JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

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Article

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J. Am. Chem. Soc., **Just Accepted Manuscript** • Publication Date (Web): 11 May 2018

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Production of Formamides from CO and Amines Induced by Porphyrin Rhodium(II) Metallo-radical

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ABSTRACT: It is of fundamental importance to transform carbon monoxide (CO) to petrochemical feedstocks and fine chemicals. Many strategies built on the activation of C≡O bond by π-back bonding from the transition metal center were developed during the past decades. Herein, a new CO activation method, in which the CO was converted to the active acyl-like metallo-radical $[(por)Rh(CO)]^{\bullet}$ (por = porphyrin), was reported. The reactivity of $[(por)Rh(CO)]^{\bullet}$ and other rhodium porphyrin compounds, such as (por)RhCHO and (por)RhC(O)NH^{n}Pr, and corresponding mechanism studies were conducted experimentally and computationally, and inspired the design of a new conversion system featuring 100% atomic economy that promotes carbonylation of amines to formamides using porphyrin rhodium(II) metallo-radical. Following this radical based pathway, the carbonylations of a series of primary and secondary aliphatic amines were examined and turnover numbers up to 224 were obtained.

INTRODUCTION

The synthetic utilization of carbon monoxide (CO) in the construction of carbonyl containing organic materials is of great significance in sustainable chemistry.[1-3] The mechanism that predominates over a myriad of CO activation strategies starts from the linear coordination of CO to the metal center, from which the strong C≡O bond is activated by the π-back bonding (Figure 1a). The final products are almost universally formed via nucleophilic attack on the weakened C≡O bond,[4-8] which reduces the scope of substrates eligible for the carbonylation and restricts the design of new CO conversion pathways. Alternative CO activation strategies aiming at breaking this limitation can be envisioned by transforming CO to more reactive intermediates, such as carbonyl cations, anions or radicals (Figure 1b),[9, 10] which can further activate other substrates with low activation energy barriers. However, very few examples have been reported till now as a consequence of the lack of suitable approaches to convert free CO to such reactive intermediates.[11]

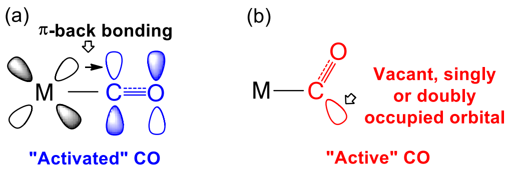


Figure 1. Activated (a) and active (b) “CO” moiety.

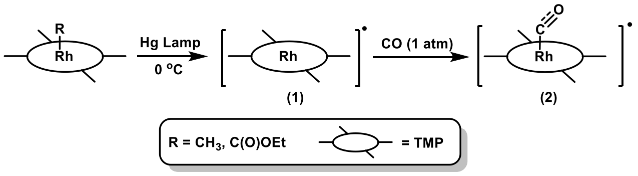
Among all these intermediates, carbonyl radical is of particular interest due to its potential applications in small molecule activation and CO coupling.[12] The $[(por)Rh(CO)]^{\bullet}$ (por = porphyrin) radicals, featuring bent Rh–CO geometries, were reported by Wayland[13] via the coordination of CO to $[(por)Rh(II)]^{\bullet}$ metallo-radical[14]. Considerable spin density was delocalized onto the bent CO ligand as confirmed by EPR measurements.[13, 15] The bent CO ligand showed radical-like reactivity with triorganostannanes to form rhodium formyl complexes (Rh–CHO), with $[(por)Rh(II)]^{\bullet}$ to form dirhodium ketone (Rh–C(O)–Rh), with alcohols to form alkoxyl carbonyl rhodium (Rh–C(O)–OR), and dimerized to form rhodium α-diketone (Rh–C(O)–C(O)–Rh).[13, 16-25] However, further transformations of the activation products are disfavored under thermal conditions because of the rigid planar porphyrin ligand, which blocked the requisite vacant coordination sites for migration-insertion and reductive elimination. Recent progresses in our lab revealed that photolysis of Rh–C bonds might be a productive route to overcome their thermal stability and obtain catalytic turnover in systems involving those novel porphyrin rhodium complexes.[26-28]

Formamides are important intermediates and precursors in organic syntheses of drugs,[29, 30] basic industrial chemicals[31] and reagents in the Vilsmeier formylation reaction.[32] A few homogeneous systems based on dehydrogenative coupling of alcohols and amines[33] showed broad applicability among diverse categories of substrates,[34-38] yet atom-economical synthesis under mild conditions for amides, especially formamides, remains a challenge.[39-42] Synthesis of formamides directly from CO and amines represents a straightforward method. Nevertheless, an efficient realization would require new methods of activation of CO and insertion of amines.[43-47] Herein, by taking advantage of the unusual reactivity of the bent CO metal complex $[(por)Rh(CO)]^{\bullet}$ with N–H bonds in amines, we report a new route for photocatalytic conversion of CO to formamides with 100% atomic economy.

RESULTS AND DISCUSSION

The Rh–C bond in (TMP)Rh–R (TMP = 5,10,15,20-tetramesitylporphyrin, R = alkyl and acyl groups such as CH_3 and C(O)OEt) could be easily photolyzed at 0 °C within 2 hours to obtain $[(TMP)Rh(II)]^{\bullet}$(**1**) (Scheme 1). Pressuring 1 atm of CO into the benzene solution of $[(TMP)Rh(II)]^{\bullet}$ results in near-quantitative formation of $[(TMP)Rh(CO)]^{\bullet}$(**2**) (Scheme 1). Both paramagnetic compounds are identified by EPR measurements (Figure S15, $g_{\perp} = 2.820$, $g_{/\!/} = 1.990$ for **1** ; Figure S16, $g_1 = 2.176$, $g_2 = 2.147$, $g_3 = 1.998$ for **2**), agreeing well with previously reported results.[15, 19]

Scheme 1. Synthesis of 1 and 2.



DFT calculations based on the model rhodium porphyrins, for which all meso-substituents are replaced by hydrogens, showed that the unpaired electron is mainly localized on the Rh metal center (Mulliken spin density: 0.99, Figure 2a) in $[(por)Rh(II)]^{\bullet}$. The optimized structure of $[(por)Rh(CO)]^{\bullet}$ revealed a bent-coordinated CO (Figure 2b) with a Rh-C-O angle of 143.7°. Considerable spin population was found on the carbonyl carbon atom (Mulliken spin density: 0.24), while the Mulliken spin density on Rh metal center is reduced to 0.72, accordingly. In comparison, only a minor fraction of the total spin is delocalized to the oxygen atom in CO (Mulliken spin density: 0.03). The calculated length (1.14 Å) and Mayer bond order (2.29) of the C–O bond in the bent CO ligand is comparable to that of free CO (1.13 Å and 2.44 Å, respectively), indicating a slightly activated C≡O bond as a result of the weak π back-bonding from Rh metal center. Therefore, the geometry and electronic analysis of $[(por)Rh(CO)]^{\bullet}$ are consistent with the presence of the acyl radical like CO ligand, which was also suggested by previous EPR studies.[13]

Inspired by the E–H (H, C, O) bond cleavage of H_2, CH_4 and ethanol by the reactive $[(por)Rh(CO)]^{\bullet}$, which lead to the stoichiometric formation of (por)RhCHO, (por)RhC(O)CH_3 and (por)RhC(O)OC_2H_5, respectively,[21, 25, 48] we speculate that **2** might activate N–H bonds in amines via a similar manner (Scheme 2), forming (TMP)RhC(O)NHR and (TMP)RhCHO (**4**). Interaction of the amine nitrogen atom with **2** is expected to be even more favored than the aforementioned substrates because of the electron deficient acyl radical character of **2**, as revealed by preceding computational studies (Mulliken atomic charges calculated for the carbonyl carbon atoms in free CO and $[(por)Rh(CO)]^{\bullet}$ are -0.013 and 0.12, respectively). At the same time, the bent geometry further reduces steric hindrance around the carbonyl carbon atom in comparison with that for the linear CO.

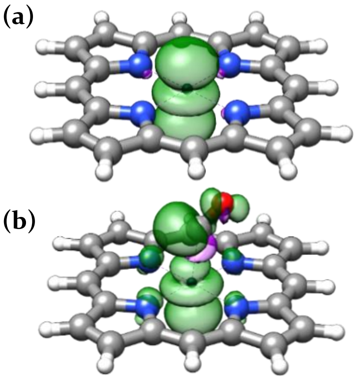
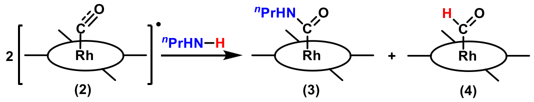


Figure 2. Calculated spin density on model rhodium porphyrin complexes $[(por)Rh(II)]^{\bullet}$ (a) and $[(por)Rh(CO)]^{\bullet}$ (b).

Scheme 2. Activation of N–H bond in amines by 2, taking $^{n}PrNH_2$ (*n*-propylamine) as example.



With these in mind, the reaction of **2** with $^{n}PrNH_2$ was examined. After addition of excess of $^{n}PrNH_2$ (18 equivalents) to the benzene solution of **2**, a set of characteristic multiplets were detected in the high field of ^{1}H NMR spectrum after 2 hours at room temperature (δ 0.60 ppm (m, 2 H, $NHC\boldsymbol{H}_2CH_2CH_3$), -0.60 ppm (m, 2 H, $NHCH_2C\boldsymbol{H}_2CH_3$), -0.67 ppm (t, 3 H, $^{3}J(H,H) = 6.8$ Hz; $NHCH_2CH_2C\boldsymbol{H}_3$), -1.82 ppm (m, 1 H, $N\boldsymbol{H}CH_2CH_2CH_3$), which is identical to that of the independently prepared (TMP)RhC(O)NH^{n}Pr (**3**) (Figure S5). The solid state structure of **3** was determined by X-ray diffraction, as shown in Figure 3a.

The assumed coproduct **4** was not directly observed due to its instability. Instead, (TMP)RhH (**5**) and ^{n}PrNHCHO (**6**) were found. Complexes **6** and **5** are likely generated by the reaction of **4** with $^{n}PrNH_2$ as implied by the independent model reaction between (TPP)Rh–CHO (TPP = 5,10,15,20-tetraphenylporphyrin, **7**, which is an analogue of **4** and can be readily prepared from (TPP)RhH (**8**), and CO)[49] and $^{n}PrNH_2$ (Scheme 3). After vacuum transfer of 1 μL of $^{n}PrNH_2$ to a benzene solution containing an equilibrium distribution of **7** (0.00116 M) and **8** (0.00101 M), which was obtained under 1 atm of CO/H_2 (1:1 v/v), at room temperature in dark, the characteristic high-field ^{1}H NMR doublet of Rh–C***H***O disappeared, accompanied by the formation of **6** after 2 h. The turnover number (TON) of formamide **6** was 42 when a large excess of $^{n}PrNH_2$ was used. During the reaction, the formation of (TPP)RhC(O)NH^{n}Pr (**9**) was also observed using ^{1}H NMR which was stable at this reaction condition thus impeding further catalytic turnover. The solid state structure of **9** was also determined by X-ray diffraction (Figure 3b).

A straightforward strategy for improving the TON of this thermal catalytic carbonylation of amines could be proposed as blocking the formation of **9**. Addition of excess amount of Me_2EtSiH, which is a hydrogen atom donor, was found to effectively increase the thermal catalytic performance (Table S1). The concentration of **2** was significantly lowered due to the hydrogen atom abstraction from Me_2EtSiH by **2**, which led to the generation of **7**, thus hindered the formation of **9** (Scheme S1). Similar reactivity was also seen for other metallocarbonyl radicals.[50, 51] With the presence of 30 equiv. of Me_2EtSiH, TONs ranged from 14 (for cyclohexylamine) to 470 (for *n*-hexylamine) were obtained at room temperature within 7 days (Table S2).

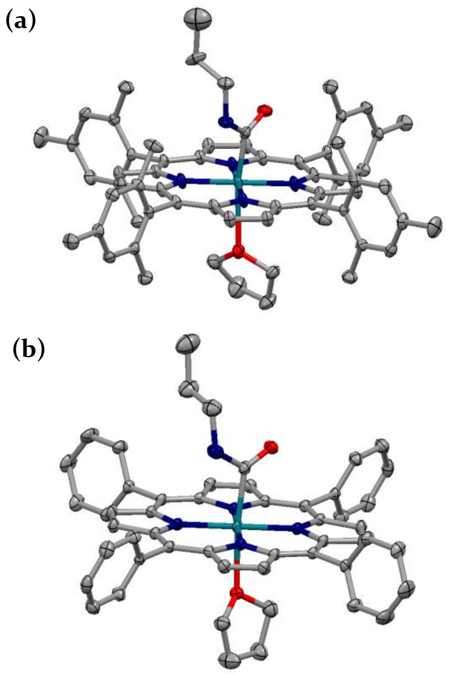
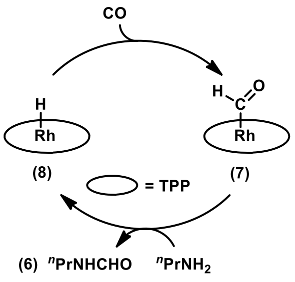


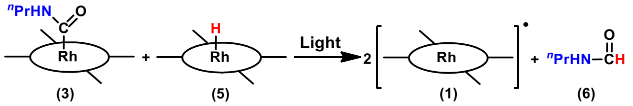
Figure 3. Solid state structures of $(TMP)RhC(O)NH^{n}Pr\cdot THF$ (a) and $(TPP)RhC(O)NH^{n}Pr\cdot THF$ (b). Thermal ellipsoids set at 50% probability; hydrogen atoms are omitted for clarity.

Scheme 3. Formation of formamide 6 from the reaction of 7 with *n*-propylamine.

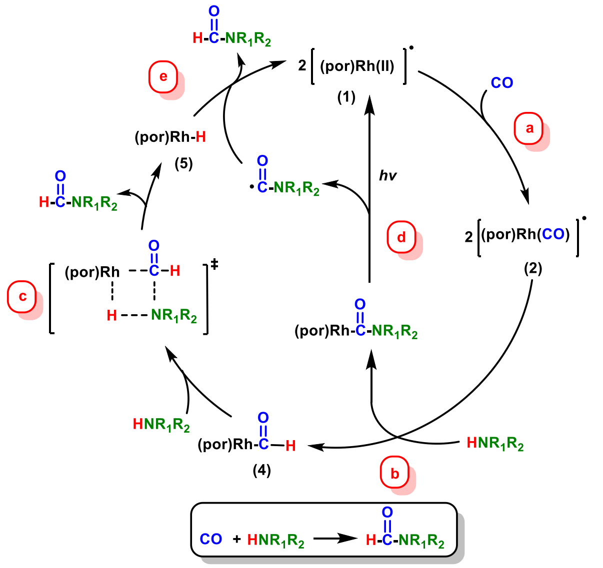


Previously, our lab had reported a photocatalytic hydroxylation protocol for Si–C(sp³) bonds, in which homolytic cleavage of $(por)Rh–CH_3$ bond by photolysis played a vital role in regenerating the active porphyrin rhodium catalyst.[28] We hypothesize that the Rh–C bond in (TMP)Rh–C(O)NHR could also be photolyzed using high voltage mercury lamp as the light source. Photolysis of benzene solution of $(TMP)Rh^{13}C(O)NH^{n}Pr$ led to the formation of $\bullet{}^{13}C(O)NH^{n}Pr$ radical, which was trapped *in situ* by 2,2,6,6-tetramethylpiperidin-1-yl (TEMPO) to form $TEMPO–{}^{13}C(O)NH^{n}Pr$ as detected by high resolution mass spectroscopy ($[M+H]^+$, m/z 244.20997). Meanwhile, generation of $[(TMP)Rh(II)]^{\bullet}$ was also demonstrated by EPR measurement. The active acyl radical could abstract the axial hydrogen atom in **5**, which was a good hydrogen atom donor, thus leading to the formation of target formamide **6** (Scheme 4). The hydrogen source for the product was further confirmed by the isotope-labelling experiment in which $D–{}^{13}C(O)NH^{n}Pr$ was observed during the light irradiation of the benzene solution containing both $(TMP)Rh^{13}C(O)NH^{n}Pr$ and (TMP)Rh–D.

Scheme 4. Formation of formamide 6 by light irradiation of the mixture of 3 and 5.



Scheme 5. Catalytic cycle of photo production of formamides from CO and amines catalyzed by $[(por)Rh(II)]^{\bullet}$.



The abovementioned elementary steps constitute the observed catalytic production cycle of **6** as illustrated in Scheme 5. The formal carbonyl insertion reaction of CO with amine is envisioned to proceed through: a) $[(por)Rh(II)]^{\bullet}$ binds with CO to form $[(por)Rh(CO)]^{\bullet}$; b) the resulting $[(por)Rh(CO)]^{\bullet}$ intermediate reacts with $R^1R^2N–H$ to produce (por)RhCHO and $(por)RhC(O)NR^1R^2$; c) nucleophilic attack of amine to (por)RhCHO releases formamide product and generates (por)RhH; d) photocleavage of Rh–C bond in $(por)RhC(O)NR^1R^2$ regenerates $[(por)Rh(II)]^{\bullet}$, and e) abstraction of H atom from (por)RhH by $\bullet C(O)NR^1R^2$ acyl radical leads to the formation of formamide product and the regeneration of

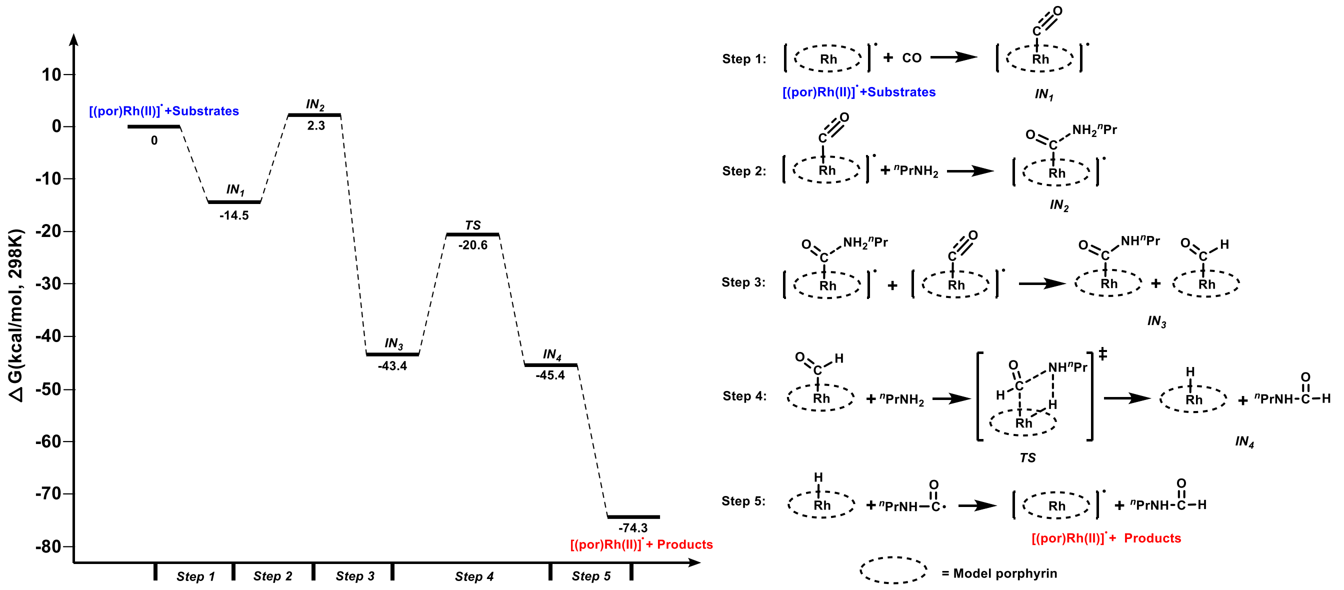


Figure 4. Calculated potential energy surface (PES) for rhodium porphyrin catalyzed production of ^{n}PrNHCHO from CO and ^{n}PrNH$_2$.

$[(por)Rh(II)]^{\bullet}$.

In order to get more insights about the aforementioned catalytic formamide productions, the proposed mechanism was further investigated by DFT calculations based on the model rhodium porphyrin. The calculated potential energy surface (PES) shows that the whole catalytic process is significantly exothermic (Figure 4). The catalytic process is initiated by the coordination of CO to the $[(por)Rh(II)]^{\bullet}$ catalyst (Figure 4, step 1) with a calculated exothermicity of 14.5 kcal/mol, which is in good accordance with the experimentally observed ease of binding of CO to $[(TPP)Rh(II)]^{\bullet}$ or $[(TMP)Rh(II)]^{\bullet}$. The formal overall *ter*-molecular reaction of $[(por)Rh(CO)]^{\bullet}$ with ^{n}PrNH$_2$ (Scheme 5, step b) is achieved by means of two individual elementary reactions to avoid the unfavorable entropy change for the *ter*-molecular pathway: the interaction of ^{n}PrNH$_2$ to the carbonyl group in $[(por)Rh(CO)]^{\bullet}$ (Figure 4, step 2), and reaction of the resulting $[(por)Rh(C(O)NH_2{}^{n}Pr)]^{\bullet}$ with another molecule of $[(por)Rh(CO)]^{\bullet}$, leading to the formation of (por)RhC(O)NH^{n}Pr and (por)RhCHO (Figure 4, step 3). Although the former reaction is endothermic, the latter reaction is strongly exoergic and provides the major driving force for this formal *ter*-molecular reaction. The following reaction of (por)RhCHO with ^{n}PrNH$_2$ producing the final product ^{n}PrNHCHO and (por)RhH (Figure 4, step 4), traverses a moderate activation energy barrier (22.8 kcal/mol). Remarkably, the computed energy barrier for step 4 well matches previously reported β-H elimination processes of rhodium porphyrin based compounds.[52-55] In comparison, no observable energy barriers are identified for other fundamental steps. Step 4 is most likely in equilibrium as indicated by the very small free energy change (~ -2.0 kcal/mol). However, this equilibrium is driven to the right side when coupled with the sequential strongly exoergic hydrogen atom abstraction in (por)RhH by •C(O)^{n}PrNH radical (Figure 4, step 5), which is produced by the photocleavage of the Rh–C bond in (por)RhC(O)NH^{n}Pr, and consequently leads to the formation of the ^{n}PrNHCHO product accompanied by the regeneration of the initial $[(por)Rh(II)]^{\bullet}$ catalyst.

Encouraged and inspired by these mechanistic insights, we optimized the reaction conditions for the catalytic transformation of ^{n}PrNH$_2$ to **6** using the less toxic toluene solvent, and a maximum TON of 224 was obtained as determined by GC (see SI for details). Control experiments showed that there was no conversion without light or catalyst **1**. The source of the carbonyl carbon in **6** was identified to be the CO gas by a ^{13}C-labelling reaction, in which ^{13}CO and ^{n}PrNH$_2$ were used as reactants and H–^{13}C(O)NH^{n}Pr was observed as the product. When ^{n}PrND$_2$ was used, the formyl hydrogen in product **6** was accordingly changed to D, which demonstrated that the hydrogen of the formyl group in the product came from one of the amino hydrogens in the substrate. And when d^8-toluene was used as the solvent, no D was found in **6**, thus excluded the possibility that toluene could act as the hydrogen source. Other substrates, including several primary and secondary amines, were also examined under identical condition with corresponding TONs ranging from 17 (for benzyl amine) to 107 (for *n*-butylamine) (Table S3).

Rhodium(I) porphyrin, which could be generated as a result of σ-donor ligand induced disproportionation of (por)Rh(II),[19] was reported to react with CO to form (por)RhCHO.[48] To further distinguish the presented radical based pathway from the close-shell pathway, the catalytic conversion of piperidine and CO to piperidine-1-carbaldehyde by **2** was monitored using electron paramagnetic resonance. A strong isotropic resonance at g=1.982, which could be tentatively assigned to the

$[(TMP)Rh(piperidine)_2]^{\cdot}$ metallo-radical, was observed and its intensity kept increasing during the measurement (Figure S23). Therefore, although the close-shell pathway could not be completely ruled out at the present stage, the radical based mechanism is thought to account for the production of formamides from amines and CO.

CONCLUSIONS

In conclusion, the reactivity and corresponding mechanism of a series rhodium porphyrins, such as $[(por)Rh(CO)]^{\cdot}$, (por)RhCHO and (por)RhC(O)NH^{n}Pr, were investigated in detail. The combination of these elementary reactions led to the selective production of formamides from CO and amines without the formation of any by-product, thus illustrating a novel metallo-radical based strategy for CO activation and conversion exhibiting 100% atomic economy. As a benefit of the active metallo-radicals and the photochemistry of rhodium porphyrins, the whole conversion proceeded under mild conditions without any sacrificial reagents. This protocol provides new mechanistic insight into conversion of CO to value-added compounds. The tandem reactions designed in this article that activates CO through one electron process may shed light into the design of new catalytic processes in transformation of metal-carbonyl complexes into useful chemicals. Further applications of this system to other substrates are underway.

ASSOCIATED CONTENT

Supporting Information. Additional experimental details, spectral data for related compounds and crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

We gratefully acknowledge financial support from Shanghai Sailing Program (18YF1401800) and National Natural Science Foundation of China (21571009).

ABBREVIATIONS

por, porphyrin; TMP, 5,10,15,20-tetramesitylporphyrin; TPP, 5,10,15,20-tetraphenylporphyrin; THF, tetrahydrofuran; TEMPO, 2,2,6,6-tetramethylpiperidin-1-yl; EPR, electron paramagnetic resonance; TON, turnover number; PES, potential energy surface; DFT, density functional theory.

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