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Hydrophosphination of CO_2 and Subsequent Formate Transfer in the 1,3,2-Diazaphospholene-Catalyzed *N*-Formylation of Amines

*Che Chang Chong and Rei Kinjo**

Abstract: *Hydrophosphination of CO_2 with 1,3,2-Diazaphospholene (NHP-H; **1**) afforded phosphorus formate (NHP-OCOH; **2**) through the formation of a bond between the electrophilic phosphorus atom in **1** and the oxygen atom from CO_2, along with hydride transfer to the carbon atom of CO_2. Transfer of the formate from **2** to Ph_2SiH_2 produced $Ph_2Si(OCHO)_2$ (**3**) in a reaction that could be carried out in a catalytic manner by using 5 mol% of **1**. These elementary reactions were applied to the metal-free catalytic N-formylation of amine derivatives with CO_2 in one pot under ambient conditions.*

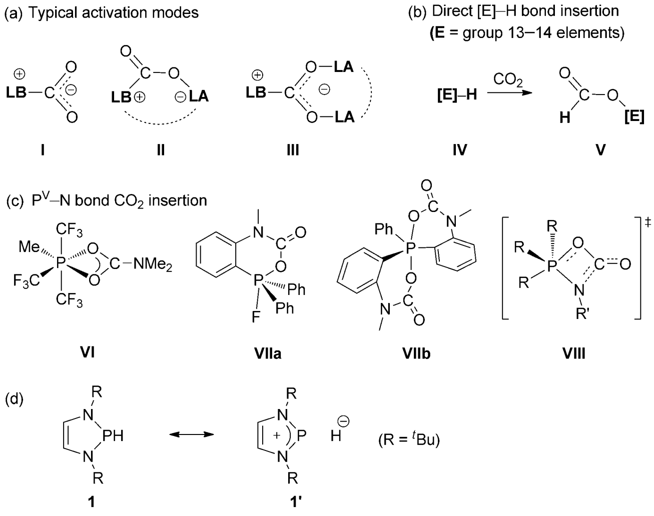

Figure 1. a) Three coordination modes in the activation of CO_2 by main-group compounds. b) Direct insertion of [E]–H bonds into CO_2. c) Examples of products and an intermediate from direct insertion of the P^V–N bond into CO_2. d) Generic structure of 2-*H*-1,3,2-diazaphospholene (**1**).

The valorization of carbon dioxide (CO_2) has attracted much attention in synthetic chemistry because of the potential use of CO_2 as a nontoxic, abundant, and inexpensive C1 source for the production of useful chemicals.[1,2] However, the considerable thermodynamic stability of CO_2 hampers facile activation. To address this issue, several metal catalysts have been employed for the transformation of CO_2, which has afforded various commodity chemicals such as formic acid derivatives, methane, methanol, CO, and formaldehyde.[3]

Metal-free catalytic systems for CO_2 valorization present an alternative method to the prevalent use of conventional metal catalysts.[4,5] The seminal work by Grimme, Stephan, Erker, et al. in 2009 demonstrated the potential of frustrated Lewis pairs (FLPs), consisting of a Lewis base (LB) and Lewis acid (LA), for CO_2 capture.[6,7] Since then, a variety of systems based on main-group compounds have been developed for the activation of CO_2.[8] Depending on the binding modes to CO_2, these systems are mainly classified into three types: one LB adduct (**I**), one LB and one LA adduct (**II**), and one LB and two LA adducts (**III**; Figure 1 a).[9] These are also recognized as key structures of initial intermediates in the functionalization of CO_2 by main-group catalysts. For instance, hydroboration of CO_2 catalyzed by main-group compounds is inferred to proceed via the activation of CO_2 to give insertion of the B–H bond into the activated C=O bond.[8g–h,10a] However, recent studies by Fontaine and Bourissou suggest that such a mechanistic pathway often involves a high activation barrier.[10b–d] Meanwhile, it has been reported that the direct reduction of CO_2 by main-group p-block hydrides [E]-H (**IV**) gives rise to formate derivatives (**V**) via insertion of the E–H bond (Figure 1 b). In this process, the main-group fragment [E] and the H atom of **IV** bond to an oxygen atom and the carbon atom of CO_2, respectively. The E–H bond thus has to be polarized as $E(\delta+)$–$H(\delta-)$ so that it concomitantly displays hydride-donor ability and electrophilic nature at the [E] moiety. As such, extant examples are limited to group 13–14 elements such as B,[11] Al,[12] Ga,[13] Ge,[14] and Sn.[15]

With group 15 elements (Figure 1 c), Cavell et al. reported the insertion of CO_2 into the P–N bond of $Me(F_3C)_3P^V$–NMe_2 over two days, which afforded the hexacoordinate phosphorus derivative **VI**.[16] Stephan et al. demonstrated that amidophosphoranes containing strained four-membered rings readily reacted with CO_2 to produce P^V heterocycles (**VIIa–b**).[17] Recently, Fontaine et al. described the activation of CO_2 with phosphazenes, in which an intermediate (**VIII**) involving CO_2 insertion into the P^V–N bond was proposed.[18] In those reactions, the P centre in the +V oxidation state acted as an electrophile to form a bond with an O atom of CO_2. Relevant sequestration of CO_2 with phosphines (R_3P^{III}) is extremely rare,[19,20] and to the best of our knowledge, formation of a phosphorus(III) formate (R_2P^{III}–OCOH) via P^{III}–H bond insertion into CO_2, that is, hydrophosphination, has not thus far been achieved. This is presumably because phosphines are typically nucleophilic, and therefore the interaction with CO_2

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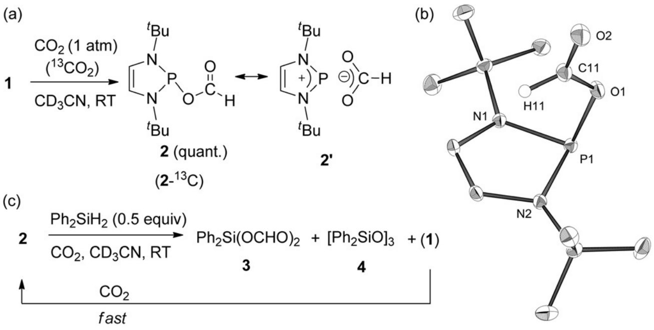
should predominantly generate adduct **I** (Figure 1 a) rather than the P^{III}–H bond insertion product.[2d,8p–q] Given the significance of CO_2 valorization, it is highly desirable to develop diverse strategies for the capture of CO_2 and its transformation into value-added compounds.

Recently, we reported that 1,3,2-diazaphospholene (**1**), which exhibits zwitterionic properties (**1′**; Figure 1 d),[21] effectively promotes the hydroboration of carbonyl compounds.[22] The reaction mechanism involved a facile insertion of the exocyclic P–H bond of **1** into the C=O bond at the initial step. This result prompted us to investigate the reactivity of **1** towards CO_2 since it possesses consecutive C=O bonds. Herein, we report a facile CO_2 insertion into the P–H bond of **1** to form the phosphorus formate **2**. Transfer of the formate from **2** to silane, and its application in the catalytic N-formylation of amines are also described.

A CD_3CN solution of **1** was exposed to 1 atm of CO_2 at ambient temperature. Instantaneously, the yellow solution darkened to a deep brown color, showing a singlet at 111.5 ppm in the ^{31}P NMR spectrum, which is shifted downfield compared to that (57.8 ppm) of **1**. After workup, product **2** was isolated as a brown solid in 93 % yield (Scheme 1 a). The ^{1}H NMR spectrum of **2** shows a characteristic peak at 8.10 ppm while the $^{13}C\{^{1}H\}$ NMR spectrum shows a singlet at 164.2 ppm. We also carried out a ^{13}C-labelling study with $^{13}CO_2$, which produced **2**-^{13}C (90 % yield). The ^{1}H NMR spectrum of **2**-^{13}C displays a doublet at 8.13 ppm that is due to coupling ($^{1}J_{H\text{-}C} = 210.8$ Hz) with the ^{13}C atom arising from $^{13}CO_2$ (see the Supporting Information). In the solid-state IR spectrum of **2**, a peak corresponding to the C=O stretching vibration was detected at 1720 cm^{-1}. These results indicate the presence of a formate group (OCHO) in **2**, which was decisively confirmed by X-ray diffractometry (Scheme 1 b). The P1–O1 distance (1.808(1) Å) is 11 % longer than a typical P–O single bond (1.63 Å). The formation of phosphorus formate **2** rather than adduct **I** (Figure 1 a) demonstrates that one of the O atoms in CO_2 attacks the electrophilic P atom, whereas the C atom in CO_2 accepts the H atom as a hydride from **1**. Note that this result presents the first example of hydrophosphination of CO_2.



Scheme 1. a) Reaction of **1** with CO_2 ($^{13}CO_2$). b) Solid-state structure of **2**. Hydrogen atoms, except for H11, are omitted for clarity. c) Formate transfer from **2** to Ph_2SiH_2 under CO_2 atmosphere.

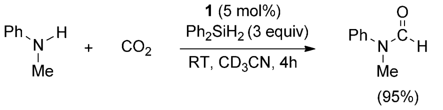
We postulated that the downfield ^{31}P NMR chemical shift and the long P–O bond in **2** indicate an ionic property of the bond that induces zwitterionic character (**2′**; Scheme 1 a), from which the formate group should be readily transferred to the appropriate acceptor. To bear out our hypothesis, we examined the reaction of **2** with a hydrosilane because the expected formation of a strong Si–O bond could be a driving force for the reaction. Under CO_2 atmosphere, treatment of **2** with a half equivalent of Ph_2SiH_2 afforded $Ph_2Si(OCHO)_2$ (**3**) as the major product, concomitant with the formation of the siloxane **4** (**3**/**4** = 2.3:1 after 15 min; Scheme 1 c). We also observed that **3** was converted into **4** after 18 h under the reaction conditions (Figures S1, S2 in the Supporting Information). The formation of **3** demonstrates the transfer of formate from **2** to Ph_2SiH_2, along with regeneration of **1**. During the reaction, however, only a peak for **2** was detected in the ^{31}P NMR spectrum, probably owing to a rapid reaction between the in situ regenerated **1** and CO_2. Therefore, we examined the subsequent addition insertion of the P–H bond of **1** into CO_2 followed by formate transfer from **2** to silane in a catalytic process.

CO_2 was introduced into a J-young NMR tube filled with a CD_3CN solution of Ph_2SiH_2 and 5 mol % of **1**, and the reaction was monitored by NMR spectroscopy. Within 1 h at room temperature, the conversion of Ph_2SiH_2 into **3** (> 95 %) was confirmed, and only small amounts of siloxane **4** (< 5 %) were detected (Scheme 2, Figure S3-1). We also performed a ^{13}C-labeling experiment for the catalytic reaction under $^{13}CO_2$ atmosphere and confirmed the clean formation of $Ph_2Si(O^{13}CHO)_2$ (**3**-^{13}C; $^{1}J_{H\text{-}C} = 232.5$ Hz; Figures S3, S4).

$$Ph_2SiH_2 \xrightarrow[CD_3CN,\ RT,\ 1h]{\mathbf{1}\ (5\ mol\ \%)\ \ CO_2} \underset{\substack{\mathbf{3}\ (>95\ \%)\\ (\mathbf{3}\text{-}^{13}C)}}{Ph_2Si(OCHO)_2} + \underset{\mathbf{4}\ (<5\ \%)}{(Ph_2SiO)_3}$$

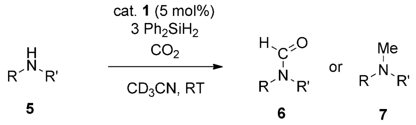
Scheme 2. Catalytic hydrosilylation of CO_2 with 5 mol % of **1**.

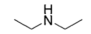
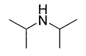
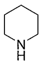
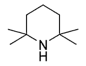
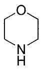
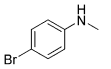
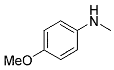
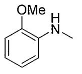
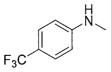
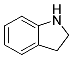
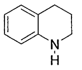
Recently, catalytic N-formylation and N-methylation of amines using CO_2 as the carbon source were reported with various organocatalysts.[23,24] In these reactions, formate derivatives are considered to be key intermediates for the formation of formamides.[23–25] Therefore, we attempted the one-pot N-formylation of amines with **1** as a catalyst. To investigate the reaction, *N*-methylaniline was utilized as a test substrate. After a brief screening of the reaction conditions (Table S3–1), we obtained the optimized conditions as shown in Scheme 3. Significantly, when $^{13}CO_2$ was used, ^{13}C-labelled *N*-methyl-*N*-phenylformamide was obtained (see the Supporting Information).



Scheme 3. N-formylation of PhMeNH with CO_2 catalyzed by **1**.

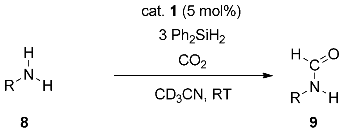
Table 1: Scope of catalytic N-formylation of secondary amines with CO_2.

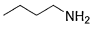
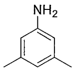
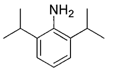
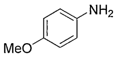
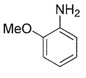
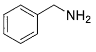
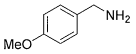
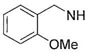
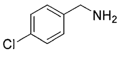
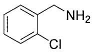


5		*t* [h]	Product	Yield [%][a]	TON	TOF [hr^{-1}]
5a		0.5	**6a**	95	19	38
5b		2	**7b**	61	12	6
5c		0.5	**6c**	94	19	38
5d		7	**7d**	53	11	2
5e		2	**6e**	94	19	10
5f		5	**6f**	87	17	4
5g		5	**6g**	93	19	4
5h		6	**6h**	78	16	3
5i		18	**6i**	71	14	1
5j		6	**6j**	94	19	3
5k		23	**6k**	64	13	0.6

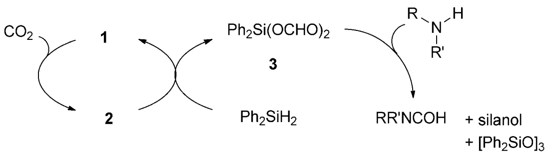
[a] Yields were determined by ^{1}H NMR spectroscopy with 1,3,5-trimethoxybenzene as an internal standard.

Table 2: Scope of the catalytic N-formylation of primary amines with CO_2.



8		*t* [h]	Product	Yield [%][a]	TON	TOF [hr^{-1}]
8a		2	**9a**	84	17	9
8b		18	**9b**	97	19	1
8c		24	**9c**	85	17	0.7
8d		10	**9d**	>99	20	2
8e		10	**9e**	72	14	1
8f		4	**9f**	97	19	5
8g		2	**9g**	91	18	9
8h		2	**9h**	99	20	10
8i		2	**9i**	82	16	8
8j		2	**9j**	90	18	9

[a] Yields were determined by ^{1}H NMR spectroscopy with 1,3,5-trimethoxybenzene as an internal standard.



Scheme 4. Proposed mechanism for the N-formylation of amines with Ph_2SiH_2 and CO_2 catalyzed by **1**.

With the optimized conditions in hand, we examined the scope of the catalytic reaction with various secondary amines (Table 1). Sterically less-hindered aliphatic amines (**5a**, **5c**, **5e**) afforded the corresponding N-formylamines in excellent yields (**6a** 95%, **6c** 94%, **6e** 94%). Meanwhile, reactions with sterically hindered and highly basic amines such as diisopropylamine (**5b**) and 2,2,4,4,-tetramethylpiperidine (**5d**), afforded N-methylated amines (**7b**: 61%, **7d**: 53%), which were probably formed by subsequent reduction of the corresponding N-formylamines (**6b**, **6d**).[24,26] Secondary amines containing aryl substituents (**5f–k**) were well tolerated and the corresponding formamides (**6f–k**) were produced in good to excellent yields (94–64%). To expand the scope of the reaction, we also tested primary amines (Table 2). All of the amines employed (**8a–j**) were well tolerated and the corresponding formamides (**9a–j**) were produced in 72–99% yields.

To gain insight into the reaction mechanism, we performed control reactions. In the absence of silane, a mixture of *N*-methylaniline and **1** under CO_2 atmosphere only afforded **2**, and no further reaction between **2** and *N*-methylaniline was observed. We also confirmed that *N*-methylaniline does not react with Ph_2SiH_2. Similarly, no apparent reaction was observed between **1** and silane. Meanwhile, addition of *N*-methylaniline to $Ph_2Si(OCHO)_2$ (**3**) gave *N*-formyl-*N*-methylaniline after 2 h at room temperature in the absence of **1** and **2**. Therefore, we propose a mechanism (Scheme 4) for the N-formylation of amines that involves the following three steps: 1) insertion of the P—H bond of **1** into CO_2 to generate **2**, 2) transfer of a formate from **2** to Ph_2SiH_2 to form $Ph_2Si(OCOH)_2$ (**3**) along with the regeneration of **1**, 3) formation of formamides and also silane byproducts such as silanols and $(Ph_2SiO)_3$ through the reaction of **3** with amines. Catalyst **1** thus acts as a reducing agent for CO_2 to form **2**, which subsequently transfers its formate moiety to silane. This mechanism differs from that proposed for the NHC–silane system in the N-formylation of amines,[23,24] where an initial activation of silane by NHC is energetically more favorable than the mechanism encompassing the formation of an NHC–CO_2 adduct.[26]

In summary, we have demonstrated the first hydrophosphination of CO_2 with **1**, subsequent transfer of formate from

2 to Ph_2SiH_2, and catalytic N-formylation of amines under metal-free and ambient conditions.

Acknowledgements

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Keywords: CO_2 activation · hydrophosphination · hydrosilylation · metal-free catalysis · N-formylation

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Angew. Chem. **2015**, *127*, 12284–12288

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