Cite this: DOI: 10.1039/c2cc33301e

COMMUNICATION

Stoichiometric CO₂ reductions using a bis-borane-based frustrated Lewis pair \dagger

Michael J. Sgro, Johannes Dömer and Douglas W. Stephan*

Received 8th May 2012, Accepted 28th May 2012 DOI: 10.1039/c2cc33301e

The bis-borane 1,2-C₆H₄(BCl₂)₂ forms an adduct with PtBu₃, but is still capable of exhibiting FLP reactivity with THF and CO₂. The resulting CO₂ species is reduced by Me₂NHBH₃ or $[C_5H_6Me_4NH_2]X$ (X = $[HB(C_6F_5)_3]$, $[HB(C_6F_5)_2(C_7H_{11})]$) followed by quenching with water to effect the stoichiometric conversion of CO₂ to methanol.

Since the industrial revolution 200 years ago, the global concentration of carbon dioxide has risen rapidly. This in turn has contributed to global warming and climate change sparking much concern worldwide. Efforts to reduce CO2 emissions have garnered considerable attention and approaches to this problem have varied, including an array of creative carbon capture technologies. However, due to the massive scale on which one has to implement such protocols, a single solution is unlikely. Another alternative involves innovative energy technologies,^{1–6} which focus on strategies to reduce consumption or employ alternative sources of energy. In that regard, one concept that addresses both CO₂ capture and an alternative energy source is the notion of the "methanol economy" put forth by Olah.^{7,8} In this approach CO_2 is used as a C1 source for fuel. This strategy would result in the "recycling" of CO2, but could in principle be "carbon neutral" if the reduction of CO2 to C1 fuels was achieved with "green" hydrogen, that is hydrogen derived from the photo-catalytic splitting of water.9,10 The other missing link in this scenario is an effective and clean process for the low temperature reduction of CO₂. While transition metal chemistry involving CO₂ has been studied, a number of recent efforts have exploited the notion of "frustrated Lewis pairs" (FLPs) for the activation of a variety of small molecules,¹¹⁻¹⁴ and CO₂ in particular. For example, we have reported the reversible capture of CO₂ employing the combination of sterically demanding phosphines and boranes (Chart 1).¹⁵ Shortly thereafter, Ashley and O'Hare demonstrated the conversion of amineborane based FLP-CO₂ species to methanol upon heating to 160 °C for 6 days.¹⁶ Subsequently, we showed that FLPs derived from aluminum halides (X = Cl or Br) and PMes₃

(Mes = $2,4,6-C_6H_2Me_3$) react with CO₂ to give the species $Mes_3P(CO_2)(AlX_3)_2$ (X = Cl; Br)) (Chart 1).¹⁷ Interestingly, while treatment of these products with ammonia borane (H₃NBH₃) and subsequent hydrolysis resulted in the stoichiometric reduction of CO₂ to methanol, simple prolonged exposure of the species Mes₃P(CO₂)(AlI₃)₂ to CO₂ resulted in the reduction of CO₂ to CO with concurrent formation of $Mes_3P(CO_2)(O(AII_2)_2)(AII_3)$ and $[Mes_3PI][AII_4]$.¹⁸ In related work, Piers et al. showed catalytic deoxygenative hydrosilylation of CO₂ employing an FLP system generating methane.¹⁹ We have also explored reduction chemistry with boron-based FLPs, involving bis-boranes, although in these cases, while binding was seen, such systems proved to be thermally labile (Chart 1).²⁰ In this manuscript, we demonstrate that while the bis-borane $1,2-C_6H_4(BCl_2)_2$ forms an adduct with PtBu₃ it still behaves as an FLP. Moreover it reacts with CO₂, forming a thermally stable species that can be stoichiometrically reduced in a sequence of reactions involving treatment with ammonia borane or ammonium borohydrides, followed by quenching with water. Interestingly, the latter transformation exploits FLP activation of CO₂ and H₂ to effect the stoichiometric conversion to methanol.

The bis-borane $1,2-C_6H_4(BCl_2)_2$ (1) was prepared following literature procedures of Kaufmann and also Williams *et al.*^{21,22} Combination of this species with $PtBu_3$ resulted in the formation of a new species (2) which could be isolated as a white solid in 84% yield. The ¹H NMR data were consistent with the formation of a 1 : 1 adduct with phosphine. The ³¹P{¹H} NMR spectrum showed a single, but broadened peak at 28.5 ppm, while the ¹¹B NMR spectrum revealed two broad resonances at 22.3 and 12.9 ppm. These data were consistent with the formulation of **2** as $1,2-C_6H_4(BCl_2)_2\cdot(PtBu_3)$. The broadening of signals in the NMR spectra suggests phosphine





Department of Chemistry, University of Toronto,

⁸⁰ St. George Street, Toronto, Ontario, Canada M5S 3H6. E-mail: dstephan@chem.utoronto.ca

[†] Electronic supplementary information (ESI) available. CCDC 881300 and 881301. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2cc33301e



Fig. 1 POV-ray depiction of **3**, C: black, B: light-pink, Cl: green; P: orange, O: red. H-atoms are omitted for clarity.

binding to boron is in slow exchange between the two boron sites.

Despite the formation of an adduct, the ability of 2 to act as an FLP was queried. We have previously shown that borane/ donor FLP systems exhibit the ability to effect THF ring opening. Thus, in an initial test, the species 2 was exposed to THF. This resulted in the formation of a new species which was ultimately obtained as colorless needles of **3** in 97% yield. The ${}^{31}P$ { ${}^{1}H$ } and ¹¹B NMR spectrum showed singlets at 48.80 and 12.00 ppm, respectively. The corresponding ¹H NMR spectrum revealed resonances consistent with the ring-opening of THF and thus the formulation of **3** as $1,2-C_6H_4(BCl_2)_2(O(CH_2)_4PtBu_3)$. This formulation of 3 was subsequently confirmed by X-ray crystallography (Fig. 1).[‡] The structural data affirm the zwitterionic nature resulting from the ring-opening of THF. The oxygen atom bridges the two boron centers giving rise to B-O bond distances of 1.532(4) and 1.533(4) Å with a B-O-B angle of $112.2(2)^{\circ}$. It is noteworthy that the constraint of the five-membered ring imposes a B-O-B angle that is markedly less than that seen for unrestricted cases such as $O(B(C_6F_5)_2)_2$ (B-O-B 139.5(2)°). The remaining metric parameters are unexceptional. The ability of 2 to activate THF is consistent with the notion that this species provides access to a reactive FLP.22-24

Having affirmed the ability of 2 to act as an FLP, a solution of 2 in toluene was exposed to an atmosphere of CO_2 and allowed to stir overnight. Subsequent work-up afforded a white, microcrystalline solid 4 in 77% yield. The ${}^{31}P{}^{1}H{}$ NMR spectrum of 4 exhibits a resonance at 48.4 ppm, while the ¹H NMR data are consistent with inclusion of phosphine and bis-borane in a 1:1 ratio. A ${}^{13}C{}^{1}H$ NMR signal is observed at 156.3 ppm. This signal also exhibits phosphorus-carbon coupling of 94.6 Hz, suggesting the inclusion of CO₂. This was further supported by the observation of an IR absorption at 1719 cm⁻¹. The ¹¹B NMR spectrum reveals a single peak at 18.0 ppm. Although this latter observation infers a molecular symmetry that would arise from the CO₂ spanning the two boron centers, X-ray diffraction data reveal the molecular structure is in fact dissymmetric (Fig. 2). In the solid state, the CO₂ fragment is captured between the phosphine and one of the boron centers. This gives rise to P-C, O-B, C-O and C=O bond lengths of 1.894(4), 1.477(5), 1.320(4) and 1.177(5) Å, respectively. While the P-C bond in 4 is similar to that seen in $tBu_{3}P(CO_{2})B(C_{6}F_{5})_{3}$ (1.8931(12) Å), $Mes_{2}PCH_{2}CH_{2}B(C_{6}F_{5})_{2}$ - (CO_2) (1.900(3) Å)¹⁵ and Mes₃PCO₂(AlCl₃)₂ (1.886(3) Å), the O-B distance in 4 is significantly shorter $tBu_3P(CO_2)B(C_6F_5)_3$: 1.5474(15) Å, Mes₂PCH₂CH₂B(C₆F₅)₂(CO₂): 1.550(4) Å and $Mes_3PCO_2(AlCl_3)_2$: 1.550(3) Å). This latter observation is



Fig. 2 POV-ray depiction of **4**, C: black, B: light-pink, Cl: green; P: orange, O: red. H-atoms are omitted for clarity.

consistent with the thermal stability of **4**. The O-C-O angle was found to be $127.0(4)^{\circ}$. It is interesting to note that despite the asymmetry of the CO₂ binding, both boron centers are four coordinate. This is achieved *via* bridging of one chlorine atom between the B centers. The bridging B-Cl distances are found to be 1.999(5) and 2.038(5) Å, while the terminal B-Cl bond distances averaged 1.838(5) Å.

Compound **4** proved to be remarkably stable with respect to loss of CO₂. No decomposition was observed on heating to 80 °C for 24 h. This stands in marked contrast to the CO₂ products derived from the FLPs $tBu_3P/B(C_6F_5)_3$ and $(C_6H_2Me_3)_2PCH_2CH_2B(C_6F_5)_2$. These species were seen to lose CO₂ at 80 °C and -20 °C, respectively. Similarly, **4** is significantly more thermally robust than the symmetric FLP-CO₂ complexes derived from the bis-boranes Me₂C = $C(BX_2)_2$ (X = Cl, C₆F₅) and PtBu₃ as these latter species were observed to lose CO₂ at 15 °C. The enhanced thermal stability is thought to arise from the bridging chlorine atom between the boron centers of **4** as this serves to enhance the Lewis acidity of the boron bound to the oxygen of CO₂. This enhanced acidity results in a strong B–O bond and explains the improved stability of the CO₂ activation product.

Given the stability of 4, efforts were undertaken to reduce the captured CO₂. Treatment with the amine-borane Me₂NHBH₃ for 15 min followed by quenching with D₂O led to the generation of methanol-d₁ in 34% yield (Scheme 1).

The FLP derived from **2** failed to activate hydrogen. Treatment of compound **4** with three equivalents of $[C_5H_6Me_4NH_2]$ - $[HB(C_6F_5)_3]$, a known salt derived from the activation of H₂ by the FLP $C_5H_6Me_4NH/B(C_6F_5)_3$, reacted slowly. After stirring for 24 h, subsequent treatment with D₂O afforded methanol in 15% yield. However, altering the salt to $[C_5H_6Me_4NH_2][HB(C_6F_5)_2(C_7H_{11})]$ (5), allowed the reaction time to be reduced to 1 h, and boosted the yield of methanol to 57%.

In conclusion, we have demonstrated that the bis-borane $1,2-C_6H_4(BCl_2)_2$ in combination with $PtBu_3$, reacts as an FLP despite formation of a phosphorus-boron adduct. Moreover this FLP is shown to bind CO₂ strongly in an asymmetric fashion, allowing further stoichiometric reactions with reducing agents. Of particular interest is the ability to reduce this species employing a product of FLP activation of H₂. Although in this case, B-O bond cleavage requires the addition of water, this finding further demonstrates the potential of FLPs to concurrently activate CO₂ and H₂ for CO₂ reduction.



Scheme 1 Synthesis of 2–4 and reduction of 4.

We are presently pursuing conceptually similar but less oxophilic FLP systems in the quest for an FLP system capable of catalytic reduction of CO_2 in the presence of H_2 .

DWS gratefully acknowledges the financial support of NSERC of Canada and the award of a Canada Research Chair. MJS is grateful for the award of an NSERC of Canada postgraduate scholarship.

Notes and references

‡ Crystallographic data. **3**: CCDC: 881300, $P\bar{1}$, a = 8.9031(5) Å, b = 11.5796(7) Å, c = 13.1403(8) Å, $\alpha = 93.817(4)^{\circ}$, $\beta = 99.079(4)^{\circ}$, $\gamma = 92.330(4)^{\circ}$, V = 1332.95(14) Å³, data = 4689, var = 280, R (>2 σ): 0.0447, $R_{\rm w}$ (all) = 0.0945, GOF = 1.012. **4**: CCDC 881301, $P2_12_12_1$,

a = 11.3108(5) Å, b = 14.2805(5) Å, c = 14.9742(7) Å, V = 2418.69(18) Å³, data = 5551, var = 262, R (>2 σ): 0.0557, R_w (all) = 0.1223, GOF = 0.990.

- 1 M. Bojic, AIP Conf. Proc., 2010, 1239, 12-21.
- 2 W. D. Grossmann, I. Grossmann and K. Steininger, *Environ. Sci. Technol.*, 2010, 44, 4849–4855.
- 3 R. Kothari, V. V. Tyagi and A. Pathak, *Renewable Sustainable Energy Rev.*, 2010, 14, 3164–3170.
- 4 A. M. Omer, Energy Costs, Int. Dev. New Dir., 2009, 39-77.
- 5 A. M. Omer, Int. J. Curr. Chem., 2010, 1, 31-62.
- 6 J. Wadsworth, Metall. Mater. Trans. A, 2010, 41A, 1047-1062.
- 7 G. A. Olah, Angew. Chem., Int. Ed., 2005, 44, 2636-2639.
- 8 G. A. Olah, G. K. S. Prakash and A. Goeppert, J. Org. Chem., 2009, 74, 487–498.
- 9 J. M. Lehn, Int. Congr. Catal., [Proc.], 8th., 1984, 1, 63-83.
- 10 M. Navarro Yerga Rufino, M. C. Alvarez Galvan, F. del Valle, A. Villoria de la Mano Jose and L. G. Fierro Jose, *ChemSusChem*, 2009, 2, 471–485.
- 11 D. W. Stephan, Org. Biomol. Chem., 2008, 6, 1535-1539.
- 12 D. W. Stephan, Dalton Trans., 2009, 3129-3136.
- 13 D. W. Stephan, Chem. Commun., 2010, 46, 8526-8533.
- 14 D. W. Stephan and G. Erker, Angew. Chem., Int. Ed., 2010, 49, 46–76.
- 15 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.
- 16 A. Ashley, A. Thompson and D. O'Hare, Angew. Chem., Int. Ed., 2009, 48, 9839–9843.
- 17 G. Ménard and D. W. Stephan, J. Am. Chem. Soc., 2010, 132, 1796–1797.
- 18 G. Ménard and D. W. Stephan, Angew. Chem., Int. Ed., 2011, 50, 8396–8399.
- 19 A. Berkefeld, W. E. Piers and M. Parvez, J. Am. Chem. Soc., 2010, 132, 10660–10661.
- 20 X. Zhao and D. W. Stephan, Chem. Commun., 2011, 47, 1833–1835.
- 21 D. Kaufmann, Chem. Ber., 1987, 120, 901-905.
- 22 V. C. Williams, W. E. Piers, W. Clegg, M. R. J. Elsegood, S. Collins and T. B. Marder, J. Am. Chem. Soc., 1999, 121, 3244–3245.
- 23 G. C. Welch, J. D. Masuda and D. W. Stephan, *Inorg. Chem.*, 2006, 45, 478–480.
- 24 S. J. Geier and D. W. Stephan, J. Am. Chem. Soc., 2009, 131, 3476–3477.