Metal-Free Activation

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Activation of CO_2 and SO_2 by Boryl(phosphino)carbenes**

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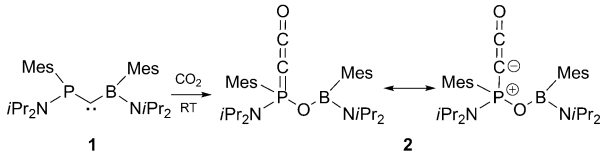
Since the isolation of the first stable (phosphino)-(silyl)carbene (PSC) in 1988,[1] followed three years later by the publication of a structurally characterized N-heterocyclic carbene (NHC),[2] important findings have regularly been reported in the field of stable carbene chemistry. To better understand the nature of these species, efforts have been devoted to the design of new stabilization modes mainly by modifying the substitution pattern at the carbene center and thus delineating various subclasses of carbene reagents (PSCs, NHCs, PHCs, CAACs, …) with a strong impact on their intrinsic reactivity.[3] Recently, great progress has been reported in using stable singlet (alkyl)(amino)carbenes for the activation of enthalpically strong E–H (E = B, Si, P) bonds and small molecules, such as CO, H_2, NH_3, or P_4.[4] In contrast, the area of the activation of carbon dioxide by carbenes is mostly limited to NHCs and dominated by the thermally reversible formation of the corresponding NHC–CO_2 adducts in which the structural integrity of both reagents is preserved.[5] In the absence of any additional reagent,[6] the imidazolium carboxylate is stable and does not evolve. The only reported example of cleaving carbon dioxide with a carbene results from the gas-phase splitting reaction of CO_2 with transient methylene.[7]

As a part of our program on the chemistry of Group-13-substituted deficient species, we have recently disclosed the isolation of the stable boryl(phosphino)carbene **1**.[8] Herein we report its reactivity towards CO_2 and SO_2 leading to the stripping of both dioxides into the corresponding phosphoryl ketenylidene and phosphoryl sulfine derivatives, respectively.

Reaction of boryl(phosphino)carbene **1**, in pentane, with a saturated CO_2 atmosphere is carried out at room temperature for five minutes. After evaporation of the solvent under vacuum and workup, phosphacumulene ylide **2** (Scheme 1)



Scheme 1. Synthesis of **2**.

was isolated as white crystals (57% yield) from a cold (−30 °C) saturated pentane solution and fully characterized by NMR and IR spectroscopy and by single-crystal X-ray diffraction.[9]

The $^{31}P\{^1H\}$ NMR spectrum of **2** shows a singlet at $\delta = 17.1$ ppm. In the $^{13}C\{^1H\}$ NMR spectrum the carbon atoms of the ketenyl moiety give rise to two characteristic doublets, downfield ($\delta = 141.6$, $^2J_{CP} = 61.7$ Hz) and upfield ($\delta = 7.1$, $^1J_{CP} = 259.3$ Hz) with a large coupling constant indicative of direct P–C bonding. In the IR spectrum of a THF solution of **2**, a strong absorption at 2118 cm^{-1} confirms the presence of the ketene fragment.[10]

The X-ray structure of **2** was determined at −80 °C (Figure 1). The phosphorus atom is in a tetrahedral environment. The P1–C1 bond length is distinctly shorter (1.644(3) Å) than an average single P–C bond (1.85 Å),[11] and in the range expected for a phosphorus ylide bond.[12]

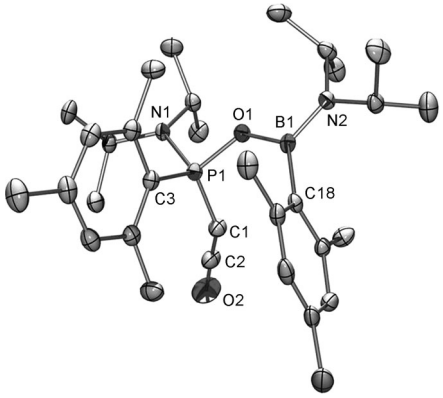


Figure 1. Molecular structure of **2**. Thermal ellipsoids set at 30% probability. H atoms are omitted for clarity.

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Compared to the dimesitylketene (Mes_2CCO; C=C 1.29(1) and C=O 1.18(1) Å),[13] the C1–C2 distance (1.234(4) Å) is shorter, exhibiting a partial triple bond character, whereas the C2–O2 bond (1.204(4) Å) is slightly elongated. The large value of the P-C1-C2 angle (144.1(3)°) is indicative of a markedly ylidic character and the geometrical parameters on whole are reminiscent of ketenylidenetriphenylphosphorane Ph_3PCCO (Table 1).[10]

To shed more light on this special feature, DFT calculations at the M05-2X/6-311 + G(d,p)//M05-2X/6-31G(d) level have been performed on the reaction pathway in pentane solution (see Figure 2). CO_2 binding to carbene **1** to give phosphonium carboxylate **3** is slightly endergonic (11.4 kcal mol^{-1}). This step is similar to the reactivity of NHCs with CO_2 generating an imidazolium carboxylate as an endpoint. In our case, however, cyclization of **3** into oxaphosphetane **4** can take place. This step is thermodynamically favored (−26.6 kcal mol^{-1}) and

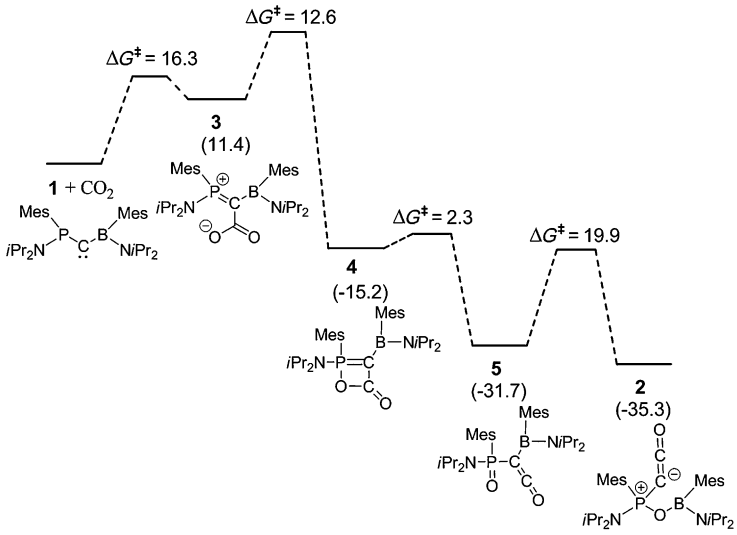
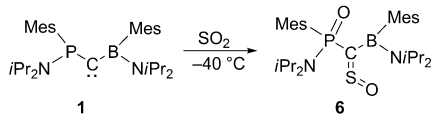


Figure 2. Gibbs energy diagram (kcal mol^{-1}) resulting in the formation of **2** (in parentheses values relative to **1** + CO_2).

Table 1: Selected geometrical parameters for **2**, Ph_3PCCO, and Mes_2CCO.[a]

Parameter	**2**	Ph_3PCCO[10]	Mes_2CCO[13]
P–C	1.644(3)	1.648(7)	
C–C	1.234(4)	1.210(10)	1.29(1)
C–O	1.204(4)	1.185(9)	1.18(1)
P-C-C	144.1(3)	145.5(7)	
C-C-O	177.2(4)	175.6(8)	176(1)

[a] Bond lengths [Å] and bond angles [°].



Scheme 2. Synthesis of **6**.

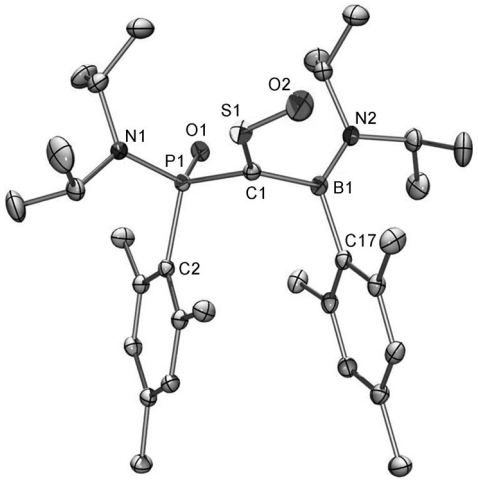


Figure 3. Molecular structure of **6**. Thermal ellipsoids set at 30% probability. H atoms are omitted for clarity.

plays a major role in the overall transformation, illustrating the crucial role of the strongly electrophilic phosphonium moiety in the activation process of CO_2. No transition state could be found for the straightforward formation of **4** by [2+2] cycloaddition to CO_2. Subsequent rearrangement of **4** into boryl(phosphonio)ketene **5** in a Wittig-like fashion is also thermodynamically favored (−16.5 kcal mol^{-1}), involving only a very low activation Gibbs energy (2.3 kcal mol^{-1}).[14] Finally, phosphacumulene ylide **2**, which is computed to be slightly more stable than **5** (−3.6 kcal mol^{-1}), results from a 1,3-boratropy with a 19.9 kcal mol^{-1} barrier process. Unfortunately, intermediate **5** could not be detected by NMR spectroscopy under the reaction conditions used.

Under similar conditions to the reaction with CO_2, **1** reacts with SO_2 leading selectively to sulfine **6** which is only stable below −25 °C (Scheme 2).[15] The product was fully characterized by NMR spectroscopy at low temperature.[16]

The structure of **6** was unambiguously determined by an X-ray diffraction analysis at −50 °C, and agrees with the spectroscopic data obtained (Figure 3).

In the case of SO_2, theoretical calculations reveal that the reaction follows a pathway comparable to that of CO_2 (Supporting Information, Scheme S1). Sulfine **6** is thermodynamically favored with respect to **1** + SO_2 (−57.6 kcal mol^{-1}). In this case, the 1,3-boratropy is endergonic (9.1 kcal mol^{-1}), explaining the absence of evolution of **6** into a phosphacumulene ylide.

In conclusion, the original push–pull boryl(phosphino)-carbene **1** exhibits unprecedented reactivity towards thermodynamically stable small organic dioxides. Its unique electronic properties enable the challenging activation of carbon dioxide and sulfur dioxide, transformations that are costly in relation to the thermodynamics. This is one of the rare examples of such a transformation with organic systems.[17]

Development of new push–pull models is underway and will allow better understanding of this type of reactivity.

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