

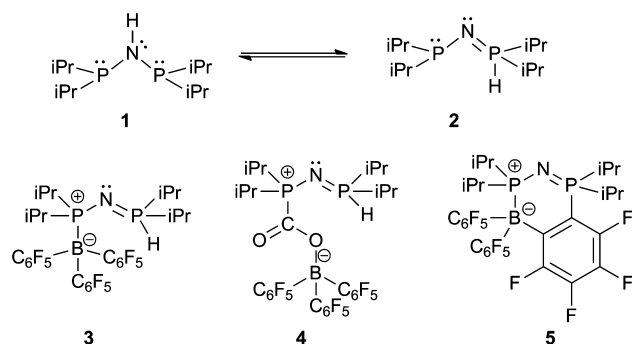
NH/PH Isomerization and a Lewis Pair for Carbon Dioxide Capture

Brian M. Barry,[†] Diane A. Dickie,[†] Luke J. Murphy,[‡] Jason A. C. Clyburne,^{*,‡} and Richard A. Kemp^{*,†,§}[†]Department of Chemistry and Chemical Biology, University of New Mexico, Albuquerque, New Mexico 87131, United States[‡]The Atlantic Centre for Green Chemistry, Department of Chemistry, Saint Mary's University, Halifax, NS, B3H 3C3, Canada[§]Advanced Materials Laboratory, Sandia National Laboratories, Albuquerque, New Mexico 87106, United States

S Supporting Information

ABSTRACT: Bis(di-*i*-propylphosphino)amine **1** reacts with B(C₆F₅)₃ to form an adduct with concomitant N/P H-isomerization. This species reacts smoothly with carbon dioxide. An attempt to prepare an anionic derivative resulted in the formation of a novel heterocycle derived from the PNP ligand and B(C₆F₅)₃.

Bis(diarylphosphino)amines, HN(PAr₂)₂, and the related bis(dialkylphosphino)amines, HN(PR₂)₂, are reliable precursors to the monoanionic ligand, [N(PR₂)₂][−]. The steric demands of these ligands are reminiscent of the *t*-butylmethylphosphino-di-*t*-butylphosphinomethane or “trichickenfootPHOS” ligand,¹ suggesting that bis(phosphine)-amines may have great potential in facilitating a wide variety of metal-mediated transformations. These ligands are ambidentate and are known to bond in a variety of modes with either transition metal or lanthanide and actinide compounds;² however, the coordination chemistry of this important ligand class with main group elements has not been extensively explored. Our group, having a longstanding interest in CO₂ interactions with main group compounds,³ has recently been successful in using the aliphatic ligand HN(P^{*i*}Pr)₂ (**1**) to prepare a novel tin-containing compound that reacts with carbon dioxide.⁴



Bis(dialkylphosphino)amines, HN(PR₂)₂, have the ability to engage in a tautomerization reaction with Lewis acids, generating phosphoranes such as **3**, discussed below. Having bulky alkyl groups such as *t*-butyl on phosphorus will facilitate this isomerization, and it is well-known that reaction of an electrophile with compounds such as **1** occurs predominantly at phosphorus, resulting in the formation of charged phosphoranimine-phosphonium salts. Recently, this prototropism has been cleverly used to prepare chiral and air-stable hydro-

genation catalysts.⁵ Here, we report the use of **1** to prepare a Lewis acid–base adduct capable of reacting selectively with carbon dioxide. It is anticipated that the isomerization reaction from **1** to **2** in the presence of a Lewis acid might facilitate break-up of the complex and be more selective *vis-à-vis* small molecule reactivity than the elegant but more reactive frustrated Lewis pair (FLP) systems.⁶

Bis(di-*i*-propylphosphino)amine **1** reacts cleanly with B(C₆F₅)₃ in benzene to produce the air-stable zwitterionic derivative **3**, which can be crystallized from benzene solution. Spectroscopic analysis of the isolated material is consistent with the formation of compound **3**. In contrast to the single resonance at 68.0 ppm (C₆D₆) in the ³¹P{¹H} NMR spectrum of **1**, **3** exhibits two signals at 26.0 and 42.6 ppm. The upfield signal is a doublet of quartets consistent with a combination of ²J_{P–P} and ³J_{B–P} coupling and has been assigned to a phosphorane resonance. The remaining quartet, assigned to the boron-bound phosphorus atom, is broadened due to the direct interaction with a quadrupolar B atom. The ¹J_{B–P} coupling can be resolved, but the broadening does not allow for ²J_{P–P} resolution. The ¹J_{B–P} coupling (97 Hz) observed in the ³¹P{¹H} spectrum is in accord with observation of a doublet in the ¹¹B{¹H} spectrum with a similar coupling. The proton-coupled ³¹P spectrum of **3** revealed a signal with a ¹J_{H–P} coupling constant of 466 Hz. This coupling was supported by the ¹H NMR spectrum that also showed the same ¹J_{P–H} coupling constant for the phosphorus bound proton. Taken *in toto*, these data are consistent with a prototropic reaction with migration of the proton from nitrogen to phosphorus upon interaction with B(C₆F₅)₃. Consistent with this, the infrared spectrum of **1** exhibits a strong N–H absorption at 3265 cm^{−1} that is noticeably absent in the infrared spectrum of **3**. For compound **3**, a new absorption appears at 2378 cm^{−1}, and this is assigned as a P–H stretch. Last, high-resolution mass spectrometry studies are in accord with the formula for **3**.

In order to confirm the atomic connectivity, crystals of **3** were isolated, and the structure was determined by single crystal X-ray diffraction. The results of the study are shown in Figure 1, and the structure shows the anticipated presence of the B(C₆F₅)₃ fragment coordinated to one of the phosphorus centers, leading to the unsymmetric nature of the PNP fragment. Important structural parameters are included in the caption of Figure 1.

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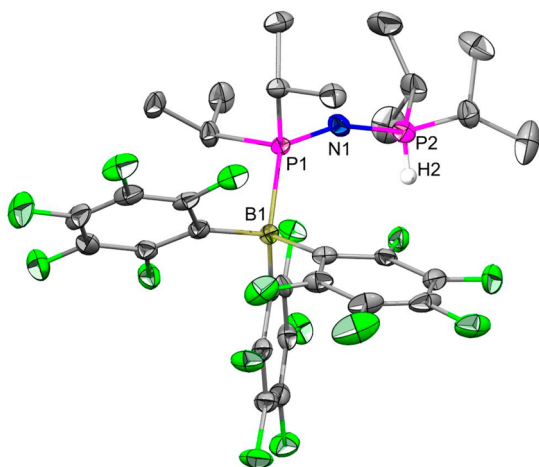


Figure 1. Molecular structure of **3** (50% ellipsoids). Hydrogens (except H2) omitted for clarity. Selected bond lengths (Å) and angles (deg): P(1)–N(1) = 1.600(4), P(2)–N(1) = 1.545(4), P(1)–B(1) = 2.083(5); P(1)–N(1)–P(2) = 156.1(3).

Compound **3** is air stable and exhibits neither oxidation nor reaction with water vapor in the air over several weeks. Furthermore, reactions of compound **3** were attempted with diphenylamine and phenyl acetylene, but no reactions were observed under the reaction conditions used (toluene, 60 °C, for 4 h). However, in benzene solution and in the presence of an atmosphere of carbon dioxide, the compound reacts readily and selectively to produce adduct **4**. Reactivity of CO₂ with **3** is indicated by the observation of an absorption in the IR spectrum at 1679 cm^{−1} characteristic of a new C=O bond.

NMR studies in C₆D₆ solution of **4** are also informative. In general, the resonances are sharper than for compound **3**. The ³¹P{¹H} spectrum of **4** shows two inequivalent doublets (37.0 and 38.4 ppm), which are coupled to each other (27 Hz) while the ¹¹B{¹H} signal is a singlet. Evidence for the formation of a P–C bond upon formal CO₂ insertion is revealed in the ¹³C{¹H} spectrum as a doublet at 167.9 ppm with a ¹J_{P–C} coupling constant of 117 Hz. High-resolution mass spectrometry studies are in accord with the formula for **4**. Last, compound **4** was also examined using thermogravimetric analysis-mass spectrometry. Evolution of carbon dioxide was observed beginning at 160 °C and completed by 180 °C. Above 225 °C, the material decomposed.

Further characterization of **4** was performed using X-ray crystallography (Figure 2). The C–O/C=O bond lengths of 1.319(3) and 1.214(3) Å, respectively, are in excellent agreement with previously reported P/B-based CO₂ adducts.⁷ Somewhat surprisingly, given the unsymmetric nature of the molecule, the P–N bonds were found to be identical (P1–N1 = 1.577(2) Å; P2–N1 = 1.575(2) Å). These measurements are halfway between the nominal P–N and P=N bonds of **3** and significantly shorter than the true single bonds in the free ligand, **1** (1.706(4) Å).⁴

Recently, we have found that weakly coordinating cations can facilitate the formation of extremely novel and highly reactive complex anions.⁸ In this light, we attempted to prepare an anionic FLP system targeting the tetramethylammonium salt of **3** that we expected could be formed *via* lithiation of **1**, followed by the addition of B(C₆F₅)₃, and subsequent cation exchange with tetramethylammonium chloride. The lithiation of **1** in benzene led to immediate formation of a white precipitate,

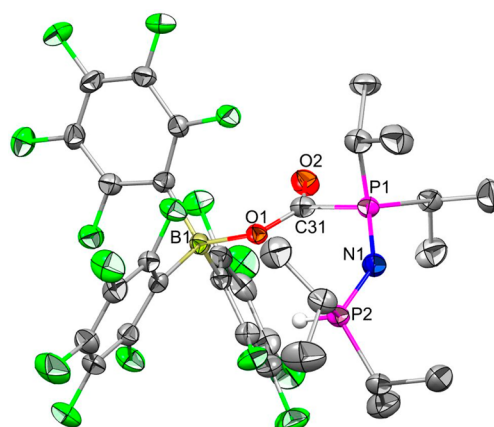


Figure 2. Molecular structure of **4** (50% ellipsoids). Hydrogens (except H2) omitted for clarity. Selected bond lengths (Å) and angles (deg): P(1)–N(1) = 1.577(2), P(2)–N(1) = 1.575(2), P(1)–C(31) = 1.880(3), C(31)–O(1) = 1.319(3), C(31)–O(2) = 1.214(3), B(1)–O(1) = 1.540(3); P(1)–N(1)–P(2) = 143.98(17), O(1)–C(31)–O(2) = 126.7(3), O(1)–C(31)–P(1) = 112.39(19), O(2)–C(31)–P(1) = 120.9(2).

which upon the addition of B(C₆F₅)₃ was only partially redissolved. Subsequent addition of tetramethylammonium chloride led to another white precipitate, presumably LiCl, that was removed *via* filtration. Solvent was removed under vacuum conditions, and the solid residue was recrystallized from pentane, resulting in an off-white crystalline material. This material was characterized using multinuclear NMR, high-resolution mass spectrometry and single crystal X-ray diffraction, and the structure was determined to be the unusual cyclic structure **5** (Figure 3) rather than the anticipated [NMe₄][*i*-Pr₂P(B(C₆F₅)₃)–N–P(*i*Pr)₂]. We also isolated 5·0.5C₆H₁₄, and its crystallographic data are included in the Supporting Information.

The formation of compound **5** was unexpected, as it requires the cleavage of a very strong carbon–fluorine bond. The cleavage of the C–F bond is not observed without the addition of tetramethylammonium chloride, indicating that cation exchange of the tightly bound lithium ion for the more weakly coordinating tetramethylammonium cation is necessary for

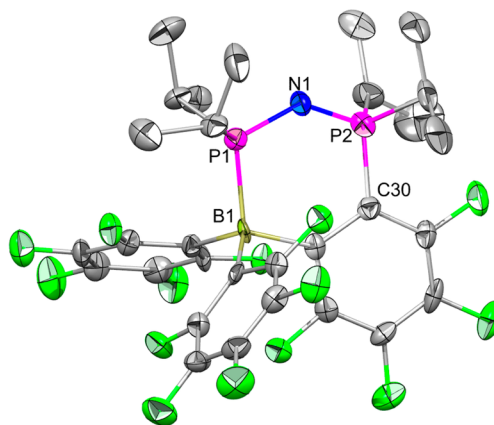


Figure 3. Molecular structure of **5** (50% ellipsoids). Hydrogens omitted for clarity. Selected bond lengths (Å) and angles (deg): P(1)–N(1) = 1.607(5), P(2)–N(1) = 1.567(5), P(1)–B(1) = 2.039(8), P(2)–C(30) = 1.814(7); P(1)–N(1)–P(2) = 131.4(4), N(1)–P(1)–B(1) = 110.6(3).

fluoride salt formation. FLP systems have previously been reported to undergo aromatic substitution at the *para* position of the fluorinated aryl borane leading to zwitterionic species.⁹ This can be prevented by using an extremely sterically congested phosphine, or by replacing the *para*-F with a hydrogen atom. In the case of **5**, the *para* position is not accessible when one phosphorus atom of the PNP ligand is bound to boron, but the *ortho* position is within reach of the other phosphorus atom. To our knowledge, this type of reaction has not been observed previously for PNP ligands, although related systems have been reported.¹⁰ In those systems, the formation of a stable, five-membered heterocycle was speculated to be the driving force for the reaction, and it seems likely that the six-membered heterocycle formed in **5** would be similarly stabilizing.

In summary, bis(*di*-*i*-propylphosphino)amine **1** reacts with B(C₆F₅)₃ to form an adduct with concomitant N/P H-isomerization. This species **3** is a mildly frustrated Lewis acid–base boron–phosphorus pair; however much of the “frustration” is released through the isomerization reaction in which the PNP angle broadens, releasing much of the steric strain. This species reacts smoothly with carbon dioxide. Last, an attempt to prepare an anionic FLP resulted in the observation of a novel cyclization of the PNP ligand with B(C₆F₅)₃.

■ ASSOCIATED CONTENT

■ Supporting Information

Synthetic procedures and spectroscopic data for compounds **3**, **4**, and **5**. Important X-ray crystallographic data for **3**, **4**, **5**, and **5·0.5C₆H₁₄** (CCDC 934157–934160). This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: jason.clyburne@smu.ca (J.A.C.C.), rakemp@unm.edu (R.A.K.).

Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Hoge, G.; Wu, H.-P.; Kissel, W. S.; Pflum, D. A.; Greene, D. J.; Bao, J. J. *Am. Chem. Soc.* **2004**, *126*, 5966.
- (2) (a) Fei, Z.; Dyson, P. J. *Coord. Chem. Rev.* **2005**, *249*, 2056. (b) Bhattacharyya, P.; Woollins, J. D. *Polyhedron* **1995**, *14*, 3367.
- (3) (a) Dickie, D. A.; Ulibarri-Sanchez, R. P., III; Jarman, P. J.; Kemp, R. A. *Polyhedron* **2013**, *58*, 92. (b) Dickie, D. A.; Gislason, K. B.; Kemp, R. A. *Inorg. Chem.* **2012**, *51*, 1162. (c) Stewart, C. A.; Dickie, D. A.; Moasser, B.; Kemp, R. A. *Polyhedron* **2012**, *32*, 14. (d) Felix, A. M.; Boro, B. J.; Dickie, D. A.; Tang, Y.; Saria, J. A.; Moasser, B.; Stewart, C. A.; Frost, B. J.; Kemp, R. A. *Main Group Chem.* **2012**, *11*, 13. (e) Harper, N. D.; Nizio, K. D.; Hendsbee, A. D.; Masuda, J. D.; Robertson, K. N.; Murphy, L. J.; Johnson, M. B.; Pye, C. C.; Clyburne, J. A. C. *Ind. Eng. Chem. Res.* **2011**, *50*, 2822. (f) Stewart, C. A.; Dickie, D. A.; Parkes, M. V.; Saria, J. A.; Kemp, R. A. *Inorg. Chem.* **2010**, *49*, 11133. (g) Dickie, D. A.; Parkes, M. V.; Kemp, R. A. *Angew. Chem., Int. Ed.* **2008**, *47*, 9955. (h) Tang, Y.; Kassel, W. S.; Zakharov, L. N.; Rheingold, A. L.; Kemp, R. A. *Inorg. Chem.* **2005**, *44*, 359. (i) Tang, Y.; Zakharov, L. N.; Rheingold, A. L.; Kemp, R. A. *Organometallics* **2005**, *24*, 836. (j) Tang, Y.; Zakharov, L. N.; Rheingold, A. L.; Kemp, R. A. *Organometallics* **2004**, *23*, 4788.
- (4) Dickie, D. A.; Coker, E. N.; Kemp, R. A. *Inorg. Chem.* **2011**, *50*, 11288.
- (5) Revés, M.; Ferrer, C.; León, T.; Doran, S.; Etayo, P.; Vidal-Ferran, A.; Riera, A.; Verdager, X. *Angew. Chem., Int. Ed.* **2010**, *49*, 9452.
- (6) (a) Ménard, G.; Hatnean, J. A.; Cowley, H. J.; Lough, A. J.; Rawson, J. M.; Stephan, D. W. *J. Am. Chem. Soc.* **2013**, *135*, 6446. (b) Courtemanche, M.-A.; Légaré, M.-A.; Maron, L.; Fontaine, F.-G. *J. Am. Chem. Soc.* **2013**, *135*, 9326. (c) Takeuchi, K.; Stephan, D. W. *Chem. Commun.* **2012**, *48*, 11304. (d) Stephan, D. W.; Erker, G. *Angew. Chem., Int. Ed.* **2010**, *49*, 46.
- (7) (a) Sajid, M.; Kehr, G.; Wiegand, T.; Eckert, H.; Schwickert, C.; Pöttgen, R.; Cardenas, A. J. P.; Warren, T. H.; Fröhlich, R.; Daniliuc, C. G.; Erker, G. *J. Am. Chem. Soc.* **2013**, *135*, 8882. (b) Sgro, M. J.; Dömer, J.; Stephan, D. W. *Chem. Commun. (Cambridge, U.K.)* **2012**, *48*, 7253. (c) Harhausen, M.; Fröhlich, R.; Kehr, G.; Erker, G. *Organometallics* **2012**, *31*, 2801. (d) Bertini, F.; Lyaskovskyy, V.; Timmer, B. J. J.; de Kanter, F. J. J.; Lutz, M.; Ehlers, A. W.; Slootweg, J. C.; Lammertsma, K. J. *Am. Chem. Soc.* **2012**, *134*, 201. (e) Zhao, X.; Stephan, D. W. *Chem. Commun.* **2011**, *47*, 1833. (f) Peuser, I.; Neu, R. C.; Zhao, X.; Ulrich, M.; Schirmer, B.; Tannert, J. A.; Kehr, G.; Fröhlich, R.; Grimme, S.; Erker, G.; Stephan, D. W. *Chem.—Eur. J.* **2011**, *17*, 9640. (g) Mömmling, C. M.; Otten, E.; Kehr, G.; Fröhlich, R.; Grimme, S.; Stephan, D. W.; Erker, G. *Angew. Chem., Int. Ed.* **2009**, *48*, 6643. (h) Kroner, J.; Nöth, H.; Polborn, K.; Stolpmann, H.; Tacke, M.; Thomann, M. *Chem. Ber.* **1993**, *126*, 1995.
- (8) MacIntosh, I. S.; Sherren, C. N.; Robertson, K. N.; Masuda, J. D.; Pye, C. C.; Clyburne, J. A. C. *Organometallics* **2010**, *29*, 2063.
- (9) (a) Travis, A. L.; Binding, S. C.; Zaher, H.; Arnold, T. A. Q.; Buffet, J.-C.; O'Hare, D. *Dalton Trans.* **2013**, *42*, 2431. (b) Geier, S. J.; Dureen, M. A.; Ouyang, E. Y.; Stephan, D. W. *Chem.—Eur. J.* **2010**, *16*, 988. (c) Welch, G. C.; Prieto, R.; Dureen, M. A.; Lough, A. J.; Labeodan, O. A.; Höltrichter-Rossmann, T.; Stephan, D. W. *Dalton Trans.* **2009**, 1559. (d) Welch, G. C.; Höltrichter-Rossmann, T.; Stephan, D. W. *Inorg. Chem.* **2008**, *47*, 1904. (e) Welch, G. C.; Cabrera, L.; Chase, P. A.; Hollink, E.; Masuda, J. D.; Wei, P.; Stephan, D. W. *Dalton Trans.* **2007**, 3407.
- (10) (a) Schnurr, A.; Vitze, H.; Bolte, M.; Lerner, H.-W.; Wagner, M. *Organometallics* **2010**, *29*, 6012. (b) Zhao, X.; Gilbert, T. M.; Stephan, D. W. *Chem.—Eur. J.* **2010**, *16*, 10304.