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Reduction of CO_2 to free CO by a Pd(I)–Pd(I) dimer†

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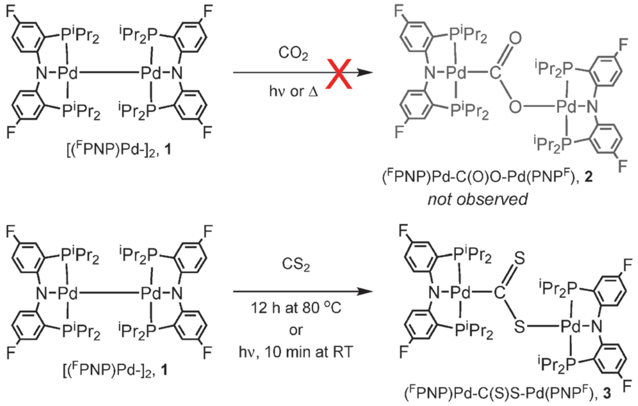
Reaction of CO_2 with a Pd(I)–Pd(I) dimer supported by amido/bis(phosphine) pincer PNP ligands produces free CO in the presence of Me_3SiCl and Me_3SiOTf.

Reduction of carbon dioxide (CO_2) to carbon monoxide (CO) is an important fundamental chemical transformation that potentially provides a path for utilization of CO_2 in making value-added chemicals and a path for storing solar energy in the form of chemical fuels.[1] In biology, this conversion is efficiently and reversibly catalysed by the carbon monoxide dehydrogenase (CODH) enzyme.[2] Synthetic electrocatalysts for reduction of CO_2 to CO have also been developed, most notably using Re,[3] Ni,[4] Pd,[5] and Ru[6] complexes. Stoichiometric chemical reduction of CO_2 to free CO has been accomplished using a variety of transition metal complexes,[7–11] uranium,[12] as well as main group elements.[13–16] In general, these reactions are successful when the formal equivalent of oxide (O^{2-}) generated in the CO_2 reduction is trapped by making strong bonds to oxophilic elements (*e.g.*, metal-oxos or Si–O and Al–O bonds) and when the transition metal compounds involved have a low affinity for binding CO as a ligand. The catalytic chemical reduction of CO_2 to CO by Sadighi *et al.*[17] exemplifies this well: a Cu(I) catalyst mediates reduction of CO_2 to CO with pinB–Bpin[18] as the reductant, consuming the oxide equivalent to form pinB–O–Bpin. A conceptually related CsF-catalyzed conversion of CO_2 to CO with $PhMe_2Si–SiMe_2Ph$ as the reductant was very recently disclosed.[19]



Scheme 1 Reactions of **1** with CO_2 and CS_2.

We were in particular intrigued by the studies[5] of Dubois *et al.* on the polyphosphine-supported Pd^{II} electrocatalysts in view of our recent work[20] with the Pd^I–Pd^I dimer$[(^FPNP)Pd–]_2$ (**1**) (Scheme 1). Dubois *et al.* arrived at the conclusion that Pd^I–Pd^I dimers were the undesirable decomposition products in their system, but that in some cases, bimetallic bis-Pd systems displayed enhanced electrocatalytic rates. Since **1** has previously been shown to activate other small molecules,[20b,c] we were encouraged to examine its reactivity with CO_2.

Exposure of C_6D_6 solutions of **1** to 1 atm of CO_2 at ambient temperature or at 80 °C, with or without illumination, did not lead to any NMR-detectable products. In contrast, treatment of **1** with CS_2, a heavier analog of CO_2, resulted in clean insertion of CS_2 into the Pd–Pd bond to give **3**; this insertion proceeded rapidly (10 min) upon illumination of the reaction mixture, and sluggishly (12 h) at 80 °C in the dark. An X-ray crystallographic study of **3** (Fig. 1) revealed an approximately square-planar environment about each Pd. The environment about C25 of the CS_2 fragment is planar, with one C–S distance *ca.* 0.05 Å shorter than the other. Solution NMR spectroscopic characterization of **3** agreed with the solid-state structure. The two different $(^FPNP)Pd$ fragments in **3** each show local C_{2v} symmetry on the NMR timescale, with the ^{19}F NMR chemical shifts being consistent with the two Pd atoms in each (PNP)Pd fragment bound to different types of substituents.[23]

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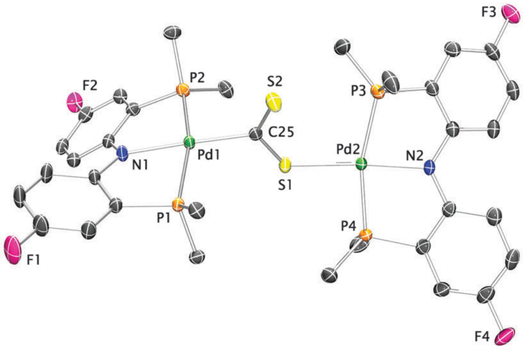
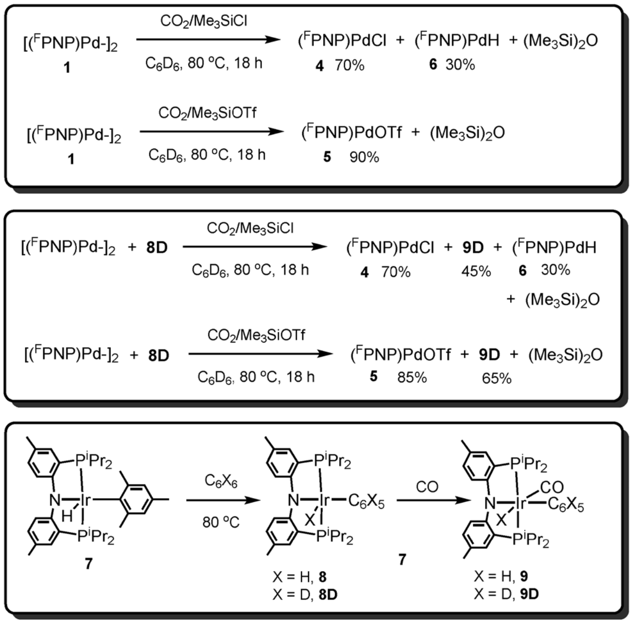


Fig. 1 POV-Ray[21] rendition of the ORTEP[22] drawing (50% thermal ellipsoids) of **3** showing selected atom labeling. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Pd1–C25, 2.019(3); C25–S1, 1.693(3); C25–S2, 1.639(3); Pd1–N1, 2.079(2); Pd2–N2, 2.042(2); P1–Pd1–P2, 164.14(3); P3–Pd2–P4, 164.42(3).



Scheme 2 Reactions of **1** with CO_2 in the presence of Me_3SiCl/Me_3SiOTf (top); reactions of **1** with CO_2 in the presence of Me_3SiCl/Me_3SiOTf and an iridium CO trap **8D** (middle); independent syntheses and identities of the $(^{Me}PNP)Ir$ complexes used to trap CO (bottom).

Insertion of CS_2 into Pd^I–Pd^I single bonds[24] in A-frame[25] types of compounds (and analogous Pt^I–Pt^I)[26,27] has been previously reported.

We hypothesized that a CO_2 insertion product **2** analogous to **3** may be kinetically accessible but not thermodynamically favorable. Related complexes with Pd^{II}–C(=O)O–Pd^{II} and Pt^{II}–C(=O)O–Pt^{II} subunits have been reported *via* condensation of metallacarboxylic acids (M^{II}–COOH) with M^{II}–OH,[28,29] and an A-frame[25] Rh^I–CO_2–Rh^I complex made *via* insertion of CO_2 into a Rh^0–Rh^0 bond has been reported as well.[30] We envisaged that CO_2 conversion may be driven forward by a subsequent favorable reaction of the Pd–O bond in the putative **2** with a Me_3Si–X reagent. Therefore, we subjected a C_6D_6 solution of **1** to CO_2 (1 atm) while in the presence of either Me_3SiCl or Me_3SiOTf (and $(^FPNP)Me$[31] as an internal NMR integration standard). Thermolysis of these two mixtures at 80 °C for 18 h resulted in complete consumption of **1** and the formation of $(^FPNP)PdCl$ (**4**) and $(^FPNP)PdOTf$ (**5**) as dominant Pd products in 70% and 90% yield (by NMR *vs.* an internal standard), respectively (Scheme 2). The balance of Pd in the reaction with Me_3SiCl was in the form of $(^FPNP)PdH$[32] (**6**) (*ca.* 30%). In both cases, $(Me_3Si)_2O$ was detected by ^1H NMR spectroscopy.[33] The balance of oxophilicity of Si and the softness of Pd must be important since no reaction was detected upon thermolysis of **3** with either Me_3SiCl or Me_3SiOTf. Stoichiometric considerations upon observation of $(Me_3Si)_2O$ and **4** or **5** suggested to us that CO may be the other major product. In order to quantify the production of CO, we selected $(^{Me}PNP)Ir(D)(C_6D_5)$ (**8D**) as *in situ* trap for free carbon monoxide. **8D** can be quantitatively prepared by thermolysis of **7**[34] in C_6D_6. Cummins *et al.* recently used another 16-electron d^6 complex $Cp^*RuCl(PCy_3)$ as a CO trap.[7]

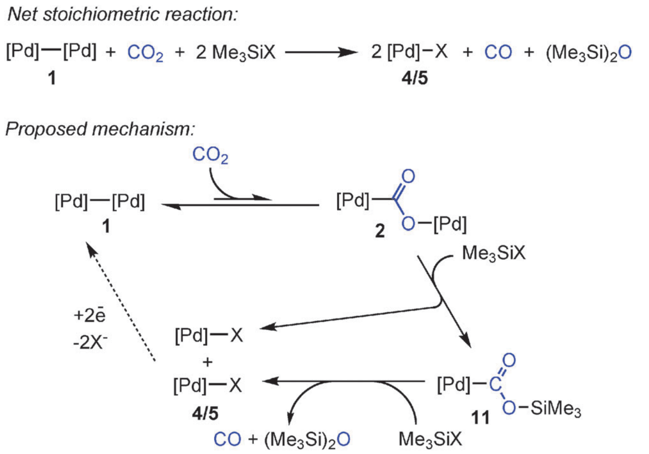
Thermolysis of **1** in C_6D_6 under 1 atm of CO_2 in the presence of Me_3SiOTf and **8D** produced 85% yield of **5** and 65% yield of $(^{Me}PNP)Ir(D)(C_6D_5)(CO)$ (**9D**). The analogous reaction with Me_3SiCl yielded 70% yield of **5**, 30% yield of $(^FPNP)PdH$[35] (**6**) and 45% yield of **9D**.

Several control reactions under the thermolysis conditions were necessary to establish that the CO in **9D** is indeed the trapped free CO generated by **1**/CO_2/Me_3SiX. Complex **8D** showed no reaction with CO_2, or separately, with Me_3SiOTf or Me_3SiCl. Thermolysis of **8D** at 80 °C for 24 h under 1 atm of CO_2 in the presence of Me_3SiOTf resulted in 60% consumption of **8D**, but **9D** was not observed as a product. Thermolysis of **8D** at 80 °C for 18 h under 1 atm of CO_2 in the presence of Me_3SiCl resulted in complete consumption of **8D** and a mixture of products that did not contain **9D**. Treatment of **8D** with Me_3SiCl (or Me_3SiOTf) and CO, followed by thermolysis resulted only in the formation of **9D**.

For Pd control reactions, we determined that **1** does react with CO upon thermolysis, with or without Me_3SiCl or Me_3SiOTf. However, **4** was only a minor product (10%) from the Me_3SiCl/CO reaction, and **5** was not observed at all in the Me_3SiOTf/CO reaction. The dimer **1** did not react with either Me_3SiCl or Me_3SiOTf alone after 18 h at 80 °C in C_6D_6. We also considered that **1** may react with Me_3SiX reversibly, with CO_2 activation proceeding *via* $(^FPNP)PdSiMe_3$ (**10**). We were able to access **10** by treating **4** with $KO^tBu/Me_3SiSiMe_3$ or by reacting **4** with excess Mg metal and Me_3SiCl. **10** did not react with CO_2 nor did it revert to **1** in the presence of **4** after 18 h at 80 °C (see ESI†). $(^FPNP)PdH$ (**6**) was also unaffected[36] when thermolyzed under a CO_2 atmosphere and thus **6** or **10** are unlikely to be involved as an intermediate.

We have not established the nature of all the products in the control reactions. However, the combination of our control results indicates that **9D** is indeed produced by trapping CO generated by **1**/CO_2/Me_3SiOTf and not *via* reduction of CO_2 in the coordination sphere of Ir. As well, **5** is indeed primarily produced in the same CO_2 reduction by **1**. With Me_3SiCl, the situation is similar, but it appears that most of **9D** observed in the **1**/CO_2/Me_3SiCl reactions does originate from the trapping of free CO.

Scheme 3 depicts the overall net reaction and the proposed mechanism. It is reasonable to expect that the reversible



Scheme 3 The net reaction for the stoichiometric reduction of CO_2 reported in this work and the possible mechanism.

formation of **2** could be followed by fast Pd–O/Si–X metathesis to give **4**/**5** and **10**. Compound **10** would then decarbonylate before or after reacting with the second equivalent of Me_3SiX. Decarbonylation of closely related (PCP)PdC(=O)OH and of (PCP)Pd–C(=O)O–Pd(PCP) has been demonstrated by Cámpora *et al.*, where PCP is κ^3-2,6(^{i}Pr$_2$PCH$_2$)$_2$C$_6$H$_3$.[28] In a previous publication, we showed that **4** can be chemically reduced to the dimer **1** (dotted reaction arrow in Scheme 3) by alkali metals.[20c] Thus, the cycle in Scheme 3 can be viewed as a synthetic cycle for the reduction of CO_2 to CO. Naturally, a practical electrochemical implementation may only be of interest if Me_3SiX can be replaced by a Brønsted acid HX.

In summary, we have demonstrated that the Pd^I–Pd^I dimer **1** can reduce CO_2 to free CO with the help of Me_3SiOTf, or less efficiently with Me_3SiCl. Release of free CO mediated by a late transition metal catalyst is a challenge because of the generally high affinity of late metal complexes in reduced oxidation states for binding CO. In our system, this problem is circumvented by the pincer ligation of Pd and by the relatively low affinity of either Pd^I or Pd^{II} oxidations states for CO as a ligand.

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