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Stepwise carbon dioxide hydrosilylation catalyzed by bimetallic complexes [CpM(CO)$_2$(μ-CO)···Pd($^{Bu^t}$PCP)]

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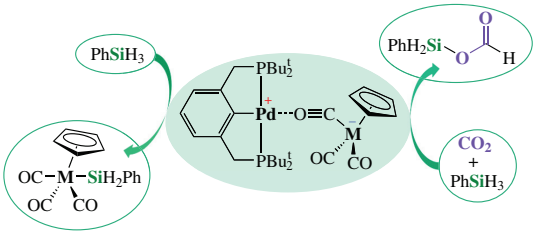
The interaction of bimetallic ($^{Bu^t}$PCP)Pd···(OC)M(CO)$_2$Cp (M = Mo, W) complexes with PhSiH$_3$ leads to an efficient heterolytic splitting of Si–H bond that is a primary step in catalytic hydrosilylation of CO$_2$. The reaction can be stopped at the formate level in the presence of the above complexes while proceeds further when catalyzed by ($^{Bu^t}$PCP)PdH.



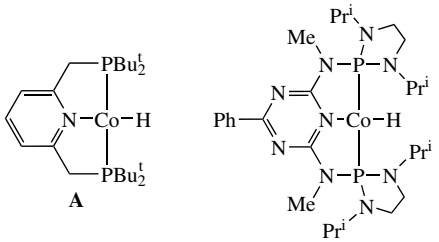
Keywords: bimetallic catalysis, pincer complexes, carbon dioxide, hydrosilylation, reaction mechanism, IR spectroscopy.

Carbon dioxide is a unique and almost unlimited source of carbon in the form of C_1 synthon, which can be involved in various chemical reactions yielding valuable chemical compounds.[1] A booming research on the catalytic CO_2 reduction with hydrogen has led to the development of a great number of transition metal complexes[2,3] some of which employ the metal–ligand cooperation. Most of these complexes catalyze two-electron (2ē) reduction of CO_2 into formic acid[4] or formate ion, whereas homogeneous cases of 4ē reduction to formaldehyde or 6ē reduction to CH_3OH are not so numerous.[2] The development of efficient homogeneous catalytic systems based on transition metal complexes that operate at relatively low H_2 pressures and temperatures remains a topical task.[2,5]

Boranes, R_2BH, or silanes, R_nSiH_{4-n}, provide a synthetically convenient alternative to H_2 as they are readily available, non-toxic and easier to handle.[6–9] Their reactions with CO_2 are also well explored, but anyway, the race for more effective catalyst continues. The use of these compounds assumes a heterolytic splitting of their E–H bonds that, as in the case of reduction with H_2, is often catalyzed by metal pincer complexes. For example, cobalt(I) pincers (**A**, **B**) operate *via* $PhSiH_3$ oxidative addition to Co(OCHO) species forming six-coordinated cobalt(III) dihydrides.[10–12]

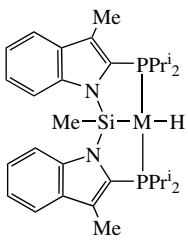
Pincer complexes of Group 10 metals catalyze CO_2 hydroboration to different oxidation levels.[13–17] Thus, among the bis(indolylphosphino)silyl (PSiP) complexes **C** the Pd catalyst exhibited moderate activity yielding boryl formate while the Ni species selectively produced bis(boryl) acetal.[17] The thorough study on (^{R}PXCYP)MH complexes **D** has shown a correlation between the steric bulk of phosphine substituents and the rate of pinacol borane (HBPin) consumption.[18] Interestingly, the presence of triphenyl borate as a Lewis acid co-catalysts altered the selectivity of CO_2 hydroboration, allowing to obtain bis(boryl) acetal and methoxyborane compounds instead of boryl formate in the presence of (^{R}PCP)PdH catalysts (**D**; X = Y = CH_2).[17] Surprisingly, CO_2 hydrosilylation has not been studied for these complexes. The mechanistic studies on catalytic CO_2 hydrosilylation[19] and hydroboration[20] suggested the sequential reaction, which proceeded as a cascade of three 2ē reduction catalytic cycles of C=O insertion into M–H bond and followed by the E–H addition.

We have previously[21–24] shown that bimetallic complexes ($^{Bu^t}$PXCYP)Pd···(OC)M(CO)$_2$Cp **1a**,**b** (M = Mo and W, respectively) displayed bifunctional properties. Palladium cationic and molybdenum/tungsten anionic metal centers are able to cooperatively activate bifunctional substrates (BH_3–NHR_2,[23] HCOOH[24]) and thereby launch further catalytic dehydrogenation. Herein, we have studied the reactivity of these bimetallic complexes in Si–H bonds activation, a primary step of the hydrosilylation reactions in general, and in catalytic hydrosilylation of CO_2 *inter alia*.



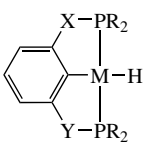
A

B



C

M = Ni, Pd, Pt



D

R = Bu^t, Cy, Pr^i
M = Pd, Ni
X, Y = CH_2, O

The IR monitoring revealed that both palladium hydrides ($^{Bu^t}$PCP)PdH (**D**; X = Y = CH_2), ($^{Bu^t}$PCOP)PdH (**D**; X = CH_2, Y = O) and bimetallic complexes **1a**,**b** catalyzed the reaction of CO_2 with $PhSiH_3$ under ambient conditions (1 bar, 25 °C).† When the CO_2 hydrosilylation is carried out in the presence of palladium hydride only (10 mol% loading), IR spectra show the presence of palladium formate [ν_{CO}(Pd(OCHO) at 1622 cm^{-1}][24] and the decrease of ν_{SiH}($PhSiH_3$) intensity without an increase of any new bands (see Online Supplementary Materials, Figure S1) suggesting a reduction to formaldehyde level (in the form of bis(silyl) acetal) or methanol level (in the form of methoxysilane). The reaction rate is ten times faster for ($^{Bu^t}$PCP)PdH ($v_0 = 3.0 \times 10^{-6}$ mol dm^{-3} s^{-1}) than for ($^{Bu^t}$PCOP)PdH ($v_0 = 2.4 \times 10^{-7}$ mol dm^{-3} s^{-1}) in accordance with higher hydricity of the former and, which resulted in facilitating CO_2 insertion.

In contrast, in the presence of complexes **1a** or **1b** IR spectra show disappearance of the starting silane (the decrease of ν_{SiH} band at 2157 cm^{-1}) and formation of different reduction product, namely, silyl formate $PhSiH_2(OCHO)$ characterized by intense ν_{CO} band at 1715 cm^{-1} (Figure 1). Within half an hour, the second ν_{CO} band appears in this region (1723 cm^{-1}) and grows in time, which we assign to silylene bis-formate $PhSiH(OCHO)_2$.[25,26]

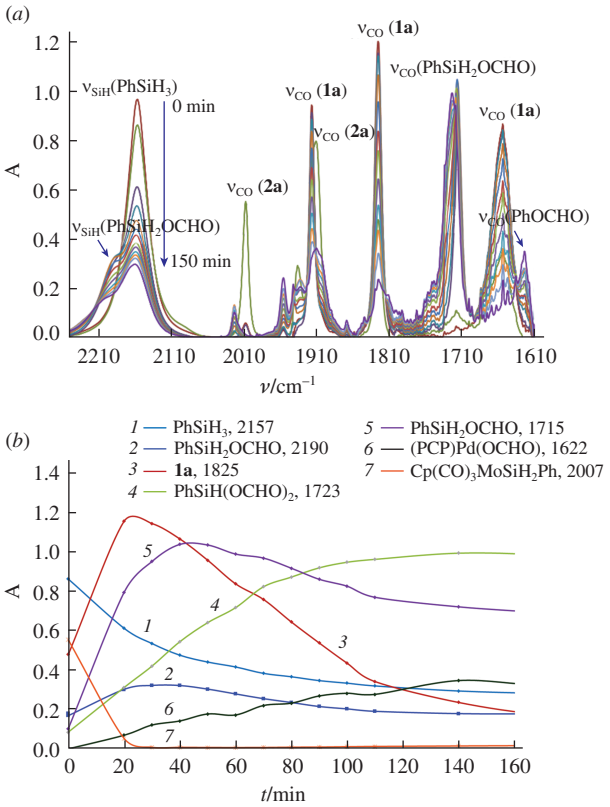


Figure 1 (*a*) Time evolution of IR spectra for the mixture of **1a** (c = 0.006 M) with $PhSiH_3$ (c = 0.06 M) under 1 bar CO_2 and (*b*) the corresponding kinetic curves A(t) for the selected bands. Toluene, l = 0.05 cm, 298 K.

† *Typical procedure for catalytic CO_2 hydrosilylation*. In an argon atmosphere a solution of bimetallic complex **1a**,**b** (c = 0.006 M) or palladium hydride complex (c = 0.006 M) in toluene (2 ml) was placed in a 25 ml Schlenk flask. Then specified amount of $PhSiH_3$ (c = 0.06 or 0.1 M) was added upon stirring at room temperature. Carbon dioxide-filled balloon was connected to the Schlenk flask using a needle through the septum cap. The resulting solution was transferred to the CaF_2 cell with metal needle connector between the home-modified cryostat and flask. IR spectrum was measured, and the solution was transferred back to the flask to keep a CO_2 atmosphere. The measurements were repeated every 10 min.

The initial reaction rates v_0 calculated from the decrease of the starting ν_{SiH} band were 4.3×10^{-6} and 3.0×10^{-6} mol dm^{-3} s^{-1} for 10 mol% **1a** and **1b**, respectively. Raising the temperature to 40 °C led to a slight increase in the initial rate for **1a** to 4.3×10^{-6} mol dm^{-3} s^{-1} that can be caused by the change of the reactant ratio due to a decrease of CO_2 solubility. Interestingly, in 2 h after mixing, the ν_{CO} bands of $PhSiH_{3-x}(OCHO)_x$ (x = 1, 2) begin to decrease until complete disappearance. This indicates a deeper reduction yielding bis(silyl) acetal $PhSiH_2$–OCH_2O–H_2SiPh and methoxysilane as confirmed by ^{1}H NMR spectra (Figure S2). The increase in $PhSiH_3$ loading to 25 equiv. leads to acceleration of the reaction to $v_0 = 1.6 \times 10^{-5}$ mol dm^{-3} s^{-1} (Figures S3, S4).

IR spectra also showed the simultaneous transformation of bimetallic complexes. For **1a**, new bands ν_{CO} were observed at 2007, 1936, 1910 cm^{-1} with a low frequency shoulder ν_{SiH} at 2090 cm^{-1} immediately after mixing [Figure 1(*a*)].‡ This species **2a** would disappear transforming back into **1a** (Table 1), whose bands slowly fade in the course of the reaction while ν_{CO} of ($^{Bu^t}$PCP)Pd(OCHO) grows in intensity [Figure 1(*b*)]. Tungsten-based complex **1b** behaves a bit differently showing the appearance of ν_{CO} bands belonging to $CpW(CO)_3H$ and formation of a higher amount of ($^{Bu^t}$PCP)Pd(OCHO) (Figure S5).

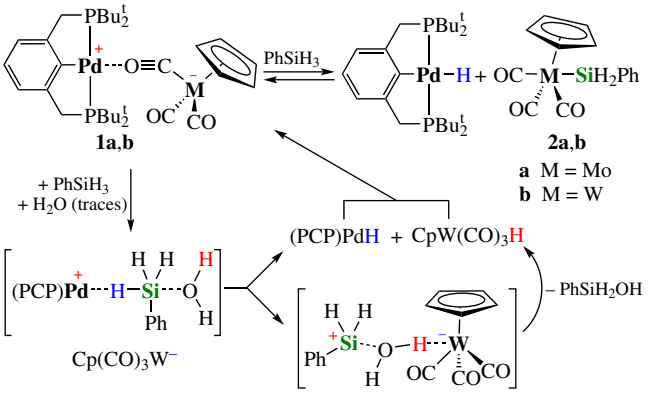
To probe the structure of **2a**, we monitored the reaction of **1a**,**b** with $PhSiH_3$ under an inert atmosphere. At equimolar **1a**/$PhSiH_3$ ratio, we observed (Figure S6) an intensity decrease for the ν_{SiH} band 2157 cm^{-1} of $PhSiH_3$ and appearance of two new low-frequency ν_{SiH} bands at 2118 and 2093 cm^{-1}. At the same time, new bands ν_{CO}(**2a**) appear at 2007, 1936, 1910 cm^{-1} together with ν_{PdH} at 1717 cm^{-1}, growing in intensity on the expense of ν_{CO} bands of **1a** (Figure S7, Table 1). NMR spectra (toluene-d_8) measured after the reaction completion show a set of new proton signals δ_H 7.70–7.33 (5 H, Ph), 5.25 (s, 2 H, SiH_2) and 4.41 (s, 5 H, Cp), the ^{29}Si resonance at 7.1 ppm, as well as the signal of ($^{Bu^t}$PCP)PdH in the ^{31}P{^{1}H} spectrum (δ_P 93.5). These IR and NMR data evidence the formation of silyl complex $Cp(CO)_3Mo(\eta^1\text{-}SiH_2Ph)$ **2a** (Scheme 1). Such complexes have been obtained, *e.g.*, by the reaction of $RSiH_2Br$ (R = Me, Ph) with $CpM(CO)_3Na$ (M = Mo, W) in cyclohexane,[27] and have spectral characteristics similar to those of **2**.[27,28] We suggest that bimetallic complex **1a** activates the SiH bond in a FLP-like fashion *via* the trimolecular complex, where heterolytic Si–H bond splitting yields palladium hydride and $Cp(CO)_3Mo(\eta^1\text{-}SiH_2Ph)$ (**2a**, see Scheme 1).

Reaction of W-containing bimetallic complex **1b** with $PhSiH_3$ exhibits some peculiarity. When silane is added to a solution of **1b** in toluene, $CpW(CO)_3H$ is instantly formed (ν_{CO} 2020 cm^{-1}) and then transforms in time into **2b** (ν_{CO} 2004, ν_{SiH} 2090 cm^{-1}) (Figure S8). We hypothesize that the silyl cation $PhSiH_2^+$ particle formed as a result of the hydride-ion transfer to the palladium

Table 1 Characteristic stretching vibrations (ν_{CO} and ν_{SiH}) for organometallic compounds and silyl formates.

Compound	ν_{CO}/cm^{-1}	ν_{SiH}/cm^{-1}
($^{Bu^t}$PCP)Pd–(OC)Mo$(CO)_2$Cp	1917, 1824, 1654	
($^{Bu^t}$PCP)Pd–(OC)W$(CO)_2$Cp	1911, 1820, 1651	
$Cp(CO)_3Mo(\eta^1\text{-}SiH_2Ph)$	2007, 1936, 1910	2118, 2093
$Cp(CO)_3W(\eta^1\text{-}SiH_2Ph)$	2004, 1933, 1907	2118, 2093
$CpMo(CO)_3H$	2023, 1933	
$CpW(CO)_3H$	2019, 1925	
$PhSiH_{3-x}(OCHO)_x$	1715 (x = 1), 1723 (x = 2)	2190 (x = 1)

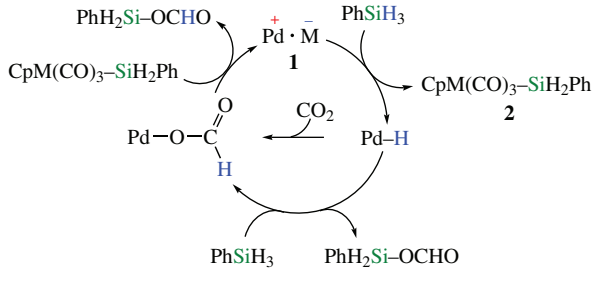
‡ Due to the peculiarities of the reaction set-up, CO_2 is introduced at the last step (*vide supra*). This delay allows **1a** and $PhSiH_3$ to react yielding compound **2a** (*vide infra*).



Scheme 1

cation can activate trace water due to its substantial Lewis acidity[29] and protonate tungsten anion within a trimolecular complex $PhSiH_2^+\cdots OH_2\cdots{}^-W(CO)_3Cp$ yielding also $PhSiH_2OH$ (see Scheme 1). This side reaction is possible for **1b** because of higher basicity of tungsten anion [$pK_a(CpWH(CO)_3) = 16.1$ in MeCN] in comparison with the molybdenum one [$pK_a(CpMoH(CO)_3) = 13.9$ in MeCN].[30,31] Despite more complicated reaction scheme for **1b**, the rate of silane consumption is quite similar for 10 mol% **1a** and **1b** ($v_0 = 1.5\times10^{-6}$ and 1.3×10^{-6} mol dm^{-3} s^{-1}, respectively) and is only twice lower than that observed in the presence of ($^{Bu^t}$PCP)PdH (*vide supra*), indicating the SiH bond cleavage is the rate-determining step. Generated *in situ* in the presence of 10 equiv. $PhSiH_3$, complex **2a** catalyzes CO_2 hydrosilylation showing the IR spectral picture (Figure S9) identical to that observed for **1a**/$PhSiH_3$/CO_2 (see Figure 1).

The data obtained show that the use of bimetallic complex **1** leads to a stepwise CO_2 hydrosilylation when the reduction can be stopped at the formate level, whereas sole ($^{Bu^t}$PCP)PdH rapidly passes this stage giving a deeper reduction. Insertion of CO_2 into Pd–H bond is a diffusion-controlled step that makes Si–H bond activation a rate-determining step (Scheme 2). The overall hydrosilylation rate (rate of $PhSiH_3$ consumption) is higher in the presence of bimetallic complexes **1** although the reaction of $PhSiH_3$ with **1** is slower than with ($^{Bu^t}$PCP)Pd(OCHO). This supports the importance of multiple non-covalent interactions at the key stage of hydride transfer to Pd^+ and the activation of Si–H bond by bimetallic complex in the FLP-fashion. It is noteworthy that upon the addition of Ph_2SiH_2 to bimetallic complex **1a** in toluene, neither palladium hydride nor silyl complex analogs to **2a** is formed. Since the hydride donating ability of Si–H is higher in Ph_2SiH_2 than in $PhSiH_3$,[32] we propose that the reaction with Ph_2SiH_2 is hampered by lower steric accessibility of the Si–H bond. Steric factors may also slow the hydrosilylation to formaldehyde or methanol levels when $PhSiH_3$ is used. The results obtained illustrate the potential of transition metal-based frustrated Lewis pairs (FLPs) in selective hydrosilylation of carbon dioxide to different levels under mild conditions. Tuning the reactivity of the Lewis base and/or Lewis acid component of this system *via* ligand modification will be a subject of our further investigations.



Scheme 2

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2024.02.010.

References

1 N. Yu. Kuznetsov, A. L. Maximov and I. P. Beletskaya, *Russ. J. Org. Chem.*, 2022, **58**, 1681 (*Zh. Org. Khim.*, 2022, **58**, 1267).
2 S. Navarro-Jaén, M. Virginie, J. Bonin, M. Robert, R. Wojcieszak and A. Y. Khodakov, *Nat. Rev. Chem.*, 2021, **5**, 564.
3 S.-T. Bai, G. De Smet, Y. Liao, R. Sun, C. Zhou, M. Beller, B. U. W. Maes and B. F. Sels, *Chem. Soc. Rev.*, 2021, **50**, 4259.
4 S. Gelman-Tropp, E. Kirillov, E. Hey-Hawkins and D. Gelman, *Chem. – Eur. J.*, 2023, e202301915.
5 J. Klankermayer, S. Wesselbaum, K. Beydoun and W. Leitner, *Angew. Chem., Int. Ed.*, 2016, **55**, 7296.
6 F. J. Fernández-Alvarez, A. M. Aitani and L. A. Oro, *Catal. Sci. Technol.*, 2014, **4**, 611.
7 F. J. Fernández-Alvarez and L. A. Oro, *ChemCatChem*, 2018, **10**, 4783.
8 J. Chen, M. McGraw and E. Y.-X. Chen, *ChemSusChem*, 2019, **12**, 4543.
9 Y. Zhang, T. Zhang and S. Das, *Green Chem.*, 2020, **22**, 1800.
10 M. L. Scheuermann, S. P. Semproni, I. Pappas and P. J. Chirik, *Inorg. Chem.*, 2014, **53**, 9463.
11 H. H. Cramer, S. Ye, F. Neese, C. Werlé and W. Leitner, *JACS Au*, 2021, **1**, 2058.
12 H. H. Cramer, B. Chatterjee, T. Weyhermüller, C. Werlé and W. Leitner, *Angew. Chem., Int. Ed.*, 2020, **59**, 15674.
13 S. Chakraborty, J. Zhang, Y. J. Patel, J. A. Krause and H. Guan, *Inorg. Chem.*, 2013, **52**, 37.
14 S. Chakraborty, Y. J. Patel, J. A. Krause and H. Guan, *Polyhedron*, 2012, **32**, 30.
15 S. Chakraborty, J. Zhang, J. A. Krause and H. Guan, *J. Am. Chem. Soc.*, 2010, **132**, 8872.
16 H.-W. Suh, L. M. Guard and N. Hazari, *Chem. Sci.*, 2014, **5**, 3859.
17 L. J. Murphy, H. Hollenhorst, R. McDonald, M. Ferguson, M. D. Lumsden and L. Turculet, *Organometallics*, 2017, **36**, 3709.
18 M. R. Espinosa, D. J. Charboneau, A. Garcia de Oliveira and N. Hazari, *ACS Catal.*, 2019, **9**, 301.
19 F. Bertini, M. Glatz, B. Stöger, M. Peruzzini, L. F. Veiros, K. Kirchner and L. Gonsalvi, *ACS Catal.*, 2019, **9**, 632.
20 F. Huang, C. Zhang, J. Jiang, Z.-X. Wang and H. Guan, *Inorg. Chem.*, 2011, **50**, 3816.
21 E. S. Osipova, N. V. Belkova, L. M. Epstein, O. A. Filippov, V. A. Kirkina, E. M. Titova, A. Rossin, M. Peruzzini and E. S. Shubina, *Eur. J. Inorg. Chem.*, 2016, 1415.
22 V. A. Levina, A. Rossin, N. V. Belkova, M. R. Chierotti, L. M. Epstein, O. A. Filippov, R. Gobetto, L. Gonsalvi, A. Lledós, E. S. Shubina, F. Zanobini and M. Peruzzini, *Angew. Chem., Int. Ed.*, 2011, **50**, 1367.
23 E. S. Osipova, E. S. Gulyaeva, E. I. Gutsul, V. A. Kirkina, A. A. Pavlov, Y. V. Nelyubina, A. Rossin, M. Peruzzini, L. M. Epstein, N. V. Belkova, O. A. Filippov and E. S. Shubina, *Chem. Sci.*, 2021, **12**, 3682.
24 E. S. Osipova, D. V. Sedlova, E. I. Gutsul, Y. V. Nelyubina, P. V. Dorovatovskii, L. M. Epstein, O. A. Filippov, E. S. Shubina and N. V. Belkova, *Organometallics*, 2023, **42**, 2651.
25 S. N. Riduan, Y. Zhang and J. Y. Ying, *Angew. Chem., Int. Ed.*, 2009, **48**, 3322.
26 B.-X. Leong, Y.-C. Teo, C. Condamines, M.-C. Yang, M.-D. Su and C.-W. So, *ACS Catal.*, 2020, **10**, 14824.
27 P. Gusbeth and H. Vahrenkamp, *Chem. Ber.*, 1985, **118**, 1143.
28 T. Watanabe, H. Hashimoto and H. Tobita, *Angew. Chem., Int. Ed.*, 2004, **43**, 218.
29 E. N. Nikolaevskaya, M. A. Syroeshkin and M. P. Egorov, *Mendeleev Commun.*, 2023, **33**, 733.
30 V. Skagestad and M. Tilset, *J. Am. Chem. Soc.*, 1993, **115**, 5077.
31 V. A. Levina, O. A. Filippov, E. I. Gutsul, N. V. Belkova, L. M. Epstein, A. Lledós and E. S. Shubina, *J. Am. Chem. Soc.*, 2010, **132**, 11234.
32 Z. M. Heiden and A. P. Lathem, *Organometallics*, 2015, **34**, 1818.

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