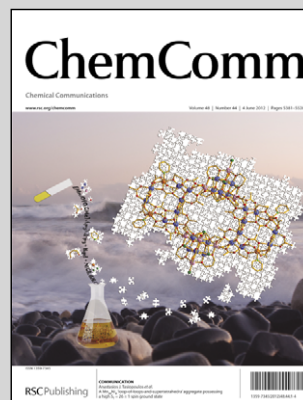


Showcasing research from Professor Datong Song's laboratory, University of Toronto, Canada

Reversible formal insertion of CO₂ into a remote C–H bond of a ligand in a Ru(II) complex at room temperature

This reversible transformation of CO₂ features an actor ligand and a spectator metal centre. The forward and backward reactions both occur spontaneously at room temperature, which is related to important processes in nature that mediate the uptake and release of CO₂ under ambient conditions.

As featured in:



See Vincent T. Annibale and
Datong Song,
Chem. Commun., 2012, **48**, 5416.

Cite this: *Chem. Commun.*, 2012, **48**, 5416–5418

www.rsc.org/chemcomm

COMMUNICATION

Reversible formal insertion of CO₂ into a remote C–H bond of a ligand in a Ru(II) complex at room temperature†

Vincent T. Annibale and Datong Song*

Received 19th December 2011, Accepted 1st February 2012

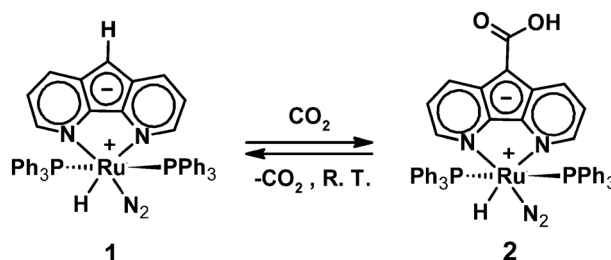
DOI: 10.1039/c2cc17933d

Here we report a reversible formal insertion of CO₂ into a remote C–H bond of the diazafluorene ligand (L[−]) in a Ru(II) complex which occurs at ambient temperature.

Two major approaches in CO₂ related research are sequestration and utilization. The majority of the research in sequestration has focused on CO₂ storage and gas-separation within porous materials,^{1–5} while CO₂ utilization has focused on reactions which utilize CO₂ as a chemical feedstock, *e.g.* in carboxylation reactions the whole {CO₂} moiety is incorporated into the product, or in reduction reactions CO₂ is reduced to a variety of products such as methanol.^{6–11} The major challenge is the remarkable thermodynamic stability of CO₂.

One area of interest is reversible reactions involving CO₂ which may lead to a new means of CO₂ sequestration or to catalyst development. Nature employs reversible reactions of CO₂ in the zinc-containing metalloenzyme carbonic anhydrase as a means of CO₂ transport. Recently a variety of phosphonium ionic liquids were applied in equimolar CO₂ capture where the anion is reversibly carboxylated.¹² *N*-Heterocyclic carbenes (NHCs) can also be carboxylated reversibly to form zwitterionic adducts which have been successfully applied as carboxylation and CO₂ reduction organocatalysts.^{13–16} Both the ionic liquid and NHC systems require heat for the decarboxylation reaction to occur.^{12,13} There are many examples of transition metal complexes which bind CO₂ reversibly, and some recent examples of main-group frustrated Lewis pairs (FLPs) capable of the same task.¹⁷ The insertion of CO₂ into transition-metal–H, –C, –N, and –O bonds has been reported; some of these insertion reactions are reversible.

Previously we reported that the zwitterionic complex **1** can reversibly split H₂ over a long-range between the Ru(II) center and a carbanion of the diazafluorene ligand (L[−]) where the distance between the Ru center and the backbone carbon is ~5.0 Å.¹⁸ Intrigued by this reactivity likely resulting from unquenched basicity on the negatively charged ligand and the

Scheme 1 Reversible carboxylation of complex **1**.

Lewis acidity of the positively charged metal center within the zwitterion we decided to explore further reactivity of **1** with other small molecules. Here we report the reactivity of **1** towards CO₂.

When the solution of complex **1** in either THF, DME, benzene or toluene is placed under an atmosphere of CO₂ an orange precipitate of complex **2** forms, where a formal insertion of CO₂ into the C–H bond in the backbone of the diazafluorene ligand has occurred (Scheme 1). It is worth noting that CO₂ does not insert into the Ru–H bond or displace the dinitrogen ligand. Complex **2** is extremely moisture- and oxygen-sensitive in the solid-state and in solution, insoluble in benzene, toluene, diethyl ether, DME, hexanes and pentane, slightly soluble in THF, and reacts with chlorinated solvents such as dichloromethane and chloroform.

The X-ray quality crystals of **2** were obtained by allowing CO₂ to slowly diffuse into a toluene solution of **1**. As shown in Fig. 1† the Ru(II) center adopts a slightly distorted octahedral geometry and has two N-donors from the chelate ligand, a hydride and dinitrogen ligand *cis* to each other, and two triphenylphosphine ligands *trans* to each other. The Ru1–N2 bond (2.275(3) Å) is longer than the Ru1–N1 bond (2.118(3) Å), likely a result of the greater *trans* influence of the hydride ligand. The N–N bond length for the dinitrogen ligand is 1.122(5) Å, slightly longer than that of a free N₂ 1.0975 Å, and similar to that in complex **1** (1.111(2) Å).¹⁸ Complex **2** forms doubly H-bonded dimers in the solid state where the O1–O2' distance is 2.624(4) Å, reminiscent of other carboxylic acids. The IR spectrum for complex **2** has a N₂ stretching frequency at 2097 cm^{−1}, and a C=O stretching frequency at 1609 cm^{−1}.¹⁹ The N₂ stretching frequency is similar to complex **1** (2092 cm^{−1}), and this indicates that very little back-donation and activation of the dinitrogen ligand is involved.²⁰

Davenport Chemical Research Laboratories, Department of Chemistry, University of Toronto, 80 St. George Street, Toronto, Ontario, Canada M5S 3H6. E-mail: dsong@chem.utoronto.ca; Fax: +1 416 978 7013; Tel: +1 416 978 7014

† Electronic supplementary information (ESI) available: Experimental and spectroscopic details of **2**. CCDC 859613. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2cc17933d

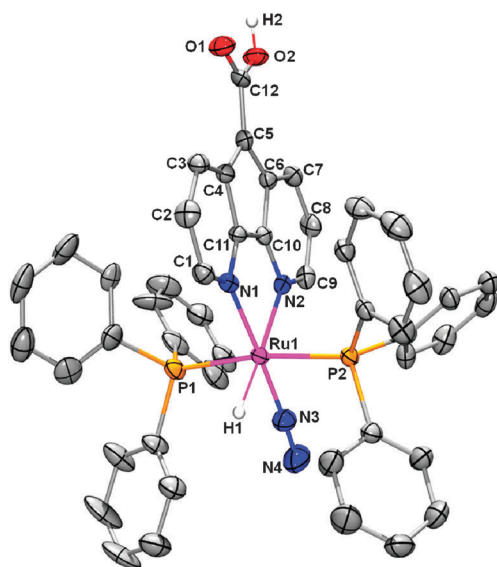
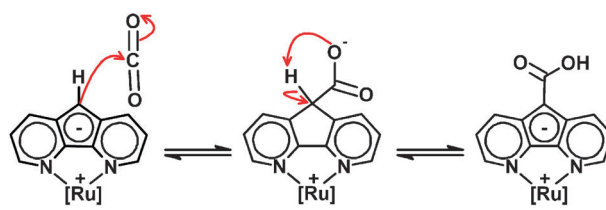


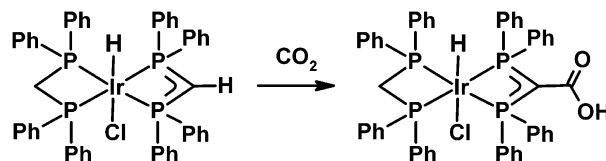
Fig. 1 Molecular structure of complex **2**. Non-H atoms are shown as 30% probability ellipsoids, and hydride and carboxylic acid H-atoms are shown as spheres of arbitrary radius, the rest of the H-atoms are omitted for clarity. Disordered phenyl rings are also omitted for clarity. Selected bond lengths (Å) and angles (°) for **2**: Ru1–N1, 2.118(3); Ru1–N2, 2.275(3); Ru1–N3, 1.890(4); Ru1–P1, 2.3473(11); Ru1–P2, 2.3800(11); N3–N4, 1.122(5); C4–C5, 1.439(6); C5–C6, 1.433(6); C5–C12, 1.430(6); O1–C12, 1.276(5); O2–C12, 1.292(5); N1–Ru1–N2, 81.23(12); N1–Ru1–P1, 91.04(9); N2–Ru1–P1, 92.70(9); N3–Ru1–P1, 87.47(12); N1–Ru1–P2, 94.76(9); N2–Ru1–P2, 93.82(8); N3–Ru1–P2, 86.57(12); N4–N3–Ru1, 177.1(4); C6–C5–C4, 107.5(3); C12–C5–C4, 124.9(4); C12–C5–C6, 127.5(4); O1–C12–O2, 122.3(4); O1–C12–C5, 119.7(4); O2–C12–C5, 118.0(4).

When an analytically pure sample of complex **2** is dissolved in THF- d_8 in a J. Young tube under dinitrogen atmosphere at room temperature, within a minute the initially bright orange solution turns brown. ^1H and ^{31}P NMR studies revealed that a mixture of **1** and **2** forms, where the major ($\sim 4.6:1$ ratio) species is **1** (see ESI† for NMR spectra). The ratio of **1** to **2** does not change significantly even after 24 h in a sealed J. Young tube. The decarboxylation can be driven to completion by either stirring complex **2** in THF in an open system under nitrogen for ~ 2 h at room temperature, or by doing three cycles of dissolving in THF under N_2 and pumping away the volatiles under vacuum. Replacing the dinitrogen atmosphere inside the J. Young tube with carbon dioxide affords clean conversion to **2** and allows for ^1H and ^{31}P NMR characterization, the poor solubility of **2** in THF- d_8 precludes the collection of ^{13}C NMR data. In the ^1H NMR spectrum, the hydride of **2** appears as a triplet at -12.75 ppm. In the ^{31}P NMR spectrum, the triphenylphosphine ligands of **2** display a signal at 48.67 ppm.

The formal insertion of CO_2 into the ligand C–H bond occurs likely *via* a nucleophilic attack of the backbone carbon of diazafluorenyl to the carbon of CO_2 , followed by proton migration (Scheme 2). The microscopic reverse process might also have a sufficiently low barrier that it occurs readily at room temperature. It is worth distinguishing the reactivity observed for complex **1** from other carbanions towards CO_2 . Carbocyclic anionic ligands such as Cp^- in ferrocene for example are carboxylated irreversibly under Friedel–Crafts



Scheme 2 Proposed mechanism for reversible carboxylation.

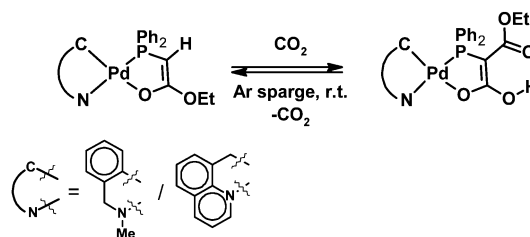


Scheme 3 Formal insertion of CO_2 into a remote C–H bond in an Ir system described by Langer and Oro.^{21,22}

conditions in the presence of a Lewis acid such as AlCl_3 ; alternatively the Cp-ring can be deprotonated and reacted with CO_2 followed by an acidic workup to give the ferrocenyl carboxylic acid. Organolithium and Grignard reagents react with CO_2 to form carboxylates and the proton does not migrate to the oxygen to form a carboxylic acid group. In these cases, the reverse reactions require forcing conditions.

An example of a formal insertion of CO_2 into a remote C–H bond of a ligand resulting in C–C bond formation is described by Langer, Oro and co-workers (see Scheme 3).^{21,22} It is worth noting that the formal insertion of CO_2 is not reversible in this Ir system, and decarboxylation can be achieved upon the addition of an acid which results in the neutral dpmm ligand on Ir(III) as opposed to the anionic diphosphanylmethanide ligand.²²

One example of a reversible carboxylation that occurs at room temperature was described by Braunstein and co-workers. When the palladium complex (Scheme 4) is reacted with CO_2 , there is formal insertion of CO_2 into the C–H bond of the P,O-chelate and the resulting COOH moiety coordinates to the metal center *via* one O atom. The reverse reaction is accomplished by an argon sparge under ambient conditions.^{23–25} It was suggested that the strong σ -donor *trans* to the O-donor might labilize the Pd–O bond and allow the polarized C–H bond to react with CO_2 .²³ A related complex with the same phosphino enolate P,O-chelate ligand, but which does not have the strong *trans*-influence of a C-donor, *cis*-[Pt($\text{Ph}_2\text{PCHC}(\text{O})\text{OEt}$) $_2$], does not react with CO_2 under the same conditions.²³ The Pd(II) centre seems to mediate the events leading to this formal insertion and elimination of CO_2 in these P,O-chelate complexes, where the corresponding alkaline metal salts do not react with CO_2 .²⁶



Scheme 4 Reversible carboxylation that occurs at room temperature described by Braunstein.^{23–25}

Our system described in this communication essentially shows the C–H bond that formally inserts CO₂ is remote from the metal centre. The role of the metal centre in our Ru(II)–diazfluorenone system might be to adjust the basicity/nucleophilicity of the carbanion, the acidity of the C–H bond involved in proton migration, and the strength of the newly formed C–C bond.²⁷ These subtle adjustments enable both the carboxylation and decarboxylation where the energy barriers are small and facile to overcome at ambient temperature.

In summary we have shown that CO₂ can formally insert into a remote C–H bond of an anionic ligand reversibly at room temperature. The metal's role is likely to modulate the strength of the resulting C–C bond and adjust basicity of the carbanion, and the acidity of the C–H bond to allow the carboxylation and decarboxylation to occur readily at room temperature. Current efforts are focussed on generalizing this concept of reactivity in order to investigate less air sensitive systems, also with less costly metals, for catalytic and sensing applications. Another avenue is to tune the C–C bond strength so that the decarboxylation can only occur at a slightly higher temperature which might be useful for sequestration applications.

We thank the Natural Science and Engineering Research Council of Canada (NSERC), the Canadian Foundation for Innovation (CFI), the Ontario Research Fund and the University of Toronto (Connaught Foundation) for funding. We thank Gabriel Ménard of the Stephan research group for assistance with the ¹³C–labelling experiment. V. T. A. gratefully thanks the NSERC for a postgraduate scholarship (PGS D2), and the government of Ontario for an Ontario Graduate Scholarship (OGS).

Notes and references

† Selected crystallographic data for **2**: $a = 24.6475(13)$ Å, $b = 9.0725(4)$ Å, $c = 21.7223(10)$ Å, $\beta = 114.311(2)^\circ$, $V = 4426.7(4)$ Å³, $Z = 4$, space group $P2_1/c$, $T = 150$ K, total data 38 160, unique data 10 124, parameters 508, GOF = 1.025, $R_1 = 0.0590$ (observed data), $wR_2 = 0.1457$ (all data) (CCDC 859613).

- 1 A. Demessence, D. M. D'Alessandro, M. L. Foo and J. R. Long, *J. Am. Chem. Soc.*, 2009, **131**, 8784–8786.
- 2 D. Britt, H. Furukawa, B. Wang, T. G. Glover and O. M. Yaghi, *Proc. Natl. Acad. Sci. U. S. A.*, 2009, **106**, 20637–20640.
- 3 S. K. Nune, P. K. Thallapally and B. P. McGrail, *J. Mater. Chem.*, 2010, **20**, 7623–7625.

- 4 A. Phan, C. J. Doonan, F. J. Uribe-Romo, C. B. Knobler, M. O'Keeffe and O. M. Yaghi, *Acc. Chem. Res.*, 2010, **43**, 58–67.
- 5 H.-S. Choi and M. P. Suh, *Angew. Chem., Int. Ed.*, 2009, **48**, 6865–6869.
- 6 W. B. Tolman, *Activation of Small Molecules: Organometallic and Bioinorganic Perspectives*, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2006.
- 7 M. Aresta and A. Dibenedetto, *Dalton Trans.*, 2007, 2975–2992.
- 8 S. N. Riduan and Y. Zhang, *Dalton Trans.*, 2010, **39**, 3347–3357.
- 9 E. E. Benson, C. P. Kubiak, A. J. Sathrum and J. M. Smieja, *Chem. Soc. Rev.*, 2009, **38**, 89–99.
- 10 N. S. Lewis and D. G. Nocera, *Proc. Natl. Acad. Sci. U. S. A.*, 2006, **103**, 15729–15735.
- 11 T. Sakakura, J.-C. Choi and H. Yasuda, *Chem. Rev.*, 2007, **107**, 2365–2387.
- 12 C. Wang, X. Luo, H. Luo, D. Jiang, H. Li and S. Dai, *Angew. Chem., Int. Ed.*, 2011, **50**, 4918–4922.
- 13 H. A. Duong, T. N. Tekavec, A. M. Arif and J. Louie, *Chem. Commun.*, 2004, 112–113.
- 14 B. R. Van Ausdall, J. L. Glass, K. M. Wiggins, A. M. Arif and J. Louie, *J. Org. Chem.*, 2009, **74**, 7935–7942.
- 15 Y. Kayaki, M. Yamamoto and T. Ikariya, *Angew. Chem., Int. Ed.*, 2009, **48**, 4194–4197.
- 16 S. N. Riduan, Y. Zhang and J. Y. Ying, *Angew. Chem., Int. Ed.*, 2009, **48**, 3322–3325.
- 17 C. M. Mömming, E. Otten, G. Kehr, R. Fröhlich, S. Grimme, D. W. Stephan and G. Erker, *Angew. Chem., Int. Ed.*, 2009, **48**, 6643–6646.
- 18 E. Stepowska, H. Jiang and D. Song, *Chem. Commun.*, 2010, **46**, 556–558.
- 19 The ¹³C-labelled isotopologue of **2**, ¹³C-**2**, was synthesized where the C=O stretch shifts to 1574 cm⁻¹. The expected C–O stretch could not be assigned. See Fig. S8 and S9 (ESI†) for IR spectra of **2** and ¹³C-**2** respectively.
- 20 B. A. MacKay and M. D. Fryzuk, *Chem. Rev.*, 2004, **104**, 385–401.
- 21 J. Langer, M. J. Fabra, P. García-Orduña, F. J. Lahoz and L. A. Oro, *Chem. Commun.*, 2008, 4822–4824.
- 22 J. Langer, M. J. Fabra, P. García-Orduña, F. J. Lahoz, H. Görls, L. A. Oro and M. Westerhausen, *Dalton Trans.*, 2010, **39**, 7813–7821.
- 23 P. Braunstein, D. Matt, Y. Dusauroy, J. Fischer, A. Mitschler and L. Ricard, *J. Am. Chem. Soc.*, 1981, **103**, 5115–5125.
- 24 P. Braunstein, D. Matt and D. Nobel, *J. Am. Chem. Soc.*, 1988, **110**, 3207–3212.
- 25 P. Braunstein, D. Matt and D. Nobel, *Chem. Rev.*, 1988, **88**, 747–764.
- 26 P. Veya, C. Floriani, A. Chiesi-Villa, C. Guastini, A. Dedieu, F. Ingold and P. Braunstein, *Organometallics*, 1993, **12**, 4359–4367.
- 27 Attempts to explore the reactivity of NaL toward CO₂ produced an unidentified solid insoluble in all common solvents. The poor solubility hints the polymeric nature of the product and prevents further investigation of the reversibility of the CO₂ reaction with NaL.