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CO_2 Reduction

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

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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 $P\textit{t}Bu_3$, 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-$((CH_2)_2NHP\textit{i}Pr_2)_3$ (**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.

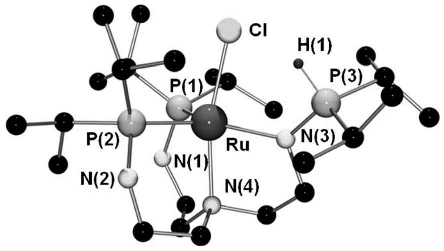

Figure 1. POV-ray depiction of the cation of **2**. Hydrogen atoms except P–H omitted for clarity.

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

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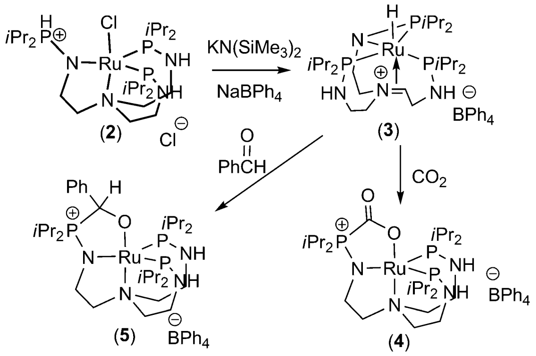
reveals an apparent doublet of triplets in the hydride region at −6.34 ppm ($^2J_{HP} = 20$, 33 Hz). Furthermore, a DEPT ^{1}H/^{13}C NMR experiment confirms the presence of a new CH fragment. While repeated attempts yielded crystals of poor quality, a preliminary X-ray study[28] was consistent with 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 $[Cp_2Zr(OC_6H_4P\mathit{t}Bu_2)(CO_2)]^+$, 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.

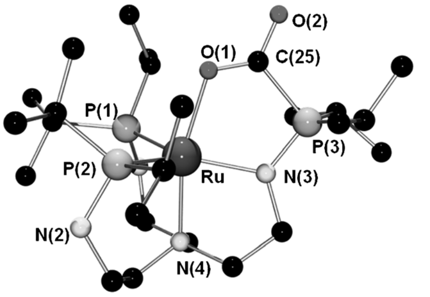


Figure 2. POV-ray depiction of the cation of **4**. Hydrogen atoms omitted for clarity.

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 mono-hydroboration 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

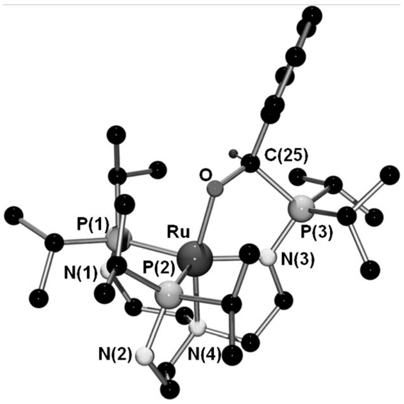
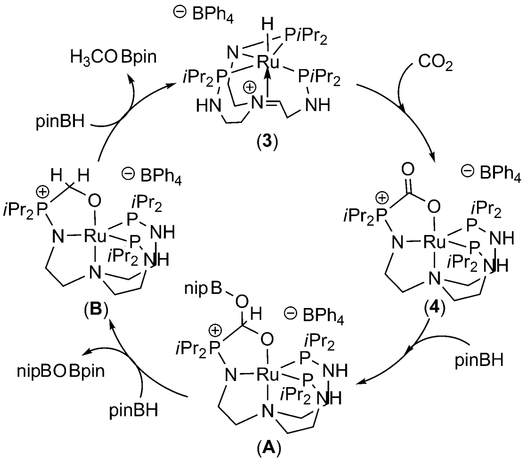


Figure 3. POV-ray depiction of the cation of **5**. Hydrogen atoms except H25 omitted for clarity.



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.

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