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Activation of CO₂ and SO₂ by Boryl(Phosphino)carbenes

Florie Lavigne, Eddy Maerten,* Gilles Alcaraz, Vicenç Branchadell, Nathalie Saffon-Merceron, Antoine Baceiredo*

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. In order 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, momentous achievements have been reported with stable singlet (alkyl)(amino)carbenes, in the field of the activation of enthalpically strong E-H (E = B, Si, P) bonds and small molecules such as CO, H₂, NH₃ or P₄.^[4] Contrastingly, 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-CO₂ 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 the dismemberment of carbene dioxide by a carbene results from the gas-phase splitting reaction of CO₂ with transient methylene.^[7]

As a part of our on-going program on the chemistry of group-13-substituted deficient species, we have recently disclosed the isolation of the stable boryl(phosphino)carbene **1**.^[8] Here we report its reactivity towards CO₂ and SO₂ leading to the stripping of both dioxides into the corresponding phosphoryl-ketenylidene and – sulfine derivatives, respectively.

Reaction of boryl(phosphino)carbene **1**, in pentane, with a saturated CO₂ atmosphere is carried out at room temperature for five minutes. After evaporation of the solvent under vacuum and workup, phosphacumulene ylide **2** was isolated as white crystals (57 % yield) from a cold (–30°C) saturated pentane solution and fully characterized by NMR, IR and X-ray diffraction analysis (Scheme 1).^[9]

Scheme 1. Synthesis of phosphacumulene ylide **2**

The ³¹P{¹H} NMR spectrum shows a singlet at δ 17.1. In the ¹³C{¹H} the carbon atoms of the ketenyl moiety appear as two characteristic doublets, at low field (141.6, ²J_{CP} = 61.7 Hz) and at high field (7.1, ¹J_{CP} = 259.3 Hz) with a large coupling constant indicative of direct P-C connectivity. 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] Compared to the dimesitylketene (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-O1 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 Ph₃PCCO (Table 1).^[10]

Figure 1. Molecular structure of phosphacumulene ylide **2**. Thermal ellipsoids with 30 % probability. H atoms are omitted for clarity.

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author.

Table 1. Selected geometrical parameters for **2**, Ph₃PCCO and Mes₂CCO (Distances in Å and angles in degrees).

	2	Ph ₃ PCCO ^[10]	Mes ₂ CCO ^[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)

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). CO₂ 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 CO₂ generating an imidazolium-carboxylate as an end-point. Here, however, cyclization of **3** into oxaphosphetane **4** can take place. This step is thermodynamically favored (−26.6 kcal.mol⁻¹) and plays a major role in the overall transformation, illustrating the crucial role of the strongly electrophilic phosphonium moiety in the dismemberment process of carbene dioxide. No transition state could be found for the straightforward formation of **4** by [2+2] cycloaddition to CO₂. 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** that is computed to be slightly more stable than **5** (−3.6 kcal.mol⁻¹) results from a 1,3-boratrophy with a 19.9 kcal.mol⁻¹ barrier process. Unfortunately, intermediate **5** could not be observed by NMR spectroscopy in the involved reaction conditions.

Figure 2: Gibbs energy diagram (kcal.mol⁻¹) resulting in the formation of **2** (in parentheses values relative to **1** + CO₂).

Under similar conditions, boryl(phosphino)carbene **1** reacts with SO₂ leading selectively to sulfine **6** that is only stable below −25°C (Scheme 2).^[15] The product was fully characterized by NMR spectroscopy at low temperature.^[16]

Scheme 2. Synthesis of boryl(phosphoxyde)-sulfine **6**.

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

Figure 3. Molecular structure of boryl(phosphoxyde)sulfine **6**. Thermal ellipsoids with 30 % probability. H atoms are omitted for clarity.

In the case of SO₂, theoretical calculations reveal that the reaction follows a pathway comparable to the one of CO₂ (see Supporting Information, Scheme S1). Sulfine **6** is thermodynamically favored with respect to **1** + SO₂ (−57.6 kcal.mol⁻¹). In this case, the 1,3-boratrophy is endergonic (9.1 kcal.mol⁻¹), explaining the absence of evolution of **6** to 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 dismemberment of carbon and sulfur dioxide, a transformation that is costly in relation to the thermodynamics. This is one of the rare examples known to date 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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Dismemberment of CO₂ and SO₂ by
Boryl(Phosphino)- carbenes

The first examples of the dismemberment of small organic dioxide molecules by the stable boryl(phosphino)carbene **1** are presented. In the presence of CO₂ and SO₂, **1** leads respectively to the original phosphacumulene ylide [Mes(iPr₂N)B-O-P(CCO)(NiPr₂)Mes] **2** and boryl(phosphoryl)sulfine [Mes(iPr₂N)B-C(SO)-P(O)(NiPr₂)Mes] **5** that have been structurally and spectroscopically characterized.