CO Oxidation by N₂O Homogeneously Catalyzed by Ruthenium Hydride Pincer Complexes Indicating a New Mechanism

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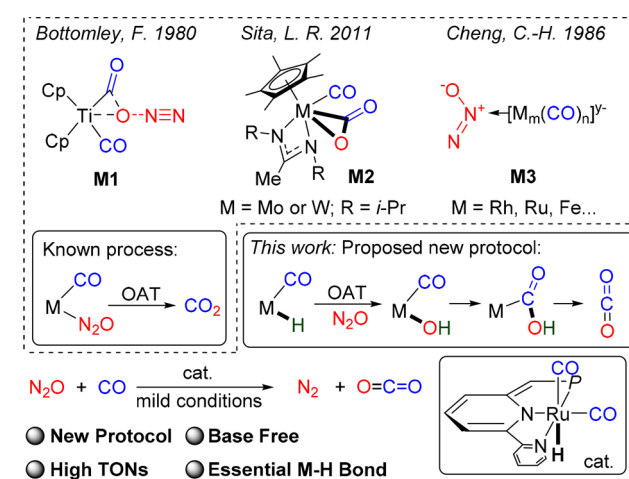
S *Supporting Information*

ABSTRACT: Both CO and N₂O are important, environmentally harmful industrial gases. The reaction of CO and N₂O to produce CO₂ and N₂ has stimulated much research interest aimed at degradation of these two gases in a single step. Herein, we report an efficient CO oxidation by N₂O catalyzed by a (PNN)Ru−H pincer complex under mild conditions, even with no added base. The reaction is proposed to proceed through a sequence of O-atom transfer (OAT) from N₂O to the Ru−H bond to form a Ru−OH intermediate, followed by intramolecular OH attack on an adjacent CO ligand, forming CO₂ and N₂. Thus, the Ru−H bond of the catalyst plays a central role in facilitating the OAT from N₂O to CO, providing an efficient and novel protocol for CO oxidation.

Scheme 1. Homogeneous Reactions of CO and N₂O

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ecause of the widespread use of nitrogenous chemicals in agriculture and industrial processes, N₂O has become the most abundant stratospheric ozone depletion substance and concomitantly one of the most potent greenhouse gases (N₂O is ca. 300 times more potent than CO₂) due to atmospheric concentration increases.[1] To address this environmental issue, efficient destruction/conversion of N₂O, including its degradation or reduction to molecular dinitrogen, is of utmost importance and has drawn much attention.[2] The reaction of CO and N₂O to produce CO₂ and N₂, which is quite exothermic and strongly driven by formation of dinitrogen, is considered an attractive reductive process due to the destruction of two environmentally harmful industrial gases in one step.[3−6] Although heterogeneously catalyzed reactions have been reported,[4] reactions homogeneously catalyzed by metal complexes are rare and desirable,[6] since they may proceed selectively under mild conditions and may provide fundamental mechanistic information.

Experiments aimed at reduction of N₂O by CO involving metal complexes were reported.[5] In early stoichiometric work by Bottomley,[5a] a CO ligand of Cp₂Ti(CO)₂ **1** was converted to free CO₂ under excess N₂O in 15% yield, and the process was suggested to involve reaction of Cp₂Ti(CO)₂ **1** with N₂O, affording [(Cp₂Ti)₄(CO₃)₂] **2**, which upon further reaction with N₂O produces free CO₂ and [Cp₂TiO] **3**. A concerted transient species **M1** (Scheme 1) was proposed, in which the O atom interacts with Ti and CO ligand directly. Sita reported stoichiometric photolytic CO oxidation with N₂O in the presence of Cp*M[η²-N(ⁱPr)C(Me)N(ⁱPr)](CO)₂ (M = Mo

or W) **4**.[5b−d] The reaction was initiated by oxidation of **4** by N₂O forming Cp*M(O)[η²-N(ⁱPr)C(Me)N(ⁱPr)] **5**, releasing N₂ and CO. O-atom transfer (OAT) in the presence of CO afforded CO₂. While catalysis was mentioned, no catalytic data were reported. Homogeneously catalyzed reaction of CO with N₂O was reported by Cheng, using metal carbonyl anions.[6] In this system N₂O was proposed to undergo nucleophilic attack by the anionic metal center of [Rh(CO)₄]⁻, [Fe₂(CO)₈]²⁻, and [Ru₄(CO)₁₃]²⁻ (**M3**, Scheme 1) followed by intramolecular OAT to form CO₂. Although catalytic, a large excess of base was required, and low turnover numbers (TONs) were obtained (maximum ca. 50). Thus, the development of mild and efficient homogeneously catalyzed N₂O reduction by CO is challenging.

As mentioned above, direct interaction between a CO ligand and N₂O was the proposed pathway for CO oxidation by N₂O to form CO₂ and N₂.[5,6] In 2017, we developed the homogeneously catalyzed hydrogenation of N₂O in high TONs, in which selective mono O-transfer from N₂O into a (PNP)Ru−H bond of the pincer catalyst was the key step in the catalysis.[7] The efficient O-transfer into Ru−H was studied computationally,[9] including specifically the (PNP)Ru−H pincer system,[9b,c] and it was concluded to proceed via nucleophilic attack of the hydride ligand on the terminal nitrogen of N₂O, followed by a concerted N₂ liberation.[9,12] This result encouraged us to explore a catalytic

CO oxidation by N_2O initiated by O-transfer into a M−H bond.[8,9] We propose that a H−M−CO complex may undergo O-transfer from N_2O into the M−H bond to generate a HO−M−CO species, followed by intramolecular interaction between M−OH and CO ligand to form a M−COOH intermediate (Scheme 1).[10] CO_2 release in the presence of CO regenerates the H−M−CO complex, thus completing the catalytic cycle. To enable such a homogeneously catalyzed CO oxidation, highly selective OAT from N_2O into M−H bond is needed, without decomposing the complex. Herein, we report the development of mild CO oxidation by N_2O catalyzed by a (PNN)Ru−H complex based on such a mechanism. The reaction proceeds smoothly, yielding high TON under mild conditions, even with no added base.

Initially, CO oxidation by N_2O was examined by treating a premixed solution of 0.01 mmol of the (PNP)Ru complex **6** (P = $P(^iPr)_2$,[11a]) and 1 equiv of *t*-BuOK in 4 mL of toluene under 1 atm of CO and 2 atm of N_2O in a 90 mL Fisher-Porter tube (1 atm of gas in 90 mL corresponds to ca. 3.7 mmol at 20 °C). After heating at 100 °C for 22 h, 0.63 mmol of CO_2 (63 TON) was detected by GC in the gas phase. The reaction occurred smoothly, even using catalytic base. In the absence of **6**, no CO_2 was formed. Moreover, replacing **6** by RuHCl(CO)(PPh$_3$)$_3$ did not lead to CO_2 formation. Other pincer Ru complexes were then screened (Table 1). The complex (PNP)Ru(CO)Cl$_2$ **7** (X-ray characterized[12]) did not lead to any CO_2, indicating that *the Ru−H bond is crucial for the transformation*. With the bulkier complex **8** (P = $P(^tBu)_2$),[11b] only a trace of CO_2 was formed. The PNN complex **9**[8c,11c] was less active than the PNNH complex

10,[11d] which yielded 62 TON of CO_2. The 2,2-bipyridine-based pincer complexes **12** (P = PPh_2)[11e] and **14** (P = $P(^tBu)_2$)[11f] were less efficient and afforded 24 and 22 TON of CO_2, respectively, while use of **13** (P = $P(^iPr)_2$)[11g] resulted in 83 TON of CO_2. Interestingly, the catalytic activity of complexes **13** and **14** in THF was higher than in toluene. In THF at 70 °C, 130 and 197 TON were obtained in the gas phase, respectively, and an additional 40 TON (when using **14**) was detected in solution. Without base, significantly lower catalytic activity was observed, forming only 30 TON of CO_2.

To gain mechanistic information on this catalytic transformation, individual stoichiometric reactions that may be involved in the catalytic cycle using complex **14** as precatalyst were explored. Reaction of **14** with *t*-BuOK is known to occur smoothly to afford the dearomatized complex **15**.[11g] Alarmingly, reaction of **15** with excess N_2O resulted in complete decomposition of the complex. On the other hand, reaction of **15** with excess CO afforded the dearomatized dicarbonyl complex **16**, in which CO coordination stabilizes the dearomatized complex (Scheme 2). Importantly, a competitive experiment of **15** under *both* N_2O and CO (1:1) resulted in the formation of **16** as the major product. Thus, the much faster reaction of **15** with CO prevents the decomposition of **15** caused by over-oxidation by N_2O and enables the catalytic cycle.

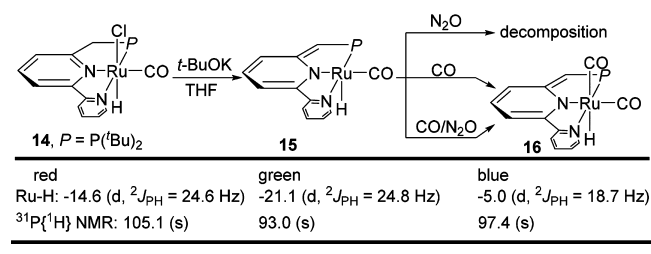**Scheme 2. Reactions of Complex 15 and Formation of 16**

	14, P = $P(^tBu)_2$	**15**	**16**
	red	green	blue
Ru-H:	-14.6 (d, $^2J_{PH}$ = 24.6 Hz)	-21.1 (d, $^2J_{PH}$ = 24.8 Hz)	-5.0 (d, $^2J_{PH}$ = 18.7 Hz)
$^{31}P\{^1H\}$ NMR:	105.1 (s)	93.0 (s)	97.4 (s)

Table 1. Catalyst Screening for CO Oxidation by N_2O^{a-d}

Crystals of complex **16** were obtained by recrystallization from pentane at −35 °C. The X-ray structure of **16** (Figure 1) reveals an octahedral geometry, the hydride ligand being located *trans* to a CO ligand. The dearomatized structure of **16** is clearly indicated by the bond length C(10)−C(11) (1.390(3) Å) being much shorter than a C−C single bond (the corresponding bond
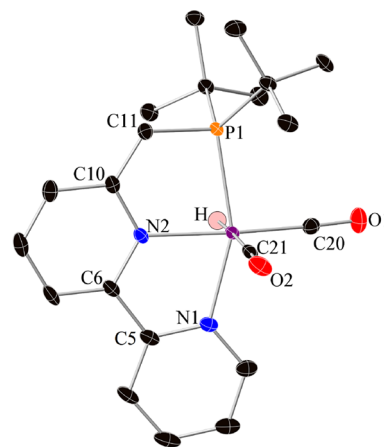

Figure 1. Crystal structure of complex **16**. Atoms are presented as thermal ellipsoids at 50% probability level. Hydrogen atoms, except for Ru−H, are not shown. For selected bond lengths and angles, see SI.

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^{a}All reactions were conducted in a 90 mL Fisher-Porter tube using the catalyst (0.01 mmol), *t*-BuOK (0.01 mmol), 3.7 mmol of CO, and 7.4 mmol of N_2O in 4 mL toluene. ^{b}The catalyst and *t*-BuOK were premixed in the solvent for 20 min and used directly for the reactions. ^{c}The TONs are based on the generated CO_2 as measured by GC of the gas phase calibrated by a standard curve. ^{d}The amount of CO_2 dissolved in toluene was not determined.[13,14] ^{e}The reaction was conducted in THF at 70 °C. ^{f}The amount of CO_2 dissolved in THF was determined as ca. 0.4 mmol (40 TON).[13]

length in complex **17** is 1.508 Å), indicating a significant double bond character.

While the corresponding dearomatized PNP pincer complexes of **6** and **8** are stable,[11a,b] the PNN complex **16** is converted slowly, even at room temperature, to the aromatic complex **17** via C−H activation at the pyridine ring (eq 1).[15,16] The Ru−H of **17** appears in ^{1}H NMR in THF at −5.3 ppm (d, [2]J_{PH} = 17.6 Hz) and ^{31}P{^{1}H} NMR shows a singlet at 88.4 ppm.[12] This transformation is much faster in toluene, providing a possible explanation for the better catalysis in THF than in toluene. Nevertheless, in real-time ^{31}P NMR analysis of the catalytic reaction of CO and N_2O using complex **14** in THF, both complexes **16** and **17** were observed. Interestingly, **17** (0.01 mmol) under 1 bar of CO and 2 bar of N_2O also catalyzed the reaction, but with much lower efficiency, affording only 54 TON of CO_2 in the gas phase. Thus, although **16** is the more active catalyst (see below), participation of **17** in the catalysis cannot be excluded.


$$ (1) $$
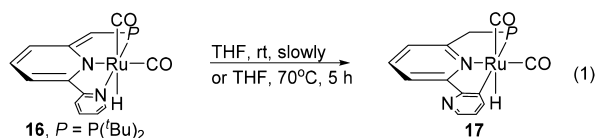
The reaction of complexes **16** or **17** with N_2O (1 equiv or excess) in the absence of CO resulted in decomposition and the Ru−OH complex was not observed. Aiming at generation of (PNN)Ru(OH)X proposed in Scheme 1, the aromatized pincer complex (PNN)RuCl$_2$(CO) **18** was prepared and crystallographically characterized.[12] Complex **18** was subjected to a reaction with 2.2 equiv of [(18-crown-6)K]OH in THF at room temperature (Scheme 3). Interestingly, while the proposed ruthenium dihydroxo complex **M4** and dearomatized ruthenium hydroxo complex **M5** were not detected, treatment of the reaction mixture with CO resulted in formation of the dearomatized hydride complex **16**, and CO_2 (detected by GC), suggesting that the reaction proceeds through halide substitution by [(18-crown-6)K]OH followed by water elimination via metal−ligand cooperation (MLC)[16] forming in the presence of CO the complex **M5**, which is unstable and leads to **16** by releasing CO_2 under CO. The relatively fast intramolecular reaction between the OH group and CO results in CO_2 formation, likely via a RuCOOH intermediate **M6**,[10] and suggests that the catalysis is enabled by O-insertion from N_2O into the Ru−H bond.[7−9] These results suggest that the turnover limiting step in the process is the oxygen-atom-transfer step.

On the basis of these observations and reported DFT studies,[9] a plausible mechanism for this reaction is proposed (Scheme 4). First, the premixed solution of precatalyst **14** and base generates the dearomatized ruthenium complex, which reacts with CO immediately, affording the dicarbonyl complex **16**.[11,12] Efficient

Scheme 3. Reaction of Complex 18 with [(18-C-6)K]OH
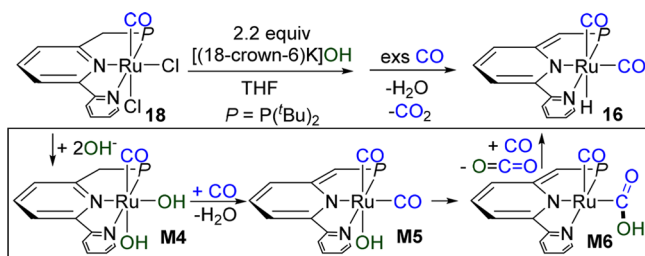
Scheme 4. Possible Mechanism
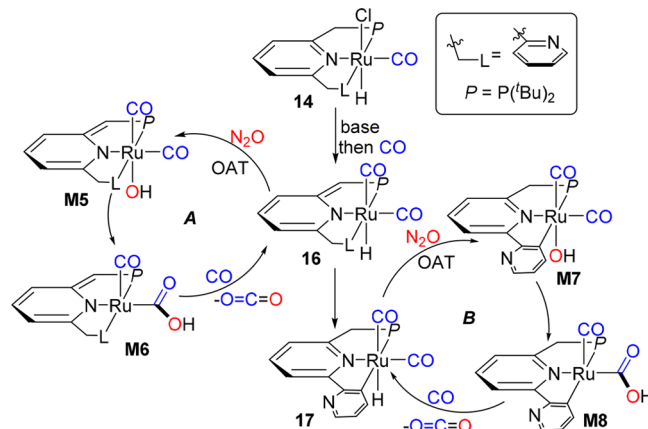
OAT from N_2O into Ru−H, which is likely initiated by nucleophilic attack of the hydride ligand on N_2O,[9] results in formation of a hydroxo intermediate **M5**,[7−9] which might undergo intramolecular nucleophilic attack by hydroxide on the adjacent CO to give a RuCOOH intermediate **M6**,[10] followed by β-H elimination to form CO_2 and regeneration of **16** under CO.[10] In addition, a less efficient mechanism involving complex **17**, obtained during catalysis via MLC[16] and C−H activation,[15] might also take place to some extent, by undergoing OAT (**M7**) and CO_2 formation (**M8**) (catalytic cycle **B**). In both processes, the Ru−H bond plays a key role in assisting OAT to CO. Throughout this catalytic cycle the formal metal oxidation state may not change, providing a novel protocol for CO oxidation by N_2O.

This plausible mechanism encouraged us to explore the catalytic reaction using complex **16** as catalyst *with no added base*. Remarkably, full conversion of CO was achieved by using 0.01 mmol of complex **16** under mild, base-free conditions (eq 2).

$$ (2) $$

$$ (3) $$
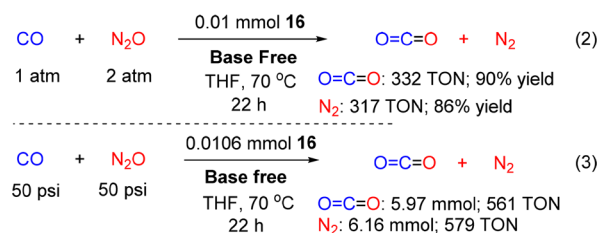
CO_2 was produced in 90% yield (2.72 mmol in the gas phase and 0.6 mmol in solution, for a total of 332 TON) and 86% yield of dinitrogen (3.17 mmol, 317 TON) was determined by GC.

In addition, the highest TONs were achieved by using 0.0106 mmol of **16** as catalyst in the presence of excess of CO (50 psi) and N_2O (50 psi). After heating for 22h, 6.16 mmol of dinitrogen (579 TON) together with 5.97 mmol of CO_2 (4.97 mmol in gas phase and ca. 1.0 mmol in solution; 561 TON) were produced (eq 3).

In summary, a new homogeneously catalyzed reaction of CO and N_2O to produce CO_2 and N_2 was developed. High efficiency and high TON were achieved using the ruthenium complex **14** as the precatalyst or the corresponding dearomatized complex **16** as the actual catalyst. The reaction catalyzed by **16** proceeds smoothly under base-free conditions, providing an efficient method for degradation of both CO and N_2O in a single step. The Ru−H bond is necessary for the catalysis. The catalytic cycle is proposed to involve selective O-atom transfer into Ru−H of

16, intramolecular CO insertion into the resulting Ru—OH, and subsequent CO_2 liberation, regenerating the catalyst **16** in the presence of CO. Quite remarkably, while N_2O alone decomposes the catalyst, this is prevented by the presence of the more reactive CO.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.8b03927.

> Experimental procedures and spectral data (PDF)
> X-ray data for complexes **7**, **16**, **17**, and **18** (CIF)

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Notes
The authors declare no competing financial interest.

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