DOI: 10.1002/anie.201205741

CO_2 Reduction

Frustrated Lewis Pair Inspired Carbon Dioxide Reduction by a Ruthenium Tris(aminophosphine) Complex**

*Michael J. Sgro and Douglas W. Stephan**

The global concentration of carbon dioxide continues to rise, contributing to global warming and climate change. While numerous creative strategies are being developed for CO_2 capture, there is an increasing interest in using carbon dioxide as a C_1 carbon source. The hydrogenation of CO_2 to formic acid and its derivatives is one such well-developed strategy based on Ru,[1–4] Ir,[5] and Fe[6,7] catalysis.[8,9]

Another particularly appealing approach is the idea of the methanol economy proposed by Olah.[10,11] In this scenario, CO_2 is reduced to the liquid fuel methanol by exploiting the existing distribution infrastructure.[10,11] It is this latter prospect that has prompted considerable recent attention in new strategies for the reduction of CO_2.[12–17] Inherent in the reduction of CO_2 to methanol is the cleavage of one of the C–O bonds. This can been achieved by employing metal-based processes using silanes, boranes, or aldehydes as oxygen scavengers. For example, the groups of Sadighi[17] and Guan[12] have achieved catalytic reduction of CO_2 using borane to CO and methoxide, respectively. Most recently, Sabo-Etienne and co-workers[13] have illuminated the mechanism of reduction of CO_2 by $[RuH_2(H_2)_2(PCy_3)_2]$ and pinacolborane (HBpin).

In a seemingly separate approach, several studies have exploited the notion of frustrated Lewis pairs (FLPs) for CO_2 activation and reduction.[18–26] For example, Ashley, Thompson, and O'Hare demonstrated that amine–borane-based FLP-CO_2 species could be reduced to methanol by heating at 160 °C for 6 days.[18] Subsequently, we showed that AlX_3–phosphine-based FLPs could be employed to effect the stoichiometric reduction of CO_2 to methanol or CO, depending on the conditions. The bis(borane) $C_6H_4(BCl_2)_2$, in combination with P*t*Bu_3, affords similar stoichiometric reductions of CO_2 to methanol,[26] while Piers et al. have utilized FLP systems in the catalytic deoxygenative hydrosilylation of CO_2, generating methane.[20]

Herein we adopt a hybrid approach to CO_2 reduction by exploiting both transition-metal systems and the concept of FLPs for activation. In this regard, we note the insightful work of Wass et al.,[27] who have described early transition-metal cations with pendant phosphine donors. These systems act as FLPs to stoichiometrically capture CO_2. The oxophilicity of early metal centers in these systems precludes catalytic activity. In the present work, we have developed a Lewis acidic ruthenium species with a pendant phosphine donor. This FLP-like system is shown to capture and activate CO_2 for catalytic reduction with boranes, yielding methoxyboranes and $O(BR_2)_2$ as products. Aspects of the mechanism of this unique approach are considered.

Targeting a Ru complex of the tripodal ligand N-$((CH_2)_2NHP{i}Pr_2)_3$ (**1**), the reaction of **1** with $[Ru(PPh_3)Cl_2]$ in CH_2Cl_2 ultimately gave **2** in 94% yield. Compound **2** exhibited two singlets at 121 and 41 ppm in a 2:1 ratio in the $^{31}P\{^1H\}$ NMR spectrum, which is consistent with two dramatically different phosphorus environments. This inequivalence was also mirrored in the ^1H NMR spectrum, as the methylene groups exhibit four different multiplets between 2.68 and 3.33 ppm. Furthermore, a single proton gave rise to a doublet of triplets ($J_{PH} = 521$, 5 Hz) at 7.16 ppm in the ^1H NMR spectrum, consistent with a diisopropylphosphonium group. A single-crystal X-ray diffraction study of **2** (Figure 1)[28] revealed a five-coordinate distorted trigonal-bipyramidal geometry about Ru. Two phosphine fragments of **1** and an amido nitrogen from the remaining arm occupy the pseudo trigonal plane, while the axial positions are completed by the central tertiary amine and a chloride atom. In the latter case, the N4-Ru-Cl angle is 166.00(4)° and the computed Cl–H distance of 2.72(1) Å is consistent with a hydrogen bonding interaction between the phosphonium proton and the bound chloride atom.

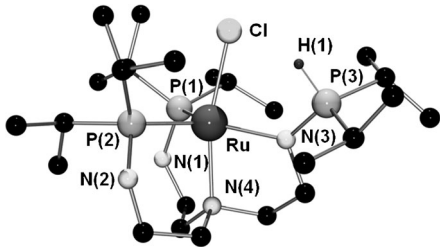


Figure 1. POV-ray depiction of the cation of **2**. Hydrogen atoms except P–H omitted for clarity.

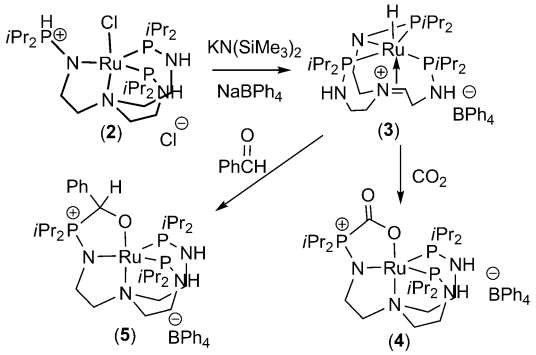
The phosphonium proton and metal bound halide are removed in the reaction of compound **2** with $KN(SiMe_3)_2$ in THF followed by anion metathesis with $NaBPh_4$. This affords **3** in 78% yield; this species gives rise to three inequivalent doublets of doublets in the $^{31}P\{^1H\}$ NMR spectrum. The coupling constants of 7, 15, and 91 Hz are consistent with both *cis* and *trans* phosphine dispositions. The ^1H NMR spectrum

[*] M. J. Sgro, Prof. Dr. D. W. Stephan
Department of Chemistry, University of Toronto
80 St. George Street, Toronto, Ontario, M5S 3H6 (Canada)
E-mail: dstephan@chem.utoronto.ca
Homepage: http://www.chem.utoronto.ca/staff/DSTEPHAN

[**] D.W.S. gratefully acknowledges the financial support of NSERC of Canada and the award of a Canada Research Chair. M.J.S. is grateful for the support of an NSERC scholarship.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201205741.

reveals an apparent doublet of triplets in the hydride region at −6.34 ppm ($^2J_{HP}$ = 20, 33 Hz). Furthermore, a DEPT ^{1}H/^{13}C NMR experiment confirms the presence of a new CH fragment. While repeated attempts yielded crystals of poor quality, a preliminary X-ray study[28] was consistent with a structure of **3** in which the Ru was pseudo octahedral (Scheme 1), with the amido nitrogen and the adjacent phosphorus atom binding to Ru affording a NPRu three-membered ring. The hydride in **3** arises from metalation of a carbon atom *alpha* to the central nitrogen atom.[28] Similar β-hydride abstractions have previously been observed.[29,30]



Scheme 1. Synthesis of **2**–**5**.

The strain in the NPRu ring in **3** suggests the ring-opened form, which links the Lewis acidic Ru and Lewis basic P, is readily accessible and prompted us to probe the reactivity with CO_2. Exposure of a solution of **3** to an atmosphere of CO_2 resulted in the immediate precipitation of the orange solid **4** in 81% yield. This species exhibits a ^{31}P{^{1}H} NMR spectrum that is comprised of two singlets at 119 and 29 ppm. The analogous reaction with $^{13}CO_2$ resulted in the ^{31}P{^{1}H} resonance at 29 ppm becoming a doublet while a doublet was also seen in the ^{13}C{^{1}H} NMR spectrum at 174 ppm with a $^1J_{CP}$ of 127 Hz. These data are consistent with the formation of a new P–C bond. The observed IR absorption at 1651 cm^{-1} provides further evidence of CO_2 activation. Structural data for **4** confirmed the capture of CO_2 by the concurrent action of the pendant phosphine base and the Lewis acidic Ru center (Figure 2).[31] The P–C, C–O, and C=O bond lengths are 1.908(6), 1.239(6), and 1.244(6) Å respectively, which are similar to the bond lengths seen in main group FLP–CO_2 complexes.[18–26] The Ru–O bond length of 2.207(3) Å is considerably longer than the Zr–O bond distance in $[Cp_2Zr(OC_6H_4PtBu_2)(CO_2)]^+$, which is consistent with the reduced oxophilicity at Ru.[27] Nonetheless, **4** proved to be thermally robust, remaining intact when heated to 80° C for over a week. The present reactivity is reminiscent of the reactions of the Erker intramolecular FLPs[19] with CO_2 in which ring strain prompts P–B dissociation and subsequent reaction.

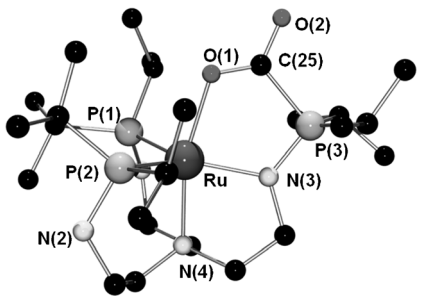


Figure 2. POV-ray depiction of the cation of **4**. Hydrogen atoms omitted for clarity.

Five equivalents of HBpin were added to a solution of **4** in CD_2Cl_2 in an attempt to reduce the bound CO_2. Monitoring the reaction by NMR spectroscopy for 24 h revealed the stoichiometric reduction of CO_2 to MeOBpin with the concomitant formation of $O(Bpin)_2$. This reaction could also be achieved in a catalytic fashion. One equivalent of **4** and 18 equivalents of HBpin were heated to 50 °C under an atmosphere of CO_2. ^{1}H NMR integration relative to an internal standard showed the slow but steady consumption of the borane and conversion into MeOBpin and $O(Bpin)_2$ with the consumption of 75% of the borane after 96 h.[28] Use of a higher excess of borane had little effect on the rate, although use of **4**:HBpin in a ratio of 1:100 resulted in a small increase in the TON to nine equivalents of MeOBpin after 96 h. Altering the CO_2 pressure from 1 to 5 atm had no effect on the product distribution.[28] Use of catecholborane (HBcat) or 9-borabicyclo[3.3.1]nonane (9-BBN) as reducing agents resulted in similar rates of reduction of CO_2 to the corresponding products MeOBcat, $O(Bcat)_2$ and MeOBBN, $O(BBN)_2$, respectively.

The mechanism of these reductions is thought to involve successive hydroborations of the CO_2 fragment of **4**. Employing $^{13}CO_2$, the reduction by **4** using HBpin was monitored by ^{13}C NMR spectroscopy. After 4 h, the presence of the monohydroboration product of CO_2 (from intermediate **A**) was evidenced by the appearance of a signal at 158 ppm. This signal is similar to that recently reported by Sabo-Etienne and co-workers.[13] Structure **A** appears initially but is fully consumed after 24 h, suggesting its intermediate nature. A subsequent reaction of **A** with HBpin is proposed to liberate $O(Bpin)_2$ and generate the intermediate **B**. While this species was not observed spectroscopically, an analogue was prepared by the reaction of **3** with benzaldehyde. The product **5** is isolated in high yield (Scheme 1) and was shown to exhibit a doublet in the ^{1}H NMR spectrum at 5.53 ppm with a $^2J_{HP}$ of 6 Hz, while the ^{13}C{^{1}H} NMR spectrum showed a doublet at 88 ppm with $^1J_{CP}$ of 69 Hz. These data are consistent with formation of a P–C bond, a fact further confirmed by crystallography.[28] The aldehyde is captured between the Ru center and the pendant phosphorus center (Figure 3) similar to that proposed for intermediate **B**. Compound **5** was shown to react with HBpin upon heating to 50 °C for 24 h to generate $PhCH_2OBpin$. Subsequent hydrolysis with D_2O afforded the isolation of [D_1]benzylalcohol ($PhCH_2OD$) in 80% yield. Moreover, compound **5** in the presence of excess HBpin and under a CO_2 atmosphere was shown to be catalytically competent in the reduction of CO_2 consistent with the proposed intermediate **B** (Scheme 2).

In summary, the species **3** activates CO_2 for reduction by HBpin to yield MeOBpin and $O(Bpin)_2$. Analogous products

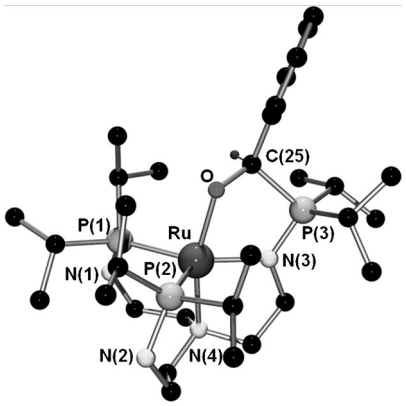
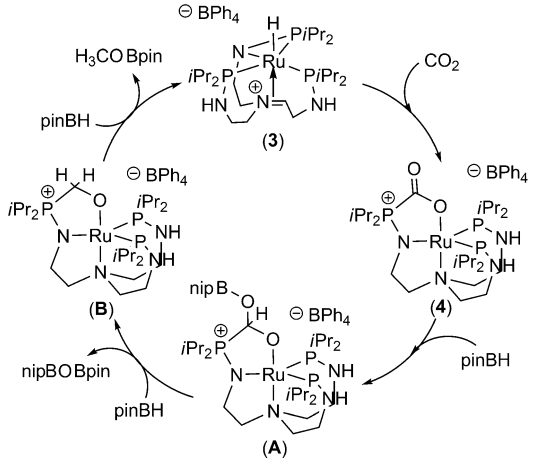


Figure 3. POV-ray depiction of the cation of **5**. Hydrogen atoms except H25 omitted for clarity.



Scheme 2. Proposed catalytic cycle for the reduction of CO_2.

are obtained with catecholborane and 9-BBN. Although these products are similar to those observed by the groups of Guan,[12] and Sabo-Etienne,[13] the RuNP ring of **3** is reminiscent of FLP systems. Moreover, the binding of CO_2 in **4** and of aldehyde in **5** exploits the cooperative action of the pendant Lewis basic phosphine and Lewis acidic Ru center. These observations demonstrate that transition metal-based catalysts can be designed based on an activation strategy that is based on an analogy to FLPs. We are continuing to develop such systems.

Received: July 18, 2012
Revised: August 23, 2012
Published online: October 4, 2012

Keywords: boranes · CO_2 reduction · frustrated Lewis pairs · homogeneous catalysis · ruthenium

[1] P. G. Jessop, T. Ikariya, R. Noyori, *Chem. Rev.* **1995**, *95*, 259 – 272.
[2] S. Wesselbaum, T. Vom Stein, J. Klankermayer, W. Leitner, *Angew. Chem.* **2012**, *124*, 7617 – 7620; *Angew. Chem. Int. Ed.* **2012**, *51*, 7499 – 7502.
[3] C. A. Huff, M. S. Sanford, *J. Am. Chem. Soc.* **2011**, *133*, 18122 – 18125.
[4] E. Balaraman, C. Gunanathan, J. Zhang, L. J. W. Shimon, D. Milstein, *Nat. Chem.* **2011**, *3*, 609 – 614.
[5] R. Tanaka, M. Yamashita, K. Nozaki, *J. Am. Chem. Soc.* **2009**, *131*, 14168 – 14169.
[6] C. Federsel, A. Boddien, R. Jackstell, R. Jennerjahn, P. J. Dyson, R. Scopelliti, G. Laurenczy, M. Beller, *Angew. Chem.* **2010**, *122*, 9971 – 9974; *Angew. Chem. Int. Ed.* **2010**, *49*, 9777 – 9780.
[7] R. Langer, Y. Diskin-Posner, G. Leitus, L. J. W. Shimon, Y. Ben-David, D. Milstein, *Angew. Chem.* **2011**, *123*, 10122 – 10126; *Angew. Chem. Int. Ed.* **2011**, *50*, 9948 – 9952.
[8] W. Leitner, *Angew. Chem.* **1995**, *107*, 2391 – 2405; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2207 – 2221.
[9] P. G. Jessop, F. Joo, C. C. Tai, *Coord. Chem. Rev.* **2004**, *248*, 2425 – 2442.
[10] G. A. Olah, *Angew. Chem.* **2005**, *117*, 2692 – 2696; *Angew. Chem. Int. Ed.* **2005**, *44*, 2636 – 2639.
[11] G. A. Olah, A. Goeppert, G. K. S. Prakash, *J. Org. Chem.* **2009**, *74*, 487 – 498.
[12] S. Chakraborty, J. Zhang, J. A. Krause, H. R. Guan, *J. Am. Chem. Soc.* **2010**, *132*, 8872 – 8873.
[13] S. Bontemps, L. Vendier, S. Sabo-Etienne, *Angew. Chem.* **2012**, *124*, 1703 – 1706; *Angew. Chem. Int. Ed.* **2012**, *51*, 1671 – 1674.
[14] A. J. M. Miller, J. A. Labinger, J. E. Bercaw, *Organometallics* **2011**, *30*, 4308 – 4314.
[15] S. N. Riduan, Y. G. Zhang, J. Y. Ying, *Angew. Chem.* **2009**, *121*, 3372 – 3375; *Angew. Chem. Int. Ed.* **2009**, *48*, 3322 – 3325.
[16] T. Matsuo, H. Kawaguchi, *J. Am. Chem. Soc.* **2006**, *128*, 12362 – 12363.
[17] D. S. Laitar, P. Muller, J. P. Sadighi, *J. Am. Chem. Soc.* **2005**, *127*, 17196 – 17197.
[18] A. E. Ashley, A. L. Thompson, D. O'Hare, *Angew. Chem.* **2009**, *121*, 10023 – 10027; *Angew. Chem. Int. Ed.* **2009**, *48*, 9839 – 9843.
[19] C. M. Mömming, E. Otten, G. Kehr, R. Fröhlich, S. Grimme, D. W. Stephan, G. Erker, *Angew. Chem.* **2009**, *121*, 6770 – 6773; *Angew. Chem. Int. Ed.* **2009**, *48*, 6643 – 6646.
[20] A. Berkefeld, W. E. Piers, M. Parvez, *J. Am. Chem. Soc.* **2010**, *132*, 10660 – 10661.
[21] M. A. Dureen, D. W. Stephan, *J. Am. Chem. Soc.* **2010**, *132*, 13559 – 13568.
[22] G. Ménard, D. W. Stephan, *J. Am. Chem. Soc.* **2010**, *132*, 1796 – 1797.
[23] G. Ménard, D. W. Stephan, *Angew. Chem.* **2011**, *123*, 8546 – 8549; *Angew. Chem. Int. Ed.* **2011**, *50*, 8396 – 8399.
[24] L. J. Hounjet, C. B. Caputo, D. W. Stephan, *Angew. Chem.* **2012**, *124*, 4792 – 4795; *Angew. Chem. Int. Ed.* **2012**, *51*, 4714 – 4717.
[25] R. C. Neu, G. Ménard, D. W. Stephan, *Dalton Trans.* **2012**, *41*, 9016 – 9018.
[26] M. J. Sgro, J. Dömer, D. W. Stephan, *Chem. Commun.* **2012**, *48*, 7253 – 7255.
[27] A. M. Chapman, M. F. Haddow, D. F. Wass, *J. Am. Chem. Soc.* **2011**, *133*, 18463 – 18478.
[28] See the Supporting Information. CCDC 892478, 892479, and 892480, 892481 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
[29] A. Friedrich, M. Drees, M. Kass, E. Herdtweck, S. Schneider, *Inorg. Chem.* **2010**, *49*, 5482 – 5494.
[30] V. F. Kuznetsov, K. Abdur-Rashid, A. J. Lough, D. G. Gusev, *J. Am. Chem. Soc.* **2006**, *128*, 14388 – 14396.
[31] Related ruthenium complex capture of CO_2 has been previously reported; see: J. F. Hartwig, R. G. Bergman, R. A. Andersen, *J. Am. Chem. Soc.* **1991**, *113*, 6499 – 6508.

