å is elongated relative to the Si–O bond in **1** (1.6792(2) Å). The C19–O2 bond length of 1.283(5) Å is consistent with a C–O bond order of

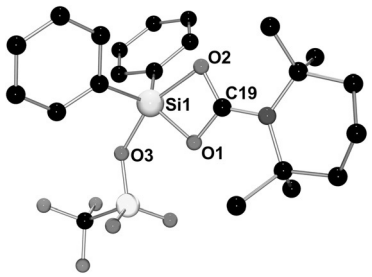
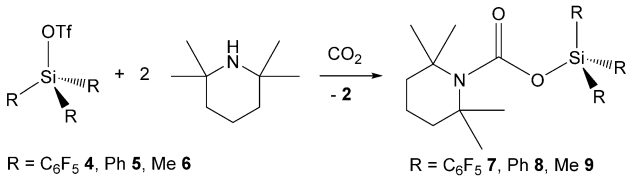


Figure 2. POV-ray depiction of the molecular structure of **3**. H atoms and disorder in the TMP moiety omitted for clarity.

less than 2, while the O1-C19-O2 angle of 107.5(3)° is significantly smaller than the idealized carbonyl bond angle of 120°. These parameters suggest the donation of electron density from O2 into the σ*-orbital of the Si–O3 bond.

The silyl triflates $(C_6F_5)_3Si(OTf)$ (**4**), $Ph_3Si(OTf)$ (**5**), and $Me_3Si(OTf)$ (**6**) were found to react in an analogous fashion when combined with two equivalents of TMP and exposed to CO_2 gas. Following reaction and removal of the salt by-product, the corresponding silyl carbamates **7**–**9** were isolated in yields of 86, 95, and 83%, respectively (Scheme 2). Single crystals of **7** and **8** suitable for X-ray diffraction analysis were obtained by slow evaporation of pentane solutions (Figures 3 and 4).



Scheme 2. Synthesis of **7**–**9**.

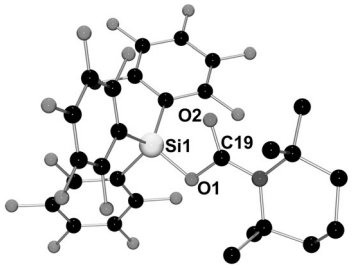


Figure 3. POV-ray depiction of the molecular structure of **7**. H atoms omitted for clarity.

The solid-state molecular structures of **7** and **8** (Figures 3 and 4) display tetrahedral geometries about silicon. In contrast to the structure of **3**, the CO_2 moieties are not bound in a chelating fashion. In fact, the Si1–O2 contact distances for **7** and **8** are quite long, with distances of 2.390(1) and 2.8280(1) Å, respectively. This suggests only weak donation from the carbonyl oxygen to silicon in **7**, while there is no evidence for such in-

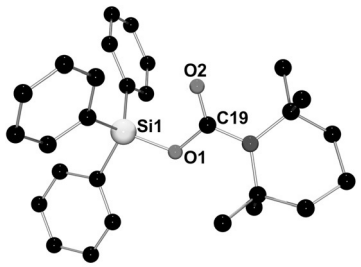


Figure 4. POV-ray depiction of the molecular structure of **8**. H atoms omitted for clarity.

teraction in **8**. The C19–O2 bond length of 1.237(2) Å and O1-C19-O2 angle of 114.2(1)° for **7** show slight deviations from typical carbamate metric parameters;[17] however, those for **8** (C19-O2 1.2200 Å; O1-C19-O2 119.44°) are consistent with a C=O double bond and very close to the idealized sp^2 hybridized carbon angle of 120°.[18] The degree of the Si1-O2 interaction in **3**, **7** and **8** appears to be strongly dependent on the electrophilicity of the silicon centre.

A comparison of the NMR data reveals that the ^{29}Si signal for compound **3** ($\delta_{Si} = -72.0$ ppm) is more upfield than those of **7** ($\delta_{Si} = -49.9$ ppm), **8** ($\delta_{Si} = -12.1$ ppm), and **9** ($\delta_{Si} = 19.2$ ppm), and the parent Lewis acid Ph_2SiOTf_2 ($\delta_{Si} = -24.6$ ppm). Such upfield shifts in the ^{29}Si NMR signal have been previously seen for five coordinate silicon[19] and suggests the κ^2 binding of CO_2 is present for **3** in solution. Furthermore, the more downfield ^{13}C carbonyl resonance of **3** ($\delta_C = 165.02$) is also consistent with a different CO_2 binding motif than in **7** ($\delta_C = 157.67$), **8** ($\delta_C = 155.92$), and **9** ($\delta_C = 156.36$).

When these silyl carbamates **3**, **7**–**9** are placed under vacuum, no release of CO_2 is observed. This stands in contrast to a related species, [TMPH][$C_9H_{18}NCO_2B(C_6F_5)_3$], reported by Piers and co-workers,[4b] which liberates CO_2 on exposure to vacuum. The increased stability of silyl carbamates **3**, **7**–**9** is presumably a consequence of the isolation from the salt by-product, which precludes the reverse reaction.

In a similar fashion, treatment of **6** with one stoichiometric equivalent of PEt_3 resulted the formation of an adduct [Me_3SiPEt_3][OTf] (**10**), as evidenced by a sharp singlet in the $^{31}P\{^1H\}$ NMR spectrum at $\delta_P = -11.5$ ppm (Figure 5). Interestingly, the ^{29}Si spectrum of this adduct did not display Si–P coupling, suggesting that the adduct dissociates reversibly on the NMR time scale. This mixture was exposed to CO_2 gas in a J-Young NMR tube, and the $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture after 20 min revealed two broad singlets at $\delta_P = -15.5$ ppm (**10**, shifted due to equilibrium) and $\delta_P = 38.4$ ppm (**11**). Repetition of this experiment with isotopically enriched $^{13}CO_2$ gas resulted in the same broad singlet at $\delta_P = -15.5$ ppm as well as a doublet at $\delta_P = 38.4$ ppm ($^1J_{PC} = 115$ Hz) in the $^{31}P\{^1H\}$ NMR spectrum. The ^{13}C NMR spectrum displayed a corresponding broad doublet at $\delta_C = 163.14$ ppm with a matching coupling constant ($^1J_{CP} = 115$ Hz). This one bond P-C coupling suggests reversible insertion of CO_2 into the Si–P adduct **10**. Insertion of CO_2 into weak Lewis acid-base adducts is known,[20] as has been reported for $PMes_3/AlX_3$ (X = Cl, Br) adducts.[7b]

Variable-temperature NMR experiments using labeled $^{13}CO_2$ demonstrate that at −20 °C, full conversion to the CO_2 insertion product is observed (Figure 5); however, due to the reversible nature of this CO_2 insertion, the product **11** was not isolable. Nonetheless, all NMR spectroscopic data supports the formulation [$Et_3PCO_2SiMe_3$][OTf] (**11**) (Scheme 3).

In a similar manner, the stoichiometric reaction of **5** with PEt_3 yields a weak adduct, [Ph_3SiPEt_3][OTf] (**12**), evidenced by the singlet in the ^{31}P NMR spectrum at $\delta_P = -16.4$ ppm which is slightly downfield from free PEt_3. Addition of CO_2 to this adduct results in the rapid formation of an equilibrium between the Si–P donor–acceptor adduct and a new species (**13**) at $\delta_P = 41.0$ ppm. The ^{13}C NMR spectrum of this mixture dis-

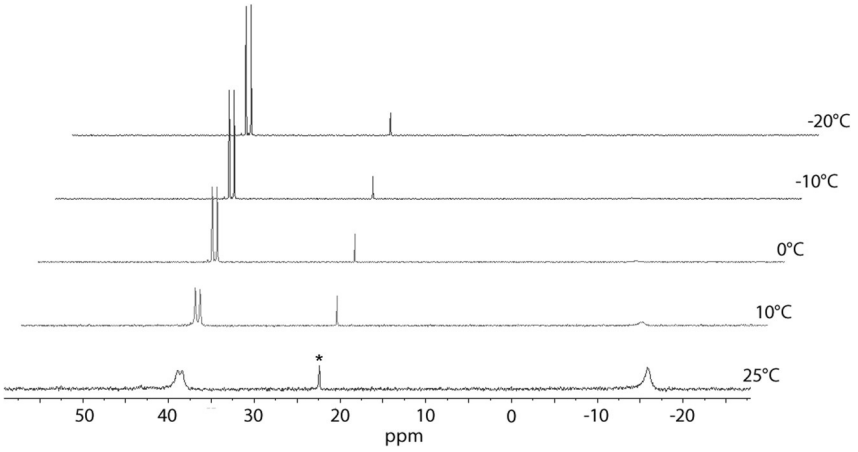
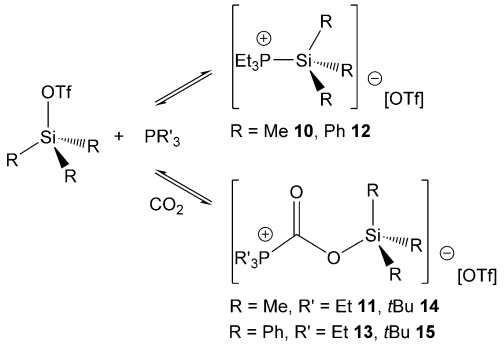


Figure 5. Variable-temperature $^{31}P\{^1H\}$ NMR study depicting the conversion between **10** and **11** in a $^{13}CO_2$ filled NMR tube. * denotes $[HPEt_3]^+$ impurity arising from moisture in the CO_2 gas.



Scheme 3. Synthesis of **10**–**15**.

plays a characteristic doublet at $\delta_C = 163.49$ ppm exhibiting a P–C coupling of 112 Hz as well as resonances for constituent silicon and phosphorus fragments. This spectroscopic data supports the reversible formation of an analogous CO_2 insertion product $[Et_3PCO_2SiPh_3][OTf]$ (**13**) (Scheme 3); similarly, attempts to isolate **13** were unsuccessful due to loss of CO_2 under a nitrogen atmosphere.

In an effort to minimize adduct formation and promote CO_2 capture, the more sterically hindered phosphine P*t*Bu$_3$ was examined as the Lewis base partner. In contrast to PEt_3, P*t*Bu$_3$ (Tolman cone angle of 182° vs 132°)[21] in combination with **6** shows no Lewis acid/base interaction by NMR spectroscopy. Exposure to $^{13}CO_2$ in a sealed J-Young NMR tube shows resonances in the ^{31}P and ^1H NMR spectra that are significantly broadened in comparison to that of free P*t*Bu$_3$; however, no phosphorus–carbon coupling was observed. The ^{13}C NMR spectrum of this mixture showed a broadened resonance attributable to free CO_2 as well as an extremely broad signal in the baseline from $\delta_C = 158$–166 ppm, suggesting very weak CO_2 binding by **6** and P*t*Bu$_3$.

Cooling of the reaction mixture to 0 °C, revealed a very broad doublet (due to ^{31}P–^{13}C coupling), visible at $\delta_P = 51.6$ ppm inferring an equilibrium with free P*t*Bu$_3$. Further cooling to −40 °C, resulted in the disappearance of the free P*t*Bu$_3$ resonance and yields a spectrum with a sharp doublet at $\delta_P = 50.2$ ppm ($^1J_{CP} = 87$ Hz) corresponding to a CO_2 captured species. The low temperature $^{13}C\{^1H\}$ NMR spectrum displays the expected resonances for the constituent silicon and phosphorus fragments, as well as a doublet at $\delta_P = 161.45$ ppm with a matching P–C coupling of 87 Hz. This spectroscopic data supports the proposed formulation $[t\text{Bu}_3PCO_2SiMe_3][OTf]$ (**14**) (Scheme 3).

It is interesting and perhaps counterintuitive that **10** is only observable in solution at low temperature. By contrast, CO_2 capture by **6** and PEt_3 readily occurs at room temperature. As P*t*Bu$_3$ is actually a slightly stronger donor than PEt_3 (Tolman electronic parameters: PEt_3 2061.7 cm^{-1}, P*t*Bu$_3$ 2056.1 cm^{-1})[21] this difference in reactivity must be attributable to steric effects. It is proposed that the weak and reversible adduct formation between **6** and PEt_3 allows for pre-association of the Lewis acid and base components and facilitates CO_2 activation. At room temperature, pre-organization of more hindered Lewis bases, such as P*t*Bu$_3$, with tetrahedral Lewis acids may be less favourable due to increased steric congestion.

The analogous reaction employing **5** similarly displayed weak CO_2 binding at room temperature. Upon addition of $^{13}CO_2$ gas to a 1:1 stoichiometric mixture of **5** and P*t*Bu$_3$, NMR spectroscopy revealed minor conversion (~10%) to a new CO_2 captured species $[t\text{Bu}_3PCO_2SiPh_3][OTf]$ (**15**) (Scheme 3) as evidenced by a small doublet in in the $^{31}P\{^1H\}$ spectrum $\delta_P = 57.5$ ppm ($^1J_{PC} = 85$ Hz) and a corresponding doublet in the ^{13}C spectrum at $\delta_C = 162.93$ ppm. Allowing this mixture to stand for a day at room temperature led to no change in composition, with free P*t*Bu$_3$ still remaining as the predominant species in solution.

We anticipated that reactions of CO_2 with **1** and trialkylphosphines would yield more stable products due to the potential for κ^2 binding of CO_2. Treatment of **1** with one stoichiometric equivalent of PEt_3 did not result in adduct formation. Following addition of CO_2, the $^{31}P\{^1H\}$ NMR spectrum revealed two new resonances at $\delta_P = 43.9$ ppm (**16**, major) and $\delta_P = 41.7$ ppm (**17**, minor). Repetition of this reaction with $^{13}CO_2$ gas revealed that both new signals in the ^{31}P NMR spectrum couple to ^{13}C nuclei with similar coupling constants of $^1J_{PC} = 112$ Hz (**16**) and $^1J_{PC} = 119$ Hz (**17**). Changing the relative ratio of the **1** and PEt_3 reagents had a significant effect on the ratio of **16** and **17** in solution (Figure 6).

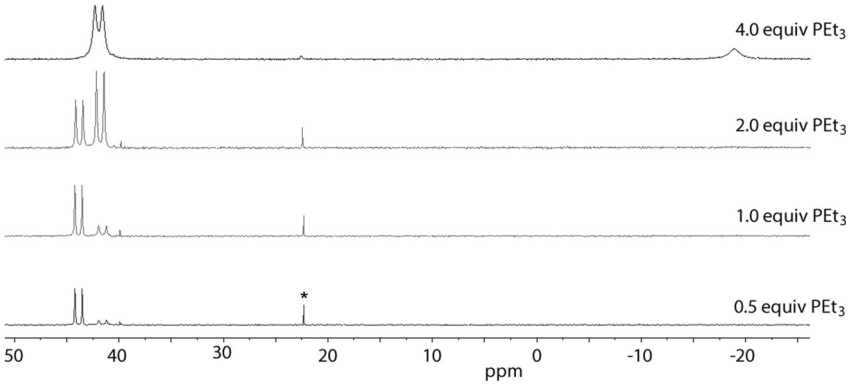


Figure 6. $^{31}P\{^1H\}$ NMR spectra depicting the activation of $^{13}CO_2$ by **1** and different stoichiometric equivalents of PEt_3. * denotes $[HPEt_3]^+$ impurity arising from moisture in the CO_2 gas.

With 0.5 stoichiometric equivalents of PEt_3, **16** is the predominant species in solution; however, with 4.0 equivalents of PEt_3, the major species, **17**, appears to be in equilibrium with free phosphine giving rise to a broadened $^{31}P\{^1H\}$ spectrum. Increasing the equivalents of phosphine in the reaction mixture presumably shifts the equilibrium towards species **17**.

The ^{13}C NMR spectra of these reaction mixtures reveal that the carbonyl carbon resonances of **16** and **17** have nearly identical chemical shifts of $\delta_C = 162.83$ and 162.65 ppm. For each reaction, the ^{19}F NMR spectrum displays only one triflate signal at room temperature. As a greater amount of PEt_3 is utilized, this ^{19}F NMR resonance shifts upfield. At 0.5 equivalents of PEt_3, the triflate signal appears at $\delta_F = -76.57$ ppm, whereas with 4.0 equivalents the resonance appears at $\delta_F = -78.78$ ppm (cf. $\delta_F = -76.10$ ppm for **1**). A more upfield resonance is consistent with a greater degree of dissociation of the triflate anion. These chemical shifts imply the dissociation of a single triflate in **16** and both triflate anions in **17**. Thus, it is proposed that **16** and **17** correspond to stepwise CO_2 activation products in which one or two molecules of CO_2 are bound, $[Et_3P(CO_2)SiPh_2(OTf)][OTf]$ (**16**) and $[(Et_3PCO_2)_2SiPh_2]$

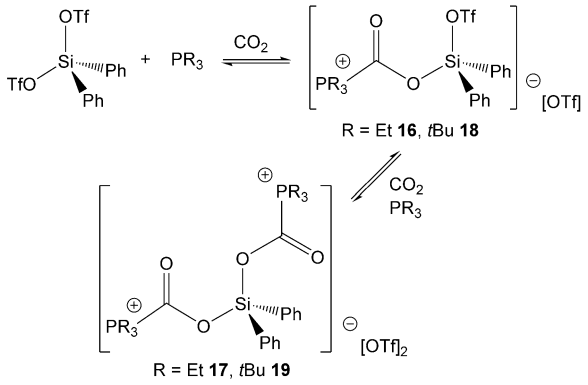
$[OTf]_2$ (**17**), respectively (Scheme 3). This is further supported by the low temperature NMR spectrum of the reaction between **1**, excess PEt_3, and CO_2. At low temperatures, the P–Et resonances of **17** and free PEt_3 split in the ^1H NMR spectrum. Although still broad, integration of the CH_2-PCO_2 resonance relative to the aromatic signals reveals a ratio of two PEt_3 moieties per equivalent of Lewis acid.

Examples of double activation of small molecules by FLP systems are relatively rare. In 2011, we reported that the bis-borane $(C_6F_5)_2B(C_6F_4)B(C_6F_5)_2$ could activate two molecules of nitrous oxide using two equivalents of P*t*Bu$_3$ to afford the bis-zwitterion *t*Bu$_3$P(N_2O)B(C_6F_5)$_2$$C_6F_4$($C_6F_5$)$_2$B($ON_2$)P*t*Bu$_3$.[22] For this system, it is proposed that N_2O activation occurs in a stepwise fashion. In 2012, our group also reported the double activation of CO_2 using the diamidophosphorane $(C_6H_4(NMe))_2PPh$.[8] This process occurs by the insertion of two molecules of CO_2 into the P–N bonds to yield the bis(carbamato)phosphorane $(C_6H_4NMe(CO_2))_2PPh$.[8] In contrast to the bis-borane system, which contains two different Lewis acidic centres, the diamidophosphorane uses a single phosphorus Lewis acidic centre for the double activation process.

Treatment of **1** with one stoichiometric equivalent of P*t*Bu$_3$ did not result in adduct formation. Addition of $^{13}CO_2$ to this mixture resulted in a $^{31}P\{^1H\}$ NMR spectrum that displayed a broadened P*t*Bu$_3$ resonance and a broad doublet ($\delta_P = 57.5$, $^1J_{PC} = 80$ Hz) corresponding to the CO_2 captured product [*t*Bu$_3$P(CO_2)SiPh$_2$(OTf)][OTf_2] (**18**) (Scheme 4). Attempts to promote the generation of a bis-CO_2 activation product analogous to **17** by addition of excess P*t*Bu$_3$ only accelerated degradation of **18**. However, upon cooling to $-30\,^\circ C$, a 1:2 stoichiometric mixture of **1** and P*t*Bu$_3$ pressurized with $^{13}CO_2$ showed consumption of P*t*Bu$_3$ and **18** and the generation of a species proposed to be [(*t*Bu$_3$P(CO_2))$_2$SiPh$_2$][OTf_2]$_2$ (**19**) (Scheme 4) (see Supporting Information). Interestingly at room temperature, there is no evidence for the formation of a bis-CO_2 activation product. Over time, decomposition of **18** occurs at room temperature. The major decomposition species can be identified by a doublet in the ^{13}C NMR spectrum at $\delta_C = 181.61$ ppm ($^1J_{PC} = 45$ Hz) and a corresponding signal in the ^{31}P NMR spectrum at $\delta_P = 49.7$ ppm. Resonances arising from isobutylene were also observed in the ^1H NMR spectrum and the product was presumed to be the phosphinoformate species, *t*Bu$_2$P(CO_2)SiPh$_2$(OTf). This could be formed by the deprotonation of a *tert*-butyl substituent of **18** and loss of isobutylene.

Conclusion

Silyl triflates and tetramethylpiperidine are shown to react with CO_2 to yield silyl carbamates in the form of $C_9H_{18}N(CO_2)SiR_3$ and the ammonium triflate salt [TMPH][OTf]. In these carbamate products, the CO_2 moiety was found to bind to silicon in either a κ^1 or κ^2 fashion depending on the electrophilicity of the silicon centre. Silyl triflates (R_3SiOTf) are also shown to be active in the complexation of CO_2 in combination with PEt_3 or P*t*Bu$_3$ to yield species of the general form [R′$_3$P(CO_2)SiR$_3$][OTf]. These species are unstable with respect to CO_2 liberation and thus are only stable in a CO_2 filled vessel. When employing



Scheme 4. Synthesis of **16**–**19**.

PEt_3 or P*t*Bu$_3$ as the Lewis base partner, $Ph_2Si(OTf)_2$ has been proposed to activate either one or two molecules of CO_2 depending on the stoichiometric equivalents of phosphine used as well as the temperature. Reactions employing P*t*Bu$_3$ tended to yield less CO_2 incorporation at equilibrium than their PEt_3 counterparts. The increased steric hindrance of P*t*Bu$_3$ is presumably less conducive to the prearrangement of the Lewis acidic and basic components when used with tetrahedral Lewis acids.

These findings illustrate that CO_2 activation can be achieved with electronically saturated Lewis acids. We are continuing to investigate the application of four-coordinate silicon Lewis acids in FLP chemistry and their use in the activation of CO_2.

Experimental Section

General methods: All preparations and manipulations were carried out under an anhydrous N_2 atmosphere using standard glovebox and Schlenk-line techniques. Glassware was oven-dried and cooled under vacuum prior to use. Unless specified, all reagents were used as received without further purifications. 2,2,6,6-Tetramethylpiperidine was distilled from CaH_2 prior to use. $(C_6F_5)_3Si(OTf)$ (**4**) was prepared by literature methods.[23] $Me_3Si(OTf)$ (**6**) was purchased from Strem Chemicals. Solvents (CH_2Cl_2 and pentane) were dried using an Innovative Technologies solvent purification system, degassed, and stored over molecular sieves. CD_2Cl_2 was dried over CaH_2, degassed, and stored over activated molecular sieves. NMR spectra were obtained on a Bruker Avance III-400 MHz, Varian 400 MHz, Agilent DD2 500 MHz, Agilent DD2 600 MHz, or Varian Mercury 300 MHz spectrometer. All NMR experiments were conducted at a temperature of 25 °C unless otherwise noted. ^1H, ^{11}B, ^{13}C, ^{19}F, ^{29}Si, and ^{31}P NMR spectra were referenced using (residual) solvent resonances relative to $SiMe_4$ (^1H and ^{13}C) or relative to an external standard (^{11}B: $(Et_2O)BF_3$, ^{19}F: $CFCl_3$, ^{29}Si: $SiMe_4$, ^{31}P: 85% H_3PO_4). Chemical shifts are reported in ppm and coupling constants as scalar values in Hz. Combustion analyses were performed by ANALEST at the University of Toronto with a PerkinElmer CHN Analyzer.

$Ph_2Si(OTf)_2$ (1): A solution of Ph_2SiCl_2 (534 mg, 2.11 mmol, 1.0 equiv) in CH_2Cl_2 (2 mL) was added to a suspension of AgOTf (1.084 g, 4.22 mmol, 2.0 equiv) in CH_2Cl_2 (3 mL). The resulting mixture was left stirring at room temperature in the dark for 24 h The AgCl precipitate was removed by filtration and the solvent was re-

moved in vacuo. The resulting solid was washed with minimal pentane (1 mL) to give a white powder (930 mg, 92%). Crystals suitable for X-ray diffraction were grown from a concentrated CH_2Cl_2 solution at room temperature. The product can also be recrystallized from pentane in the freezer at −35 °C. ^{1}H NMR (400.0 MHz, CD_2Cl_2): δ = 7.61 (dd, 4H, $^3J_{HH}$ = 8 Hz, $^3J_{HH}$ = 8 Hz, *m*-C_6H_5), 7.76 (tt, 2H, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz, *p*-C_6H_5), 7.83 ppm (dd, 4H, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz, *o*-C_6H_5); ^{13}C{^{1}H} NMR (75.4 MHz, CD_2Cl_2): δ = 118.60 (q, $^1J_{CF}$ = 318 Hz, CF_3), 122.73 (s, *i*-C_6H_5), 129.47 (s, *m*-C_6H_5), 134.75(s, *p*-C_6H_5), 135.60 ppm (s, *o*-C_6H_5); ^{19}F{^{1}H} NMR (376.4 MHz, CD_2Cl_2): δ = −76.10 ppm (s, CF_3); ^{29}Si NMR (79.5 MHz, CD_2Cl_2): δ = −24.6 ppm (s); elemental analysis calcd for (%): $C_{14}H_{10}F_6O_6S_2Si$: C 35.00, H 2.10; found: C 34.57, H 2.39.

[TMPH][OTf] (2): The precipitate from reactions yielding **3**, **7**–**9** was isolated by filtration of the reaction mixtures. The white solid was washed with CH_2Cl_2 and pentane (5 mL) and then dried in vacuo. NMR spectroscopy and X-ray diffraction identified this species as [TMPH][OTf]. Single crystals suitable for X-ray diffraction were grown at room temperature from CH_2Cl_2. ^{1}H NMR (400.0 MHz, CD_3CN): δ = 1.41 (s, 12H, CH_3), 1.65 (m, 4H, CH_2), 1.74 (m, 2H, CH_2), 6.53 ppm (brt, 2H, $^1J_{HN}$ = 12 Hz, NH); ^{13}C{^{1}H} NMR (75.4 MHz, CD_3CN): δ = 16.71 (s, CH_2), 27.39 (s, CH_3), 35.36 (s, CH_2), 59.04 (s, *C*-Me_2), 121.78 ppm (q, $^1J_{CF}$ = 320 Hz, CF_3); ^{19}F{^{1}H} NMR (376.4 MHz, CD_3CN): δ = −79.39 ppm (s, CF_3).

$C_9H_{18}N(CO_2)SiPh_2(OTf)$ (3): A J-Young NMR tube was charged with **1** (34 mg, 0.0708 mmol, 1.0 equiv) and 2,2,6,6-tetramethylpiperidine (20 mg, 0.142 mmol, 2.0 equiv) in CD_2Cl_2 (1 mL). The J-Young was degassed and filled with CO_2. Following this, a white solid started to precipitate from solution. The progress of the reaction was monitored by ^{1}H NMR spectroscopy; upon reaction completion, the contents of the J-Young were transferred to a vial and pentane was added (3 mL). The mixture was filtered to remove the precipitate **2**. Volatiles were removed from the filtrate in vacuo affording **3**. The product is a white solid which can be recrystallized from pentane or CH_2Cl_2/pentane solutions at −30 °C (32 mg, 88%). Single crystals suitable for X-ray diffraction were grown by slow evaporation of a pentane solution. ^{1}H NMR (400.0 MHz, CD_2Cl_2): δ = 1.58 (s, 12H, CH_3), 1.66 (m, 2H, CH_2), 1.76 (m, 4H, CH_2), 7.45 (ddm, 4H, $^3J_{HH}$ = 7 Hz, $^3J_{HH}$ = 7 Hz, *m*-C_6H_5), 7.51 (tt, 2H, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 2 Hz, *p*-C_6H_5), 7.84 ppm (ddd, 4H, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 1 Hz, $^4J_{HH}$ = 1 Hz, *o*-C_6H_5); ^{13}C{^{1}H} NMR (100.6 MHz, CD_2Cl_2): δ = 16.14 (s, CH_2), 29.16 (s, CH_3), 41.52 (s, CH_2), 61.22 (s, *C*-Me_2), 119.29 (q, $^1J_{CF}$ = 318 Hz, CF_3), 128.49 (s, *m*-C_6H_5), 131.42 (s, *p*-C_6H_5), 132.84 (s, *i*-C_6H_5), 135.53 (s, *o*-C_6H_5), 165.02 ppm (s, NCO_2); ^{19}F{^{1}H} NMR (376.4 MHz, CD_2Cl_2): δ = −77.77 (s, CF_3); ^{29}Si NMR (79.5 MHz, CD_2Cl_2): δ_{Si} = −72.0 ppm (s); elemental analysis calcd for (%) $C_{23}H_{28}F_3NO_5SSi$: C 53.58, H 5.47, N 2.72; found: C 53.88, H 5.69, N 3.23.

$Ph_3Si(OTf)$ (5): A solution of Ph_3SiCl (460 mg, 1.56 mmol, 1.0 equiv) in CH_2Cl_2 (2 mL) was added to a suspension of AgOTf (400 mg, 1.56 mmol, 1.0 equiv) in CH_2Cl_2 (3 mL). The resulting mixture was stirred in the dark for 12 h. The AgCl precipitate was removed by filtration and the solvent was removed in vacuo, affording a white solid (495 mg, 78%). Single crystals suitable for X-ray diffraction were grown from a concentrated pentane solution at room temperature. ^{1}H NMR (400.0 MHz, CD_2Cl_2): δ = 7.53 (dd, 6H, $^3J_{HH}$ = 8 Hz, $^3J_{HH}$ = 8 Hz, *m*-C_6H_5), 7.63 (t, 3H, $^3J_{HH}$ = 8 Hz, *p*-C_6H_5), 7.75 ppm (d, 6H, $^3J_{HH}$ = 8 Hz, *o*-C_6H_5); ^{13}C{^{1}H} NMR (100.6 MHz, CD_2Cl_2): δ = 118.86 (q, $^1J_{CF}$ = 318 Hz, CF_3), 128.94 (s, *m*-C_6H_5), 129.11 (s, *i*-C_6H_5), 132.46 (s, *p*-C_6H_5), 136.03 ppm (s, *o*-C_6H_5); ^{19}F{^{1}H} NMR (376.4 MHz, CD_2Cl_2): δ = −76.87 ppm (s, CF_3); ^{29}Si{^{1}H} NMR (79.5 MHz, CD_2Cl_2): δ = 1.7 ppm (s); elemental analysis calcd for (%) $C_{19}H_{15}F_3O_3SSi$: C 55.87, H 3.70; found: C 55.84, H 3.92.

$C_9H_{18}N(CO_2)Si(C_6F_5)_3$ (7), $C_9H_{18}N(CO_2)SiPh_3$ (8) and $C_9H_{18}N(CO_2)SiMe_3$ (9): These compounds were prepared in a similar fashion to **3** and thus only one preparation is detailed. **7**: Scale: **4** (20 mg, 0.0295 mmol, 1.0 equiv), 2,2,6,6-tetramethylpiperidine (8 mg, 0.0590 mmol, 2.0 equiv). The product was obtained as a white solid (20 mg, 95%). Single crystals suitable for X-ray diffraction were grown by slow evaporation of a pentane solution. ^{1}H NMR (500.0 MHz, CD_2Cl_2): δ = 1.41 (s, 12H, CH_3), 1.61 (m, 2H, CH_2), 1.68 ppm (t, 4H, $^3J_{HH}$ = 6 Hz, CH_2); ^{13}C{^{1}H} NMR (125.73 MHz, CD_2Cl_2): δ = 16.10 (s, CH_2), 29.37 (s, CH_3), 41.36 (s, CH_2), 58.89 (s, *C*-Me_2), 106.99 (t, $^2J_{CF}$ = 28 Hz, *i*-C_6F_5), 137.81 (dm, $^1J_{CF}$ = 253 Hz, *m*-C_6F_5), 142.78 (dm, $^1J_{CF}$ = 257 Hz, *p*-C_6F_5), 149.19 (dm, $^1J_{CF}$ = 245 Hz, *o*-C_6F_5), 157.67 ppm (s, NCO_2); ^{19}F{^{1}H} NMR (376.4 MHz, CD_2Cl_2): δ = −128.35 (d, 6F, $^3J_{FF}$ = 18.1 Hz, *o*-C_6F_5), −149.22 (t, 3F, $^3J_{FF}$ = 19.9 Hz, *p*-C_6F_5), −161.16 ppm (m, 6F, *m*-C_6F_5); ^{29}Si NMR (79.5 MHz, CD_2Cl_2): δ = −49.9 ppm (s); elemental analysis calcd for (%) $C_{28}H_{18}F_{15}NO_2Si$: C 47.13, H 2.54, N 1.96; found: C 46.89, H 2.26, N 2.00.

8: Scale: **5** (30 mg, 0.0734 mmol, 1.0 equiv), 2,2,6,6-tetramethylpiperidine (21 mg, 0.147 mmol, 2.0 equiv). The product was obtained as a white solid (27 mg, 83%). Single crystals suitable for X-ray diffraction were grown by slow evaporation of a pentane solution. ^{1}H NMR (400.0 MHz, CD_2Cl_2): δ = 1.47 (s, 12H, C-CH_3), 1.64 (m, 2H, CH_2), 1.71 (t, 4H, $^3J_{HH}$ = 6 Hz, CH_2), 7.39 (dd, 6H, $^3J_{HH}$ = 7 Hz, $^3J_{HH}$ = 7 Hz, *m*-C_6H_5), 7.45 (t, 3H, $^3J_{HH}$ = 7 Hz, *p*-C_6H_5), 7.66 ppm (d, 6H, $^3J_{HH}$ = 7 Hz, *o*-C_6H_5); ^{13}C{^{1}H} NMR (125.73 MHz, CD_2Cl_2): δ = 15.95 (s, CH_2), 29.94 (s, CH_3), 40.40 (s, CH_2), 57.06 (s, *C*-Me_2), 128.13 (s, *m*-C_6H_5), 130.39 (s, *p*-C_6H_5), 134.23 (s, *i*-C_6H_5), 136.04 (s, *o*-C_6H_5), 155.92 ppm (s, NCO_2); ^{29}Si NMR (79.5 MHz, CD_2Cl_2): δ = −12.1 ppm (s); elemental analysis calcd for (%) $C_{13}H_{27}NO_2Si$: C 75.80, H 7.50, N 3.16; found: C 76.49, H 7.50, N 2.97.

9: Scale: **6** (30 mg, 0.135 mmol, 1.0 equiv), 2,2,6,6-tetramethylpiperidine (38 mg, 0.270 mmol, 2.0 equiv). The product was obtained as a colourless oil (30 mg, 86%). ^{1}H NMR (500.0 MHz, CD_2Cl_2): δ = 0.26 (s, 9H, Si-CH_3), 1.39 (s, 12H, C-CH_3), 1.58 (m, 2H, CH_2), 1.64 ppm (t, 4H, $^3J_{HH}$ = 6 Hz, CH_2); ^{13}C{^{1}H} NMR (125.73 MHz, CD_2Cl_2): δ = 0.24 (s, Si-CH_3), 16.25 (s, CH_2), 29.94 (s, C-CH_3), 41.11 (s, CH_2), 56.53 (s, *C*-Me_2), 156.36 ppm (s, NCO_2); ^{29}Si NMR (79.5 MHz, CD_2Cl_2): δ = 19.2 ppm (s); elemental analysis calcd for (%) $C_{13}H_{27}NO_2Si$: C 60.65, H 10.57, N 5.44; found: C 60.05, H 11.01, N 6.13.

$[Me_3SiPEt_3][OTf]$ (10) and $[Ph_3SiPEt_3][OTf]$ (12): These compounds were prepared in a similar fashion and thus only one is detailed.

10: **6** (30 mg, 0.135 mmol, 1.0 equiv) and PEt_3 (10 mg, 0.135 mmol, 1.0 equiv) were combined in CD_2Cl_2 and the resulting adducts were examined by multinuclear NMR spectroscopy. ^{1}H NMR (400.0 MHz, CD_2Cl_2): δ = 0.53 (s, 9H, Si-CH_3), 1.16 (dt, 9H, $^3J_{HP}$ = 16 Hz, P-CH_2CH_3), 1.83 ppm (m, 6H, P-CH_2); ^{13}C{^{1}H} NMR (100.6 MHz, CD_2Cl_2): δ = −0.53 (s, Si-CH_3), 8.26 (s, P-CH_2CH_3), 14.81 (br, P-CH_2), 119.73 ppm (q, $^1J_{CF}$ = 318 Hz, CF_3); ^{19}F{^{1}H} NMR (376.4 MHz, CD_2Cl_2): δ = −78.09 ppm (s, CF_3); ^{29}Si NMR (79.5 MHz, CD_2Cl_2): δ = 30.9 ppm (s); ^{31}P{^{1}H} NMR (161.9 MHz, CD_2Cl_2): δ = −11.5 ppm (s);

12: Scale: **5** (22 mg, 0.0539 mmol, 1.0 equiv), PEt_3 (4 mg, 0.0539 mmol, 1.0 equiv); ^{1}H NMR (400.0 MHz, CD_2Cl_2): δ = 1.04 (dt, 9H, $^3J_{HP}$ = 15 Hz, $^2J_{HH}$ = 8 Hz, CH_3), 1.53 (qd, 6H, $^2J_{HH}$ = 8 Hz, $^2J_{HP}$ = 2 Hz, P-CH_2), 7.52 (ddm, 6H, $^3J_{HH}$ = 7 Hz, $^3J_{HH}$ = 7 Hz, *m*-C_6H_5), 7.62 (tm, 3H, $^3J_{HH}$ = 7 Hz, *p*-C_6H_5), 7.69 ppm (dm, 6H, $^3J_{HH}$ = 7 Hz, *o*-C_6H_5); ^{13}C{^{1}H} NMR (100.6 MHz, CD_2Cl_2): δ = 9.01 (d, $^1J_{CP}$ = 8 Hz, P-CH_2), 17.41 (s, P-CH_2CH_3), 119.40 (q, $^1J_{CF}$ = 318 Hz, CF_3), 128.24 (brs, *i*-C_6H_5), 129.13 (s, *m*-C_6H_5), 132.58 (s, *p*-C_6H_5), 136.13 ppm (s, *o*-C_6H_5); ^{19}F{^{1}H} NMR (376.4 MHz, CD_2Cl_2): δ = −77.32 ppm (s, CF_3); ^{29}Si{^{1}H} NMR (HMBC) (99.3 MHz, CD_2Cl_2): δ = −1.0 ppm (s); ^{31}P{^{1}H} NMR (161.9 MHz, CD_2Cl_2): δ_P = −16.4 ppm (s).

[$Et_3PCO_2SiMe_3$][OTf] (11), [$Et_3PCO_2SiPh_3$][OTf] (13), [$tBu_3PCO_2SiMe_3$][OTf] (14), [$tBu_3PCO_2SiPh_3$][OTf] (15): These compounds were prepared in a similar fashion and thus a general procedure is detailed. A J-Young NMR tube was charged with the appropriate silyl triflate (1.0 equiv) and PEt_3 (1.0 equiv) in CD_2Cl_2 (1 mL); The reaction mixture was then examined for adduct formation by multinuclear NMR spectroscopy. Following this, the J-Young NMR tube was degassed and CO_2 gas was added. In each case, NMR spectra obtained after one hour revealed the presence a CO_2 sequestered species in equilibrium with free starting materials or an adduct. The Si/P CO_2 captured species were not isolable and thus were characterized in a CO_2-filled J-Young NMR tube.

11: Scale: **6** (30 mg, 0.135 mmol, 1.0 equiv), PEt_3 (10 mg, 0.135 mmol, 1.0 equiv); (Reaction mixture with **10**): ^{1}H NMR (400.0 MHz, CD_2Cl_2): $\delta = 0.48$ (s, Si-CH_3), 1.16–1.42 (br, 11 P-Et), 1.54–1.80 (br, 10 P-Et), 2.25–2.40 (br, 10 P-Et), 2.40–2.90 ppm (br, 11 P-Et); ^{13}C{^{1}H} NMR (100.6 MHz, CD_2Cl_2): $\delta = -0.10$ (s, Si-CH_3), 6.36 (br, P-CH_2CH_3), 12.45 (br, P-CH_2), 120.06 (q, $^1J_{CF} = 319$ Hz, CF_3), 125.28 (br, free CO_2), 163.14 ppm (brd, $^1J_{CP} = 115$ Hz, P-CO_2); ^{19}F{^{1}H} NMR (376.4 MHz, CD_2Cl_2): $\delta = -78.39$ ppm (s, CF_3); ^{29}Si{^{1}H} NMR (HMBC) (99.3 MHz, CD_2Cl_2): $\delta = 40.3$ ppm (br); ^{31}P{^{1}H} NMR (161.9 MHz, CD_2Cl_2): $\delta = -13.9$ (br, 10), 38.4 ppm (br, 11).

13: Scale: **5** (22 mg, 0.0539 mmol, 1.0 equiv), PEt_3 (4 mg, 0.0539 mmol, 1.0 equiv); (Reaction mixture with **12**): ^{1}H NMR (400.0 MHz, CD_2Cl_2): $\delta = 1.04$ (brm, 12 P-CH_2CH_3), 1.28 (dt, $^3J_{HP} = 20$ Hz, $^3J_{HH} = 8$ Hz, 13 P-CH_2CH_3), 1.48 (brm, 12 P-CH_2), 2.62 (dq, $^2J_{HP} = 14$ Hz, $^3J_{HH} = 8$ Hz, 13 P-CH_2), 7.51 (br, *m*-C_6H_5), 7.60 (br, *p*-C_6H_5), 7.68 ppm (br, *o*-C_6H_5); ^{13}C{^{1}H} NMR (100.6 MHz, CD_2Cl_2): $\delta = 6.24$ (d, $^2J_{PC} = 6$ Hz, 13 P-CH_2CH_3), 9.05 (br, 12 P-CH_2CH_3), 12.62 (d, $^1J_{PC} = 42$ Hz, 13 P-CH_2), 17.58 (br, 12 P-CH_2), 118.90 (q, $^1J_{CF} = 318$ Hz, CF_3), 125.27 (s, free CO_2), 128.86 (s, 12 *i*-C_6H_5), 128.95 (s, 13 *m*-C_6H_5), 129.00 (s, 12 *m*-C_6H_5), 129.15 (s, 13 *i*-C_6H_5), 132.27 (s, 12 *p*-C_6H_5), 132.46 (s, 13 *p*-C_6H_5), 136.02 (s, 13 *o*-C_6H_5), 163.49 ppm (d, $^1J_{CP} = 112$ Hz, P-CO_2); ^{19}F{^{1}H} NMR (376.4 MHz, CD_2Cl_2): $\delta = -78.20$ ppm (s, CF_3); ^{29}Si{^{1}H} NMR (HMBC) (99.3 MHz, CD_2Cl_2): $\delta = -0.5$ (s, 12), 0.5 ppm (s, 13); ^{31}P{^{1}H} NMR (161.9 MHz, CD_2Cl_2): $\delta = -15.2$ (s, 12), 41.0 ppm (s, 13).

14: Scale: **6** (22 mg, 0.0990 mmol, 1.0 equiv), P*t*Bu_3 (20 mg, 0.0990 mmol, 1.0 equiv); Reaction mixture (25 °C): ^{1}H NMR (400.0 MHz, 25 °C, CD_2Cl_2): $\delta = 0.49$ (s, 9H, Si-CH_3), 1.19–1.50 ppm (br, 27H, PC(CH_3)$_3$); ^{13}C{^{1}H} NMR (100.6 MHz, 25 °C, CD_2Cl_2): $\delta = 0.32$ (s, Si-CH_3), 32.36 (br, PC(CH_3)$_3$), 34.70 (br, P-C), 119.54 (q, $^1J_{CF} = 319$ Hz, CF_3), 161.97 ppm (br, P-CO_2); ^{19}F{^{1}H} NMR (376.4 MHz, CD_2Cl_2): $\delta = -77.86$ ppm (s, CF_3); ^{29}Si{^{1}H} NMR (HMBC) (99.3 MHz, CD_2Cl_2): $\delta = 43.7$ ppm(s); ^{31}P{^{1}H} NMR (161.9 MHz, 25 °C, CD_2Cl_2): $\delta = 62.5$ (brs); (−40 °C): ^{1}H NMR (500.0 MHz, −40 °C, CD_2Cl_2): $\delta = 0.44$ (s, 9H, Si-CH_3), 1.65 ppm (d, 27H, $^3J_{HP} = 15$ Hz, PC(CH_3)$_3$); ^{13}C{^{1}H} NMR (100.6 MHz, −40 °C, CD_2Cl_2): $\delta = -0.67$ (s, Si-CH_3), 29.86 (s, PC(CH_3)$_3$), 40.99 (d, $^1J_{CP} = 18$ Hz, P-C), 120.49 (q, $^1J_{CF} = 321$ Hz, CF_3), 161.45 ppm (d, $^1J_{CP} = 87$ Hz, P-CO_2); ^{19}F{^{1}H} NMR (376.4 MHz, CD_2Cl_2): $\delta_F = -79.07$ ppm (s, CF_3); ^{29}Si{^{1}H} NMR (HMBC) (99.3 MHz, CD_2Cl_2): $\delta = 38.2$ ppm (s); ^{31}P{^{1}H} NMR (202.4 MHz, −40 °C, CD_2Cl_2): $\delta = 50.23$ ppm (d, $^1J_{CP} = 87$ Hz).

15: Scale: **5** (30 mg, 0.0734 mmol, 1.0 equiv), P*t*Bu_3 (15 mg, 0.0734 mmol, 1.0 equiv); Reaction mixture: ^{1}H NMR (400.0 MHz, CD_2Cl_2): $\delta = 1.31$ (d, $^3J_{HP} = 10$ Hz, free P*t*Bu_3), 1.66 (d, $^3J_{HP} = 15$ Hz, 15 P-C(CH_3)$_3$), 7.51 (dd/br, $^3J_{HH} = 7$ Hz, $^3J_{HH} = 7$ Hz, *m*-C_6H_5), 7.61 (brt, $^3J_{HH} = 7$ Hz, *p*-C_6H_5), 7.71 ppm (brd, $^3J_{HH} = 7$ Hz, *o*-C_6H_5); ^{13}C{^{1}H} NMR (100.6 MHz, CD_2Cl_2): $\delta = 30.69$ (br, P-C), 32.61 (d, $^3J_{CP} = 13$ Hz, P-C(CH_3)$_3$), 119.43 (q, $^1J_{CF} = 321$ Hz, CF_3), 125.32 (s, free CO_2), 128.91 (s, *m*-C_6H_5), 129.09 (s, *i*-C_6H_5), 132.44 (s, *p*-C_6H_5), 136.02 (s, *o*-C_6H_5), 162.93 ppm (brd, $^1J_{PC} = 85$ Hz, 15 P-CO_2); ^{19}F{^{1}H} NMR (376.4 MHz, 25 °C, CD_2Cl_2): $\delta = -77.42$ ppm (brs, CF_3); ^{29}Si NMR (HMBC) (79.5 MHz, CD_2Cl_2): $\delta = 1.6$ ppm (s); ^{31}P{^{1}H} NMR (161.9 MHz, CD_2Cl_2): $\delta = 57.5$ (brs, 15), 62.5 ppm (brs, free P*t*Bu_3).

[$Et_3P(CO_2)SiPh_2(OTf)$][OTf] (16) and [$(Et_3PCO_2)_2SiPh_2$][OTf]$_2$ (17): A J-Young NMR tube was charged with **1** (1.0 equiv) and PEt_3 (0.5, 1.0, 2.0, or 4.0 equiv) in CD_2Cl_2 (1 mL). No adduct formation was observed between $Ph_2Si(OTf)_2$ and PEt_3 by ^{31}P NMR spectroscopy. The J-Young NMR tubes were degassed and CO_2 gas was added. The relative amounts of **16** and **17** observed in the reaction mixtures are strongly dependent on the number of equivalents of PEt_3 used. NMR spectroscopic data is provided for the reactions using 0.5 equiv and 4.0 equiv PEt_3.

Reaction mixture with 0.5 equiv PEt_3: Scale: **1** (29 mg, 0.0604 mmol, 1.0 equiv), PEt_3 (2 mg, 0.0302 mmol, 0.5 equiv); ^{1}H NMR (400.0 MHz, CD_2Cl_2): $\delta = 1.35$ (m, 16 PCH_2CH_3), 2.69 (brm, 16 P-CH_2), 7.61 (brdd, $^3J_{HH} = 8$ Hz, $^3J_{HH} = 8$ Hz, *m*-C_6H_5), 7.76 (tt, $^3J_{HH} = 8$ Hz, $^4J_{HH} = 2$ Hz, *p*-C_6H_5), 7.83 ppm (dm, $^3J_{HH} = 8$ Hz, *o*-C_6H_5); ^{13}C{^{1}H} NMR (100.6 MHz, CD_2Cl_2): $\delta = 6.15$ (d, $^2J_{PC} = 6$ Hz, 16 P-CH_2CH_3), 12.66 (d, $^1J_{PC} = 42$ Hz, 16 P-CH_2), 118.97 (q, $^1J_{CF} = 318$ Hz, CF_3), 122.84 (s, *i*-C_6H_5), 125.30 (s, free CO_2), 129.52 (s, *m*-C_6H_5), 134.79 (s, *p*-C_6H_5), 135.65 (s, *o*-C_6H_5), 162.83 ppm (d, $^1J_{PC} = 112$ Hz, 16 P-CO_2); ^{19}F{^{1}H} NMR (376.4 MHz, CD_2Cl_2): $\delta = -76.57$ ppm (s, CF_3); ^{29}Si NMR (79.5 MHz, CD_2Cl_2): $\delta = -24.6$ ppm (s, 16); ^{31}P{^{1}H} NMR (161.9 MHz, CD_2Cl_2): $\delta = 41.7$ (br, trace, 17), 43.9 ppm (s, 16).

Reaction mixture with 4.0 equiv PEt_3: Scale: **1** (29 mg, 0.603 mmol, 1.0 equiv), PEt_3 (18 mg, 0.241 mmol, 4.0 equiv); ^{1}H NMR (400.0 MHz, CD_2Cl_2): $\delta = 0.90$–1.50 (br, overlapping PEt_3 and 17 P-Et), 2.40–2.80 (br, 17 P-CH_2CH_3), 7.59 (dd, $^3J_{HH} = 7$ Hz, $^3J_{HH} = 7$ Hz, *m*-C_6H_5), 7.69 (t, $^3J_{HH} = 7$ Hz, *p*-C_6H_5), 7.83 ppm (dd, $^3J_{HH} = 7$ Hz, $^4J_{HH} = 1$ Hz, *o*-C_6H_5); ^{13}C{^{1}H} NMR (100.6 MHz, CD_2Cl_2): $\delta = 6.00$ (br, 17 P-CH_2CH_3), 9.30 (br, PEt_3 P-CH_2CH_3), 12.24 (br, 17 P-CH_2), 18.48 (br, PEt_3 P-CH_2), 121.14 (q, $^1J_{CF} = 320$ Hz, CF_3), 124.56 (s, *i*-C_6H_5), 125.25 (br, free CO_2), 129.33 (s, *m*-C_6H_5), 133.92 (s, *p*-C_6H_5), 135.66 (s, *o*-C_6H_5), 162.65 ppm (brd, $^1J_{PC} = 119$ Hz, PCO_2); ^{19}F{^{1}H} NMR (376.4 MHz, CD_2Cl_2): $\delta = -78.78$ ppm (s, CF_3); ^{29}Si NMR (79.5 MHz, CD_2Cl_2): $\delta_{Si} = -21.0$ ppm (s, 17); ^{31}P{^{1}H} NMR (161.9 MHz, CD_2Cl_2): $\delta = -18.6$ (br, PEt_3), 41.7 (br, 17), 43.9 ppm (br, trace, 16).

[$tBu_3P(CO_2)SiPh_2(OTf)$][OTf_2] (18) and [$(tBu_3PCO_2)_2SiPh_2$][OTf]$_2$ (19): A J-Young NMR tube was charged with **1** (1.0 equiv) and P*t*Bu_3 (1.0 or 2.0 equiv) in CD_2Cl_2 (1 mL). No adduct formation was observed between **1** and P*t*Bu_3 by ^{31}P NMR spectroscopy. The J-Young NMR tubes were degassed and CO_2 gas was added. Partial conversion to **18** was observed at room temperature, while formation of **19** was only observable at low temperature (−30 °C).

18: Reaction mixture with 1.0 equiv P*t*Bu_3: Scale: **1** (30 mg, 0.0624 mmol, 1.0 equiv), P*t*Bu_3 (13 mg, 0.0624 mmol, 1.0 equiv); (25 °C): ^{1}H NMR (400.0 MHz, CD_2Cl_2): $\delta = 1.30$ (br, free P*t*Bu_3), 1.70 (br, 18 P-C(CH_3)$_3$), 7.62 (dd/br, $^3J_{HH} = 8$ Hz, $^3J_{HH} = 8$ Hz, *m*-C_6H_5), 7.76 (brt, $^3J_{HH} = 8$ Hz, *p*-C_6H_5), 7.81 ppm (dd, $^3J_{HH} = 8$ Hz, $^4J_{HH} = 1$ Hz, *o*-C_6H_5); ^{13}C{^{1}H} NMR (125.7 MHz, CD_2Cl_2): $\delta = 30.58$ (br), 32.51 (br), 34.63 (brd, $^1J_{CP} = 30$ Hz, P-C), 42.76 (brd, $^1J_{CP} = 12$ Hz, P-C), 119.41 (q, $^1J_{CF} = 319$ Hz, CF_3), 122.80 (brs, i-C_6H_5), 122.89 (brs, i-C_6H_5), 125.29 (brs, free CO_2), 129.51 (brs, *m*-C_6H_5), 129.75 (brs, *m*-C_6H_5), 134.80 (s, overlapping *p*-C_6H_5), 135.58 (brs, overlapping *o*-C_6H_5), 162.96 ppm (brd, $^1J_{CP} = 80$ Hz, PCO_2); ^{19}F{^{1}H} NMR (376.4 MHz, CD_2Cl_2): $\delta = -77.32$ ppm (s, CF_3); ^{29}Si{^{1}H} NMR (HMBC) (99.3 MHz, CD_2Cl_2): $\delta = -24.6$ (s, $Ph_2Si(OTf)_2$), −20.7 ppm (s, 18); ^{31}P{^{1}H} NMR (161.9 MHz, CD_2Cl_2): $\delta = 57.5$ (brs, 18), 62.5 ppm (brs, free P*t*Bu_3).

19: Reaction mixture with 2.0 equiv P*t*Bu_3: Scale: **1** (29 mg, 0.0603 mmol, 1.0 equiv), P*t*Bu_3 (24 mg, 0.121 mmol, 2.0 equiv); (−30 °C): ^{1}H NMR (500.0 MHz, CD_2Cl_2): $\delta = 1.64$ (d, 54H, $^3J_{HP} = 16$ Hz, P-C(CH_3)$_3$), 7.62 (dd, 4H, $^3J_{HH} = 8$ Hz, $^3J_{HP} = 8$ Hz, *m*-C_6H_5), 7.76 ppm (m, 6H, overlapping *p*-C_6H_5 *o*-C_6H_5); ^{13}C{^{1}H} NMR (125.7 MHz,

CD_2Cl_2): $\delta = 29.91$ (s, P-C(CH_3)$_3$), 45.04 (d, $^1J_{CP} = 16$ Hz), 120.57 (q, $^1J_{CF} = 320$ Hz, CF_3), 122.08 (s, *i*-C_6H_5), 129.55 (s, *m*-C_6H_5), 134.49 (s, *p*-C_6H_5), 135.09 (s, *o*-C_6H_5), 163.26 ppm (d, $^1J_{CP} = 80$ Hz, PCO_2); $^{19}F\{^1H\}$ NMR (470.4 MHz, CD_2Cl_2): $\delta = -78.9$ ppm (s, CF_3); $^{31}P\{^1H\}$ NMR (202.4 MHz, CD_2Cl_2): $\delta = 55.6$ (d, $^1J_{PC} = 81$ Hz, 18, *trace*), 56.1 ppm (d, $^1J_{PC} = 80$ Hz, 19); $^{29}Si\{^1H\}$ NMR (HMBC) (99.3 MHz, CD_2Cl_2): $\delta = -17.7$ ppm(s).

X-ray diffraction studies: Single crystals were coated with Paratone-N oil and mounted under a cold nitrogen stream. Data sets were collected on a Bruker Kappa Apex II CCD diffractometer using a graphite monochromater with $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). Data reduction was performed using the Bruker SMART software package. Data sets were corrected for absorption effects using SADABS. The structures were solved by direct methods using XS and refined by full-matrix least-squares on F^2 using XL as implemented in the SHELXTL suite of programs. All non-hydrogen atoms were refined anisotropically unless noted otherwise. Hydrogen atoms were placed in calculated positions using an appropriate riding model and coupled isotropic temperature factors. In the case of $C_9H_{18}N(CO_2)SiPh_2(OTf)$ (**3**), this structure was both twinned and disordered. The TMP moiety is disordered over two positions (50:50). The disordered atoms were refined isotropically, while the remaining non-hydrogen atoms were refined anisotropically.

CCDC 1400630, 1400631, 1400632, 1400633 and 1400634 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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[1] IPCC, **2014**: *Climate Change 2014: Synthesis Report.* Contribution of Working Groups I, II and III to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change (Eds.: R. K. Pachauri, L. A. Meyer), Geneva, Switzerland, **2014**, p. 151.

[2] a) C. Maeda, Y. Miyazaki, T. Ema, *Catal. Sci. Technol.* **2014**, *4*, 1482 – 1497; b) D. M. D'Alessandro, B. Smit, J. R. Long, *Angew. Chem. Int. Ed.* **2010**, *49*, 6058 – 6082; *Angew. Chem.* **2010**, *122*, 6194 – 6219; c) M. Cokoja, C. Bruckmeier, B. Rieger, W. A. Herrmann, F. E. Kuhn, *Angew. Chem. Int. Ed.* **2011**, *50*, 8510 – 8537; *Angew. Chem.* **2011**, *123*, 8662 – 8690; d) Q. Liu, L. Wu, R. Jackstell, M. Beller, *Nat. Commun.* **2015**, *6*, 10.1038/ncomms6933.

[3] C. M. Mömming, E. Otten, G. Kehr, R. Fröhlich, S. Grimme, D. W. Stephan, G. Erker, *Angew. Chem. Int. Ed.* **2009**, *48*, 6643 – 6646; *Angew. Chem.* **2009**, *121*, 6770 – 6773.

[4] a) F. A. LeBlanc, W. E. Piers, M. Parvez, *Angew. Chem. Int. Ed.* **2014**, *53*, 789 – 792; *Angew. Chem.* **2014**, *126*, 808 – 811; b) A. Berkefeld, W. E. Piers, M. Parvez, *J. Am. Chem. Soc.* **2010**, *132*, 10660 – 10661.

[5] A. E. Ashley, A. L. Thompson, D. O'Hare, *Angew. Chem. Int. Ed.* **2009**, *48*, 9839 – 9843; *Angew. Chem.* **2009**, *121*, 10023 – 10027.

[6] a) M.-A. Courtemanche, J. Larouche, M.-A. Légaré, W. Bi, L. Maron, F.-G. Fontaine, *Organometallics* **2013**, *32*, 6804 – 6811; b) M.-A. Courtemanche, M.-A. Légaré, L. Maron, F.-G. Fontaine, *J. Am. Chem. Soc.* **2014**, *136*, 10708 – 10717; c) R. Declercq, G. Bouhadir, D. Bourissou, M.-A. Légaré, M.-A. Courtemanche, K. S. Nahi, N. Bouchard, F.-G. Fontaine, L. Maron, *ACS Catal.* **2015**, *5*, 2513 – 2520; d) F.-G. Fontaine, M.-A. Courtemanche, M.-A. Légaré, *Chem. Eur. J.* **2014**, *20*, 2990 – 2996; e) M.-A. Légaré, M.-A. Courtemanche, F.-G. Fontaine, *Chem. Commun.* **2014**, *50*, 11362 – 11365; f) M. A. Courtemanche, M. A. Legare, L. Maron, F. G. Fontaine, *J. Am. Chem. Soc.* **2013**, *135*, 9326 – 9329.

[7] a) G. Ménard, D. W. Stephan, *Dalton Trans.* **2013**, *42*, 5447 – 5453; b) G. Ménard, D. W. Stephan, *J. Am. Chem. Soc.* **2010**, *132*, 1796 – 1797; c) G. Ménard, D. W. Stephan, *Angew. Chem. Int. Ed.* **2011**, *50*, 8396 – 8399; *Angew. Chem.* **2011**, *123*, 8546 – 8549; d) G. Ménard, T. M. Gilbert, J. A. Hatnean, A. Kraft, I. Krossing, D. W. Stephan, *Organometallics* **2013**, *32*, 4416 – 4422; e) M. J. Sgro, J. Dömer, D. W. Stephan, *Chem. Commun.* **2012**, *48*, 7253 – 7255; f) T. Wang, D. W. Stephan, *Chem. Eur. J.* **2014**, *20*, 3036 – 3039; g) T. Wang, D. W. Stephan, *Chem. Commun.* **2014**, *50*, 7007 – 7010.

[8] L. J. Hounjet, C. B. Caputo, D. W. Stephan, *Angew. Chem. Int. Ed.* **2012**, *51*, 4714 – 4717; *Angew. Chem.* **2012**, *124*, 4792 – 4795.

[9] A. Schäfer, W. Saak, D. Haase, T. Muller, *Angew. Chem. Int. Ed.* **2012**, *51*, 2981 – 2984; *Angew. Chem.* **2012**, *124*, 3035 – 3038.

[10] a) A. Schäfer, M. Reißmann, A. Schäfer, M. Schmidtmann, T. Müller, *Chem. Eur. J.* **2014**, *20*, 9381; b) M. Reissmann, A. Schafer, S. Jung, T. Muller, *Organometallics* **2013**, *32*, 6736 – 6744.

[11] a) T. J. Herrington, A. J. W. Thom, A. J. P. White, A. E. Ashley, *Dalton Trans.* **2012**, *41*, 9019 – 9022; b) T. J. Herrington, B. J. Ward, L. R. Doyle, J. McDermott, A. J. P. White, P. A. Hunt, A. E. Ashley, *Chem. Commun.* **2014**, *50*, 12753 – 12756.

[12] G. R. Whittell, E. I. Balmond, A. P. M. Robertson, S. K. Patra, M. F. Haddow, I. Manners, *Eur. J. Inorg. Chem.* **2010**, 3967 – 3975.

[13] a) K. Hara, R. Akiyama, M. Sawamura, *Org. Lett.* **2005**, *7*, 5621; b) K. Kubota, C. L. Hamblett, X. Wang, J. L. Leighton, *Tetrahedron* **2006**, *62*, 11397; c) Y. Sakaguchi, Y. Iwade, T. Sekikawa, T. Minami, Y. Hatanaka, *Chem. Commun.* **2013**, *49*, 11173.

[14] a) N. Iwasawa, T. Mukaiyama, *Chem. Lett.* **1987**, 463; b) M. Sai, M. Akakura, H. Yamamoto, *Chem. Commun.* **2014**, *50*, 15206 – 15208.

[15] A. D. Dilman, S. L. Ioffe, *Chem. Rev.* **2003**, *103*, 733.

[16] A. L. Liberman-Martin, R. G. Bergman, T. D. Tilley, *J. Am. Chem. Soc.* **2015**, *137*, 5328 – 5331.

[17] B. H. Bracher, R. W. H. Small, *Acta Crystallogr.* **1967**, *23*, 410.

[18] F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen, R. Taylor, *J. Chem. Soc. Perkin Trans.* **1987**, S1 – S19.

[19] a) J. A. Cella, J. D. Cargioli, E. A. Williams, *J. Organomet. Chem.* **1980**, *186*, 13 – 17; b) A. D. Dilman, V. V. Levin, A. A. Korlyukov, P. A. Belyakov, M. I. Struchkova, M. Y. Antipin, V. A. Tartakovsky, *J. Organomet. Chem.* **2008**, *693*, 1005 – 1019.

[20] a) J. Boudreau, M. A. Courtemanche, F. G. Fontaine, *Chem. Commun.* **2011**, *47*, 11131 – 11133; b) F. Bertini, F. Hoffmann, C. Appelt, W. Uhl, A. W. Ehlers, J. C. Slootweg, K. Lammertsma, *Organometallics* **2013**, *32*, 6764 – 6769.

[21] C. A. Tolman, *Chem. Rev.* **1977**, *77*, 313 – 348.

[22] R. C. Neu, E. Otten, A. Lough, D. W. Stephan, *Chem. Sci.* **2011**, *2*, 170 – 176.

[23] V. V. Levin, A. D. Dilman, P. A. Belyakov, A. A. Korlyukov, M. I. Struchkova, V. A. Tartakovsky, *Eur. J. Org. Chem.* **2004**, 5141 – 5148.

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