

# Dalton Transactions

An international journal of inorganic chemistry

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## COMMUNICATION

CO<sub>2</sub> Activation by Manganese Pincer Complexes Through Different Modes of Metal-Ligand CooperationAmit Kumar,<sup>a</sup> Prosenjit Daw,<sup>a</sup> N. A. Espinosa-Jalapa,<sup>a</sup> Gregory Leitus,<sup>b</sup> Linda J. W. Shimon,<sup>b</sup> Yehoshoa Ben-David,<sup>a</sup> David Milstein<sup>a\*</sup>Received 00th January 20xx,  
Accepted 00th January 20xx

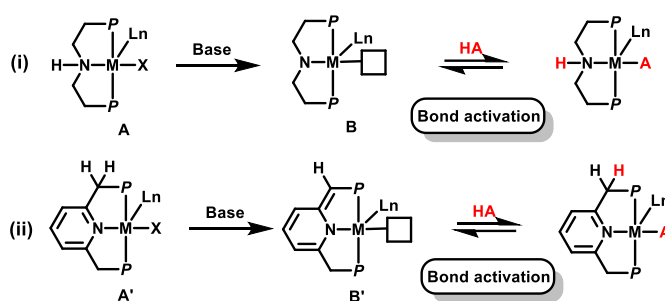
DOI: 10.1039/x0xx00000x

*Dedicated to Prof. Robin Perutz on the occasion of his 70<sup>th</sup> Birthday.*

We report here the activation of CO<sub>2</sub> using two Mn-PNN pincer complexes that can exhibit different modes of metal-ligand cooperation – amido/amino mode that involves [1,2]-activation of CO<sub>2</sub> and dearomatization/ aromatization mode that involves [1,3]-activation of CO<sub>2</sub>. We also compare their catalytic activity for CO<sub>2</sub> hydrogenation.

The increasing amount of CO<sub>2</sub> in our environment is a global concern. The activation of CO<sub>2</sub>, which is renewable, abundant, inexpensive and non-flammable, and its conversion to useful chemicals can lead to potential environmentally benign technologies. Indeed, significant efforts have been made to develop efficient catalysts for the utilization of CO<sub>2</sub> as C1 carbon source.<sup>1</sup> In the direction of developing sustainable homogeneous catalysts, recently there has been much interest in exploring pincer catalysts based on earth-abundant metals as these metals are cheaper, more abundant and usually less toxic compared to the precious metals. We and others have recently reviewed the recent progresses on pincer catalysts of earth-abundant metals for hydrogenation and dehydrogenation reactions.<sup>2,3</sup> Many of these catalysts operate via a synergy between metal and ligand, a concept commonly known as metal-ligand cooperation (MLC) and has been employed for a variety of transition metals. The two modes of MLC most exploited in bond activation and catalytic (de)hydrogenation reactions are: (i) MLC via amido / amine functionalities<sup>4</sup> and (ii) MLC via aromatization / dearomatization,<sup>5</sup> a concept introduced by our group (Scheme 1).

Pincer complexes of earth-abundant metals such as Fe,<sup>6</sup> Co<sup>7</sup> and Ni<sup>8</sup> have also been explored for CO<sub>2</sub> reactivity. One of the base-metals that has been extensively explored for green homogeneous catalysis in recent years is manganese.<sup>3</sup> A suitable precursor, Mn(CO)<sub>5</sub>Br, allows formation of stable



**Scheme 1.** Bond activation via different modes of metal-ligand cooperation: by amido/amino mode (i) and by dearomatization/aromatization mode (ii).  $P = PR_2$ ,  $X = Br, Cl$ ;  $Ln$  = monodentate ligands e.g. carbonyl or/and hydride;  $M$  = transition metals e.g. Ru, Ir, Fe, Mn, Co etc.

diamagnetic manganese pincer complexes containing CO and bromide ligands. Treatment with base results in the formation of coordinatively unsaturated manganese complexes (**B** or **B'** in Scheme 1) with the ability to perform catalysis. Regarding manganese-CO<sub>2</sub> reactivity, Prakash has recently reported sequential hydrogenation of CO<sub>2</sub> to methanol in presence of amines catalysed by a manganese pincer complex based on Macho type PNP ligands (Macho PNP:  $HN(CH_2CH_2PR_2)_2$ , Scheme 1(i)).<sup>9</sup> Kirchner and Gonsalvi also reported hydrogenation of CO<sub>2</sub> to formate as well as reduction of CO<sub>2</sub> to methanol in presence of hydrosilanes, both catalysed by a Mn pincer complex.<sup>10</sup> Leitner has recently reported an efficient Mn pincer catalyst for the hydroboration of CO<sub>2</sub> under atmospheric pressure.<sup>11</sup> Khusnutdinova has reported conversion of CO<sub>2</sub> to formate and formamide using manganese (I) complexes.<sup>12</sup> DFT calculations describing Macho type Mn-PNP complexes as promising catalysts for the hydrogenation of CO<sub>2</sub> to formate have also been reported.<sup>13</sup> A general first step in these catalytic reactions is the deprotonation of N-H proton and concomitant removal of bromide ligand from the precatalyst (**A**) to form an amido complex (**B**) that is directly involved in catalysis. Despite a few mechanistic studies on these systems, direct reactivity of CO<sub>2</sub>

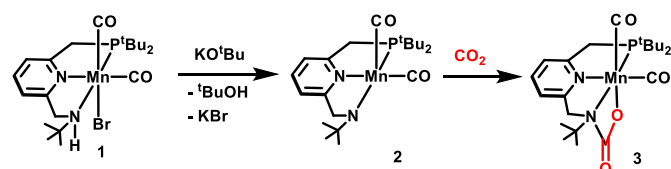
<sup>a</sup> Department of Organic Chemistry, Weizmann Institute of Science, Rehovot 76100, Israel.

<sup>b</sup> Department of Chemical Research Support, Weizmann Institute of Science, Rehovot 76100, Israel.

Electronic Supplementary Information (ESI) available: Experimental procedures, NMR and IR spectral data and crystallographic details. See DOI: 10.1039/x0xx00000x

and its coordination chemistry with an amido (**B**) or a dearomatized complex (**B'**) of manganese has not been studied. We report here the reactivity of CO<sub>2</sub> with coordinatively unsaturated manganese (I) complexes and their coordination chemistry involving different modes of metal-ligand cooperation and corresponding catalytic activity for the hydrogenation of CO<sub>2</sub>.

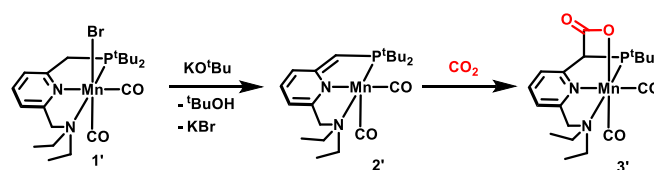
We have earlier reported the Mn-PNNH complex **1** which catalyzes the hydrogenation of esters and organic carbonates, as well as the synthesis of amides by acceptorless dehydrogenative coupling (ADC) of alcohols and amines.<sup>14</sup> Complex **1** in presence of a base such as KO<sup>t</sup>Bu generates the catalytically active amido complex **2** that has been shown to activate H-H or O-H bonds via amido/amino type MLC. Noticing useful catalytic applications of complex **2** for (de)hydrogenation reactions, we explored the reactivity of complex **2** with CO<sub>2</sub>. Reaction of one bar of CO<sub>2</sub> with a (blue coloured) solution of complex **2** in pentane resulted in the precipitation of a yellow solid in one hour at 298 K. <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of a CD<sub>2</sub>Cl<sub>2</sub> solution of the solid showed a signal at δ 117.6 (s) ppm, shifted downfield from that of complex **2** (δ 135.0). The <sup>13</sup>C{<sup>1</sup>H} NMR spectrum showed a signal at δ 161.2 (s) corresponding to the activated CO<sub>2</sub> carbon. The IR spectrum showed two strong absorptions at 1917 and 1824 cm<sup>-1</sup> in almost equal intensity, consistent with two carbonyl ligands disposed at approximately 90° from each other. A third band characteristic of a carboxylate moiety was detected at 1716 cm<sup>-1</sup>. A single crystal X-ray diffraction of the crystals grown from a CH<sub>2</sub>Cl<sub>2</sub>/pentane solution revealed the structure of the new complex (**3**) as a 2 + 2 addition product where CO<sub>2</sub> has been activated by the MLC forming new Mn-O and N-C bonds (Figure 1). This results in the formation of two metallacycles - one four membered and another seven membered. Similar [1,2]-activation of CO<sub>2</sub> has been reported by Berke using Mo and W complexes of the macho type PNP ligands.<sup>15</sup> Analogous [1,2]-activation of CO<sub>2</sub> has been reported recently using a Macho Fe-amido complex by Hazari and Bernskoetter.<sup>16</sup> The molecular structure of the CO<sub>2</sub>-bound complex **3** exhibits an octahedral complex bearing two CO ligands mutually disposed at 90.94 (9) degree and a carboxylate ligand in an axial position. The newly formed C–N bond (C22–N2 = 1.516(2) Å) is slightly elongated compared to the C1–N2 single bond [1.487 (2) Å]. A similar elongation of the new C–N bond upon [1,2]-CO<sub>2</sub> activation was also observed by Berke for W-complexes.<sup>15</sup>



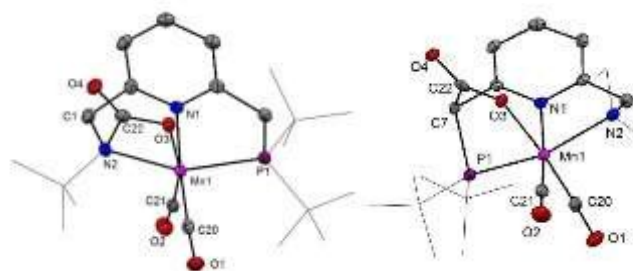
**Scheme 2.** Formation of complex **2** and its reactivity with CO<sub>2</sub> via MLC using amido/amino mode.

We further explored the reactivity of CO<sub>2</sub> with the dearomatized complex **2'** which was formed by treatment of complex **1'** with KO<sup>t</sup>Bu.<sup>14b</sup> Addition of one bar of CO<sub>2</sub> to a

pentane solution of complex **2'** resulted in immediate formation of a yellow precipitate which was isolated in 78% yield. <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of the yellow solid dissolved in CD<sub>2</sub>Cl<sub>2</sub> showed a singlet at δ 143.2 significantly shifted downfield compared to that of complex **2'** (<sup>31</sup>P{<sup>1</sup>H} NMR signal in C<sub>6</sub>D<sub>6</sub>: δ 103.7). The <sup>13</sup>C{<sup>1</sup>H} NMR spectrum showed a signal at δ 174.1 (d, <sup>2</sup>J<sub>PC</sub> = 8.7 Hz) corresponding to a manganese-carboxylate complex. A strong band at 1641 cm<sup>-1</sup> was observed in the IR spectrum corresponding to the bound carboxylate moiety. These spectral features are very similar to the [1,3]-CO<sub>2</sub> adduct of the PNP pincer complexes of Ru,<sup>17</sup> Re,<sup>18</sup> Ir<sup>19</sup> and Fe<sup>20</sup> reported earlier by us. The structure was finally confirmed by a single crystal X-ray diffraction measurement that showed a distorted octahedral geometry around the manganese centre in which the PNP ligand occupies a meridional position and two CO ligands are mutually cis to each other (Figure 1). [1,3]-binding of CO<sub>2</sub> with the side arm and manganese along with formation of new C-C and Mn-O bonds were also observed. Similar to the CO<sub>2</sub>-bound complex **3**, two new metallacycles are formed but they are now five and six membered as compared with **3** that contains four and seven membered metallacycles. Both the C-O bond lengths of the bound CO<sub>2</sub> are slightly longer for the CO<sub>2</sub>-bound complex **3'** compared to those of CO<sub>2</sub>-bound complex **3** (Figure 1). The bound C-O bond lengths are also similar to those observed in [1,3]-CO<sub>2</sub> activated complex of Ru-PNN as reported earlier by Sanford.<sup>19</sup>



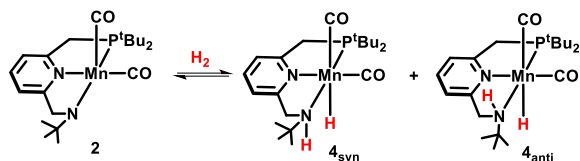
**Scheme 3.** Formation of complex **2'** and its reactivity with CO<sub>2</sub> via MLC by the aromatization/dearomatization mode.



**Figure 1.** Molecular structure of complexes **3** (left) and **3'** (right) at 50% ellipsoid probability level (<sup>t</sup>Bu and ethyl groups are drawn as wire frames). Hydrogen atoms are omitted for clarity. Selected bond lengths in Å (i) for complex **3**: Mn1–O3 = 2.0760(14); Mn1–N2 = 2.1186(16); Mn1–P1 = 2.2893(6); N2–C22 = 1.516(2); C22–O3 = 1.274(2); C22–O4 = 1.220(2); N2–C1 = 1.487(2); (ii) for complex **3'**: Mn1–O3 = 2.088(2); Mn1–N2 = 2.174(2); Mn1–P1 = 2.2727(9); C7–C22 = 1.551(4); C22–O3 = 1.281(4); C22–O4 = 1.231(4); C7–P1 = 1.863(3).

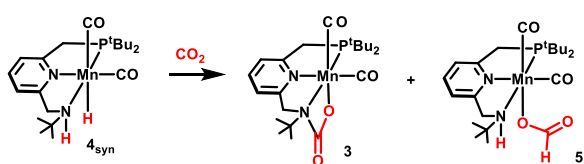
We previously reported the activation of hydrogen by complex **2** to form the manganese hydride complex **4<sub>syn</sub>** that loses hydrogen slowly at room temperature to form the amido

complex **2**. Additionally, appearance of an anti-isomer **4<sub>anti</sub>** was also observed (Scheme 4).<sup>14a</sup>



**Scheme 4.** Activation of hydrogen by complex **2** via MLC using amido/amino mode.

We further studied the reactivity of manganese hydride complex **4<sub>syn</sub>** with CO<sub>2</sub>. Addition of 4 atm of CO<sub>2</sub> in an NMR tube containing a toluene-d<sub>8</sub> solution of complex **4<sub>syn</sub>** resulted in an immediate colour change from dark green to yellow. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum showed a signal corresponding to the [1,2]-CO<sub>2</sub> bound complex **3**. A new signal was detected at δ 116.0. IR spectrum of the product showed two strong stretching frequencies at 1917 and 1832 cm<sup>-1</sup> corresponding to two CO ligands in *cis* arrangement. A strong band at 1717 cm<sup>-1</sup> was also observed corresponding to the bound CO<sub>2</sub> stretch of complex **3**. Additionally, a strong band was observed at 1599 cm<sup>-1</sup> which corresponds to the stretching frequency of metal-bound formates.<sup>10</sup> In support of the formation of formate, <sup>1</sup>H NMR spectrum also revealed a sharp signal at δ 8.34 characteristic of formates. Insertions of CO<sub>2</sub> into a manganese-hydride bond in analogous manganese pincer complexes were reported earlier and the compounds were well-characterized.<sup>10</sup> Based on the spectral evidence observed here and compared to those reported earlier, we suggest that reaction of CO<sub>2</sub> with complex **4<sub>syn</sub>** forms a mixture of the [1,3]-CO<sub>2</sub> addition product **3**, presumably via the existing equilibrium between **4<sub>syn</sub>** and **2**, and a formate complex **5** (Scheme 5). The formate complex **5** was also independently synthesized and characterized by the reaction of complex **2** with HCOOH (see SI for details).

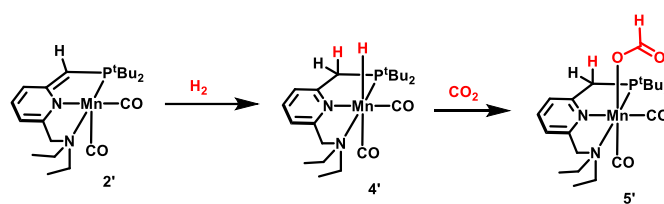


**Scheme 5.** Reactivity of complexes **7** and **8** and with CO<sub>2</sub>.

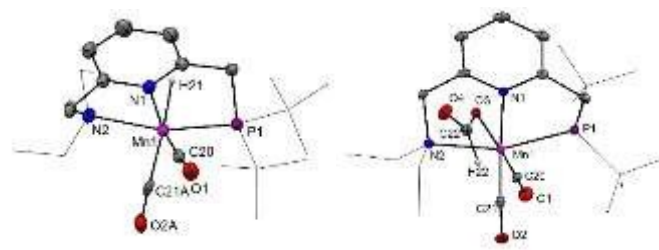
In order to explore the reactivity of complex **2'** with hydrogen, 1 bar of hydrogen was added to a pentane solution of complex **2'** (Scheme 6). The reaction led to the formation of a red precipitate which was isolated in 89% yield and characterized as the manganese hydride complex **4'**. The <sup>1</sup>H NMR spectrum showed signals corresponding to an aromatized pyridine ring and a new manganese hydride signal was detected at δ -1.52 (d, <sup>2</sup>J<sub>HP</sub> = 55.5 Hz). The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum also showed a new signal at δ 143.1 shifted downfield by 39.4 ppm compared to that of complex **2'** (δ 103.7).<sup>14b</sup> The structure was also confirmed by a single crystal X-ray diffraction that showed an octahedral manganese complex bearing the PNN ligand in a

meridional geometry and two carbonyl ligands in mutually *cis* sites (Figure 2). A hydride ligand was not located on the Fourier map and therefore placed at the axial position trans to one of the carbonyl ligands (see SI for the details).

Interestingly, reaction of complex **4'** in toluene-d<sub>8</sub> with 1 bar of CO<sub>2</sub> immediately changed the colour of the reaction mixture from dark orange to light orange. The newly formed species was spectrally characterized as complex **5'**. The signal corresponding to the bound formyl proton in the <sup>1</sup>H NMR spectrum of complex **5'** was detected at δ 8.4. Complex **5'** was stable at room temperature in toluene-d<sub>8</sub> for 24 hours. Crystals suitable for single crystal X-ray diffraction was obtained by keeping a toluene solution of complex **5'** under CO<sub>2</sub> atmosphere overnight. The structure of **5'** was also confirmed by the single crystal X-ray diffraction that showed an octahedral manganese complex with two CO at 88.19 (7) degree and the formyl group trans to a CO ligand (Figure 2).



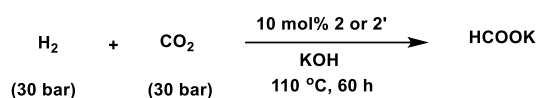
**Scheme 6.** Formation of complexes **4'** and **5'**.



**Figure 2.** Molecular structure of complexes **4'** (left) and **5'** (right) at 50% ellipsoid probability level ('Bu and ethyl groups are drawn as wire frames). Except for the Mn-H in complex **4'** (left) that has been displayed as a white ball, the remaining hydrogen atoms are omitted for clarity. Selected bond lengths in Å (i) for complex **5'**: Mn1-N1 = 2.0300(16); Mn1-N2 = 2.1797(16); Mn1-P1 = 2.2531(5); (ii) for complex **5'**: Mn1-O3 = 2.0338(11); Mn1-N2 = 2.2350(14); Mn1-P1 = 2.3122(6); C22-O4 = 1.2236(19).

Upon exploring the fundamental reactivity of CO<sub>2</sub> via different modes of metal-ligand cooperativity using complexes **2** and **2'**, we compared their effects in catalysis for the hydrogenation of CO<sub>2</sub>. A THF solution of KOH (5 mmol) and 10 mol% manganese catalyst (0.05 mmol **2** or **2'**) was heated at 110 °C under 30 bar of CO<sub>2</sub> and 30 bar of hydrogen for 60 hours (Scheme 7). Analysis of the reaction mixture by the <sup>1</sup>H NMR spectroscopy after the completion of the reaction showed 23% formation of formate in case of catalyst **2** whereas only 6% formate was observed in case of catalyst **2'**.





**Scheme 7.** Catalytic hydrogenation of CO<sub>2</sub> using catalysts **2** or **2'**.

## Conclusions

In conclusion, we report here CO<sub>2</sub> activation by manganese pincer complexes using two different modes of metal-ligand cooperation: [1,2]-CO<sub>2</sub> activation via amido/amino functionality (complex **3**) and [1,3]-CO<sub>2</sub> activation via dearomatization/aromatization mode (complex **3'**). Insertion of CO<sub>2</sub> to the Mn-H bonds forming the formate complexes **5** and **5'** are also reported. We also observed a relatively higher catalytic activity of complex **2** compared to that of **2'** for the hydrogenation of CO<sub>2</sub> to formate.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

D.M. holds the Israel Matz Professorial Chair. P.D. and A.K. are thankful to the Planning and Budgeting Committee (PBC) for a postdoctoral fellowship. PD also thanks Weizmann Institute of Science for a senior postdoctoral fellowship. N. A. E.-J. thanks Mr. Armando Jinich for a postdoctoral fellowship.

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DOI: 10.1039/C9DT03088C

Activation of CO<sub>2</sub> by manganese pincer complexes using two different modes of metal-ligand cooperativity (amido/amino mode and dearomatization/aromatization mode) is reported.

