Design, Identification, and Evolution of a Surface Ruthenium(II/III)
Single Site for CO Activation

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Abstract: RuII compounds are widely used in catalysis, photocatalysis, and medical applications. They are usually obtained in a reductive environment as molecular O2 can oxidize RuII to RuIII and RuIV. Here we report the design, identification and evolution of an air-stable surface [bipy-RuII(CO)2Cl2] site that is covalently mounted onto a polyphenylene framework. Such a RuII site was obtained by reduction of [bipy-RuIII(Cl4)]+ with simultaneous ligand exchange from Cl- to CO. This structural evolution was witnessed by a combination of in situ X-ray and infrared spectroscopy studies. The [bipy-RuII(CO)2Cl2] site enables oxidation of CO with a turnover frequency of 0.73 × 10−2 s−1 at 462 K, while the RuIII site is completely inert. This work contributes to the study of structure-activity relationship by demonstrating a practical control over both geometric and electronic structures of single-site catalysts at molecular level.

Introduction

RuIII complexes were first discovered in the 19th century.[3] Their chemistry is diverse and has sparked wide interest in homogeneous catalysis,[2] photocatalysis,[3] and biomedical applications.[4] Most RuII compounds function as reducing agents and only a few RuII complexes with strong-field π-acceptor ligands are air-stable.[5] The standard reduction potentials $E^\circ$ of RuII/RuIII in [Ru(H2O)6]3+/2+ and [Ru(NH3)6]3+/2+ are 0.23 V, 0.10 V, 0.21 V, 0.86 V and 1.24 V, respectively. Nonetheless, the RuII system can be oxidized by molecular O2 at elevated temperatures, limiting its study and application in heterogeneous oxidation chemistry.

Inspired by the relatively high reduction potential of [Ru(bipy)3]3+/2+ pair, we covalently bind bidentate bipyridine (bipy) ligand into the polyphenylene (PPhen) framework via a C–C coupling reaction, converting the bipy ligands from solute molecules into surface binding sites. This enables the design of surface single-site and single-atom catalysts, which mimic molecular catalysts and have unique coordination and electron configuration compared with particles and clusters.[7] These reported single sites, usually supported by metal oxide or carbon, have shown unique activity or selectivity in the water-gas-shift reaction,[8] hydrochlorination,[9] methane activation,[10] CH3OH steam reforming,[11] and hydrogenation.[12] In this work, we successfully designed and prepared the surface [bipy-RuII(CO)2Cl2] single site via simultaneous RuII to RuIII transition and Cl-/CO ligand exchange. Such solid/gas interface coordination chemistry, including both geometric and electronic structures, is monitored by a combination of in situ X-ray absorption fine structure (XAFS), diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), ex situ far-FTIR, X-ray photoelectron spectroscopy (XPS), and density functional theory (DFT) calculations. The [bipy-RuII(CO)2Cl2] site is stable in air for at least 400 days. It enables CO oxidation with a turnover frequency (TOF) of 0.73 × 10−2 s−1 at 462 K, while the RuIII site is completely inert. Such distinct catalytic performance could result from the geometric configuration of...
the [bipy-RuIICl4] site and its optimized energy level that boost CO conversion.

Building a surface single site on PPhen with bipy ligands is proven to be a general and versatile method. Eleven types of uniform and well-defined surface single sites are obtained, including [bipy-FeCl4]−, [bipy-CoCl4]2−, [bipy-Ni(H2O)4]2−, [bipy-CuCl4]2−, [bipy-Cu(H2O)4]2+, [bipy-ZnCl2], [bipy-RuCl4]−, [bipy-RuBr4]−, [bipy-RhCl4]−, [bipy-PdCl4], and [bipy-PtCl4]. This variety of selection including both metal cations and ligands suggests great potential in catalysis and mechanistic understandings.

**Results and Discussion**

**Design and determination of the [bipy-RuIIICl4] single site.**

Our strategy utilizes Suzuki cross-coupling with 5,5-dibromo-2,2′-bipyridine, 1,2,4,5-tetrabromobenzene, and benzene-1,4-diboronic acid as the building blocks (Figure 1 a). The latter two comprise the backbone of the PPhen framework[13] while 5,5-dibromo-2,2′-bipyridine provides bipy ligand functionality. We choose PPhen as the backbone for its pure aromatic structure, microporosity and high thermal stability under air (up to 400°C), as reported previously.[13] Bipy is a typical chelating ligand that can stabilize metal cations.[14] It has been functionalized within the UiO-67[15] and polystyrene system recently.[16] The ratio between 5,5-dibromo-2,2′-bipyridine and 1,2,4,5-tetrabromobenzene determines the amount of bipy ligands in relation to the PPhen-bipy polymer, thereby the loading of single metal sites. The ratio is set to 1:3 for that raising the content of dibromo molecule will increase the linear content of the polymer, decrease the overall surface area and consequently reduce the accessibility to the bipy sites.[17] The PPhen-bipy is Pd free, as shown in the energy dispersive spectroscopy (EDS; Supporting Information, Figure S1).

The PPhen-bipy reacts with RuCl3 to form a [bipy-RuCl4] single site in the presence of HCl, in which the bipy ligand anchors the Ru3+ while Cl− anions are balancing the +3 charge. High density and good dispersion of single sites are achieved, with more than 200 Ru ions identified over 40 nm2 of high angle annular dark field-scanning transmission electron microscopy (HAADF-STEM) image (Figure 1 b). The loading of Ru and Cl is confirmed in the EDS and X-ray photoelectron spectroscopy (Supporting Information, Figures S2, S3). The absorption edge position of Ru K-edge X-ray absorption near-edge structure (XANES) is identical to RuCl3, rather than Ru2 foil or RuO2, suggesting that the oxidation state is Ru3+ (Figure 1 c). The extended X-ray absorption fine structure (EXAFS) further confirms the single-site nature, showing only Ru–N and Ru–Cl scattering with no Ru–Ru scattering (Figure 1 d). The coordination numbers and bond lengths of Ru–N and Ru–Cl scattering are 2.0 ± 0.02 Å and 4.0 ± 0.4 at 2.35 ± 0.01 Å, respectively (Supporting Information, Table S1). The calculated bipy-RuIICl4 structure using DFT (Figure 1 d inlet; Supporting Information, Figure S4a) shows very similar values of Ru–N at 2.096 Å and Ru–Cl at 2.400 Å (Supporting Information, Table S2). The bond lengths in both EXAFS and DFT calculations match the reported value of molecular K[bipy-RuIICl4] complex (2.36 Å for Ru–Cl and 2.02 Å for Ru–N; Supporting Information, Table S3 entry 18).[18] The PPhen-[bipy-RuIICl4]− is stable in air up to 350°C (Supporting Information, Figure S5), suggesting its capability for reactions at elevated temperature even in oxidative environments. The 5.8 wt % Ru loading is calculated from the difference in weight residue between the PPhen-[bipy-RuIICl4]− and PPhen-bipy. The value is smaller than the circa 8.6 wt % Ru loading calculated from the ratio of the bipy ligand in the PPhen-bipy (see calculation in Supporting Information). The possible reasons are the loss of bipy during PPhen-bipy synthesis and the formation of inaccessible bipy site. The BET equivalent surface area is 465 m2 g−1, providing the porous framework for heterogeneous catalysis (Supporting Information, Figure S6 and Table S4). Obtaining such well-defined [bipy-RuIICl4]− site is crucial for determining the solid/gas...
H₂ reduces [bipy-RuIII(Cl)]⁻ into Ru nanoparticles (Supporting Information, Figure S7), owing to the fact that H₂ takes away Cl⁻ and no other ligand is available at the surface to maintain the hexacoordinated octahedral structure. Consequently, CO, as a reductive gas phase ligand, is selected for this ligand exchange reaction at the solid/gas interface. O₂ is co-fed, thereby any detection of the RuII will guarantee its stability under molecular O₂. At room temperature, the initial [bipy-RuIIICl₄]⁻ remains unchanged (Supporting Information, Figure S8), showing no ligand exchange with CO. The release of HCl is observed starting from 433 K (Figure 2a). A surface adsorbed C=O vibration is found in the DRIFTS spectra at 2057 cm⁻¹ (Figure 2b). This vibration absorption corresponds well to the FTIR spectrum of molecular mer(Cl)-[Ru(bipy)-(CO)Cl] (Supporting Information, Table S5 complex D). The fitted EXAFS spectrum shows the decrease of Ru–Cl coordination number from 4.0 ± 0.4 to 3.2 ± 0.2 while maintaining the bond distance at 2.35 ± 0.01 Å (Figure 2c; Supporting Information, Figures S9b, S10b, Table S1). A new Ru–CO scattering is observed at 1.88 ± 0.02 Å with a coordination number of 1.1 ± 0.2 (Figure 2c; Supporting Information, Table S1). The bond lengths are the same as the values reported for molecular mer(Cl)-[Ru(bipy)(CO)Cl] (Ru–N 2.08 Å, Ru–Cl 2.33 Å, and Ru–C 1.89 Å; Supporting Information, Table S5 complex D).[19] Similar bond lengths are also confirmed by the DFT calculations (Supporting Information, Figure S4b, Table S2). No obvious edge shift is observed in the XANES, suggesting the unchanged oxidation state of RuIII (Supporting Information, Figure S9a, S10a). We conclude that majority of the RuII surface complex becomes mer(Cl)-[bipy-RuII(CO)Cl] via:

\[
\text{mer(Cl)}-\text{[bipy-RuII(CO)Cl]} \rightarrow \text{mer(Cl)}-\text{[bipy-RuII(CO)Cl]+ HCl}
\]

A further increase in the temperature does not result in any significant changes in the online MS profile, in situ DRIFTS and XAFS spectra (Figure 2a; Supporting Information, Figure S9). This shows that CO can only replace Cl⁻, while the reduction of Ru⁺ requires H₂. H₂ is added to the feed in order to reduce Ru and remove another Cl⁻ ligand. HCl is detected in the MS, suggesting the reaction between H₂ and the Cl⁻ ligand (Figure 3a). DRIFTS and FTIR spectra show a second C=O stretching vibration absorption at 1996 cm⁻¹ when H₂ is introduced (Figure 3b; Supporting Information, Figure S12a). The far-FTIR spectra shows only one type of Ru–Cl stretching at 331 cm⁻¹ (Supporting Information, Figure S12b). These results match the FTIR spectrum of molecular cis(CO)-trans(Cl)-[Ru(bipy)-(CO)Cl] (Table S5, complex E) but are different from cis(CO)-cis(Cl)-[Ru(bipy)(CO)Cl] (Supporting Information, Table S5, complex F, 2040 and 1980 cm⁻¹).[20] From analysis of the EXAFS spectrum, the Ru–Cl coordination number is reduced to 2.2 ± 0.3 with a slight increase of bond length to 2.39 ± 0.01 Å, confirming the ligand exchange of Cl⁻ via CO with the help of H₂ (Figure 3c; Supporting Information, Figures S10a and Table S1). As a result, the coordination number of Ru–CO at 1.88 ± 0.01 Å increases to 1.9 ± 0.3 (Supporting Information, Table S1).[21] DFT calculations are performed accordingly with cis(CO)-trans(Cl)-[Ru(bipy)-(CO)Cl], showing similar Ru–Cl bond length (2.339 Å) and a slightly longer Ru–CO bond length (2.002 Å; Supporting Information, Figure S4c, Table S2).

Ru L-edge and Cl K-edge XAFS spectra were measured to determine the oxidation state of Ru. At Ru L₁-edge region, two absorption features A at 2838.0 eV and B at 2840.9 eV have been found for the initial [bipy-RuIIICl]⁻ site (Fig-
This proves that Ru 4d εg orbitals are not completely filled and are in the form of Ru II 4d εg, which is in good agreement with the Ru K-edge XANES spectrum (Figure 1c). For cis(CO)-trans(Cl)-[RuII(bipy)(CO)2Cl2] sites, feature A disappears, and a new feature C appears at 2843.0 eV. The absence of feature A suggests completely filled Ru II 4d εg orbitals. Thus, the reduction from Ru III to Ru II is confirmed. The additional feature C is assigned to Ru 2p3/2 → CO π* transition. The CO π* orbitals are formed above Ru 4d εg as a result of Ru–CO π backbonding. Similar electronic structures are also obtained from the Ru L3-edge XAFS spectra (Supporting Information, Figures S13, S14). The Ru K-edge spectra show no obvious changes, resulting from the dipole forbidden 1s → 4d transition that prevents the detection of valence orbitals (Supporting Information, Figures S10c, S15, Table S7).

In Ru–Cl complexes, d–p hybridization enables the transition from Cl 1s to Ru 4d.[23] The Ru K-edge XAFS can also validate the Ru oxidation state. There is a strong pre-edge absorption feature E at 2823.8 eV for both [bipy-RuIII(Cl)4] and cis(CO)-trans(Cl)-[RuII(bipy)(CO)2Cl2] sites in the Cl K-edge XAFS, representing the Cl 1s → Ru 4d εg transition (Figure 3c). The [bipy-RuIII(Cl)4]- site shows a feature D at 2820.8 eV, which is absent in cis(CO)-trans(Cl)-[RuII(bipy)(CO)2Cl2] site. This feature originates from Cl 1s to unfulfilled Ru III 4d εg. Therefore, the reduction is further verified via Cl K-edge XAFS. It also suggests that the Cl is not an outer shell counter anion but is in a close coordination environment with Ru cation.[25b, 26] The energy differences between features A and B as well as D and E are 2.9 eV and 3.0 eV, respectively. Such ligand field splitting energy Δ0 at core hole state is between 23400 to 24200 cm⁻¹, which corresponds well with the absorption at 352 nm in UV/Vis spectra (Supporting Information, Figure S16). Furthermore, XPS at the Ru 3d region also confirms the change of oxidation states, showing a decrease of the Ru 3d5/2 binding energy from 282.4 eV to 281.8 eV (Supporting Information, Figure S17 and Table S8). As such, we confirm that the reaction mechanism followed is:

\[ 2\text{mer(Cl)}:\text{[bipy-Ru}^{III}\text{(CO)Cl}_4] + 2\text{CO} + \text{H}_2 \rightarrow 2\text{cis(CO)-trans(Cl)}:\text{[Ru}^{II}\text{(bipy)(CO)Cl}_2] + 2\text{HCl} \] (2)

Molecular O2 is constantly present in the system and an air stable cis(CO)-trans(Cl)-[RuII(bipy)(CO)2Cl2] site is achieved.

**CO Oxidation over RuII and RuIII Single Sites**

Further increasing the temperature shows the release of CO2 from 503 K (Figure 3a). This suggests that cis(CO)-trans(Cl)-[RuII(bipy)(CO)2Cl2] is active for CO oxidation. We perform CO oxidation for both mer(Cl)-[bipy-RuIII(CO)Cl4] and cis(CO)-trans(Cl)-[RuII(bipy)(CO)2Cl2] sites. The former shows no conversion whereas the latter gives a light off at 388 K and 35% conversion at 453 K. \( p_{\text{CO}} = 0.01 \) bar and weight hourly space velocity (WHSV) of 60,000 mLh⁻¹g⁻¹ (Supporting Information, Figure S18). An activation energy \( (E_a) \) of 90 kJmol⁻¹ is determined at the WHSV of 60,000 mLh⁻¹g⁻¹. Based on the EXAFS study of the cis(CO)-trans(Cl)-[RuII(bipy)(CO)2Cl2] site and its narrow full width at half maximum (FWHM) of CO absorption in FTIR spectra (Supporting Information, Figure S12a), we assume that all the RuII sites are identical and perform the same in CO oxidation. The corresponding TOFs are then calculated as \( 0.73 \times 10^{-2} \) s⁻¹, \( 1.77 \times 10^{-3} \) s⁻¹, and \( 3.89 \times 10^{-3} \) s⁻¹ at 462, 479 and 498 K, respectively. The TOF and \( E_a \) are similar to the
state-of-the-art Cu and Pt single site over metal oxide support for CO oxidation (Supporting Information, Table S9). HAADF-STEM images show the high density of Ru\textsuperscript{ii} cations well dispersed on the polymer framework after catalysis for cis(CO)-trans(Cl)-[Ru\textsuperscript{ii}(bipy)(CO)\textsubscript{3}Cl\textsubscript{2}] site (Supporting Information, Figure S19). There is no sign of aggregation or cluster formation, which is further proved via ex situ XRD studies (Supporting Information, Figure S19a–f).

The Ru\textsuperscript{ii} retains the cis(CO)-trans(Cl)-[Ru\textsuperscript{ii}(bipy)(CO)\textsubscript{3}Cl\textsubscript{2}] structure, as indicated in the XAFS (Supporting Information, Figure S19g–i) and FTIR (Supporting Information, Figure S12c) studies after catalysis. The PPhen-bipy polymer remains unchanged, according to the post catalysis FTIR and scanning electron microscopy analysis (Supporting Information, Figure S12c and Figure S20). This is because of its high stability in air at elevated temperatures (Supporting Information, Figure S5c). The activity of cis(CO)-trans(Cl)-[Ru\textsuperscript{ii}(bipy)(CO)\textsubscript{3}Cl\textsubscript{2}] is stable during the 24 h on stream stability test (Supporting Information, Figure S21). The distinct differences in CO oxidation activity between mer(Cl)-[bipy-Ru\textsuperscript{ii}(CO)\textsubscript{3}Cl\textsubscript{2}] single site and cis(CO)-trans(Cl)-[Ru\textsuperscript{ii}(bipy)(CO)\textsubscript{3}Cl\textsubscript{2}] single site are resulted from their geometric and electronic properties. Geometrically, the former has three Cl\textsuperscript{-} ligands, which are strong binding ligands in metal complexes (poisonous for metal active center) and leaves only one CO ligand to be exchanged during catalysis. In comparison, the latter offers two exchangeable CO ligands in cis configuration, enabling the local activation of CO within the Ru coordination environment. Electronically, the Ru\textsuperscript{ii} is in a reduced form, which is reported to activate CO in water-gas-shift reaction.\[27\]

The role of the halogen ligand is further studied via [bipy-Ru\textsuperscript{ii}Br\textsubscript{4}]\textsuperscript{-} single site, where Br\textsuperscript{-} is a better leaving group than Cl\textsuperscript{-} according to solution based coordination chemistry. The transition from [bipy-Ru\textsuperscript{ii}Br\textsubscript{4}]\textsuperscript{-} to [bipy-Ru\textsuperscript{ii}(CO)Br\textsubscript{2}] takes place at room temperature while the reduction from [bipy-Ru\textsuperscript{ii}(CO)\textsubscript{3}Br\textsubscript{2}] to [bipy-Ru\textsuperscript{ii}(CO)Br\textsubscript{2}] requires 513 K (Supporting Information, Figure S22 and Table S2). This is 40 K higher than the temperature required to reduce the Cl coordinated Ru single sites. Without the presence of solvent, the bond breaking and formation here at the solid/gas interface are different.

General Synthetic Strategy

The homogeneity of the single sites is crucial to provide a key platform to investigate the structure–activity relationship. [26] Here in the PPhen-bipy system, the bidentate nitrogen is a key platform to investigate the structure–activity relationship. The homogeneity of the single sites is crucial to provide a key platform to investigate the structure–activity relationship. We have designed an air-stable cis(CO)-trans(Cl)-[Ru\textsuperscript{ii}(CO)\textsubscript{3}Cl\textsubscript{2}] single site over a PPhen-bipy framework with molecular-level accuracy. Compared to the completely inert Ru\textsuperscript{ii} site, the Ru\textsuperscript{ii} site is active for CO oxidation owing to its unique electronic and geometric structure. Such a Ru\textsuperscript{ii} single site can only be formed in the simultaneous Ru\textsuperscript{ii} to Ru\textsuperscript{ii} reduction by H\textsubscript{2} and the ligand exchange from Cl\textsuperscript{-} to CO. With the help of a well-defined pristine single site, such solid/gas interface coordination chemistry can be used to explain the surface bond breaking and formation at molecular level. The design method is generally applicable and is versatile for metal centers that are ubiquitous in catalysis, as supported by the synthesis of [bipy-MX\textsubscript{n}] sites for another nine elements.

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Figure 4. HAADF-STEM and EXAFS identifications of single site PPhen-[bipy-MX₄] structure. Cs-corrected HAADF-STEM images show the single metal ions supported on PPhen-bipy for a) Fe³⁺, b) Co²⁺, c) Ni²⁺, d) Cu²⁺, e) Zn²⁺, f) Rh³⁺, g) Pd²⁺, and h) Pt⁴⁺. Clusters and nanoparticles are observed in HAADF-STEM images for PPhen-bipy supported i) Ag⁺, j) Sn⁴⁺, k) Ir³⁺, and l) Au³⁺. Corresponded experimental and fitted EXAFS results are shown in a) [bipy-FeCl₄]⁻, b) [bipy-CoCl₂], c) [bipy-Ni(H₂O)₄]²⁺, d) [bipy-CuCl₂], e) [bipy-ZnCl₂], f) [bipy-RhCl₄]¹⁻, g) [bipy-PdCl₂], and h) [bipy-PtCl₄], respectively. The coordination number and distance of M⁻Cl and M⁻N are listed in the Supporting Information, Table S3.
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The authors declare no conflict of interest.

Keywords: heterogeneous catalysis · ruthenium(II/III) complexes · single site · surface coordination chemistry · X-ray absorption spectroscopy

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