ORGANOMETALLICS

Carbon Dioxide Reduction to Silyl-Protected Methanol Catalyzed by an Oxorhenium Pincer PNN Complex

Michael G. Mazzotta,[†] Manxi Xiong,[‡] and Mahdi M. Abu-Omar^{*,‡}

[†]Department of Chemistry, Brown Laboratory, Purdue University, 560 Oval Drive, West Lafayette, Indiana 47907, United States [‡]Department of Chemistry and Biochemistry, University of California, Santa Barbara, California 93106-9510, United States

Supporting Information

ABSTRACT: Reaction of the rhenium pincer PNN complex $[(PNN)Re(O)_2][OTf]$ (2) with Me₂PhSiH results in addition of Si-H across the Re=O bond and a complex capable of reducing CO₂ under mild conditions (ambient temperature and 100 psig) to silyl formate in 95% yield. Reaction of 2 with PhSiH₃ yields a more reactive complex that catalytically reduces silyl formate to silyl formal (85% yield) and over longer times to silyl methanol (53% yield) with extrusion of



siloxane. This system represents the unusual case of a high-valent metal oxo complex capable of reducing CO_2 in a two-step, onepot reaction to methanol.

C atalytic reduction of CO_2 to formate or methanol is an active area of research because of interest in its use as a C1 synthon, which remains a major challenge.¹⁻⁵ While a number of heterogeneous transition-metal catalysts are capable of hydrogenating CO_2 to formic acid, most methodologies require high temperature and pressure.⁶⁻⁹ A growing number of homogeneous catalytic systems have been reported to achieve hydrogenation of CO_2 to methanol under mild conditions.¹⁻⁵

The inherent stability of the Si–O bond and the propensity for Si–H bond scission to form metal hydrides render organosilanes ideal for CO₂ reduction.^{10–15} Hydrosilylation of CO₂ generally yields silyl formate and silyl formal, which are versatile products that can be used as building blocks for making organic molecules and polymers.¹⁶ Ruthenium- and iridium-catalyzed hydrosilylations of CO₂ have produced silyl formate with varying quantities of siloxane byproduct. However, most systems require high CO₂ pressure, display low catalytic activity, or cannot convert CO₂ directly to methanol in a single-pot reaction.¹⁷

We have recently reported the synthesis of the high-valent dioxorhenium PNN pincer complex [(PNN)Re(O)₂][OTf] (**2**; OTf = CF₃SO₃⁻).¹⁸ In this communication, we describe the catalytic conversion of CO₂ to silvl formate under mild conditions (25 °C, 100 psig) with Me₂PhSiH as the reductant. In a subsequent step, and with the same catalyst, silvl formate is reduced further to silvl methanol via silvl formal with the addition of PhSiH₃ (Scheme 1).

Reaction of CO₂ (100 psig) with Me₂PhSiH (0.44 mmol) in CH₂Cl₂ (DCM) at 25 °C in the presence of a catalytic amount of **2** (0.02 mmol, 4.5 mol %) produces the silyl formate HC(O)(OSiMe₂Ph) in 95% yield (by NMR). The characteristic singlet at δ 8.1 (¹H NMR) of HC(O)(OSiMe₂Ph) was used to confirm the product.¹¹ Furthermore, a singlet at δ 161





in the $^{13}C\{^1H\}$ NMR spectrum was observed when $^{13}CO_2$ was employed. The remaining features of the 1H and ^{13}C spectra were fully consistent with HC(O)(OSiMe_2Ph) as the product.

The use of Me₂PhSiH gave clean conversion to silvl formate. Additional reductant and increased temperature did not result in further reduction of the silvl formate. However, upon addition of a primary silane, PhSiH₃ (0.88 mmol), further reduction of silvl formate was observed. Initially rapid conversion (within 30 min) yielded silvl formal in 85% yield (Figure 1). This conversion is marked by the characteristic resonance of the formal protons at δ 5.2 (¹H NMR). Over a longer reaction time of 24 h, the silvl formal is reduced to silvl methanol¹³⁻¹⁵ in approximately 53% yield (Figure 1). A unique characteristic of this system is the kinetic resolution of the different reduction products. One can select for silvl formate by using a tertiary silane such as Me₂PhSiH, stop at the silyl formal with PhSiH₂ and halt the reaction after 30 min, or go all the way to silyl methanol after 24 h reaction with 2 equiv of PhSiH₃. The reaction profile in Figure 1 shows that the

Received: March 25, 2017



Figure 1. Typical time profile. Conditions: CO_2 100 psi, Me_2PhSiH (0.44 mmol) in DCM at 25 °C. At 24 h PhSiH₃ (0.88 mmol) was added. The lines are to guide the eye.

hydrosilylation of CO_2 to silyl formate takes place over the course of 24 h with excellent chemoselectivity (no formal observed). Upon addition of 2 equiv of PhSiH₃, the immediate formation of the bis(silyl)formal was observed, along with the simultaneous, and extremely rapid, consumption of the formate. Reduction of the bis(silyl)formal to silyl methanol proceeds over the course of 24 h; a longer reaction time gave no additional production of silyl methanol or further reduction to methane.

Attempts to perform this reaction all in a single step $(Me_2PhSiH + PhSiH_3 + CO_2)$ rather than by sequential addition of organosilanes were unsuccessful. This puzzling result indicated that two distinct and silane-dependent oxorhenium species were responsible for the respective catalytic products, and thus, we sought to confirm this hypothesis. Reaction of 2 with 1 equiv of Me_2PhSiH in DCM yielded a clean reaction to afford the siloxy hydride [(PNN)Re(H)(O)-(OSiMe_2Ph)][OTf] (3-H) (Scheme 2), which is analogous to

Scheme 2



 $(PPh_3)_2Re(H)(O)(OSiMe_2Ph)(I)$ reported by Toste and coworkers.¹⁹ The ³¹P{¹H} NMR spectrum of **3-H** exhibits a singlet at δ 60 and the ¹H NMR spectrum a doublet at δ 7.7 (J= 14 Hz), which is assigned to Re–H. Toste and co-workers observed the Re–H in $(PPh_3)_2Re(H)(O)(OSiMe_2Ph)(I)$ at δ 6.5. Our assignment of the Re–H was confirmed by using Me₂PhSiD, which had a signal at δ 7.7 in the ²H spectrum and

was absent from the ¹H spectrum. Additionally, the ¹H{³¹P} NMR spectrum of **3-H** gave a singlet at δ 7.7, verifying that the coupling is to the P of the PNN ligand.

Attempts to obtain single crystals of **3-H** were not successful, in part because of its reactivity. Nevertheless, reaction of 1 equiv of Me_3SiOTf with complex **2** gave the analogous siloxy triflate [(PNN)Re(O)(OTf)(OSiMe_3)][OTf] (**3-OTf**). X-rayquality crystals of **3-OTf** allowed structural determination (Figure 2), providing credence to the proposed addition of a



Figure 2. ORTEP drawing of the molecular structure of **3-OTf**. Hydrogen atoms and the outer-sphere triflate anion are omitted for clarity.

Si-X bond across the oxo ligand of 2. Many features of the 1 H NMR spectrum of 3-OTf resemble those observed for 3-H, further supporting the proposed siloxy hydride species.

Stoichiometric reaction of 3-H with CO₂ produces silyl formate at a comparable rate to that of the catalytic reaction, thus implicating this species as a viable active complex for CO₂ hydrosilylation. It is conceivable that initially PhMe₂SiH associates as a η^1 - or η^2 -silane to Re, as has been reported by our group; however, we were not able to definitively observe such a silane adduct.^{20,21} Wei and co-workers have extensively reported with computational studies that silane adducts (primarily the η^1 complex) are pervasive in oxorheniumcatalyzed hydrosilylations and may even function as the active catalyst.²² The $[Re(O)_2(PNN)]^+$ complex is Lewis acidic and thus activates the Si-H bond by addition across the Re=O bond. To establish the need for the rhenium center, we performed the reaction with only AgOTf, CO₂, and PhMe₂SiH under identical conditions and found no formation of silyl formate. The reaction between 3-H and CO₂ likely proceeds through formation of rhenium formate, as has been detailed extensively by Darensbourg,^{23,24} followed by silylium transfer, as has been shown by Oro, Piers, and Stephan.^{11,25,26} A complete catalytic cycle for the first-step reduction of CO₂ is shown in Scheme 3.

The reduction of silvl formate to formal and all the way to silvl methanol is proposed to proceed initially via a mechanism similar to that in Scheme 3, with the exception of having $[-SiPhH_2]$ on the oxo ligand. This subtle difference appears to influence the subsequent reactivity in a significant way. The

Scheme 3



evidence for this claim is presented next. Reaction of 2 with 1 equiv of PhSiH₃ in DCM yielded compound 4, which has spectroscopic features similar to those of 3-H. The ¹H NMR resonance of the Re-H appears as a doublet at δ 8.0. An AB quartet, with signals at δ 4.50 and 4.64, was identified as two diastereotopic protons of the -SiPhH₂ moiety, which we tentatively propose as residing on one of the oxo ligands, as observed with the Si-Me groups of 3-H.27 While structurally similar, complexes 3-H and 4 differ dramatically in their reactivity. Fernandes and co-workers have articulated similar observations as to the enhanced reactivity of their oxorhenium catalysts with the use of primary versus secondary organosilanes.²⁸ Zheng and Chan proposed a unique mechanism for ketone hydrosilylation with Rh complexes that was specific to primary versus secondary organosilanes.²⁹ We propose a similar mechanistic distinction for oxorhenium hydrosilylation catalysis. In this mechanism, the silane undergoes an initial oxidative addition on Rh followed by the ketone (or formal) coordinating to the silicon and inserting into an Si-H bond. We postulate a similar sequence of events for our oxorhenium catalyst: (1) addition of Si-H across the Re=O bond to form the siloxy hydride 4, (2) coordination of silyl formate (or silyl formal in the last reduction step) and insertion into an Si-H bond of -SiPhH₂ (Scheme 4), and (3) product elimination to regenerate the dioxorhenium cationic catalyst. It has been noted previously that primary organosilanes possess more silvlene character when they are activated by metals and it is this character that leads to this enhanced activity toward Si-H bond insertion into substrates.³⁰ Recent observations by Ison and co-workers that the rhenium-oxo bond acts as the basic

Scheme 4



component of a frustrated Lewis pair sheds additional light on this duality; one can imagine that subtle variations of the -R group within the organosilane yield vastly different reactivities.³¹

The reported catalytic system herein marks the first example of a high-valent metal oxo catalyst that is capable of reducing CO_2 to silyl formate, silyl formal, and all the way to silyl methanol, depending on the organosilane employed and time of reaction. Schemes 3 and 4 illustrate the salient features of the operating mechanisms and the way each product can be obtained selectively. Further studies are aimed at exploring the extent to which these transformations can be generalized to other high-valent metal oxo complexes.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organo-met.7b00223.

Full characterization data for 3-OTf, 3-H, and 4 and experimental procedures for all catalytic reactions (PDF) Crystallographic data (CIF)

AUTHOR INFORMATION

Corresponding Author

*E-mail for M.M.A.-O.: abuomar@chem.ucsb.edu.

ORCID 0

Mahdi M. Abu-Omar: 0000-0002-4412-1985

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Financial support was provided by the DOE, Office of Science, Basic Energy Sciences (Grant no. DE-FG-02-06ER15794). Many thanks to Dr. Ram Pichaandi for useful discussions and Dr. John Harwood and Dr. Huaping Mo for their assistance with NMR.

REFERENCES

- (1) Appel, A. M.; et al. Chem. Rev. 2013, 113 (8), 6621-6658.
- (2) Arakawa, H.; et al. Chem. Rev. 2001, 101 (4), 953-996.
- (3) Huff, C. A.; Sanford, M. S. J. Am. Chem. Soc. 2011, 133 (45), 18122-18125.
- (4) Huff, C. A.; Sanford, M. S. ACS Catal. 2013, 3 (10), 2412–2416.
 (5) Rezayee, N. M.; Huff, C. A.; Sanford, M. S. J. Am. Chem. Soc.
- 2015, 137 (3), 1028–1031.
- (6) Leitner, W. Angew. Chem., Int. Ed. Engl. 1995, 34 (20), 2207–2221.
- (7) Choudhury, J. ChemCatChem 2012, 4 (5), 609-611.
- (8) Li, Y. N.; Ma, R.; He, L. N.; Diao, Z. F. Catal. Sci. Technol. 2014, 4, 1498–1512.
- (9) Spencer, M. S. Top. Catal. 1999, 8, 259-266.
- (10) Jansen, A.; Pitter, S. J. Mol. Catal. A: Chem. 2004, 217 (1-2), 41-45.
- (11) Lalrempuia, R.; Iglesias, M.; Polo, V.; Sanz Miguel, P. J.; Fernández-Alvarez, F. J.; Pérez-Torrente, J. J.; Oro, L. A. Angew. Chem., Int. Ed. **2012**, *51* (51), 12824–12827.
- (12) Park, S.; Bézier, D.; Brookhart, M. J. Am. Chem. Soc. 2012, 134 (28), 11404–11407.
- (13) Riduan, S. N.; Zhang, Y.; Ying, J. Y. Angew. Chem., Int. Ed. 2009, 48 (18), 3322–3325.
- (14) Riduan, S. N.; Ying, J. Y.; Zhang, Y. ChemCatChem 2013, 5 (6), 1490–1496.

С

Organometallics

- (15) Metsänen, T. T.; Oestreich, M. Organometallics 2015, 34 (3), 543–546.
- (16) Schäfer, A.; Saak, W.; Haase, D.; Müller, T. Angew. Chem., Int. Ed. 2012, 51 (12), 2981–2984.
- (17) Deglmann, P.; Ember, E.; Hofmann, P.; Pitter, S.; Walter, O. Chem. Eur. J. 2007, 13 (10), 2864–2879.
- (18) Mazzotta, M. G.; Pichaandi, K. R.; Fanwick, P. E.; Abu-Omar, M. M. Angew. Chem., Int. Ed. **2014**, 53 (32), 8320–8322.
- (19) Nolin, K. A.; Krumper, J. R.; Pluth, M. D.; Bergman, R. G.; Toste, F. D. J. Am. Chem. Soc. **2007**, 129 (47), 14684–14696.
- (20) Ison, E. A.; Corbin, R. A.; Abu-Omar, M. M. J. Am. Chem. Soc. 2005, 127 (34), 11938–11939.
- (21) Ison, E. A.; Trivedi, E. R.; Corbin, R. A.; Abu-Omar, M. M. J. Am. Chem. Soc. 2005, 127 (44), 15374–15375.
- (22) Gu, P.; Wang, W.; Wang, Y.; Wei, H. Organometallics 2013, 32 (1), 47-51.
- (23) Darensbourg, D. J.; Wiegreffe, H. P.; Wiegreffe, P. W. J. Am. Chem. Soc. 1990, 112 (25), 9252-9257.
- (24) Darensbourg, D. J.; Wiegreffe, P.; Riordan, C. G. J. Am. Chem. Soc. 1990, 112 (15), 5759-5762.
- (25) Houghton, A. Y.; Hurmalainen, J.; Mansikkamäki, A.; Piers, W. E.; Tuononen, H. M. Nat. Chem. 2014, 6 (11), 983–988.
- (26) Weicker, S. A.; Stephan, D. W. Chem. Eur. J. 2015, 21 (37), 13027-13034.
- (27) Zuzek, A. A.; Parkin, G. J. Am. Chem. Soc. 2014, 136 (23), 8177–8180.
- (28) Fernandes, T. A.; Bernardo, J. R.; Fernandes, A. C. ChemCatChem 2015, 7 (7), 1177–1183.
- (29) Zheng, G. Z.; Chan, T. H. Organometallics 1995, 14 (1), 70–79.
 (30) Gigler, P.; Bechlars, B.; Herrmann, W. A.; Kühn, F. E. J. Am. Chem. Soc. 2011, 133 (5), 1589–1596.
- (31) Lambic, N. S.; Sommer, R. D.; Ison, E. A. ACS Catal. 2017, 7 (2), 1170–1180.