VIP CO_2 Binding

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Reversible Metal-Free Carbon Dioxide Binding by Frustrated Lewis Pairs**

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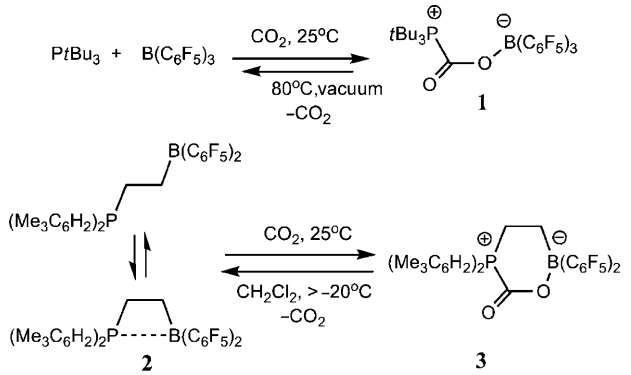
Dedicated to Prof. Helmut Werner on the occasion of his 75th birthday

Carbon dioxide is a gas that is changing our environment. Its role as a greenhouse gas is clear with the onset of global warming. In efforts to address this issue, ambitious and creative schemes are targeting materials including zeolites, silica gels, aluminas, and activated carbons,[1] as well as sophisticated metal–organic frameworks (MOFs)[2] for the benign capture and storage of carbon dioxide.[3] An alternative approach is focused on the potential use of carbon dioxide as a C_1 chemical feedstock.[4] To this end, strategies typically target the potential of transition-metal-based chemistry and catalysis.[4,5] For example, ruthenium-based catalysts have been shown to effect the hydrogenation of carbon dioxide to formic acid derivatives.[4e]

The fundamental difficulty in addressing strategies to either sequester or chemically modify carbon dioxide is its remarkable thermodynamic stability and its limited reactivity. In the absence of water, carbon dioxide is known to react with strong nucleophiles and coordinatively unsaturated transition-metal species, while organic bases readily convert it to bicarbonate salts in the presence of hydroxide.[6] On the other hand, reactions of carbon dioxide with main-group systems are poorly explored.[3] While CO_2 is known to insert into P–N, As–N, and Si–N bonds,[7,8] only recently have reports described the carboxylation of N-heterocyclic carbenes.[9,10] Reactions of CO_2 with main-group metal amides were also reported.[11]

We recently developed a new approach to main-group reactivity, derived from the concept of "frustrated Lewis pairs",[12] that is, systems in which steric congestion precludes neutralization. These systems offer latent Lewis acidity and basicity for reaction with small molecules. In this vein, we[13] and others[14] have exploited this notion for the heterolytic activation of dihydrogen and subsequent application of the resulting systems in metal-free catalytic hydrogenation and addition to olefins.[15,16] Herein, we demonstrate that the concept of frustrated Lewis pairs can be exploited to effect the reversible binding of carbon dioxide under mild conditions.

A solution of $B(C_6F_5)_3$ and $PtBu_3$ in C_6H_5Br was covered with an atmosphere of carbon dioxide, resulting in the immediate precipitation of a white solid (**1**), which was isolated in 87% yield (Scheme 1). This product exhibited



Scheme 1. Reversible CO_2 uptake and release by frustrated phosphine–borane Lewis pairs.

resonances in the $^{31}P\{^1H\}$ and $^{11}B\{^1H\}$ NMR spectra at $\delta = 46.1$ and -2.7 ppm, respectively. The ^{19}F NMR spectrum showed signals at $\delta = -133.5$, -160.4, and -166.0 ppm, typical of C_6F_5 substituents on a four-coordinate boron center. The ^{13}C NMR spectrum of **1** showed resonances expected for the constituent phosphorus and boron fragments as well as a signal at $\delta =$ 161.6 ppm, which exhibited a P–C coupling of 93 Hz; the IR spectrum of **1** showed an absorption at 1695 cm^{-1} attributable to a C=O stretch. Collectively, these data support the formulation of **1** as $tBu_3P(CO_2)B(C_6F_5)_3$.

In a similar manner, pressurizing a pentane solution of the "antagonistic"[17] Lewis pair $(Me_3C_6H_2)_2PCH_2CH_2B(C_6F_5)_2$ (**2**)[18] with 2 bar carbon dioxide results in formation of a

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white solid (**3**) in 79% yield. The product **3** exhibits an IR C=O stretching band (1694 cm^{-1}), a ^{11}B NMR resonance ($\delta = -2.4$ ppm), and a ^{13}C NMR signal ($\delta = 160.5$ ppm, $^{1}J_{PC} = 89$ Hz) that are similar to those observed for **1**. In addition, the ^{1}H NMR spectrum of **3** features signals at $\delta = 3.06$ and 1.47 ppm resulting from the methylene groups linking P and B. The latter signal exhibits a large $^{3}J_{PH}$ coupling constant of approximately 30 Hz. These data are consistent with the formulation of **3** as *cyclo*-$(Me_3C_6H_2)_2PCH_2CH_2B(C_6F_5)_2$-$(CO_2)$.

Compounds **1** and **3** were characterized by X-ray crystallography. The structural data for these compounds confirm the above formulations in which carbon dioxide reacts with phosphine and borane to form P–C and O–B bonds, resulting in pseudo-tetrahedral geometries at P and B (Figure 1).[19] In

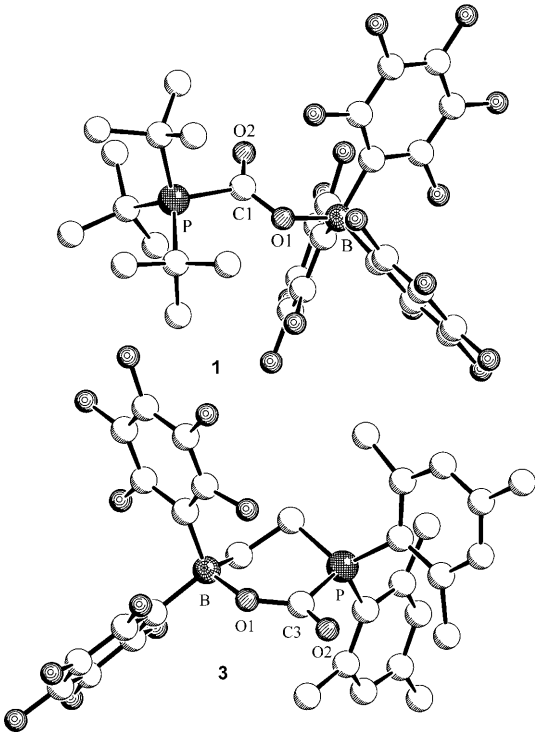

Figure 1. Molecular structures of **1** and **3**.

the case of **3**, the resulting six-membered ring exhibits a distorted half-chair conformation (Figure 1, bottom). The internal bond angle at the boron atom (O-B-C 109.6(3)°) is consistent with the pyramidalization of the B center. The corresponding internal angle at the distal phosphorus atom of 102.5(2)° is slightly smaller, reflecting the steric demands of the mesityl substituents. In both species, the geometries about the carbon atom from the CO_2 molecule are approximately trigonal-planar; the sum of angles is nearly 360°. The P–C and B–O bonds were found to be 1.8931(12) and 1.5474(15) Å in **1** and 1.900(3) and 1.550(4) Å in **3**. The C=O/C–O bond lengths in **1** and **3** are 1.2081(15)/1.2988(15) Å and 1.209(4)/1.284(4) Å, respectively. These metric parameters are comparable to those reported for the acetatoborate species $[Me_4N][(MeCO_2)B(C_6F_5)_3]$ (B–O: 1.514(2) Å, C=O: 1.217(2) Å, and C–O: 1.324(2) Å).[20] The slightly longer B–O and shorter C–O bonds in **1** and **3** are consistent with their zwitterionic character.

The thermal stabilities of the two carbon dioxide derivatives **1** and **3** were examined. Heating a solution of **1** in bromobenzene to 80 °C for 5 h in an ampoule sealed under vacuum resulted in liberation of about 50% of the carbon dioxide with the concurrent generation of the starting frustrated Lewis pair mixture. Interestingly, when this sealed sample was allowed to stand at room temperature for several hours, the complete reformation of **1** was observed. In contrast, while compound **3** is reasonably stable as a solid, it rapidly looses carbon dioxide in dichloromethane or toluene above approximately −20 °C to cleanly re-form the starting material **2**. At sufficiently low temperature the carbon dioxide addition product **3** could be handled in solution without appreciable decomposition.

This reversible carbon dioxide binding was further probed by DFT calculations.[21] The structures of **1** and **3** were optimized and shown to agree well with experimental data. The largest deviations of 0.02–0.09 Å were observed for P–C bonds. The mechanism of the reaction of **2** with CO_2 was investigated. All relevant stationary points on the energy hypersurface as well as the relevant thermochemical data were computed at the B97-D/TZVPP′, B2PLYP-D/TZVPP′, and B2PLYP-D/QZVP(-g, -f) levels of theory (Figure 2).

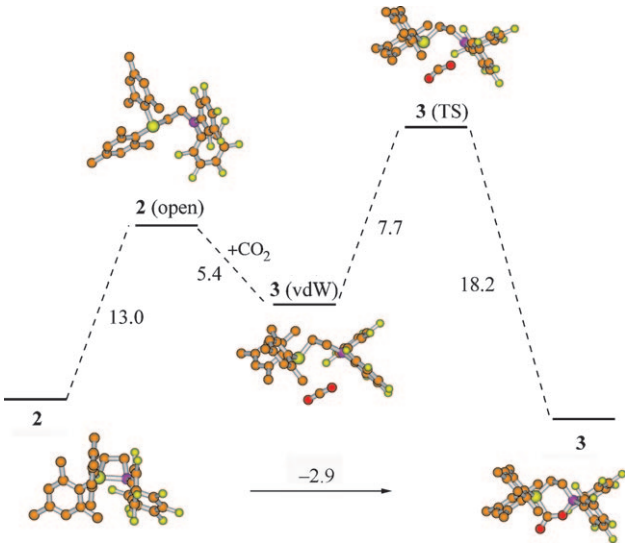

Figure 2. Relative energies (kcal mol^{-1}) for stationary points on the **2** + CO_2 hypersurface. The values refer to relative energies at the B2PLYP-D/QZVP(-g, -f)//B97-D/TZVPP' level. See the Supporting Information for computational details. P large yellow spheres, B pink, O red, C orange, F small yellow spheres.

As previously noted, the energetically favored form of **2** is a four-membered ring.[18] However, the B–P bond is relatively weak so that an open form with a *gauche* conformation is only about 13 kcal mol^{-1} higher in energy (below, we only discuss the B2PLYP-D/QZVP(-g, -f) data). This open form, **2**(open), is the active species that first forms a typical van der Waals complex with CO_2 with a binding energy of 5.4 kcal mol^{-1}. In

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this complex, **3**(vdW), the CO_2 molecule is located between the P and B atoms but is closer to the phosphorus (P···C 3.6 Å.) than to the boron atom (B···O 4.1 Å). This arrangement is interpreted as a kind of donor–acceptor interaction between the phosphorus lone pair and the carbonyl carbon atom. This kind of unsymmetrical orientation of CO_2 changes in the transition state of the reaction, **3**(TS) (Figures 2 and 3),

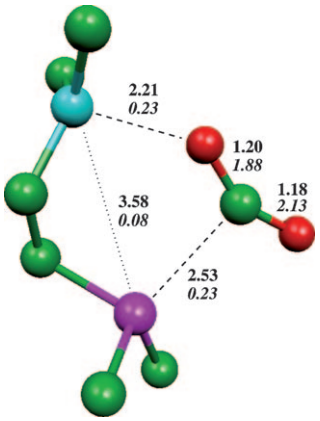

Figure 3. Structure of the transition state **3**(TS). Bond lengths and interatomic distances are given in Å; covalent bond orders are written in italics. Remaining atoms of the mesityl and C_6F_5 rings are not shown. B blue, P purple, O red, C green.

which lies only 7.7 kcal mol^{-1} above **3**(vdW). The P–C and B–O bonds are formed in a synchronous and concerted manner, as indicated by covalent bond orders of 0.23 each in the transition state (Figure 3). The difference between the P–C and B–O bond lengths is also consistent with that seen in the product **3**. These values, together with the small bending of the CO_2 moiety (151°) indicate an "early" transition state. The reverse reaction from **3** to CO_2 and **2** has a calculated energy barrier of approximately 18.2 kcal mol^{-1}, which is consistent with the experimental observations. The overall reaction is almost thermoneutral, with net changes in energy of −2.9 kcal mol^{-1}, in accord with its observed reversibility even at low temperature.

The corresponding calculations for the formation of **1** reveal a more exothermic overall reaction. The calculated energy of separation of the frustrated pair was found to be 15.6 kcal mol^{-1} (B2PLYP-D/TZVPP′), consistent with the value of 11.5 kcal mol^{-1} reported at the SCS-MP2/cc-pVTZ level of theory for this reaction.[16c] The formation of **1** from the separated reactants results in a calculated reaction energy of −35.0 kcal mol^{-1} (B2PLYP-D/TZVPP′).

To our knowledge, compounds **1** and **3** represent the first examples of a novel type of carbonic acid derivative.[10c] A few years ago, it was shown that carbonic acid itself in the absence of water is kinetically stable as a dimer under ambient conditions.[22] In contrast, these new carbon dioxide binding products **1** and **3** are favored thermodynamically to some extent over the precursor components and carbon dioxide, thus allowing controlled uptake and release of carbon dioxide. Alternatively, the species **1** and **3** may be regarded as phosphonium analogues of carbamic acid derivatives,[23,24] stabilized by O-coordination to boron. The potential of the present species in subsequent chemistry and the further exploitation of the concept of frustrated Lewis pairs are the subjects of study in our laboratories.

Experimental Section

General considerations: All manipulations were performed in inert atmosphere (N_2 vacuum line with Schlenk glassware or N_2 or Ar gloveboxes). The N_2 gas was dried with a Dri-rite column. Solvents (Aldrich) were dried using an Innovative Technologies solvent system or comparable apparatus. P*t*Bu$_3$ was purchased from the Strem Chemical Co.

Synthesis of **1**: A solution of B(C_6F_5)$_3$ (100 mg, 0.195 mmol) and P*t*Bu$_3$ (40 mg, 0.195 mmol) in C_6H_5Br (2 mL) was degassed and the reaction flask filled with CO_2 (1 bar). Immediate precipitation of a white solid was observed. The reaction mixture was allowed to sit under CO_2 (1 bar) overnight. Pentane (10 mL) was added, after which the supernatant was decanted. Washing the residue with pentane (10 mL) and drying in vacuo afforded *t*Bu$_3$P(CO_2)B(C_6F_5)$_3$ (**1**) as a white powder (129 mg, 0.170 mmol, 87 %). Crystals suitable for X-ray crystal structure analysis were obtained by recrystallization from CH_2Cl_2/cyclohexane. ^{1}H NMR (400 MHz, 298 K, CD_2Cl_2): δ = 1.60 ppm (d, $^3J_{PH}$ = 14.5 Hz, *t*Bu). ^{31}P{^{1}H} NMR (162 MHz, 298 K, CD_2Cl_2): δ = 46.1 ppm. ^{19}F NMR (377 MHz, 298 K, CD_2Cl_2): δ = −133.5 (m, 2F, *o*-F), −160.4 (m, 1F, *p*-F), −166.0 ppm (m, 2F, *m*-F). ^{11}B{^{1}H} NMR (128 MHz, 298 K, CD_2Cl_2): δ = −2.7 ppm (s). ^{13}C NMR (101 MHz, 298 K, CD_2Cl_2): δ = 161.6 (d, J_{PC} = 93 Hz, PCO_2), 147.4 (dm, J_{FC} = 243 Hz, *o*-C_6F_5), 138.9 (dm, J_{FC} = 238 Hz, *p*-C_6F_5), 136.4 (dm, J_{FC} = 236 Hz, *m*-C_6F_5), 119.5 (br, *ipso*-C_6F_5), 40.5 (d, J_{CP} = 20, $PCMe_3$), 29.9 ppm ($PCMe_3$). IR (film from CH_2Cl_2 on NaCl): $\tilde{\nu}$ = 1695 cm^{-1} (C=O). Elemental analysis calcd (%) for $C_{37}H_{27}BF_{15}O_2P$: C 49.10, H 3.59; found: C 49.14, H 3.35.

Synthesis of **3**: Dimesitylvinylphosphine (100 mg, 0.34 mmol) and HB(C_6F_5)$_2$ (117 mg, 0.34 mmol) were dissolved in pentane (7 mL) and stirred for 15 min. After degassing the solution, carbon dioxide (2 bar) was introduced for 30 min, whereupon a white powder precipitated after 5 min. The precipitate was collected by cannula filtration after 2 h and washed with pentane (2×2 mL). All volatile components were removed in vacuo to yield **3** (184 mg, 79 %). Single crystals suitable for X-ray crystal structure analysis were grown from a layered dichloromethane/pentane solution under CO_2 (2 bar) at −36 °C. ^{1}H NMR (500 MHz, 223 K, CD_2Cl_2): δ = 7.00 (4H, d, $^2J_{PH}$ = 4.3 Hz, *m*-Mes), 3.06 (2H, m, PCH_2), 2.30 (6H, s, *p*-CH_3^{Mes}), 2.21 (12H, s, *o*-CH_3^{Mes}), 1.47 ppm (2H, dm, $^3J_{PH}$ = 28.8 Hz, BCH_2). ^{13}C{^{1}H} NMR (126 MHz, 223 K, CD_2Cl_2): δ = 160.5 (d, $^1J_{PC}$ = 89.0 Hz, C=O), 147.2 (dm, $^1J_{FC}$ = 237 Hz, C_6F_5), 144.9 (d, $^4J_{PC}$ = 2.1 Hz, *p*-Mes), 142.6 (d, $^2J_{PC}$ = 9.2 Hz, *o*-Mes), 138.9 (dm, $^1J_{FC}$ = 254 Hz, C_6F_5), 136.6 (dm, $^1J_{FC}$ = 254 Hz, C_6F_5), 132.1 (d, $^3J_{PC}$ = 11.4 Hz, *m*-Mes), 120.5 (br, *ipso*-C_6F_5), 115.9 (d, $^1J_{PC}$ = 73.6 Hz, *ipso*-Mes), 26.1 (d, $^1J_{PC}$ = 34.4 Hz, PCH_2), 23.2 (d, $^3J_{PC}$ = 4.2 Hz, *o*-CH_3^{Mes}), 20.9 (*p*-CH_3^{Mes}), 12.7 ppm (br, BCH_2). ^{11}B{^{1}H} NMR (160 MHz, 223 K, CD_2Cl_2): δ = −2.4 ppm. ^{31}P{^{1}H} NMR (202 MHz, 223 K, CD_2Cl_2): δ = 0.6 ppm ($\nu_{1/2}$ = 6 Hz). ^{19}F NMR (470 MHz, 223 K, CD_2Cl_2): δ = −135.6 (4F, *o*-C_6F_5), −159.8 (2F, *p*-C_6F_5), −164.9 ppm (4F, *m*-C_6F_5). IR (KBr): $\tilde{\nu}$ = 1694 cm^{-1} (vs, C=O). Elemental analysis calcd (%) for $C_{33}H_{26}BF_{10}O_2P$: C 57.75, H 3.82; found C 57.49, H 3.68.

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[19] X-ray data: CCDC 722645 and 724493 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. **1**: $a=11.3777(5)$, $b=15.0238(6)$, $c=18.5397(7)$ Å, $\alpha=89.614(2)$, $\beta=83.862(2)$, $\gamma=87.456(2)°$, $V=3147.8(2)$ Å^3, $Z=4$, space group $P\bar{1}$, $T=150$ K, unique data: 19590 ($R_{int}=0.077$), observed data ($I>2\sigma(I)$): 14703, parameters: 919, $R=0.0378$, $wR_2=0.1008$. **3**: $a=14.7987(12)$, $b=13.7596(9)$, $c=15.5471(11)$ Å, $\beta=104.334(4)°$, $V=3067.2(4)$ Å^3, $Z=4$, space group $P2_1/n$, $T=223$ K, unique data: 5344 ($R_{int}=0.0274$), observed data ($I>2\sigma(I)$): 3738, parameters: 430, $R=0.059$, $wR_2=0.144$.

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