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Diphosphination of CO₂ and CS₂ mediated by frustrated Lewis pairs - catalytic route to phosphanyl derivatives of formic and dithioformic acid

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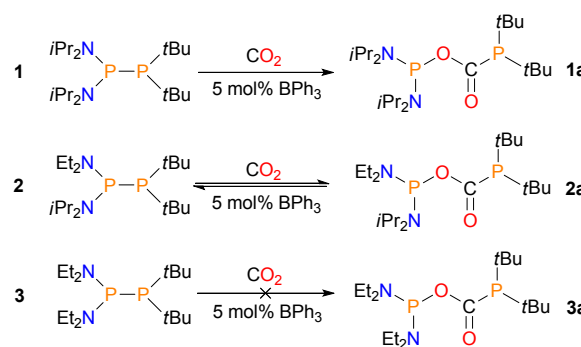
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The first example of CO₂ diphosphination is described. Reactions of unsymmetrical diphosphanes with CE₂ (E = O, S) catalyzed by BPh₃ insert a CE₂ molecule into the P-P bond with formation of the products of the general formula R₂P-E-C(=E)-PR₂. The obtained CO₂ adducts arise from synergistic interaction of diphosphane and borane with CO₂ molecule.

Carbon dioxide is an inexpensive, safe and abundant building block for the production of chemicals and fuels. Studies on the direct activation and transformation of carbon dioxide with simple nonmetallic systems have become one of the most active branches of modern catalysis research. Amid the great variety of compounds capable of activating CO₂, the frustrated Lewis pairs (FLPs)¹ reported by Stephan, which are combinations of sterically hindered Lewis acids and bases that do not form classical adducts, contributed significantly to this field.^{2–6} In the case of FLP systems based on phosphorus as the basic center, the activation of CO₂ proceeds *via* the formation of a P-C bond, and depending on the type of reactive acidic site, B-O,^{6,7} Al-O^{8,9} or Ga-O¹⁰ bonds often in a reversible manner. An interesting feature of FLP-activated CO₂ is that it can be converted into methanol under mild conditions.^{8,11} Apart from phosphines that usually act as P-containing Lewis bases, there are also reports on P-P bond-containing systems such as symmetrical diphosphanes that when used with an equimolar amount of highly Lewis acidic B(C₆F₅)₃ were found to react with H₂ and phenylacetylene.^{12,13} Although they are expensive, B(C₆F₅)₃ and its fluorinated derivatives are widely employed in FLPs due to their high reactivity towards small molecules. Notably, the presence of a Lewis acidic component is not necessary for capturing CO₂. Recently, it was reported that highly nucleophilic phosphines can reversibly form simple adducts with CO₂.¹⁴ Despite wide laboratory and industrial

applications, the fixation of CS₂ is not well studied. To date, there are only a few reports regarding the activation of CS₂ by FLPs involving the formation of Lewis base-acid adducts LB-C(S)-S-LA^{7,15,16} and the diphosphination of CS₂ with persistent (H₂C)₂(NDipp)₂P• radicals generated in solution from the parent symmetrical diphosphane.¹⁷ Unsymmetrical diphosphanes were also utilized in diphosphination reactions; however, they were reacted with activated acetylenes.^{18,19} To the best of our knowledge, there are no reports on the activation of small inorganic molecules, such as CO₂ or CS₂, involving unsymmetrical systems with polarized P-P bonds.

Based on our long-term interest in the chemistry of compounds possessing P-P functionalities^{20–27} and the recent developments in FLP chemistry,^{10,28} we decided to study the reactivity of unsymmetrical diphosphanes as Lewis basic components in combination with weakly Lewis acidic BPh₃. From the set of recently developed systems with polarized P-P bonds,²⁹ we selected three species, *t*Bu₂P-P(*i*Pr₂N)₂ (**1**), *t*Bu₂P-P(*i*Pr₂N)(NEt₂) (**2**) and *t*Bu₂P-P(NEt₂)₂ (**3**), with highly nucleophilic P-atoms. We found that mixtures of BPh₃ and a base (**1**, **2** or **3**) not only form stable FLPs that do not quench each other but also react with CO₂ and/or CS₂ in an unusual manner. The reaction of a stoichiometric mixture of **1** and BPh₃ in toluene under 1 atm of CO₂ at ambient temperature for 24 hours led to complete conversion of **1** into **1a** (Scheme 1).


 Scheme 1. Reactions of 1-3 with CO₂ catalyzed by BPh₃

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The ^{31}P NMR spectrum of the reaction mixture showed two doublets at 113.4 ppm ($\text{P}(\text{N}/\text{Pr}_2)_2$) and 47.4 ppm (PtBu_2) (**1a**). Relative to the signals of starting diphosphane **1**, the doublet attributed to the $\text{P}(\text{N}/\text{Pr}_2)_2$ group is shifted downfield, whereas the signal of PtBu_2 is shifted upfield (for **1**: 88.2 ppm and 62.6 ppm, respectively). Furthermore, the absolute value of the P-P coupling constant is significantly reduced from 358.2 Hz (**1**) to 14.5 Hz (**1a**), indicating the absence of a direct P-P bond in newly formed **1a**. Surprisingly, the ^{11}B NMR spectrum of the reaction mixture only showed a signal attributable to BPh_3 . We did not observe any resonances for zwitterionic species bearing B-O moieties, which are typically formed in reactions of phosphorus-boron FLPs with CO_2 . This observation suggested the Lewis acid was serving as a catalyst in the described reaction. To verify this hypothesis, we performed reactions of **1** with CO_2 in the presence of 25 mol% and 5 mol% BPh_3 and without the Lewis acid under the same conditions. Indeed, in the case of reactions involving catalytic amounts of BPh_3 , we observed complete conversion of **1** into **1a**, while the absence of BPh_3 resulted in no reaction of **1** with CO_2 . Compound **1a** was isolated by crystallization from the concentrated reaction mixtures at -20°C . The reaction with 5 mol% catalyst loading gave the highest isolated yield (90%) and purity as the isolated product was not contaminated by BPh_3 . Further spectroscopic analysis of isolated **1a** also indicated the incorporation of a CO_2 molecule between the two phosphorous atoms. The ^{13}C NMR spectrum of **1a** showed a very characteristic doublet of doublets at 178.2 ppm ($^1J_{\text{PC}} = 29.4$ Hz, $^2J_{\text{PC}} = 4.4$ Hz) attributed to the CO_2 moiety. Moreover, the IR data for **1a** showed an absorption band at 1667 cm^{-1} , which is typical for a C=O group. The X-ray diffraction data of **1a** conclusively confirmed the insertion of CO_2 into the P-P bond (Figure 1). The CO_2 moiety is located between two phosphanyl groups; the PtBu_2 group is bound to the carbonyl C9-atom, while the $\text{P}(\text{N}/\text{Pr}_2)_2$ group is connected to one of the oxygen atoms. The C9-O1 (1.348(3) Å) and C9=O2 (1.205(3) Å) bond lengths are in the range typical for carboxylic esters ($\sim 1.33 - 1.41$ Å and $\sim 1.19 - 1.20$ Å, respectively).³⁰ Furthermore, the P1-C9 (1.870(2) Å) and P2-O1 (1.736(2) Å) bonds are slightly longer than typical P-C and P-O single bonds ($\sim 1.80 - 1.85$ Å and $\sim 1.56 - 1.69$ Å, respectively).³⁰

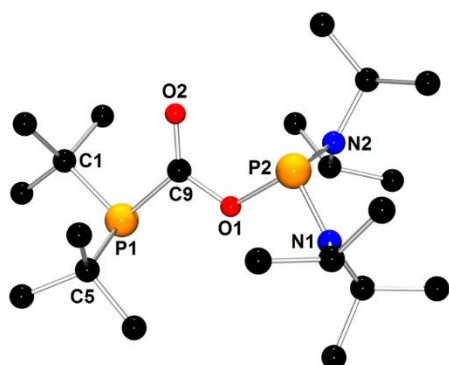


Figure 1. X-ray structure of **1a** showing the atom-numbering scheme. The H atoms are omitted for clarity.

As expected, the C9 atom exhibits trigonal planar geometry ($\angle 359.96^\circ$), while P1 and P2 are pyramidal ($\angle 314.24^\circ$ and $\angle 302.94^\circ$, respectively). P1 and P2 are located almost in the same plane as the CO_2 moiety (torsion O2-C9-O1-P2: 5.9°). The geometries around N1 and N2 are almost planar due to the interaction of their lone pairs with the P-atoms, and the same structural feature was observed for **1**.²⁹ According to NBO analysis of structure **1a**, the unusual planar array of P1-C9(=O2)-O1-P2 atoms results from sp^2 hybridization of both, C9 and O1 atoms. Furthermore, unhybridized p orbital of O1 (the one possessing a lone pair) interacts with antibonding $\pi^*(\text{C9-O2})$ orbital what is in accord with decreased occupancy (1.77) of the first one, and the increased occupancy (0.24) of the latter one. The colorless crystals of **1a** are stable under an argon atmosphere or under vacuum, and regeneration of **1** was not observed. Moreover, warming the toluene solution of **1a** to 50°C in the presence of BPh_3 for several days did not lead to decomposition of **1a**. Interestingly, in contrast to **1**, **1a** is air-stable both in the solid-state and in solution.

Experiments involving **2** and **3** indicated that small differences in the structural features of **1**, **2** and **3** have dramatic effects on the reactivity of these systems towards CO_2 . Stirring toluene solutions of **2** and BPh_3 (100 mol%/25 mol%/5 mol%) under a CO_2 atmosphere (1 atm) for 24 hours resulted in complete conversion of **2** into **2a** (Scheme 1). The spectral data of **2a** correspond to the spectral parameters determined for **1a** and confirm the insertion of a CO_2 molecule into the P-P bond. Unlike the reaction of **1**, the reaction of **2** with CO_2 is reversible. Heating a solution of **2a** with 5 mol% BPh_3 to 45°C for 24 hours under argon led to regeneration of **2** (molar ratio **2**:**2a** \approx 4:1) (Figure 2). In contrast to **1** and **2**, **3** does not react with CO_2 under identical conditions, and corresponding adduct **3a** is not formed (Scheme 1).

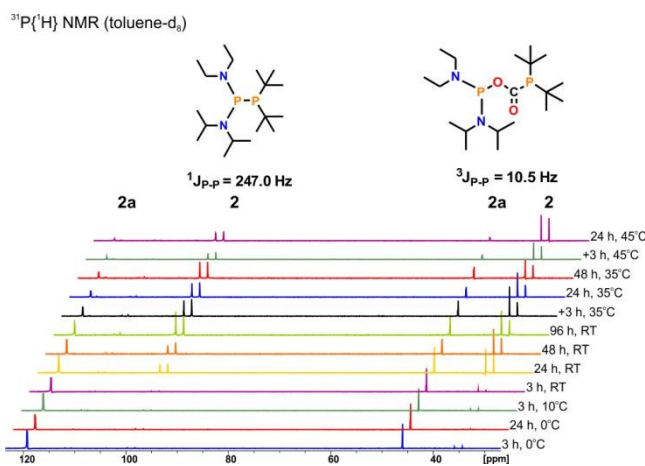
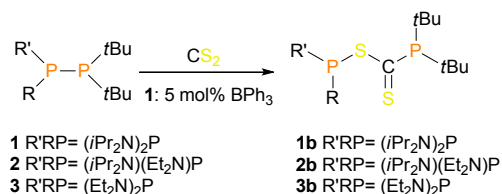


Figure 2. Variable-temperature $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **2a**.

To our delight, unsymmetrical diphosphane **1** reacted smoothly with CS_2 in the presence of BPh_3 . The desired product **1b** was obtained upon mixing a toluene solution of **1** and BPh_3 (100 mol%/25 mol%/5 mol%) with an approximately threefold excess of CS_2 at room temperature (Scheme 2). Monitoring the deep green reaction mixtures by $^{31}\text{P}\{^1\text{H}\}$ NMR revealed complete conversion of **1** into **1b** after 48 hours. Diphosphanes

2 and **3** react with CS₂ even in absence of BPh₃, and the reactions are completed after 30 minutes. However, the formation of the CS₂ adducts **2b** and **3b** proceeds by using six-fold excess of CS₂.



Scheme 2. Reactions of **1-3** with CS₂.

The obtained products were characterized by ¹H, ³¹P{¹H}, and ¹³C NMR, IR, and UV-Vis spectroscopy (see the ESI for details). Representative compound **1b** exhibits two doublets at 106.6 ppm (P(NiPr₂)₂) and 75.0 ppm (PtBu₂) (³J_{PP} = 14.5) in its ³¹P{¹H} NMR spectrum, a signal of the CS₂ moiety at 250.8 ppm (dd, ¹J_{PC} = 64.5 Hz, ²J_{PC} = 20.9 Hz) in its ¹³C NMR spectrum and a C=S absorption band at 1045 cm⁻¹ in its IR spectrum. Collectively, these data confirm the incorporation of CS₂ molecules into the diphosphane. Compounds **1b** and **2b** were characterized by X-ray analyses (Figure 3, Figure S3). The structural analysis of **1b** and **2b** showed that the CS₂ molecule was inserted in the P-P bond of the starting diphosphane with the formation of new P-C and P-S bonds. The geometries of **1b** and **2b** resemble that of **1a** with the two phosphanyl groups linked by the CS₂ unit. Similar to **1a**, the C9 atoms in **1b** and **2b** are in trigonal planar geometries, whereas the P-atoms are pyramidal. In contrast to **1a**, the products of the reactions with CS₂ are air-sensitive. Moreover, **3b** is not stable in toluene solutions, and according to NMR studies, it rearranges into more thermodynamically stable species.

The reaction products of unsymmetrical diphosphanes **1-3** with CO₂ or CS₂ may be regarded as phosphanyl derivatives of formic and dithioformic acid. Very recently, free phosphinoformic acid was detected in the gas phase,³¹ and its isolable derivatives are rare.³²⁻³⁴ To the best of our knowledge, compounds with the R₂P-E-C(=E)-PR₂ skeleton have not been described in the literature for E = O and are quite rare for E = S.¹⁷

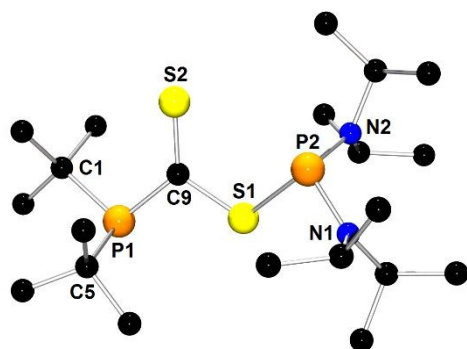
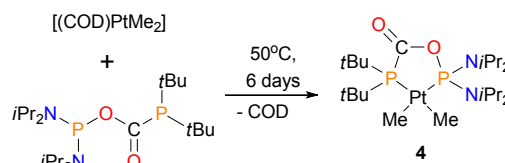


Figure 3. X-ray structure of **1b** showing the atom-numbering scheme. The H atoms are omitted for clarity

The presence of P,O-donor atoms in **1a** prompted us to examine its reactivity towards transition metal centers. The reaction of

1a with [(COD)PtMe₂] in toluene at 50°C cleanly afforded **4** (Scheme 3).
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Scheme 3. Synthesis of **4**.

Slow evaporation of the reaction mixture led to precipitation of crystalline **4** (yield 90%), which was further characterized by ¹H, ³¹P{¹H}, and ¹³C NMR spectroscopy and X-ray analysis. These data revealed that **1a** acts as a bidentate P-donor ligand, resulting in an almost planar five-membered metallacycle (Figure S4). Interestingly, the ligand geometry changes upon complexation. In free-**1a**, the P-atoms are *trans* to one another along the C–O bond, while in complexed-**1a**, they are *cis*. Differences in the reactivity of diphosphanes **1-3** and the stability of the obtained CE₂ adducts (E = O or S) were investigated by DFT calculations (see the ESI for details). The free energies ΔG₂₉₈ determined for the formation of the respective adducts confirmed that only **1a**, **1b**, and **2b** should form stable products in exergonic reactions (Table 1), and the formations of **2a**, **3a** and **3b** are not thermodynamically favorable. For the CS₂ and CO₂ adducts of **3**, only **3b** may be obtained in an endogenic reaction as an intermediate that rearranges to other presumably more stable species. By calculating the condensed nucleophilic Fukui functions (Table S12), we found that in each case, PtBu₂, as the more nucleophilic center, preferred to attack electrophilic CE₂. Second, the less nucleophilic P-center reacts with electron-rich E-atoms. In general, we can assume that the more nucleophilic P-centers react more quickly. In contrast, the more nucleophilic phosphorus centers, the less stable products are formed.

Table 1. Values of enthalpies (ΔH), free energies (ΔG) of reactions **1a-3a** and **1b-3b**

Reaction	1a	2a	3a	1b	2b	3b
ΔH kcal.mol ⁻¹	-13.0	-7.2	-5.6	-12.5	-8.4	-5.0
ΔG kcal.mol ⁻¹	-4.6	1.7	3.4	-4.1	-0.1	5.8

Experimental data provides us information about the reaction mechanism. We evidenced that presence of BPh₃ is crucial for obtaining **1a** and **2a**, and because of steric hindrance, borane does not form adducts with diphosphanes **1-3**. It is worth mentioning that neither BPh₃ nor diphosphanes **1-3** react with CO₂ alone. Even at low temperatures (between +25°C and -50°C), we did not observe formation of simple CO₂-adducts similar to those reported by Dielmann.¹⁴ We also did not notice formation of any other reaction products. Hence, we may eliminate the radical mediated reaction mechanism as phosphanyl R₂P radicals tend to react with the solvent or the

other radical giving symmetrical diphosphanes. Altogether, these observations suggest that formation of **1a** and **2a** can be considered as a result of synergistic interactions of diphosphane (Lewis base) and borane (Lewis acid) with CO₂ which is a characteristic reactivity pattern for FLPs.

Reactivity of diphosphanes **1-3** towards CS₂ seems to be more diversified. Although presence of BPh₃ also facilitates the formation of respective CS₂ adducts, in the case of highly nucleophilic systems **2** and **3**, reaction may proceed without Lewis acid by applying great excess of CS₂. Detailed reaction mechanisms are the subject of ongoing studies.

In conclusion, the reactivity of unsymmetrical diphosphanes towards CO₂ and CS₂ constitute a bridge between the reactivity of FLPs, highly nucleophilic phosphines and diphosphorus species. The diphosphination reactions described herein open new pathways for the activation of small molecules.

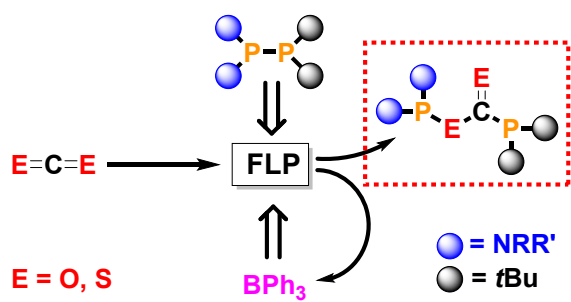
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Conflicts of interest

There are no conflicts to declare.

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