# Formal Oxidation States and Coordination Environments in the Catalytic Reduction of CO to Methanol

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## Abstract

Fundamental insight into multi-electron, multi-proton redox reactions with organometallic catalysts is greatly facilitated by knowledge of the formal oxidation state of the metal center in each of the elementary reaction steps that comprise the catalytic cycle. X-ray absorption near edge structure (XANES) is utilized herein to quantify the oxidation states and coordination environment of the organometallic resting state and intermediates in a newly proposed catalytic reduction of carbon monoxide to methanol.

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The formal oxidation state of an organometallic catalyst has been defined as "the charge left on the central metal atom when each shared electron pair is assigned to the more electronegative atom.[1]" Knowledge of formal oxidation states enables one to understand and predict reactivity that is of particular interest for multi-electron, multi-proton transfer transformations.[2] However, stripping the ligands off a metal and assigning a formal oxidation state is non-trivial, especially when non-innocent redox active ligands are present. Oxidation states assignments are hence a particular challenge for the catalytic reduction of CO or $CO_2$ that typically includes both ligand- and metal-based reductions.[3] Herein, X-ray absorption near edge structure spectroscopy (XANES), is utilized to characterize the reduction of CO to methanol for the first time in a newly proposed catalytic cycle that utilizes renewable organic hydrides.[4]

Figure 1a shows the proposed catalytic cycle for *cis*-$[Ru(bpy)_2(CO)_2]^{2+}$, where reduction by a dihydrobenzimidazole hydride results in quantitative generation of a formyl intermediate, *cis*-$[Ru(bpy)_2(CO)(CHO)]^+$ that was suggested to occur by an electron transfer – proton-coupled electron transfer (ET-PCET) mechanism with a kinetic isotope effect (KIE) of 9.6.[4] The initial and uphill electron transfer to a bipyridine ligand followed by downhill PCET to a carbonyl ligand is mechanistically entangled and represents an overall hydride transfer process. Hence the formal oxidation state of the metal center was thought to be Ru(II). The second mechanistic step is reduction of the formyl to the hydroxymethyl complex, *cis*-$[Ru(bpy)_2(CO)(CH_2OH)]^+$, that requires both a hydride transfer and a proton transfer. Here again, the reduction was presumed to be ligand based with maintenance of the Ru(II) state, yet the reaction stoichiometry was unclear.[4] Attempts to hydrolyze the hydroxymethyl ligand with acid were unsuccessful and instead visible light excitation resulted in methanol formation. The subsequent coordination of CO is proposed to regenerate the resting state completing the catalytic cycle.[4]

Figure S1 shows the Ru K edges for the resting state of three key Ru complexes in the catalytic cycle. The deep absorption edges for all these Ru complexes were fully consistent with a formal oxidation state of II,[3,5,6] and differed significantly from the spectrum expected of Ru complexes with an oxidation state of III.[7] In addition, a similar geometry for the ligands around the Ru metal center led to pre-edges with a close position and intensity.[6] Overall, there are no substantial changes in the electronic properties of the Ru center when switching ligands in the catalytic cycle of Figure 1a. Hence the X-ray data support the prior assertion that multi-electron and multi-proton reduction of this metal carbonyl complex is entirely ligand based without involvement of metal centered redox chemistry and suggest that catalysis would be operative with alternative metal carbonyl complexes that are stable in a single oxidation state.

The top panel in Figure 1b shows the corresponding Ru $L_3$ edge (2p → 4d) spectra. The $L_3$ edge is more sensitive to changes in the metal-ligand interactions than the K-edge.[3,8-10] Importantly, there were no features near 2838 eV where Ru(III) complexes are known to absorb.[3,8-10] A comparative analysis of the spectra for the Ru-complexes in the catalytic cycle reveals that the main edge energy is the same (~2842 eV) which again supports the Ru(II) assignment.[8-10] Also noted is the strong edge feature for these complexes. Detailed analysis of the Ru $L_3$-edge features typically requires higher levels of theory,[3,8-10] yet the results of our TD-DFT calculations (Figure S2) corroborate the experimental results in Figure 1b that point to strong bonding interactions

between the Ru center and the $CH_2OH$ ligand that can be challenging when closing the catalytic cycle.[4] CO is known to increase the intensity of Ru $L_3$-edge spectra by withdrawing electron density through a bonding mechanism that involves π-backdonation.[11] The –COH and $–CH_2OH$ ligands have a formal charge of –1 and donate more charge to Ru than CO. While this appears to be the first XANES spectra reported for a hydroxymethyl complex, evidence for a strong bond exists in previously reported $^1$H NMR spectra and reactivity studies of hydroxmethyl complexes.[4] An AB pattern for -$CH_AH_B$-OH (δ 4.34, 4.37, 4.45, and 4.47 ppm; $^2J_{AB}$ = 7.24 Hz) was assigned to diastereotopic H atoms in the -$CH_2$ group[4,12] indicative of hindered rotation and a higher bond-order for the Ru–C bond. A related ABX pattern -$CH_AH_BOH_x$ (δ 5.55, 5.15 and 3.94 ppm; $^3J_{AX}$ = 6.1 Hz, $^3J_{BX}$ = 5.5 Hz, $^2J_{Ab}$ = 9.3 Hz was reported for [Re(Cp)(CO)(NO)($CH_2OH$)][13] while a singlet was observed in [Re(bpy)$(CO)_3$($CH_2OH$)] indicating a similar environment for the H atoms and free rotation about the M–C bond in the latter.[14] The computed Re-C distances in Re-$CH_2OH$ of 2.107 Å for [Re(Cp)(CO)(NO)($CH_2OH$)] and 2.193 Å for [Re(bpy)$(CO)_3$($CH_2OH$)] indicate a stronger Re-C bond in the former complex that explains the diastereotopic nature of the -$CH_2$ protons in this complex. Such bonding behavior has not been previously reported and represents an important consideration for this critical intermediate in methanol synthesis and Fischer-Tropsch catalysis.[1]

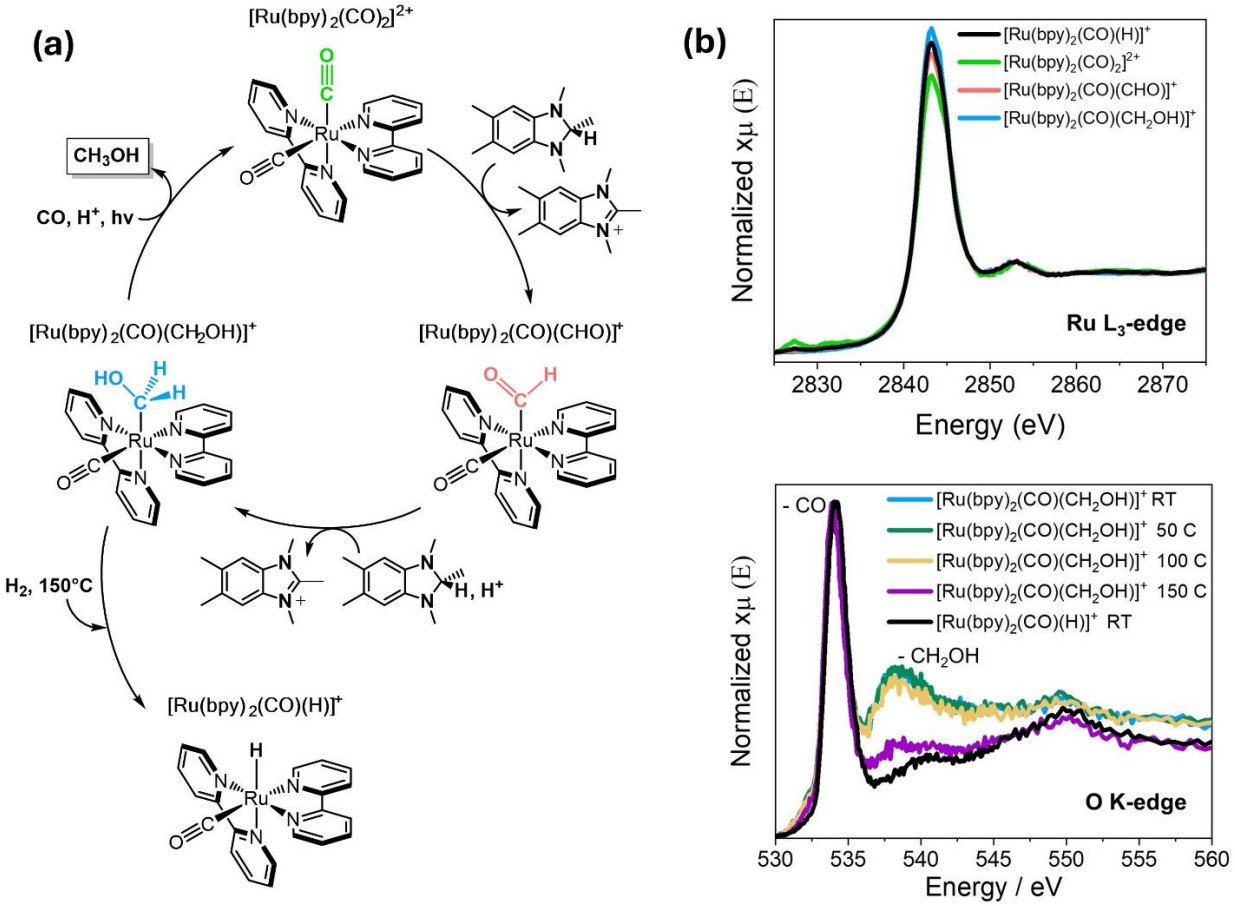

**Figure 1.** a) The proposed catalytic cycle for reduction of CO to methanol with renewable dihdrobenzimidazole organic hydrides. b) The XANES Ru $L_3$ and O K-edge spectra of organometallic Ru complexes present in the catalytic cycle. In the experiments at the O K edge, we started with a solid $[Ru(bpy)_2(CO)(CH_2OH)]^+$ complex that was exposed to gaseous $H_2$ (10 Torr) at different temperatures. By 150 ºC, the $CH_2OH$ group was hydrogenated and the transformation into $[Ru(bpy)_2(CO)(H)]^+$ was complete, presumably with release of methanol.

Measurements at the O K-edge (Figure S3) show distinctive features for the Ru complexes that have been assigned to CO, HCO and $CH_2OH$ ligands (see SI for details). *In situ* measurements at the O K-edge border were used to examine the stability of the $[Ru(bpy)_2(CO)(CH_2OH)]^+$ complex under a $H_2$ atmosphere (bottom panel in Figure 1b). Consistent with the results at the Ru $L_3$-edge, a strong bond between Ru and the $CH_2OH$ ligand resulted in a relatively high temperature (150 ºC) for complete $[Ru(bpy)_2(CO)(CH_2OH)]^+ \rightarrow [Ru(bpy)_2(CO)(H)]^+$ conversion.

In conclusion, X-ray absorption spectroscopy is shown to be a powerful tool for the characterization of species involved in the mechanism of CO reduction to methanol, providing insights into the bonding and stability of key species. The data reveal that methanol generation by renewable organic hydrides occurs by multi-electron, multi-proton transfer to the CO ligand while the metal center remains in the Ru(II) formal oxidation state. The Ru $L_3$ and O K edge features indicate a strong Ru–C bond in $[Ru(bpy)_2(CO)(CH_2OH)]^+$ that is consistent with the resilience of this complex in fluid solution and at high temperatures. These types of insights could not have been garnered from conventional techniques and indicate that X-ray absorption spectroscopy is not restricted to the oxidizing conditions necessary for water oxidation[15] and will emerge as a new means to characterize important catalytic reductions.

## Associated Content

## Supporting Information

Additional experimental details, materials, theoretical methods; XAS spectra for the investigated compounds.


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