Carbon Dioxide Capture

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Phosphorus as a Lewis Acid: CO_2 Sequestration with Amidophosphoranes**

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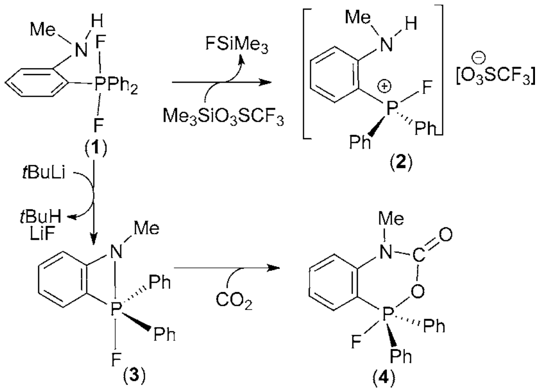
The role of CO_2 as a greenhouse gas has prompted widespread efforts for carbon capture. To date, a number of strategies have been developed to sequester this gas using materials such as alumina, silica, zeolites, activated carbon, and metal–organic frameworks (MOFs).[1] While some of these systems are being applied on increasing scale, efforts to discover fundamentally unique strategies for CO_2 capture continue. In this regard, the use of metal-free, frustrated Lewis pairs (FLPs) has received recent attention.[2] In 2009, we reported the reversible binding of CO_2 by borane/phosphine-based FLPs.[3] Subsequent work by the groups of O'Hare[4] and Piers,[5] as well as ourselves,[6] has demonstrated the use of B/P, B/N, and Al/P-based FLPs for the conversion of CO_2 into methanol, methane, or CO.

While Group 13/15 Lewis acid/base combinations continue to reveal new aspects of FLP chemistry, less attention has been paid to expanding the variety of FLP systems available. A creative departure from the original systems has been described by Alcarazo and co-workers.[7] In that work, all-carbon-based FLPs of N-heterocyclic carbenes and Lewis acidic allenes were described. Another alternative has been developed by Wass and co-workers,[8] who exploited Group 4 metal Lewis acids with bulky phosphines to activate a variety of small molecules. While considering new approaches, we noted the innovative examples of organic transformations and anion capture that are facilitated by Lewis acidic phosphonium cations[9] and queried the viability of such species in FLP chemistry. Herein, we describe the syntheses of aminophosphonium salts, which incorporate Lewis basic and acidic pnictogen functionalities within an intramolecular system. These species serve as hypothetical intermediates for the generation of ring-strained amidophosphoranes, which are shown to sequester CO_2.

Reaction of the *o*-phosphinoaniline $Ph_2P(o\text{-}C_6H_4NHMe)$[10] with XeF_2[11] at −35 °C in CH_2Cl_2 produces the off-white difluorophosphorane, $Ph_2PF_2(o\text{-}C_6H_4NHMe)$, **1** (Scheme 1). The $^{31}P\{^1H\}$ NMR spectrum of **1** reveals a high-field triplet at $\delta = -45.6$ ppm ($^1J_{PF} = 625$ Hz), while the ^1H NMR spectrum depicts the NH resonance as a broad quartet at $\delta = 4.68$ ppm ($^3J_{HH} = 5.0$ Hz) that couples to the *N*-methyl signal at $\delta = 2.67$ ppm. With the amine functionality unaffected by fluorination, facile F^- abstraction from **1** by $Me_3SiO_3SCF_3$ yields $[Ph_2PF(o\text{-}C_6H_4NHMe)][O_3SCF_3]$ (**2**), a rare example of a compound containing both acidic phosphonium and pendant amine functionalities. The $^{31}P\{^1H\}$ NMR spectrum of **2** reveals a strongly deshielded P nucleus with a doublet resonance at $\delta = 94.4$ ($^1J_{PF} = 980$ Hz), while the ^1H spectrum is largely unchanged, except for a downfield shift of the NH signal to $\delta = 5.20$.



Scheme 1. Synthesis of **2**–**4**.

The combination of unquenched Lewis acidic and basic pnictogens within **2** prompted our investigation of its potential behavior as an FLP in reactions with CO_2. Exposure of **2** to an overpressure of $^{13}CO_2$ in CD_2Cl_2 resulted in no reaction, and attempts to deprotonate the amine with one equiv of Et_3N or *n*BuLi in THF yielded a mixture of products that could not be separated. However a new, bright-yellow species (**3**) was cleanly prepared from **1** in good yields by the slow addition of an *n*-pentane solution of *t*BuLi to a THF solution of the compound at −78 °C. The ^1H NMR spectrum of **3** suggests the presence of a P–N bond, as the *N*-methyl signal is split into a doublet of doublets ($^3J_{PH} = 4.4$ Hz and $^4J_{FH} = 2.4$ Hz). The $^{31}P\{^1H\}$ NMR signal of **3** was observed as a doublet at $\delta = -44.6$ ppm ($^1J_{PF} = 679$ Hz), and the corresponding ^{19}F resonance was seen at $\delta = -44.4$ ppm. These data suggest the formulation of **3** as the amidophosphorane $Ph_2PF(o\text{-}C_6H_4NMe)$. The X-ray structure of **3** confirmed this formulation, demonstrating a distorted trigonal bipyramidal geometry at P, which is contained within a strained four-membered ring (Figure 1).[12] Although rare (a few amidofluorophosphoranes have previously been prepared),[13] compound **3** is the first to be crystallographically characterized. The P–N bond was found to be exceptionally long (1.842(7) Å and 1.839(6) Å)[13] within each of two

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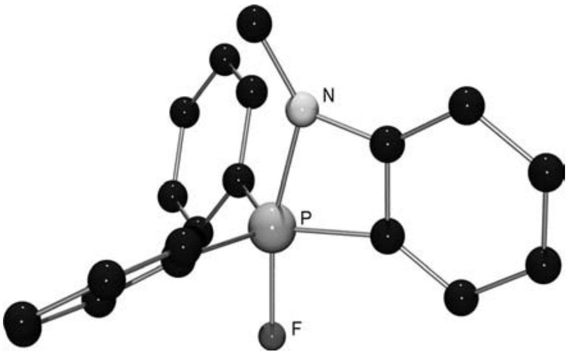


Figure 1. POV-ray depiction of **3**.

crystallographically independent molecules. The N atom occupies an axial position opposite F, although the N–P–F angles (164.4(3)° and 165.1(3)°) are somewhat distorted from linearity, presumably in response to constraints imposed by the equatorially disposed anilido C_{ipso}. The geometry of the amido unit is nearly planar, as the sum of the angles about N is 356° and the N–C_{ortho} distances of 1.439(9) Å and 1.442(10) Å are typical of single bonds. The C–C bonds within the anilido ring are similar to those within neighboring Ph rings, in contrast to the dearomatization observed within metal complexes of the amidophosphine ligand.[14]

The exposure of a bright-yellow THF solution of **3** to 1 atm of CO_2 at ambient temperature results in its immediate discoloration, and NMR analysis performed shortly thereafter indicates complete conversion to a new species (**4**). The ^{1}H NMR spectrum of **4** shows a singlet *N*-methyl resonance at $\delta = 3.15$ ppm, and the loss of its coupling to both P and F is consistent with rupture of the P–N bond within **3** to accommodate CO_2. The $^{13}C\{^1H\}$ NMR spectrum shows the CO_2 unit as a doublet at $\delta = 153.1$ ppm with $^2J_{PC} = 8$ Hz, while the $^{31}P\{^1H\}$ spectrum shows a doublet at $\delta = -57.0$ ppm, with $^1J_{PF} = 664$ Hz. The corresponding ^{19}F NMR signal is seen at $\delta = -34.2$ ppm. IR data for **4** show a characteristic carbonyl absorption band at 1696 cm^{-1}. Collectively, these data suggest that **4** is the carbamatofluorophosphorane $Ph_2PF(o\text{-}C_6H_4N(Me)CO_2)$, and this formulation was confirmed by X-ray crystallography (Figure 2).[12] Insertion of CO_2 into the activated P–N bond of **3** results in a six-membered ring with an elongated P–O bond (1.775(1) Å and 1.778(1) Å) in each of two molecules in the asymmetric unit. Within **4**, the geometry about P is trigonal bipyramidal with the carbamato O occupying an axial position *trans* to F. The C–O and C=O bonds in the CO_2 fragment of **4** average 1.330(2) and 1.212(2) Å, respectively, which are slightly longer than those seen in $t\mathrm{Bu}_3PCO_2B(C_6F_5)_3$ (1.299(2) Å, 1.208(2) Å) and $(Me_3C_6H_2)_2PCH_2CH_2B(C_6F_5)_2(CO_2)$ (1.284(4) Å, 1.209(4) Å). Compounds **3** and **4** are both rare examples of crystallographically characterized phosphoranes, and to the best of our knowledge, **4** is also the first known pentacoordinate phosphorane containing a carbamato substituent. Although kinetically hindered insertion of CO_2 into the P–N bond of $(CF_3)_3PMe(NMe_2)$ has been previously reported to proceed over several days to give a six-coordinate zwitterionic carbamatophosphate,[13] the facile insertion of CO_2 into the P–N bond of **3**, relieves strain within the four-membered ring, thereby dramatically accelerating the reaction. It is noteworthy that **4** is thermally robust, as it is unchanged on heating to 120 °C in toluene for 1 h.

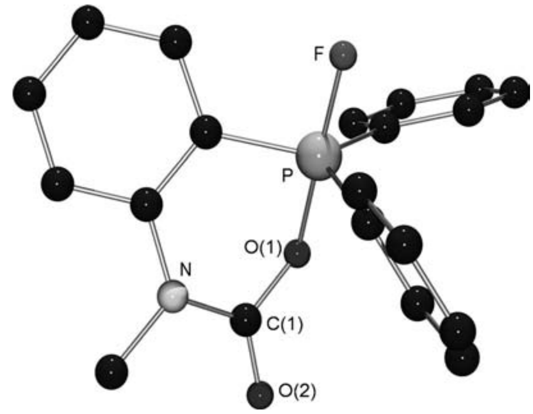
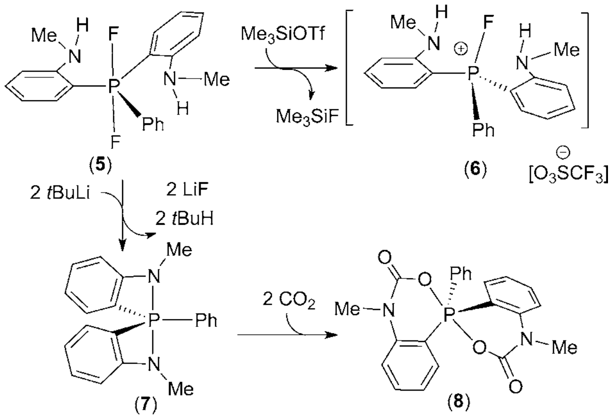


Figure 2. POV-ray depiction of **4**.

Related compounds incorporating a second *o*-*N*-methylaniline group were prepared (Scheme 2). Oxidative fluorination of $PhP(o\text{-}C_6H_4NHMe)_2$ with XeF_2 produced the phosphorane $PhPF_2(o\text{-}C_6H_4NHMe)_2$ (**5**), and subsequent fluoride ion abstraction by $Me_3SiO_3SCF_3$ generated the salt $[PhPF(o\text{-}C_6H_4NMeH)_2][O_3SCF_3]$ (**6**). The spectral parameters of these compounds closely matched those of their monoaniline derivatives. Crystallographic data of **6** confirmed the formulation and revealed P···N separations of 3.05–3.12 Å. Interestingly, both amine H atoms are oriented towards F, suggesting hydrogen bonding, although the H···F separations of about 2.4 Å indicate that this interaction is weak.[15] Consistent with the reactivity described above, the addition of 2 equiv of *t*BuLi to **5** resulted in the diamidophosphorane, $PhP(o\text{-}C_6H_4NMe)_2$ (**7**), which was isolated as a yellow solid in 75 % yield. The $^{31}P\{^1H\}$ NMR spectrum shows a shielded P nucleus with a singlet at $\delta = -58.7$ ppm, and the ^{1}H NMR spectrum demonstrates the C_2 molecular symmetry with a single NMe resonance at $\delta = 2.55$ ppm (d, $^3J_{PH} = 6.8$ Hz). Treatment of **7** with 1 atm of CO_2 under ambient conditions



Scheme 2. Synthesis of **6**–**8**.

instantly produced PhP(o-$C_6H_4N(Me)CO_2)_2$ (**8**), which was isolated in 80% yield. The $^{31}P\{^1H\}$ NMR spectrum of **8** showed a single peak at $\delta = -68.6$ ppm, and the loss of $^3J_{PH}$, which was made evident by the singlet NCH_3 signal in the ^1H NMR spectrum, was consistent with CO_2 insertion into each of the chemically equivalent P–N bonds. The ^1H and $^{13}C\{^1H\}$ NMR data were also consistent with the formulation of **8** as the double insertion product. Use of $^{13}CO_2$ revealed a strong signal at $\delta = 152.8$ ppm in the $^{13}C\{^1H\}$ NMR spectrum and IR spectroscopy of **8** showed the expected carbonyl absorption at 1697 cm^{-1}.

The formulation of **8** was also confirmed by its X-ray structure (Figure 3),[12] which showed the pseudo-C_2-symmetric geometry of the dicarbamatophosphorane, wherein oxygen donors occupy both axial positions, while the C_{ipso} atoms of the aryl groups lie in the equatorial plane. The lengths of mutually *trans* P–O bonds were found to be 1.7635(8) and 1.7773(8) Å, with an O–P–O angle of 174.27(4)°. The C–O and C=O bonds in **8** average 1.339(1) and 1.215(2) Å, respectively, and are slightly longer than those in **4**, which is consistent the Lewis acidity of the P^V center. Although several examples of dicarboxylatophosphoranes are known,[16] compound **8** is to our knowledge the first example of a dicarbamatophosphorane. Moreover, its generation from **7** is the first example of double CO_2 activation by a phosphorane.

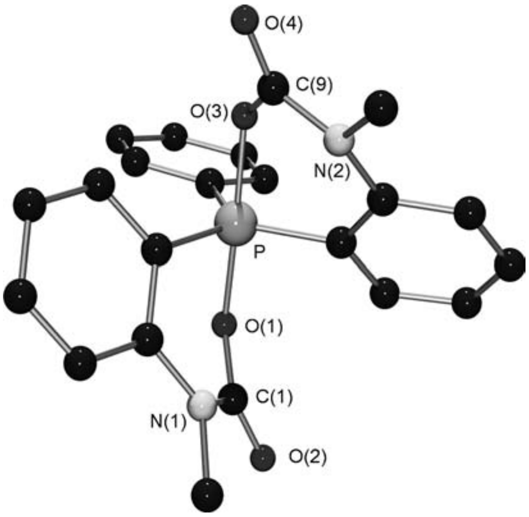
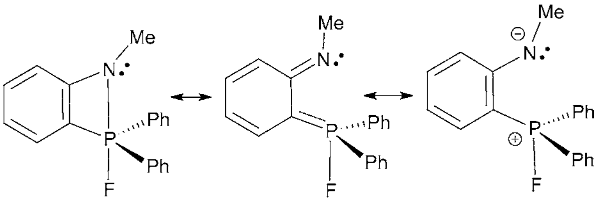


Figure 3. POV-ray depiction of **8**.

The formation of **4** and **8** result from insertion of CO_2 into the P–N bonds of **3** and **7**, respectively, and structural data for **3** suggest that ring strain within these species results in their kinetically enhanced reactivity toward CO_2. However, fluoride abstraction from **3** with $Me_3SiO_3SCF_3$ affords the salt $[Ph_2P(o\text{-}C_6H_4NMe)][O_3SCF_3]$ (**9**), which does not react with CO_2, even at 60°C for several hours. Nonetheless, the targeted species $[Ph_2P(o\text{-}C_6H_4N(Me)CO_2)][O_3SCF_3]$ (**10**) could be prepared by fluoride abstraction from **4** using $Me_3SiO_3SCF_3$. The precise details of the mechanism of CO_2 insertion remains unproven. While a concerted process is a possibility, it is also noteworthy that the resonance forms of **3** (Scheme 3) suggest the possibility of an FLP-type description in which a charge-separated P–N bond consists of an amido donor and a phosphonium acceptor. This view of **3** is reminiscent of a B/P FLP, $(C_6H_2Me_3)_2PCH_2CH_2B(C_6F_5)_2$, developed by Erker and co-workers.[16] In this regard, the CO_2 insertion chemistry discussed herein is also analogous to that reported for the four-membered rings of boron imidinates, $HC(NR)_2B(C_6F_5)_2$, which are also thought to react with small molecules via an open FLP form.[17]



Scheme 3. Resonance forms of **3**.

In summary, amidophosphoranes **3** and **7**, containing the four-membered rings, react rapidly to capture of one and two equivalents of CO_2, respectively. These compounds bind the substrate in a manner analogous to related FLP systems. These findings have prompted further study of the acceptor capabilities of electron-poor phosphonium cations to provide P^V Lewis acid centers for FLP chemistry. The results of these efforts will be reported in due course.

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[12] X-ray crystallography data for **3**: $P\bar{1}$, $a = 12.6080(7)$, $b = 13.8369(8)$, $c = 19.2878(11)$ Å, $\alpha = 96.396(2)$, $\beta = 97.763(2)$, $\gamma = 101.782(2)°$, $V = 3230.1(3)$ Å^3, $Z = 2$, data ($> 2\sigma$) = 15134, variables = 906, $R(>2\sigma) = 0.0736$, R(all) = 0.2289, GOF = 1.018. **4**: monoclinic, $P2_1/c$, $a = 17.0345(9)$, $b = 11.3459(7)$, $c = 18.3854(10)$ Å, $\beta = 107.910(2)°$, $V = 3381.2(3)$ Å^3, $Z = 8$, data ($> 2\sigma$) = 7735, variables = 451, $R(>2\sigma) = 0.0514$, R(all) = 0.1494, GOF = 1.040. **6**: triclinic, $P\bar{1}$, $a = 12.3510(6)$, $b = 14.1873(8)$, $c = 15.2817(9)$ Å, $\alpha = 111.662(3)$, $\beta = 98.057(3)$, $\gamma = 102.996(3)°$, $V = 2350.1(2)$ Å^3, $Z = 4$, data ($> 2\sigma$) = 8202, variables = 604, $R(>2\sigma) = 0.0533$, R(all) = 0.1546, GOF = 1.034. **8**: monoclinic, $C2/c$, $a = 28.4415(13)$, $b = 9.3453(5)$, $c = 15.5756(7)$ Å, $\beta = 98.410(2)°$, $V = 4095.4(3)$ Å^3, $Z = 8$, data ($> 2\sigma$) = 7801, variables = 281, $R(>2\sigma) = 0.0384$, R(all) = 0.1057, GOF = 1.027. See also the Supporting Information. CCDC 867814 (**3**), 867815 (**4**), 867816 (**6**), and 867817 (**8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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