

Carbon Dioxide Fixation

Double Phosphinoboration of CO₂: A Facile Route to Diphospha-UreasJames H. W. LaFortune,^[a] Zheng-Wang Qu,^{*,[b]} Karlee L. Bamford,^[a] Alina Trofimova,^[a] Stephen A. Westcott,^[c] and Douglas W. Stephan^{*,[a]}

Abstract: The reactions of CO₂ with a series of phosphinoboranes, including R₂PBpin (R = Ph, tBu; pin = pinacol), R₂PBMe₂ (R = Ph, tBu; Mes = 2,4,6-Me₃-C₆H₂), and R₂PBcat (R = Ph, tBu, Mes; cat = catechol) are described. Although R₂PBpin and R₂PBMe₂ afford products of the form R₂PCO₂Bpin (R = Ph **1**, tBu **4**) and R₂PCO₂BMe₂ (R = Ph **2**, tBu **3**), respectively, R₂PBcat lead to further reaction affording the diphospha-ureas, (R₂P)₂CO (R = Ph **5**, tBu **6**, Mes **7**), together with O(Bcat)₂. Computational studies provide insight into the mechanism, revealing an intermediate derived from double phosphinoboration of CO₂.

The anthropogenic emission of carbon dioxide (CO₂) continues to climb, prompting global climate change.^[1] This issue has spurred widespread interest in various aspects of CO₂ chemistry. Even though efforts targeting CO₂ capture^[2] or its conversion to C1 chemical feedstocks^[3] have garnered much interest in recent years, there is also growing interest in the utility of CO₂ as a reagent in synthetic chemistry. Although transition-metal chemistry has dominated such developments, main-group reagents have also emerged, providing unique approaches to the reactivity of CO₂. A decade ago, Stephan, Erker, and co-workers reported the use of frustrated Lewis pairs (FLPs) to capture CO₂.^[4] In the intervening years, a variety of B/N,^[5] B/P,^[6] Al/P,^[7] and Si/P^[5a,8] systems have been developed to capture or effect stoichiometric or catalytic reduction of CO₂. Apart from FLPs, basic main-group reagents have been

exploited in reactions with CO₂. For example, the carboxylations of N-heterocyclic carbenes^[9] as well as silyl and germyl amides^[10] have been reported whereas Dielmann and co-workers have described CO₂ capture by highly basic phosphines incorporating imidazolin-2-ylidenamino substituents.^[11]

In recent studies, ureas have been prepared from CO₂ and aliphatic amines exploiting transition-metal-based catalysts^[12] or cesium-based catalysts.^[13] In 2018, we reported indium-based Lewis acid catalysts for the conversion of silylamines and CO₂ to ureas with liberation of silylethers.^[14] Interestingly, even though the direct reaction of CO₂ with amines^[12c,15] generally requires high pressure (14–140 atm) and high temperature (130–170 °C), we have recently shown that judicious choice of solvent promotes the reaction of CO₂ and silylamines to give silylcarbamates and ureas.^[16]

In contrast to ureas, the phosphorus analogues, diphospha-ureas, (R₂P)₂CO are rare. The first example of a diphospha-urea (R = Ph) was prepared in low yield by the reaction of Ph₂PSiMe₃ with phosgene at –110 °C.^[17] Subsequently, the reduction of dimeric phosphaketenes, RPCO was reported to give an alternative route to a diphospha-urea.^[18] Although transition-metal-supported diphospha-ureas have also been reported,^[19] we have recently described a synthetic route exploiting nucleophilic attack of the phosphaketene Ph₃GePCO by phosphides and subsequent alkylation.^[20] In targeting new strategies to CO₂ reduction to diphospha-ureas, we note that we had some time ago reported the reactions of the phosphinoboranes R₂PB(C₆F₅)₂ with H₂ through a FLP-type reaction.^[21] Subsequently, Westcott and co-workers reported related addition reactions in which Ph₂PBpin reacts with unsaturated multiple bonds prompting phosphinoboration of ketones, imines, aldehydes,^[22] N-heterocycles,^[23] and a series of heteroallenes.^[24] In the present study, we describe the reactions of CO₂ with a series of phosphinoboranes, demonstrating that suitable modification of the B/P reagent prompts CO₂ reduction to afford a unique and facile route to diphospha-ureas. Computational studies provide insight into the mechanism, revealing an intermediate derived from double phosphinoboration of CO₂.

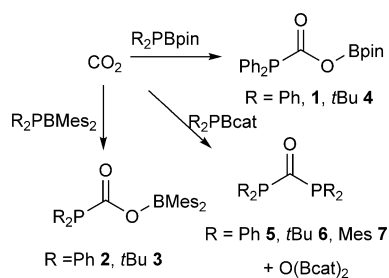
We previously described the stoichiometric reaction of Ph₂PBpin with CO₂.^[24] Based on the spectroscopy alone, the compound was formulated as Ph₂PCO₂Bpin **1** (Scheme 1). Repetition of the reaction afforded X-ray quality crystals and the subsequent diffraction study confirmed the formulation (Figure 1). In this product of phosphinoboration of CO₂, the newly formed P–C bond was found to be 1.850(2) Å whereas the O–B bond was found to be 1.383(3) Å. The slightly distort-

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Scheme 1. Synthetic pathways to 1–7.

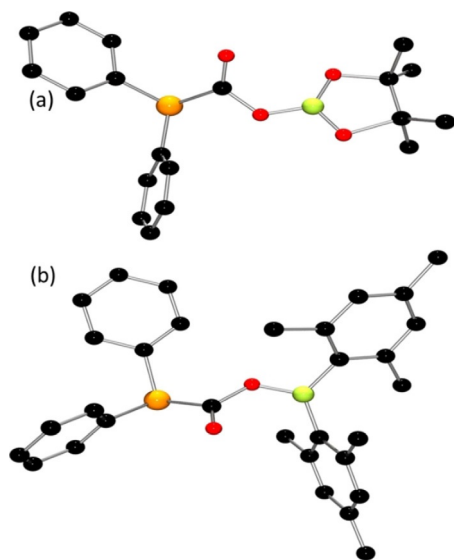


Figure 1. POV-ray depictions of the molecular structures of (a) 1; (b) 2; hydrogen atoms are omitted for clarity. C: black, O: red, P: orange, B: yellow-green.

ed trigonal-planar geometry at the central carbon atom results in a P–C–O angle of $111.12(16)^\circ$, whereas the C–O distances of $1.197(3)$ Å and $1.360(3)$ Å are consistent with formal double and single bonds, respectively.

Probing substituent effects, the phosphinoborane $\text{Mes}_2\text{PB}(\text{C}_6\text{F}_5)_2$ ^[21] was prepared, however it showed no reaction with 4 atm of CO_2 . In contrast, Ph_2PBMe_2 ^[25] reacted with CO_2 slowly over 3 days to give upon workup **2** as a white solid in 86% yield. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **2** showed a single resonance at $\delta = -1.5$ ppm with coupling to the carbon of CO_2 of $J = 19$ Hz in the ^{13}C -labelled product. The corresponding $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum revealed a resonance at 178.1 ppm with the same coupling constant in addition to resonances attributable to the remaining carbon atoms. The $^{11}\text{B}\{^1\text{H}\}$ NMR spectroscopic data showed a single resonance at 53.1 ppm. These data were consistent with the formulation of **2** as $\text{Ph}_2\text{PCO}_2\text{BMe}_2$. This assignment was confirmed crystallographically (Figure 1). The geometry of **2** is similar to that seen in **1** with the newly formed P–C and O–B distances being $1.8590(14)$ and $1.4099(18)$ Å, respectively.

In a similar fashion, the species $t\text{Bu}_2\text{PBMe}_2$ and $t\text{Bu}_2\text{PBpin}$ were prepared (see the Supporting Information) and reacted with CO_2 to give the analogous phosphinoboration products

$t\text{Bu}_2\text{PCO}_2\text{BMe}_2$ (**3**) and $t\text{Bu}_2\text{PCO}_2\text{Bpin}$ (**4**), which were isolated in 82 and 89% yield, respectively (Scheme 1). Interestingly, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **3** showed a resonance at 47.3 ppm with a coupling to the carbon atom of 40 Hz, whereas the spectrum of **4** showed a resonance at 48.2 ppm with a coupling constant to the carbon atom of 35 Hz in the ^{13}C -labelled products, consistent with significant increases in the P–C bond strengths.

The related phosphinoboranes R_2PBcat ($\text{R} = \text{Ph}$,^[22] $t\text{Bu}$, Mes) were also prepared (see the Supporting Information) and their reactions with CO_2 were examined. These reactions gave products quite distinct from **1–4**. The reaction of Ph_2PBcat with CO_2 proceeds over several days at ambient temperature to give a yellow solution. Monitoring of the solution in situ by NMR spectroscopy revealed the appearance of a $^{11}\text{B}\{^1\text{H}\}$ NMR signal at 24.4 ppm. In addition, performing the reaction with $^{13}\text{CO}_2$, a doublet $^{31}\text{P}\{^1\text{H}\}$ resonance at 30.5 ppm showed P–C coupling of 70 Hz, whereas the corresponding triplet $^{13}\text{C}\{^1\text{H}\}$ NMR resonance appeared at 239.0 ppm with the same coupling constant. These data are consistent with the generation of the diphospha-urea, $(\text{Ph}_2\text{P})_2\text{CO}$ (**5**) and the corresponding by-product $\text{O}(\text{Bcat})_2$. Efforts to isolate **5** were plagued by its thermal and photochemical instability. It is noteworthy that this species has been previously prepared by Becher and Langer using phosgene and $\text{Ph}_2\text{PSiMe}_3$. These authors also noted its instability.^[17]

The corresponding reaction of $t\text{Bu}_2\text{PBcat}$ with CO_2 also proceeds over several days at ambient temperature to give a yellow solution. The product solution displayed a $^{11}\text{B}\{^1\text{H}\}$ NMR signal at 22.5 ppm whereas the $^{31}\text{P}\{^1\text{H}\}$ NMR resonance appears at 75.5 ppm. Again, use of $^{13}\text{CO}_2$ reveals P–C coupling of 83 Hz, whereas the corresponding triplet $^{13}\text{C}\{^1\text{H}\}$ NMR resonance appears at 245.5 ppm. These data are consistent with the generation of the diphospha-urea, $(t\text{Bu}_2\text{P})_2\text{CO}$ (**6**). Although compound **6** crystallizes from pentane, X-ray data collection was complicated by the photochemical instability of **6**, despite collection at -123°C in the dark. Nonetheless, the preliminary X-ray data confirmed the connectivity (see the Supporting Information), although prudence precludes a discussion of the metric data.

The corresponding reaction of Mes_2PBcat under CO_2 proceeds similarly. After 6 days at ambient temperature, workup afforded a yellow solid **7** in 34% yield of isolated material. This product exhibited a $^{31}\text{P}\{^1\text{H}\}$ NMR resonance at 14.4 ppm with P–C coupling of 73 Hz and the corresponding triplet $^{13}\text{C}\{^1\text{H}\}$ NMR signal at 227.5 ppm in the ^{13}C -labelled product. This species was crystallized from pentane and the X-ray data were collected at -123°C in the dark. The structural data affirmed the formulation of **7** as $(\text{Mes}_2\text{P})_2\text{CO}$ (Figure 2), revealing P–C(O) bond lengths of $1.914(2)$ and $1.905(2)$ Å and a C–O bond length of $1.192(2)$ Å. The resulting P–C–P angle was $102.29(10)^\circ$ and the P–C–O angles were $130.03(16)^\circ$ and $127.65(16)^\circ$. These parameters are comparable to those recently reported for $t\text{Bu}_2\text{PC}(\text{O})\text{P}(\text{GePh}_3)_2$ (P–C: $1.887(3)$, $1.848(3)$; C–O: $1.219(3)$ Å) and $(\text{Ph}_3\text{Ge})_2\text{PC}(\text{O})\text{P}(t\text{Bu})_2$ (P–C: $1.887(3)$, $1.892(3)$; C–O: $1.212(3)$ Å).

The mechanism of the reactions of Ph_2PBpin , Ph_2PBcat , and $t\text{Bu}_2\text{PBcat}$ with CO_2 were probed by state-of-the-art DFT calcu-

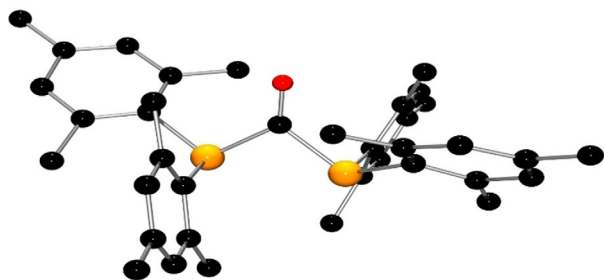


Figure 2. POV-ray depiction of the molecular structure of **7**; hydrogen atoms are omitted for clarity. C: black, O: red, P: orange.

lations at the PW6B95-D3/def2-QZVP + COSMO-RS//TPSS-D3/def2TZVP + COSMO level of theory^[26] in CH₂Cl₂ solution. As shown in Scheme 2, the direct addition of the P–B single bond of Ph₂PBpin to a C=O bond of CO₂ is –2.3 kcal mol^{–1} exergonic over a moderate barrier of 23.4 kcal mol^{–1} via the transition structure (TS) of **TS1**, affording the product of Ph₂P(O)OBpin **1'** with a *cis*-arrangement of the boryl and phosphanyl substituents, which is slightly (0.3 kcal mol^{–1}) more favorable in solution than the crystallographically observed *trans*-conformer **1**. Further addition of another Ph₂PBpin equivalent to the C=O bond of **1'** is –3.3 kcal mol^{–1} exergonic but over a sizable barrier of 28.2 kcal mol^{–1} via **TS2** to give the complex (Ph₂P)₂C(OBpin)₂ (**8**) that may further eliminate O(Bpin)₂ over a lower barrier of 24.1 kcal mol^{–1} via **TS3** to form the diphospha-urea (Ph₂P)₂CO (**5**). Direct access to diphospha-urea **5** through P–B/C–O bond metathesis between Ph₂PBpin and **1'** is prevented by an even higher barrier of 31.6 kcal mol^{–1} via **TS4**. These computations are consistent with the observed slow formation of **1** instead of the more desirable **5** at ambient temperature.

We note that prolonged exposure of **1** to excess Ph₂PBpin in pentane at –35 °C afforded crystals of (Ph₂P)₂C(OBpin)₂ **8**, albeit in low yield. Unfortunately, efforts to isolate **8** or measure its HRMS and NMR spectroscopic data proved fruitless

due to its instability in the solid state at ambient temperature and in solution at –35 °C. However, an X-ray diffraction study of **8** confirmed the formulation (Figure 3) and the pseudo-tetrahedral nature of the central carbon atom. The P–C bond lengths were 1.9116(17) and 1.9388(18) Å, whereas the newly formed B–O bond lengths were 1.370(2) and 1.364(2) Å.

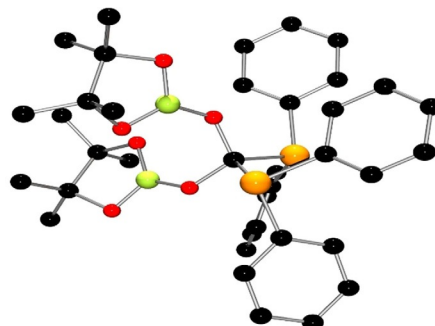
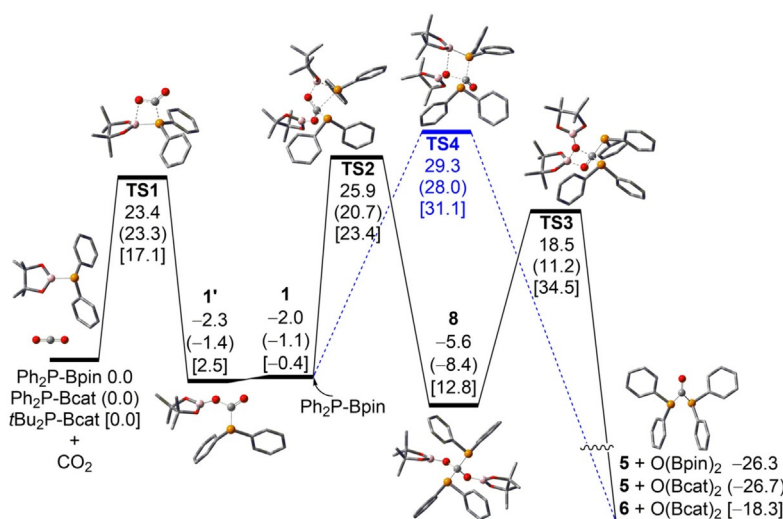


Figure 3. POV-ray depiction of the molecular structure of **8**; hydrogen atoms are omitted for clarity. C: black, O: red, P: orange, B: yellow-green.

The isolation of **8**, although supporting the computed mechanism, is surprising given its lower dissociation barrier to the conversion to **5**. Nonetheless, this is consistent with the thermal and photochemical instability of **5** as well as the observation that compound **8** is stable in the solid state at –35 °C but immediately degrades in solution, as evidenced by spectroscopic data.

As shown in Scheme 2, very similar reaction paths are also found for the reactions of Ph₂PBcat and *t*Bu₂PBcat with CO₂, despite evidently changed energetics. The introduction of the more Lewis acidic boryl Bcat leads to nearly the same barrier of 23.3 kcal mol^{–1} for the first P–B/C=O addition (dominating electrophilic attack at P). On one hand, lower barriers of 22.1 and 19.6 kcal mol^{–1} for the second P–B/C=O addition and the subsequent O(Bcat)₂ elimination steps were computed. This is



Scheme 2. DFT-computed free-energy paths in CH₂Cl₂ solution (in kcal mol^{–1}, at 298 K and 1 M reference concentration) for the reactions of Ph₂PBpin (Ph₂PBcat and *t*Bu₂PBcat values in parentheses and in brackets, respectively, for comparison) with CO₂.

in accord with the observed facile formation of diphospha-urea **5** with the rate-limiting step being the first P–B/C=O addition over a barrier of 23.3 kcal mol⁻¹. On the other hand, when the more bulky and Lewis basic phosphanyl *t*Bu₂P is further introduced, the first P–B/C=O addition becomes almost neutral in free energy over an evidently lower barrier of 17.1 kcal mol⁻¹, whereas further P–B/C=O addition followed by O(Bcat)₂ elimination is now prevented by a high overall barrier of 34.9 kcal mol⁻¹ via the high-lying **8**-like intermediate. In this case, **TS4**-like P–B/C–O bond metathesis over a barrier of 31.5 kcal mol⁻¹ after the first P–B/C=O addition is more likely to afford the slower formation of diphospha-urea **6**, as was observed experimentally.

In summary, we have described the reactions of CO₂ with a series of phosphinoboranes, illustrating a sequence of B/P additions to the carbonyl fragments. This provides access to species of the form R₂PCO₂BR'₂ initially whereas Bcat-containing B/P reagents afford a unique and facile route to diphospha-ureas. The computed mechanism proceeds through a double-addition product that was supported by experimental data. With this facile synthetic route in hand, we are now exploring the chemistry of diphospha-ureas as well as other applications of phosphinoboration reactions.^[27]

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Conflict of interest

The authors declare no conflict of interest.

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