Reversible Metal-Free Carbon Dioxide Binding by Frustrated Lewis Pairs

Cornelia M. Mömmling, Edwin Otten, Gerald Kehr, Roland Fröhlich, Stefan Grimme,*
Douglas W. Stephan,* and Gerhard Erker*

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 C1 chemical feedstock.[4] To this end, strategies typically target the potential of transition-metal-based chemistry and catalysis.[5,6] For example, ruthenium-based catalysts have been shown to effect the hydrogenation of carbon dioxide to formic acid derivatives.[6e]

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 CO2 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 CO2 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(C6F5)3 and PrBu3 in C6H4Br 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 resonances in the 31P{1H} and 11B{1H} NMR spectra at δ = 46.1 and −2.7 ppm, respectively. The 19F NMR spectrum showed signals at δ = −133.5, −160.4, and −166.0 ppm, typical of C6F5 substituents on a four-coordinate boron center. The 13C NMR spectrum of 1 showed resonances expected for the constituent phosphorus and boron fragments as well as a signal at δ = 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 PrBu3P(CO2)B(C6F5)3.

In a similar manner, pressurizing a pentane solution of the “antagonistic”[17] Lewis pair (Me3C6H2)2PCH2CH2B(C6F5)3 (2) with 2 bar carbon dioxide results in formation of a...
white solid (3) in 79% yield. The product 3 exhibits an IR C=O stretching band (1694 cm⁻¹), a ¹¹B NMR resonance (δ = −2.4 ppm), and a ¹³C NMR signal (δ = 160.5 ppm, JPC = 89 Hz) that are similar to those observed for 1. In addition, the ¹H NMR spectrum of 3 features signals at δ = 3.06 and 1.47 ppm resulting from the methylene groups linking P and B. The latter signal exhibits a large ¹JPC coupling constant of approximately 30 Hz. These data are consistent with the formulation of 3 as cyclo-(Me₃C₆H₂)₂PCH₂CH₂B(C₆F₅)₂-(CO₂). 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). In 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 106.6(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 CO₂ molecule are approximately trigonal-planar; the sum of angles is nearly 360°. As previously noted, the energetically favored form of 2 is a four-membered ring [19]. 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 CO₂ with a binding energy of 5.4 kcal mol⁻¹. In contrast, while compound 3 is reasonably stable as a solid, it rapidly loses 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.

Figure 1. Molecular structures of 1 and 3.

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 loses 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 CO₂ 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).

As previously noted, the energetically favored form of 2 is a four-membered ring [19]. 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 CO₂ with a binding energy of 5.4 kcal mol⁻¹. In
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), 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. PhBu$_3$ was purchased from the Strem Chemical Co.

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$_6$F$_5$ 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 O bonds are formed in a synchronous and concerted manner, the separated reactants results in a calculated reaction energy of separation of the frustrated pair was found to be 2.9 kcal mol$^{-1}$ (B2PLYP-D/TZVPP) represent the first examples of a novel type of carbonic acid derivative.$^{[20]}$ 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.$^{[21]}$ 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.$^{[22,23]}$
These are not the final page numbers!
Hot and bothered? Frustrated Lewis pairs comprising phosphine and borane react to reversibly bind and release CO$_2$, offering a rare example of metal-free CO$_2$ sequestration. The mechanism of formation of these CO$_2$ derivatives 1 and 2 (see scheme) by almost simultaneous P–C and O–B bond formation was characterized by quantum chemical calculations.