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Volume 52 | Number 1 | 4 January 2016 | Pages 1–216

ChemComm
Chemical Communications
www.rsc.org/chemcomm

ISSN 1359-7345

ROYAL SOCIETY OF CHEMISTRY

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Journal Name

COMMUNICATION

Diphosphination of CO_2 and CS_2 mediated by frustrated Lewis pairs - catalytic route to phosphanyl derivatives of formic and dithioformic acid

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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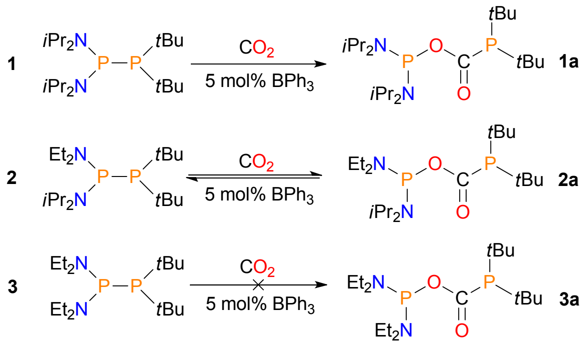
The first example of CO_2 diphosphination is described. Reactions of unsymmetrical diphosphanes with CE_2 (E = O, S) catalyzed by BPh_3 insert a CE_2 molecule into the P-P bond with formation of the products of the general formula R_2P-E-C(=E)-PR_2. The obtained CO_2 adducts arise from synergistic interaction of diphosphane and borane with CO_2 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 CO_2, 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 CO_2 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-O[10] bonds often in a reversible manner. An interesting feature of FLP-activated CO_2 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 $B(C_6F_5)_3$ were found to react with H_2 and phenylacetylene.[12,13] Although they are expensive, $B(C_6F_5)_3$ 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 CO_2. Recently, it was reported that highly nucleophilic phosphines can reversibly form simple adducts with CO_2.[14] Despite wide laboratory and industrial applications, the fixation of CS_2 is not well studied. To date, there are only a few reports regarding the activation of CS_2 by FLPs involving the formation of Lewis base-acid adducts **LB**-C(S)-S-**LA**[7,15,16] and the diphosphination of CS_2 with persistent $(H_2C)_2(NDipp)_2P\bullet$ 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 CO_2 or CS_2, 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 BPh_3. From the set of recently developed systems with polarized P-P bonds,[29] we selected three species, tBu$_2$P-P(NiPr$_2$)$_2$ (**1**), tBu$_2$P-P(NiPr$_2$)(NEt$_2$) (**2**) and tBu$_2$P-P(NEt$_2$)$_2$ (**3**), with highly nucleophilic P-atoms. We found that mixtures of BPh_3 and a base (**1**, **2** or **3**) not only form stable FLPs that do not quench each other but also react with CO_2 and/or CS_2 in an unusual manner. The reaction of a stochiometric mixture of **1** and BPh_3 in toluene under 1 atm of CO_2 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 BPh_3

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Electronic Supplementary Information (ESI) available: experimental, crystallographic, and computational details. See DOI: 10.1039/x0xx00000x

The ^{31}P NMR spectrum of the reaction mixture showed two doublets at 113.4 ppm (P(N*i*Pr$_2$)$_2$) and 47.4 ppm (P*t*Bu$_2$) (**1a**). Relative to the signals of starting diphosphane **1**, the doublet attributed to the P(N*i*Pr$_2$)$_2$ group is shifted downfield, whereas the signal of P*t*Bu$_2$ 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 ($^1J_{PC}$ = 29.4 Hz, $^2J_{PC}$ = 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 P*t*Bu$_2$ group is bound to the carbonyl C9-atom, while the P(N*i*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 (~1.33 – 1.41 Å and ~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 (~1.80–1.85 Å and ~1.56–1.69 Å, respectively).[30]

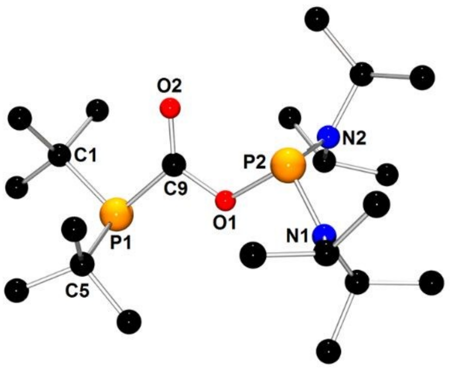

Figure 1. X-ray structure of **1a** showing the atom-numbering scheme. The H atoms are omitted for clarity.

As expected, the C9 atom exhibits trigonal planar geometry (Σ 359.96°), while P1 and P2 are pyramidal (Σ 314.24° and Σ 302.94°, 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 π*(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** ≈ 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).

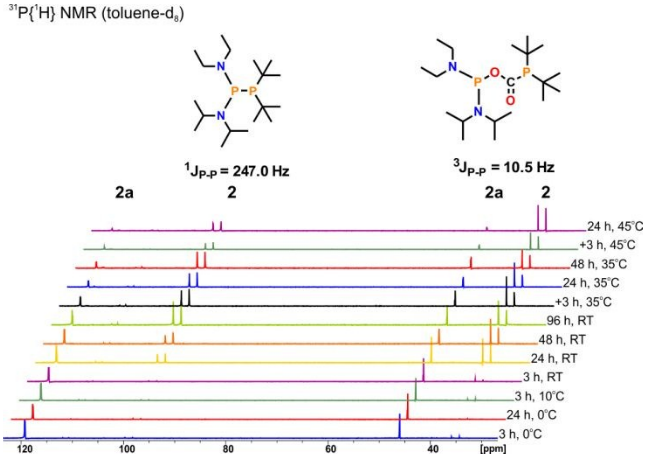

Figure 2. Variable-temperature $^{31}P\{^1H\}$ NMR spectra of **2a**.

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 $^{31}P\{^1H\}$ NMR revealed complete conversion of **1** into **1b** after 48 hours. Diphosphanes

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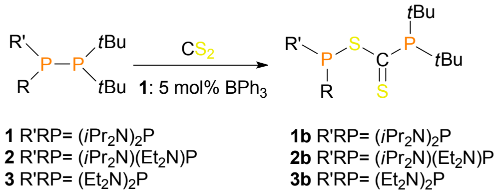
2 and **3** react with CS_2 even in absence of BPh_3, and the reactions are completed after 30 minutes. However, the formation of the CS_2 adducts **2b** and **3b** proceeds by using six-fold excess of CS_2.



Scheme 2. Reactions of **1-3** with CS_2.

The obtained products were characterized by ^{1}H, $^{31}P\{^{1}H\}$, and ^{13}C NMR, IR, and UV-Vis spectroscopy (see the ESI for details). Representative compound **1b** exhibits two doublets at 106.6 ppm ($P(NiPr_2)_2$) and 75.0 ppm ($PtBu_2$) ($^{3}J_{PP}$ = 14.5) in its $^{31}P\{^{1}H\}$ NMR spectrum, a signal of the CS_2 moiety at 250.8 ppm (dd, $^{1}J_{PC}$ = 64.5 Hz, $^{2}J_{PC}$ = 20.9 Hz) in its ^{13}C NMR spectrum and a C=S absorption band at 1045 cm^{-1} in its IR spectrum. Collectively, these data confirm the incorporation of CS_2 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 CS_2 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 CS_2 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 CS_2 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 CO_2 or CS_2 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 R_2P-E-C(=E)-PR_2 skeleton have not been described in the literature for E = O and are quite rare for E = S.[17]

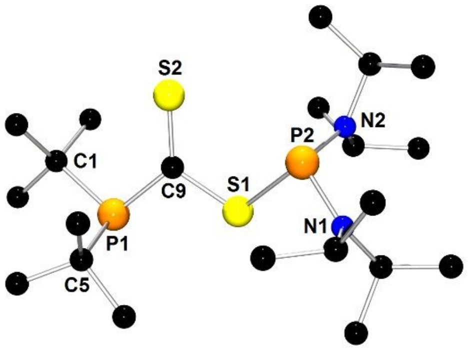
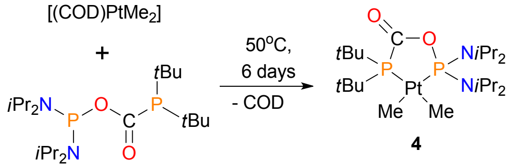


Figure 3. X-ray structure of 1b showing the atom-numbering scheme. The H atoms are omitted for clarity

The presence of P,O-donor atoms in **1a** prompted us to examine its reactivity towards transition metal centers. The reaction of **1a** with $[(COD)PtMe_2]$ in toluene at 50°C cleanly afforded **4** (Scheme 3).



Scheme 3. Synthesis of 4.

Slow evaporation of the reaction mixture led to precipitation of crystalline **4** (yield 90%), which was further characterized by ^{1}H, $^{31}P\{^{1}H\}$, and ^{13}C 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 CE_2 adducts (E = O or S) were investigated by DFT calculations (see the ESI for details). The free energies ΔG_{298} 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 CS_2 and CO_2 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, **P**tBu_2, as the more nucleophilic center, preferred to attack electrophilic **C**E_2. 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 BPh_3 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 BPh_3 nor diphosphanes **1-3** react with CO_2 alone. Even at low temperatures (between +25°C and -50°C), we did not observe formation of simple CO_2-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 R_2P radicals tend to react with the solvent or the

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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 CO_2 which is a characteristic reactivity pattern for FLPs.

Reactivity of diphosphanes **1-3** towards CS_2 seems to be more diversified. Although presence of BPh_3 also facilitates the formation of respective CS_2 adducts, in the case of highly nucleophilic systems **2** and **3**, reaction may proceed without Lewis acid by applying great excess of CS_2. Detailed reaction mechanisms are the subject of ongoing studies.

In conclusion, the reactivity of unsymmetrical diphosphanes towards CO_2 and CS_2 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.

The authors thank the National Science Centre NCN, Poland (Grant 2016/21/B/ST5/03088) for their financial support and TASK Computational Center for access to computational resources.

Conflicts of interest

There are no conflicts to declare.

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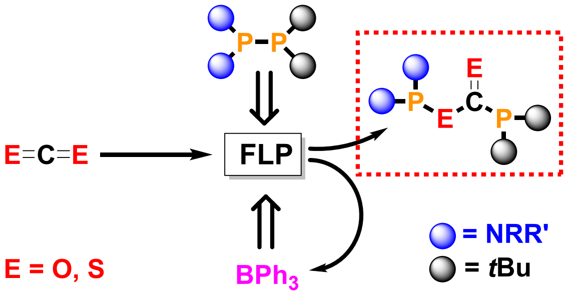

The first example of CO_2 diphosphination is described.