

Hydrogenation and Hydrosilylation of Nitrous Oxide Homogeneously Catalyzed by a Metal Complex

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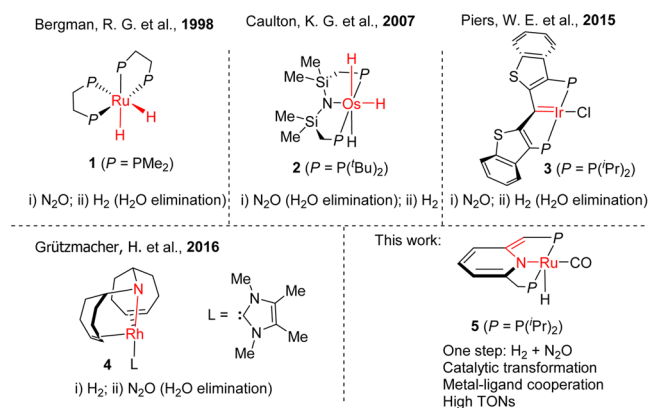
S Supporting Information

ABSTRACT: Due to its significant contribution to stratospheric ozone depletion and its potent greenhouse effect, nitrous oxide has stimulated much research interest regarding its reactivity modes and its transformations, which can lead to its abatement. We report the *homogeneously* catalyzed reaction of nitrous oxide (N_2O) with H_2 . The reaction is catalyzed by a PNP pincer ruthenium complex, generating efficiently only dinitrogen and water, under mild conditions, thus providing a green, mild methodology for removal of nitrous oxide. The reaction proceeds through a sequence of dihydrogen activation, “O”-atom transfer, and dehydration, in which metal–ligand cooperation plays a central role. This approach was further developed to catalytic O-transfer from N_2O to Si–H bonds.

Nitrous oxide (N_2O), emitted due to agriculture activities, industrial processes, combustion of fossil fuels and biomass, is a potent greenhouse gas and regulator of atmospheric ozone concentrations.^{1,2} Although accounting for only 6% of all greenhouse gas emissions from human activities, nitrous oxide shows ca. 300 times greater warming potential than CO_2 .³ Due to its highly destructive environmental effects, the degradation, reduction, and/or application of nitrous oxide have drawn much attention.⁴ Hydrogenation of nitrous oxide using dihydrogen, which is driven by release of dinitrogen and water, is considered an attractive reductive process. Although there are reports on catalytic hydrogenation reactions of N_2O by heterogeneous systems, (metal surfaces, zeolites),⁵ *homogeneously* catalyzed reactions by metal complexes are highly desirable, as they may be more amenable to catalytic design by catalyst structural modifications, and might occur under mild, selective conditions. Such systems may also shed light on mechanistic steps of importance regarding N_2O activation.

Stoichiometric hydrogenation of N_2O involving metal complexes was reported (Scheme 1).⁶ In seminal work by Bergman in 1998,^{6b} the reaction of $(DMPE)_2Ru(H)_2$ **1** ($DMPE = 1,2$ -bis(dimethylphosphino)ethane) with 1 equiv N_2O afforded the hydroxoruthenium complex $(DMPE)_2Ru(H)(OH)$, which further reacted with hydrogen gas to regenerate complex **1** and release a water molecule, representing stepwise stoichiometric hydrogenation of N_2O .⁷ Using excess N_2O , the dihydroxoruthenium complex $(DMPE)_2Ru(OH)_2$ was formed, preventing water formation and thus prohibiting catalytic hydrogenation. In 2007, Caulton reported that the reaction of $(PNP)Os(H)_3$ (**2**) ($PNP = N(SiMe_2CH_2P^tBu_2)_2$) with 1 atm of N_2O resulted in

Scheme 1. Homogeneous Hydrogenation of N_2O



formation of H_2O and $(PNP)OsH(N_2)$. A separate reaction of the latter with hydrogen slowly formed the complex $(PNP)Os(H)_3$ (**2**).^{6c} No catalysis was reported. In 2015, Piers reported a formal stoichiometric hydrogenation of N_2O using a $PC_{sp^2}P$ iridium pincer carbene complex **3**,^{6d} which reacts with N_2O with loss of N_2 to form an iridiaepoxide complex; reaction of the latter with H_2 followed by heating resulted in release of H_2O . However, no catalytic turnover was observed. In 2016, Grützmacher reported the Rh-catalyzed dehydrogenative coupling of alcohols using N_2O as a hydrogen acceptor, which proceeds by metal–ligand cooperation.^{6e} Mechanistic studies of this system showed that reaction of N_2O with H_2 in the presence of complex **4** generated N_2 , and catalysis was mentioned, but catalytic data (TON, conversion, or yield) was not reported. To the best of our knowledge, there is currently no detailed report on homogeneously catalyzed hydrogenation of nitrous oxide.

To enable homogeneously catalyzed hydrogenation of nitrous oxide, several challenges have to be met: first, high selectivity in the sequential reaction of N_2O and H_2 in the catalytic cycle is required because nitrous oxide and dihydrogen are in large excess relative to the catalyst. In addition, over-reduction by hydrogen or overoxidation by nitrous oxide can inhibit the catalytic efficiency of the reaction. Third, the catalyst should be active in the presence of excess amount of the generated water.

Here we report the development of the homogeneously catalyzed hydrogenation of N_2O with H_2 . The reaction is catalyzed by ruthenium pincer complexes and it very likely involves a unique mechanism based on metal–ligand cooperation (MLC). The reaction proceeds smoothly in high TON

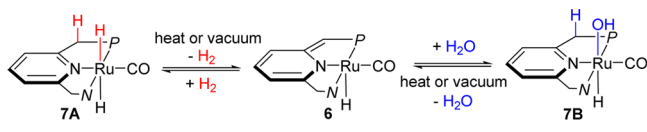
Received: March 2, 2017

Published: April 6, 2017

(TON = turnover number) under very mild conditions, thus providing a highly efficient method for hydrogenation of nitrous oxide. Moreover, the reaction was extended to catalytic O-transfer from N₂O into Si–H bonds.

In recent years, our group has developed a series of transition metal complexes with pyridine- and acridine-based LNL'-type (L = N or P) pincer ligands, capable of facile activation of various X–H bonds, including H–H, O–H, N–H, C–H, B–H, and S–H bonds via metal–ligand cooperation.⁸ As a typical example, the pyridine-based PNN-ruthenium complex **6**, first reported by us in 2005,⁹ can undergo a reversible hydrogenation/dehydrogenation sequence via metal–ligand cooperation (MLC) (Scheme 2).⁹

Scheme 2. Reversible Activation of H₂ and H₂O by **6**



Similarly, O–H bond activation of H₂O with dearomatized complex **6** takes place smoothly and reversibly at room temperature.¹⁰ Both reactions proceed with no change in the formal metal oxidation state. These two reversible reactions, and the stability of the complex under excess of water, encouraged us to explore the catalytic hydrogenation of nitrous oxide by pyridine-based pincer Ru complexes, based on metal–ligand cooperation.

Initially, the hydrogenation of N₂O was examined using 0.01 mmol of the PNN-ruthenium complex **6** (0.08 mol % catalyst) and ca. 13 mmol of N₂O¹¹ and 50 psi of H₂ in a 90 mL of Fisher-Porter tube (50 psi of H₂ corresponds to 13 mmol at rt). After heating in 5 mL THF at 65 °C for 36 h, 0.13 mmol of H₂O was detected by ¹H NMR of the reaction mixture using mesitylene as internal standard with calibration. A control experiment without the catalyst failed to afford products. Thus, the homogeneously catalyzed reaction (13 TON, 1% conversion for N₂O) has been realized. The relatively low turnover number is probably due to decomposition of the catalyst since the free PNN ligand and the corresponding phosphine oxide were observed by ³¹P{¹H} NMR of the reaction mixture. Various pyridine-based dearomatized ruthenium pincer complexes were then examined (Table 1). Replacing the diethylaminomethylene group (Et₂NCH₂–) of the pincer ligand by a 2-pyridinyl group resulted in a significant yield increase. Thus, using the PN(Py) complexes **8** (P = P(^tBu)₂)^{12a} and **9** (P = P(ⁱPr)₂) resulted in an increase in the TONs to 53 (4% conversion for N₂O) and 28 (2% conversion for N₂O), respectively. However, complete decomposition of the catalysts was observed by ³¹P{¹H} NMR spectroscopy. Compared to the PNN or PN(Py) complexes, the PNP ruthenium complex **10** (P = P(^tBu)₂)^{12b} exhibited higher stability and led to a higher TON (110 TONs/37 h, 8% conversion for N₂O). The phosphine group of the PNP ligands were then modified; whereas use of the PNP complex **12** (P = PPh₂)^{12c} resulted in a lower TON (10 TONs/36 h, <1% conversion of N₂O), complex **5** (P = P(ⁱPr)₂) achieved the best result, namely 2.2 mmol of water (220 TONs, 17% conversion for N₂O) were formed in 36 h. Significantly, the NMR spectra of the reaction solution showed that most of the starting ruthenium complex was converted to the complex (PNP)RuH(CO)(OH) **14** (spectrum iv in Figure 1; ¹H NMR for Ru–H bond, δ = –14.7 ppm (t, ²J_{PH} = 18.0 Hz); ³¹P{¹H} NMR, δ = 74.0 ppm (s); ESI analysis, MS-ESI for C₂₀H₃₆NOP₂Ru (MW = 470, (M–OH)⁺; for full mass data,

Table 1. Catalyst Screening for Hydrogenation of N₂O^{a,b,c}

N ₂ O + H ₂		Pincer [*] Ru(H)L (0.01 mmol)		N ₂ + H ₂ O	
13 mmol	13 mmol	THF, 65 °C			
6 , P = P(^t Bu) ₂ , N = NEt ₂ 13 TON / 36 h 1% conversion	8 , P = P(^t Bu) ₂ 53 TON / 69 h 4% conversion	9 , P = P(ⁱ Pr) ₂ 28 TON / 36 h 2% conversion			
10 , P = P(^t Bu) ₂ 110 TON / 37 h 8% conversion	11 , P = P(^t Bu) ₂ 61 TON / 36 h 5% conversion	12 , P = PPh ₂ 10 TON / 36 h <1% conversion			
5 , P = P(ⁱ Pr) ₂ 220 TON / 36 h 17% conversion	13 , P = P(ⁱ Pr) ₂ ^b 94 TON / 36 h 7% conversion	14 , P = P(ⁱ Pr) ₂ 307 TON / 37 h 24% conversion			

^aAll the reactions were conducted in a 90 mL Fisher-Porter tube using 13 mmol of H₂ and N₂O in 5 mL THF. ^bAll the complexes except **13** were freshly prepared from the corresponding aromatized (pincer)-RuH(Cl)(L) with 1 equiv ^tBuOK in THF and used directly in the reactions. Complex **13** was obtained similarly using KHMDs as base. ^cThe TONs are based on the generated H₂O as measured by ¹H NMR of the reaction mixture using mesitylene as internal standard (see SI for details).

see SI). Complex **14** was independently synthesized from **5** and H₂O (spectrum v in Figure 1). Moreover, the corresponding reaction using **14** as catalyst led to an even better result (307 TONs/37 h, 24% conversion for N₂O), indicating that complex **14** is very likely involved in the catalytic cycle, and is the resting state of the catalytic cycle. Replacing the CO ligand by N₂ decreased the yield significantly (110 TON for **10** vs 61 TON for **11**^{12d}). The acridine-based PNP ruthenium complex **13**^{12e} was less efficient than complex **5**, affording 94 TON (7% conversion for N₂O) in 36 h.

To have a better understanding of this catalytic transformation and to further develop it, the reaction mechanism was explored by studying individual steps that might be involved in the catalytic cycle (Scheme 3, Table S1 (see SI), and Figure 1). First, the reaction of the dearomatized ruthenium complex **5** (spectrum i in Figure 1) with dihydrogen is known to occur smoothly to afford the ruthenium *trans*-dihydride complex **15** (spectrum ii in Figure 1, pathway a in Scheme 3).¹³ On the other hand, in the absence of H₂, N₂O was found to decompose complex **5**, resulting in a complicated mixture (pathway e), which failed to convert to the ruthenium hydroxo complex **14** in the presence of excess H₂ (pathway f). Importantly, the competitive experiment of **5** in the presence of both N₂O and H₂ (1:1 mixture) resulted in formation of the ruthenium *trans*-dihydride complex **15** as the only product. Thus, the much faster reaction of **5** with H₂ than with N₂O inhibits the decomposition of **5** and enables the whole catalytic cycle. Because the hydrogenation of **5** is a reversible reaction, via metal–ligand cooperation (pathway b), catalyst **5** can be regenerated from **15**, as observed under vacuum or upon heating.¹³

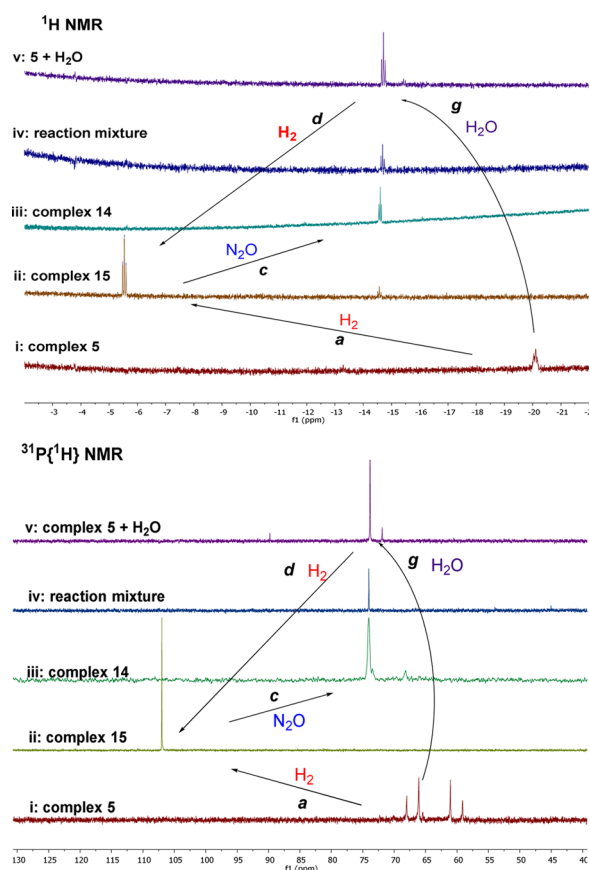
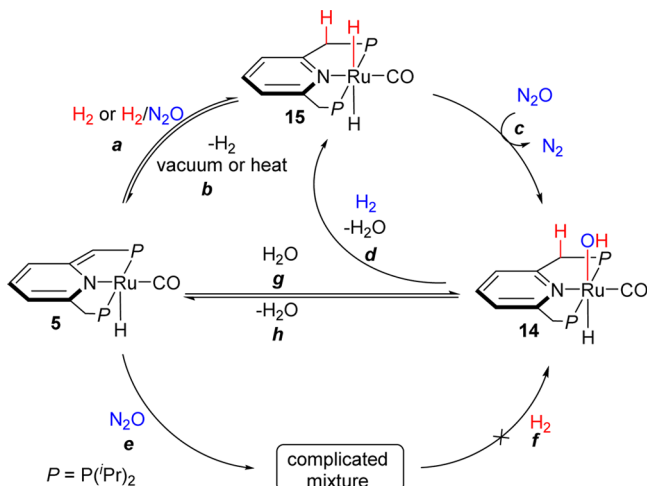


Figure 1. ^1H NMR of Ru–H bonds and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of complexes **5**, **14**, and **15** in THF and the corresponding reactions.

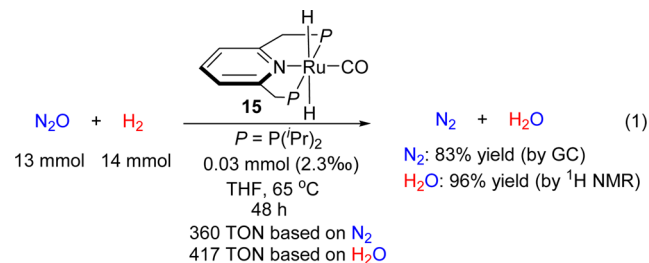
Scheme 3. Mechanistic Studies of Individual Steps



Moreover, even in the presence of 2 equiv N_2O , only mono “O”-atom transfer took place upon reaction with **15**, highly efficiently forming the hydrido hydroxo complex **14** (spectrum **iii** in Figure 1, pathway **c** in Scheme 3).¹⁴ This is important because double insertion to give the dihydroxo complex (as observed by Bergman^{6a,b}) would hinder subsequent water elimination. Reversible water elimination from complex **14** is facilitated by the *trans* effect of Ru–H bond, affording the dearomatized PNP pincer catalyst **5** under vacuum (pathway **h**). Furthermore, the ruthenium *trans*-dihydride complex **15** was regenerated directly by the reaction of ruthenium hydroxide **14** with H_2 , combining

water release and hydrogen addition via metal–ligand cooperation (pathway **d**).

Complex **15** was found to be the best catalyst in the hydrogenation of N_2O . Full conversion of nitrous oxide and the highest TON were achieved by generating **15** *in situ* from complex **5** (0.03 mmol, 0.23% of catalyst) and increasing the reaction time to 48 h (eq 1). The produced 83% yield of dinitrogen (360 TON based on N_2) was determined carefully by GC, and 96% yield of H_2O (417 TON based on H_2O) was measured by ^1H NMR with calibration.¹¹



On the basis of these results, we propose that the mechanism of hydrogenation of nitrous oxide follows the reaction sequence of pathway **a–c–h**, involving hydrogenation of the dearomatized PNP pincer complex **5** by metal–ligand cooperation (MLC) to afford the ruthenium *trans*-dihydride compound **15**, followed by (likely rate determining) selective mono oxygen transfer from nitrous oxide to give complex **14**, and water release by MLC to regenerate complex **5**, thus completing an efficient, selective catalytic cycle. Essentially, each one of the complexes **5**, **14** and **15**, which are involved in the catalytic cycle, can serve as a catalyst, as we indeed observed. However, due to the potential decomposition of **5** if N_2O is added prior to H_2 , complex **15** is practically the best catalyst. To be mentioned, due to the reversible hydration/dehydration sequence via metal–ligand cooperation, it is difficult to isolate complex **14** and it was characterized *in situ*.

Silicon–oxygen bond formation of silane with nitrous oxide is the key process for deposition of nonstoichiometric silicon oxide or semi-insulating polysilicon (SIPOS), which is used as a substitute for silicon dioxide as passivation material in high voltage power devices.¹⁵ Thus, homogeneous “O”-atom transfer of nitrous oxide into silane was then examined by using catalyst **5** under N_2O atmosphere (50 psi) (Table 2): the reaction of PhMe_2SiH **16a** with nitrous oxide took place smoothly using 1 mol % of catalyst, affording the desired silanol **17a** together with disilyl ether **18a** in 32% and 64% yields, respectively. H_2 was detected by GC, indicating the disilyl ether is formed from the direct dehydrogenative coupling reaction of formed silanol and residual silane. Ph_2MeSiH **16b**, which contains a bulkier substituent (Ph over Me group), exhibited lower reactivity and afforded 30% of silanol **17b** together with 46% of disilyl ether **18b** using 2 mol % of catalyst and increasing reaction time to 3 days. Substrate **16c** with *tert*-butyl group afforded only silanol **17c** in 46% yield together with 54% of recovered starting material. No disilyl ether **18c** was formed because of the steric hindrance of the bulky substituents.

In summary, the *homogeneously* catalyzed hydrogenation of nitrous oxide by a metal complex has been developed. High efficiency and high TON are achieved using the PNP pincer ruthenium complex **15** as the catalyst. Studies of stoichiometric steps indicate that the reaction involves metal–ligand cooperation (MLC). Thus, H_2 addition to the dearomatized catalyst **5** takes place with aromatization to form complex **15**, followed by mono-oxygen transfer from N_2O to a Ru–H bond, and

Table 2. Catalytic Oxygen Transfer to Si–H Bond Using Nitrous Oxide^a

Silane	Time / h	Product / Isolated yield
1.	36	17a, 32% + 18a, 64%
2.	66	17b, 30% +
3.	72	17c, 46% ^{b,c} + 18c, nd

^aThe reactions were conducted using a THF solution containing 0.01 mmol of catalyst **5** and 1.0 mmol (for PhMe₂SiH) or 0.5 mmol (for Ph₂MeSiH and ^tBuMe₂SiH) of substrate under 50 psi of N₂O. ^bThe yields (based on the silane) were determined by GC using standard curve due to the low boiling point of the product. ^c54% of the starting material was recovered.

subsequent water release by MLC, regenerating the dearomatized complex. Moreover, catalytic “O”-atom transfer from nitrous oxide to Si–H bonds of silanes, catalyzed by the dearomatized **5**, was also demonstrated. Further studies in this area are being carried out in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.7b02124.

Experimental procedures; spectral data (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This research was supported by the European Research Council (ERC AdG 692775). D.M. holds the Israel Matz Professorial Chair of Organic Chemistry. R.Z. thanks the Faculty of Chemistry for being awarded a Dean’s Fellowship.

■ REFERENCES

- Prather, M. *Science* **1998**, 279, 1339.
- Ravishankara, A. R.; Daniel, J. S.; Portmann, R. W. *Science* **2009**, 326, 123. Highlight: Dameris, M. *Angew. Chem., Int. Ed.* **2010**, 49, 489.
- (a) U.S. Greenhouse Gas Inventory Report 1990–2014, U.S. EPA.; (b) Hansen, J.; Sato, M. *Proc. Natl. Acad. Sci. U. S. A.* **2004**, 101, 16109.

- (4) For selected reviews on N₂O chemistry, see: (a) Tolman, W. B. *Angew. Chem., Int. Ed.* **2010**, 49, 1018. (b) Konsolakis, M. *ACS Catal.* **2015**, 5, 6397. (c) Severin, K. *Chem. Soc. Rev.* **2015**, 44, 6375. (d) Parmon, V. N.; Panov, G. I.; Uriarte, A.; Noskov, A. S. *Catal. Today* **2005**, 100, 115. (e) Pauleta, S. R.; Dell’Acqua, S.; Moura, I. *Coord. Chem. Rev.* **2013**, 257, 332. (f) Leont’ev, A. V.; Fomicheva, O. A.; Proskurnina, M. V.; Zefirov, N. S. *Russ. Chem. Rev.* **2001**, 70, 91. (g) Lee, D.-H.; Mondal, B.; Karlin, K. D. *Nitrogen Monoxide and Nitrous Oxide Binding and Reduction in Activation of Small Molecules*; Tolman, W. B., Ed.; WILEY-VCH Verlag GmbH & Co. KGaA: Weinheim, 2006; pp 43–79.

- (5) For selected reports on heterogeneous hydrogenation of nitrous oxide, see Pt: (a) Cassel, H.; Glükauf, E. Z. *Physik. Chem.* **1932**, 19B, 47. (b) Dixon, J. K.; Vance, J. E. *J. Am. Chem. Soc.* **1935**, 57, 818. Ag: (c) Benton, A. F.; Thacker, C. M. *J. Am. Chem. Soc.* **1934**, 56, 1300. Alumina: (d) Vance, J. E.; Dixon, J. K. *J. Am. Chem. Soc.* **1941**, 63, 176. Ru, Rh, Ir, or Pt: (e) Miyamoto, A.; Baba, S.; Mori, M.; Murakami, Y. *J. Phys. Chem.* **1981**, 85, 3117. Cu: (f) Dandekar, A.; Vannice, M. A. *Appl. Catal., B* **1999**, 22, 179. Au: (g) Gluhoi, A. C.; Dekkers, M. A. P.; Nieuwenhuys, B. E. *J. Catal.* **2003**, 219, 197. Fe: (h) Delahay, G.; Mauvezin, M.; Guzmán-Vargas, A.; Coq, B. *Catal. Commun.* **2002**, 3, 385. (i) Nobukawa, T.; Yoshida, M.; Okumura, K.; Tomishige, K.; Kunimori, K. *J. Catal.* **2005**, 229, 374. Ir(1,1,0): (j) Carabineiro, S. A.; Nieuwenhuys, B. E. *Surf. Sci.* **2001**, 495, 1. For the relative photo or radiative chemistry, see: (k) Zabor, J. W.; Noyes, W. A., Jr. *J. Am. Chem. Soc.* **1940**, 62, 1975. (l) Cheek, C. H.; Swinnerton, J. W. *J. Phys. Chem.* **1964**, 68, 1429.

- (6) (a) Kaplan, A. W.; Bergman, R. G. *Organometallics* **1997**, 16, 1106. (b) Kaplan, A. W.; Bergman, R. G. *Organometallics* **1998**, 17, 5072. (c) Lee, J.-H.; Pink, M.; Tomaszewski, J.; Fan, H.; Caulton, K. G. *J. Am. Chem. Soc.* **2007**, 129, 8706. (d) Doyle, L. E.; Piers, W. E.; Borau-Garcia, J. *J. Am. Chem. Soc.* **2015**, 137, 2187. (e) Gianetti, T. L.; Annen, S. P.; Santiso-Quinones, G.; Reiher, M.; Driess, M.; Grützmacher, H. *Angew. Chem., Int. Ed.* **2016**, 55, 1854. (f) Co complex catalyzed O-transfer from N₂O to phosphines: Gianetti, T. L.; Rodríguez-Lugo, R. E.; Harmer, J. F.; Trincado, M.; Vogt, M.; Santiso-Quinones, G.; Grützmacher, H. *Angew. Chem., Int. Ed.* **2016**, 55, 15323.

- (7) The mechanism of O insertion into Ru–H was studied by DFT, see: Yu, H.; Jia, G.; Lin, Z. *Organometallics* **2008**, 27, 3825.

- (8) (a) Gunanathan, C.; Milstein, D. *Acc. Chem. Res.* **2011**, 44, 588. (b) Gunanathan, C.; Milstein, D. *Science* **2013**, 341, 1229712. (c) Gunanathan, C.; Milstein, D. *Chem. Rev.* **2014**, 114, 12024. (d) Khusnutdinova, J. R.; Milstein, D. *Angew. Chem., Int. Ed.* **2015**, 54, 12236. (e) Zell, T.; Milstein, D. *Acc. Chem. Res.* **2015**, 48, 1979.

- (9) Zhang, J.; Leitius, G.; Ben-David, Y.; Milstein, D. *J. Am. Chem. Soc.* **2005**, 127, 10840.

- (10) Kohl, S. W.; Weiner, L.; Schwartsburd, L.; Konstantinovski, L.; Shimon, L. J. W.; Ben-David, Y.; Iron, M. A.; Milstein, D. *Science* **2009**, 324, 74.

- (11) For details regarding calibration of the amount of N₂O considering its solubility in THF, see SI.

- (12) (a) Balaraman, E.; Gnanaprakasam, B.; Shimon, L. J.; Milstein, D. *J. Am. Chem. Soc.* **2010**, 132, 16756. (b) Khaskin, E.; Iron, M. A.; Shimon, L. J. W.; Zhang, J.; Milstein, D. *J. Am. Chem. Soc.* **2010**, 132, 8542. (c) Jia, G.; Lee, H. M.; Williams, I. D.; Lau, C. P.; Chen, Y. *Organometallics* **1997**, 16, 3941. (d) Zhang, J.; Gandelman, M.; Shimon, L. J. W.; Rozenberg, H.; Milstein, D. *Organometallics* **2004**, 23, 4026. (e) Gunanathan, C.; Milstein, D. *Angew. Chem., Int. Ed.* **2008**, 47, 8661.

- (13) Zhang, J.; Leitius, G.; Ben-David, Y.; Milstein, D. *Angew. Chem., Int. Ed.* **2006**, 45, 1113.

- (14) For “O”-atom transfer into M–H bond of N₂O to form M–OH, see: M = Ru: refs **6a**, **6b**, **7**, and **10**; for M = Rh, see ref **6e**; for M = Hf, see: (a) Vaughan, G. A.; Rupert, P. B.; Hillhouse, G. L. *J. Am. Chem. Soc.* **1987**, 109, 5538.

- (15) Fayolle, F.; Couderc, J.-P.; Duverneuil, P. *Chem. Vap. Deposition* **1996**, 2, 255 and the references therein..