Following CO and H insertion into Ru-C bonds with X-ray photoelectron and absorption spectroscopies

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Abstract

Insertion reactions play a central role in the catalytic synthesis of higher alcohols. X-ray photoelectron and absorption spectroscopies have been used to follow migratory CO insertion and C─C coupling in a $[Ru(2,2'\text{-bipyridine})_2(CO)(CH_3)]^+$ complex heated in vacuum or exposed to CO. Heating of the Ru complex in vacuum to temperatures above 50 ^oC induced spontaneous migration of CO into the Ru─CH_3 bond to yield a ─$COCH_3$ ligand. After adding CO to the background gas, the CO insertion reaction was seen at room temperature, opening the door for the synthesis of ethanol and more energy dense liquids.

In homogeneous and heterogeneous catalysis, CO insertion into metal-alkyl bonds plays a central role in the synthesis of ethanol and higher alcohols.[1,2,3,4,5] It is also the key C-C bond forming step in many organic reactions focused on the preparation of commodity goods or pharmaceutical compounds.[6] In homogeneous catalysis, the nature of the solvent can affect the rate of CO insertion into metal-alkyl bonds.[6] In principle, the solvent (S) can accelerate the insertion reaction by taking the place of CO in the first coordination sphere of the metal center {OC-M-R + S → S-M-C(O)R}, or it can surround CO and the metal center substantially slowing down the insertion process.[6] At a conceptual level, a better understanding of CO insertion reactions with and without a solvent is important for an optimization of catalytic processes in liquid, liquid-solid, and gas-solid media.

Recently, ruthenium polypyridyl complexes are receiving a lot of attention due to their central roles in the catalytic conversion of CO_2 or CO to light alcohols.[7,8,9,10] For example, $[Ru(bpy)_3]^{2+}$ (bpy = 2,2'-bipyridine) photoactive centers were incorporated into Cu-based metal-organic frameworks for catalytic CO_2 hydrogenation to ethanol under 2 MPa of H_2/CO_2 = 3:1 at 150 °C.[8] More recently, the conversion of CO to methanol mediated by *cis*-$[Ru(bpy)_2(CO)_2]^{2+}$ has been achieved at room temperature and ambient pressure, using organic hydrides and light.[7] In this transformation, key intermediates such as *cis*-$[Ru(bpy)_2(CO)(CHO)]^{+}$ and *cis*-$[Ru(bpy)_2(CO)(CH_2OH)]^{+}$, shown in Figure 1a, were detected and characterized.[7] X-ray Absorption Near-Edge Structure (XANES) experiments at the Ru K- and L_3-edges, as well as at the O K-edge, indicate that the Ru remains in a formal oxidation state of II during the CO → CH_3OH conversion, with all the reduction chemistry occurring at a single carbonyl ligand,[11] a behavior consistent with other experimental data. A strategy to extend this carbonyl chemistry for the generation of ethanol, with a larger energy density than methanol, is proposed (right side of Figure 1a) and tested herein.

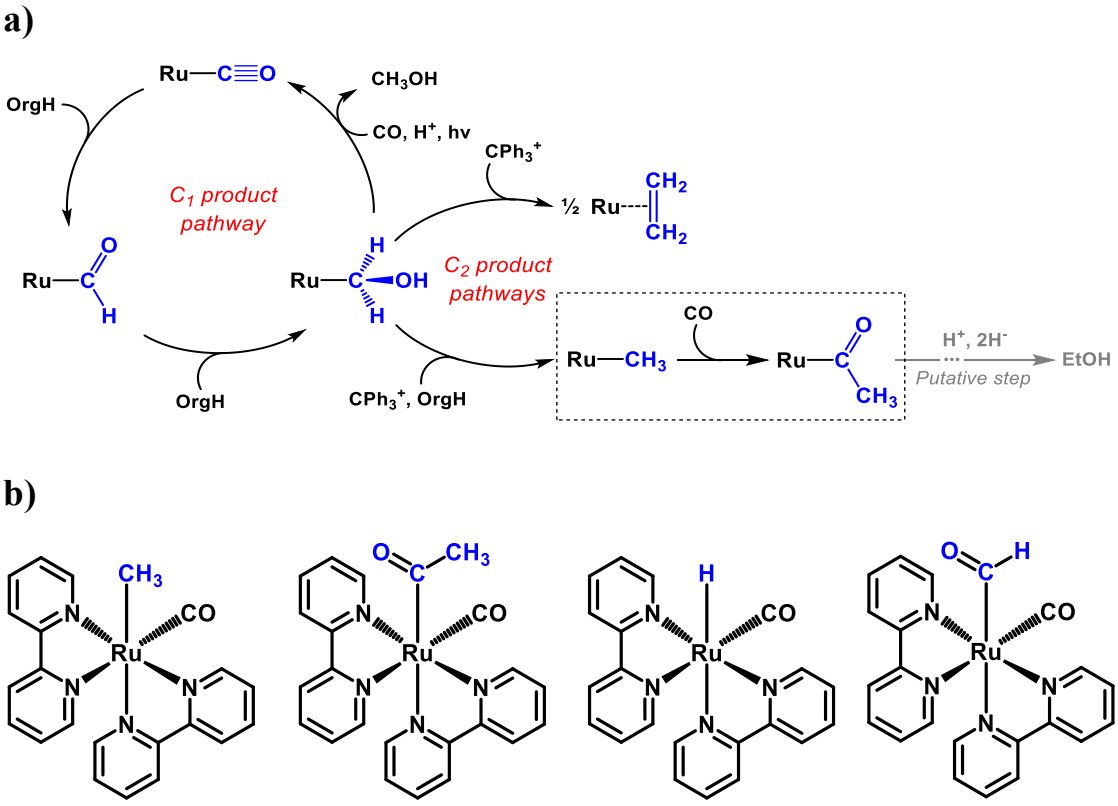

Figure 1. a) Proposed pathways for the catalytic production of methanol and for the generation of ethanol promoted by reaction of *cis*-$[Ru(bpy)_2(CO)_2]^{2+}$ with organic hydrides. b) Structures of the involved Ru complexes.

In this study, four well known Ru complexes,[7,12,13,14] whose structure is shown in Figure 1b, have been investigated. X-ray photoelectron spectroscopy (XPS) and XANES were utilized to follow the insertion of CO into a Ru-CH_3 bond at the solid-gas interface. As a background to the studies reported below, it is important to clarify several steps in the catalytic cycle depicted in Figure 1a. Reaction of *cis*-$[Ru(bpy)_2(CO)(CH_2OH)]^+$ with a trityl (CPh_3^+) carbocation in a weakly coordinating solvent resulted in the formation of a transient carbene complex.[15,16] This carbene complex reacted further to form an ethylene ligated complex $[Ru(bpy)_2(CO)(H_2C{=}CH_2)]^{2+}$ (Figure 1a) as confirmed by ^{1}H Nuclear Magnetic Resonance (NMR) spectroscopy, Figure S1. This chemistry has been recently studied in detail.[17] On the other hand, the sequential addition of the organic hydride PMBIH and CPh_3^+ resulted in the formation of the methyl complex *cis*-$[Ru(bpy)_2(CO)(CH_3)]^+$ (see Figure 1a). This finding was also corroborated by ^{1}H NMR and high-resolution mass spectrometry (Figures S2 and S3). PMBIH was the organohydride of choice due to its large hydricity and well characterized reactivity with

ruthenium carbonyls.[7] The next step to higher nuclearity alcohols involves CO insertion into the Ru─CH_3 bond to form Ru─$COCH_3$. Indeed, $[Ru(bpy)_2(CO)(CH_3)]^+$ and $[Ru(bpy)_2(CO)(COCH_3)]^+$ are both known species,[12,13] Figures S4-S6, that were independently synthesized. Such C─C coupling reactions are usually proposed as a single mechanistic step in a catalytic cycle but are rarely observed experimentally, especially for heterogenous catalysts.[18,19] Attempts to insert CO into the Ru-CH_3 bond of $[Ru(bpy)_2(CO)(CH_3)]^+$ to yield the corresponding acetyl intermediate in dichloromethane or acetonitrile solutions of the complex were unsuccessful. Even under a very high CO pressure of 2.026 x 10^6 Pa (20 atmospheres), there was no evidence for C-C bond formation. However, as we will see below, the reaction of the isolated solid complex with CO in the gas phase provided an alternative approach that was successful.

The oxidation state of the four Ru complexes was examined through ex-situ measurements of the Ru K-edge. Metallic Ru and Ru(IV)O_2 have a distinctive line shape that is very different from that observed in Ru(II) containing compounds.[20-26] As demonstrated in Figure 2a and 2b, the results of the Ru K-edge indicate that all of the Ru complexes present the same formal oxidation state, which is Ru(II).[20,21] Furthermore, the assignment of the Ru(II) oxidation state was further confirmed by the spectral features observed at the Ru L_3-edge, which match those expected for a Ru(II) center (see Figure 2c).[22,23,24] An analysis of the extended X-ray absorption fine structure (EXAFS) region, shown in Figure 2d, revealed no evidence for the formation of Ru-Ru bonds, indicating that all complexes possess a mononuclear molecular structure. In the EXAFS of the Ru complexes (Figure 2d), the strong features near 2 Å contain contributions from Ru-N(bpy) and Ru-C (CO, CH_3, CHO, $COCH_3$) bonds,[25,26] while the smaller peaks at 3-3.5 Å probably come from Ru-C(bpy) and Ru-O(CO) interactions.[25-27]

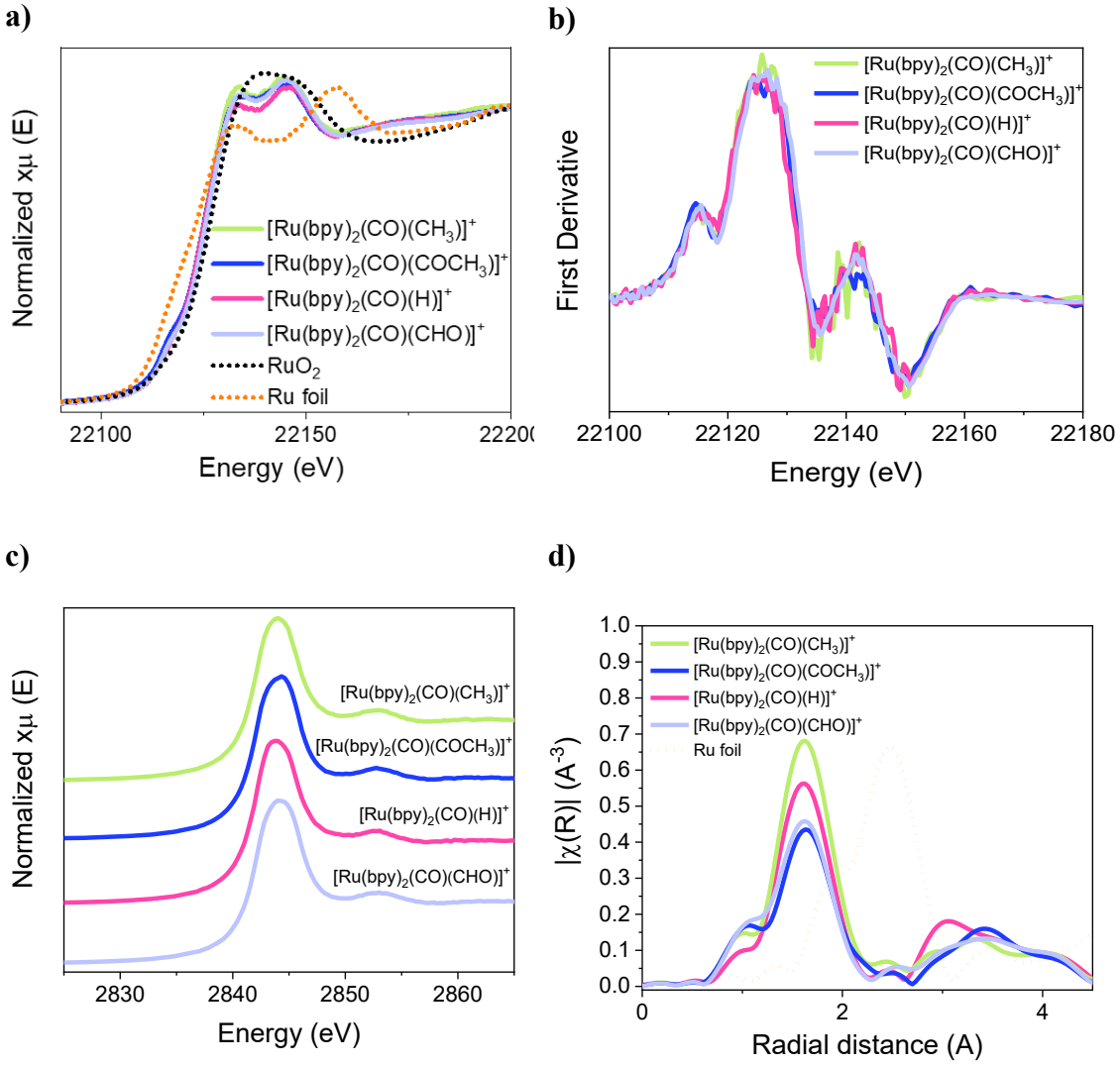

Figure 2. XANES measurement of cis-$[Ru(bpy)_2(CO)(CH_3)]^+$, cis-$[Ru(bpy)_2(CO)(COCH_3)]^+$, cis-$[Ru(bpy)_2(CO)(H)]^+$ and cis-$[Ru(bpy)_2(CO)(CHO)]^+$. a) Ru K-edge, b) First derivative, c) Ru L_3-edge, d) EXAFS region of Ru K-edge. Included for comparison are spectra for metallic Ru and RuO_2 in part a, and EXAFS features for a Ru foil in part d.

XPS has previously been used to follow ligand changes during chemical reactions.[28,29,30,31] For the Ru-complexes under study here, the C 1s XPS is of limited use due to the presence of dominant carbon features that originate from the bpy ligands that obscure small changes in other ligands.[28,29] As shown in Figure 3a, which presents the C 1s–Ru 3d core level spectra of $[Ru(bpy)_2(CO)(CH_3)]^+$ measured at 25 °C, the peak observed around 286 eV arises from a convolution of the Ru $3d_{3/2}$ signal and four distinct

carbon contributions. Two of these contributions originate from the bpy ligands, designated as type b (C_b) and c (C_c), while the remaining components correspond to carbon atoms from the CO and CH_3 groups (Figure 3a,b). However, the position of the Ru $3d_{5/2}$ peak offers particularly valuable insight into the oxidation state of the metal center. Its binding energy is consistent with the presence of Ru(II),[25-28] in agreement with the conclusions obtained from the XAS analysis. In addition, the oxidation state of the metal center was found to remain stable upon heating from 25 °C to 100 °C (Figure S7a).

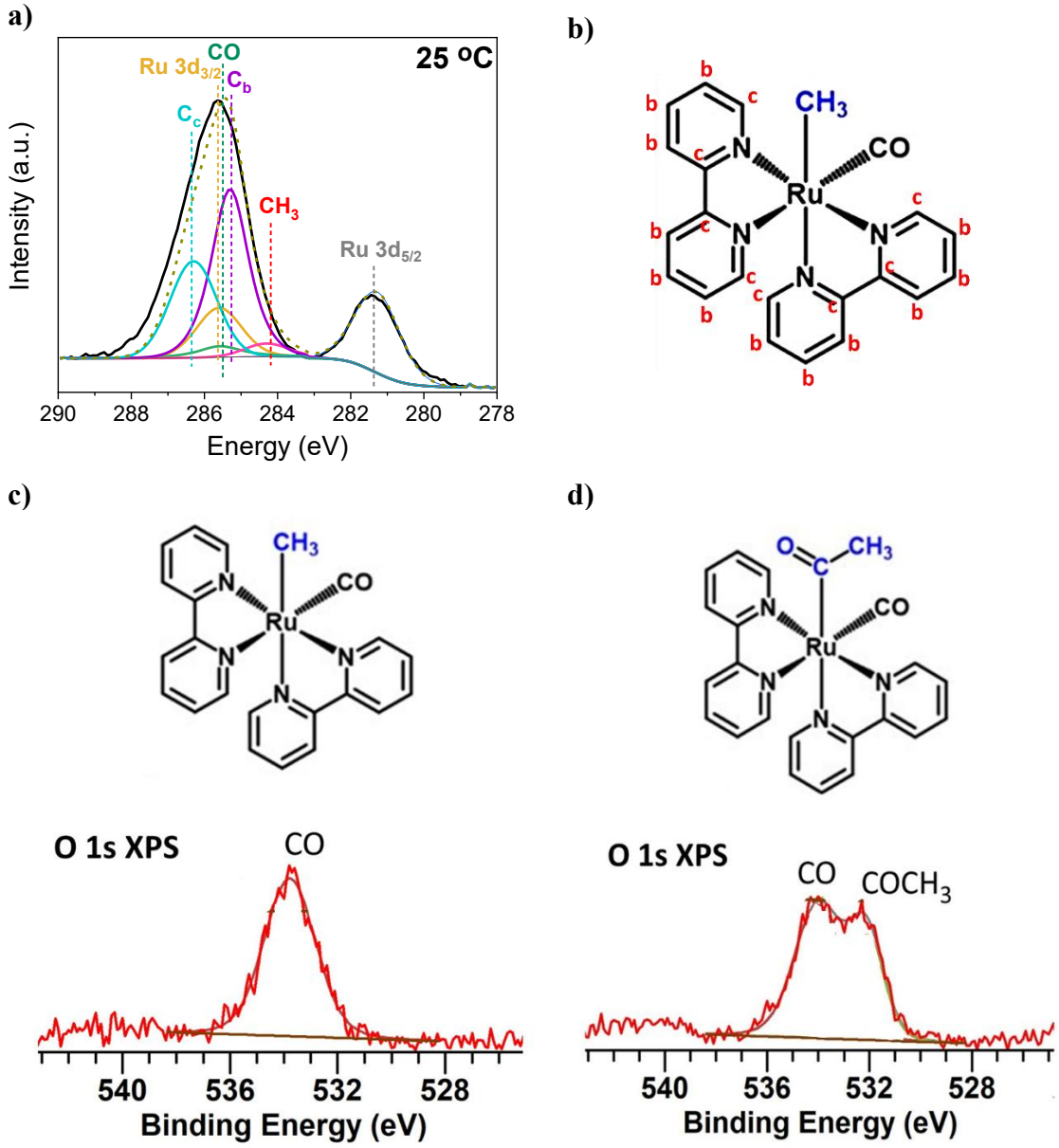

Figure 3. Part a) The C1s-Ru 3d XPS core level spectra of $[Ru(bpy)_2(CO)(CH_3)]^+$. Part b) Chemical structure of $[Ru\text{-}(bpy)_2(CO)(CH_3)]^+$ showing different types of carbons in the bpy ligands (b and c type). Parts c and d) O 1s spectra of $[Ru(bpy)_2(CO)(CH_3)]^+$ and $[Ru(bpy)_2(CO)(COCH_3)]^+$.

In the N 1s region (Figure S7b), we saw a single peak coming from the N atoms in the bpy ligands [25-28] that did not change upon heating from 25 ºC to 100 ºC under ultra-high vacuum (UHV) conditions (Figure S7b). This finding indicates that the bpy ligands exhibit stability and resist degradation under these heating conditions.

The O 1s XPS region displayed contributions from the ─CO, ─CHO and ─$COCH_3$ ligands.[26] Figure 3c,d, presents ex-situ XPS results for the $[Ru(bpy)_2(CO)(CH_3)]^+$ and $[Ru(bpy)_2(CO)(COCH_3)]^+$ complexes. As shown in Figure 3c, the O 1s spectrum of the $[Ru(bpy)_2(CO)(CH_3)]^+$ complex displays a single peak centered at approximately 534 eV, which is attributed to the oxygen atom of the coordinated CO ligand. In contrast, the O1s spectrum of the $[Ru(bpy)_2(CO)(COCH_3)]^+$ complex (Figure 3d) exhibits a second peak at around 532 eV, which is clearly associated with the oxygen atom of the acetyl ($COCH_3$) group.

XPS measurements were performed for the $[Ru\ (bpy)_2(CO)(CH_3)]^+$ complex while heating from 25 to 100 °C under UHV (Figure 4a) and under a CO atmosphere (Figure 4b). Under UHV, a shoulder developed towards lower binding energy at ~ 532 eV that is consistent with the presence of -$COCH_3$ (Figure 3d) formed by migratory insertion of CO into the Ru-CH_3 bond or by reaction of the Ru complex with the CO always present in the gas background of the XPS chamber. This shoulder clearly grew under a small pressure (6.666 pascal; 50 mTorr) of CO gas (Figure 4b). The formation of -$COCH_3$ was detected at room temperature and was predominant above 45 ºC. At 100 ºC, an O 1s spectrum similar to that of the synthesized *cis*-$[Ru(bpy)_2(CO)(COCH_3)]^+$ complex (Figure 3d) was seen. The apparent activation energy of this reaction was calculated by analyzing the temperature dependence of the peak intensity in the XPS measurements as a function of inverse temperature (1/T) in an Arrhenius-type plot, see Figure S8. The slope of the linear fit yielded an apparent activation energy of 7.4 kJ/mol. To our knowledge, this is the first report of the activation energy for this specific transformation, and the relatively low value is consistent with a facile CO insertion mechanism under mild conditions. Interestingly, during the insertion reaction, there was no significant change in the Ru $3d_{5/2}$ peak position, which always remained within experimental uncertainty at the value observed for Ru(II) in this type of complexes[25,26] and very different from those reported for $Ru(IV)O_2$, $Ru(VI)O_3$, and $Ru(VIII)O_4$.[30,31] In the experiments of Figure 4b, the CO could be moving in a concerted way from the Ru center into the CH_3 to form a C-C bond,[6,32] with a second CO molecule replacing the ligand that reacts. As mentioned above, attempts to insert CO into the Ru-CH_3 bond in dichloromethane or acetonitrile solutions of the complex to yield the corresponding acetyl intermediate were unsuccessful, even under high pressures (2.026×10^6 Pa; 20 atm) of CO, probably due to site blocking by the solvent.

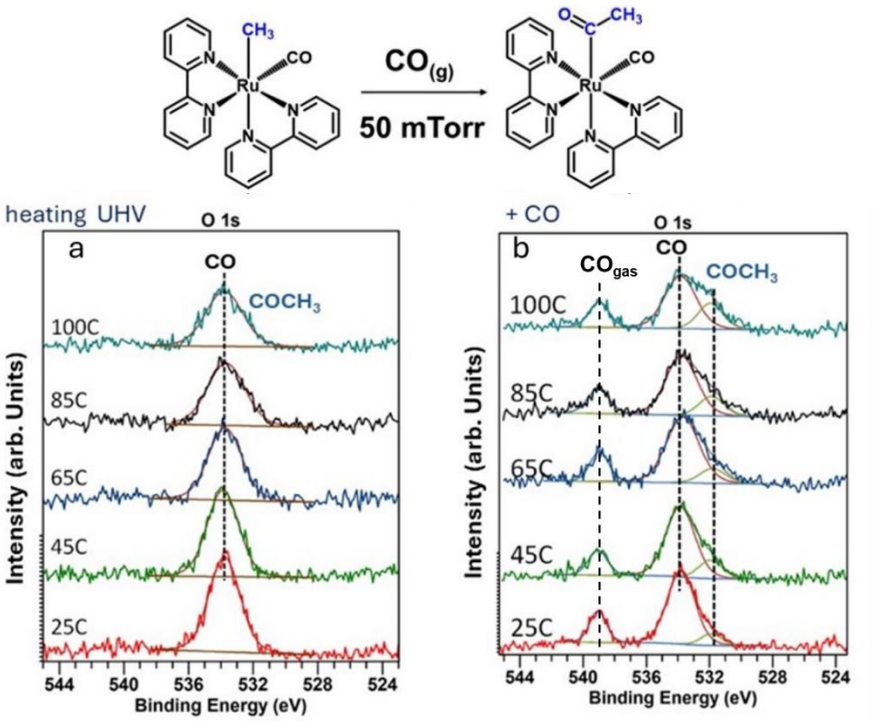

Figure 4. O 1s XPS spectra collected while heating the cis-$[Ru(bpy)_2(CO)(CH_3)]^+$ complex under ultra-high vacuum (UHV) conditions (a) and under 6.666 Pa (50 mTorr) of CO (b). The molecular complex was heated from 25 to 100 ºC.

Next, in an attempt to form ethanol, $[Ru(bpy)_2(CO)(COCH_3)]^+$ was exposed to 6.666 Pa (50 mTorr) of H_2 in the XPS chamber at 50-100 ºC. We saw no signs of reaction. XANES measurements at the O K-edge are sensitive to variations in the ligand composition of the Ru complex[7] and could be performed after exposing the sample to 1.333×10^3 Pa (10 Torr) of H_2 at 50 ºC, Figure 5a. Reduction of the CO or acyl group would lead to significant changes in the O K-edge spectra (Figure 5b). For example, the CO group appears at 534 eV, while the C=O in HCO and $COCH_3$ is located around 532 eV.[12,33] Exposure to H_2 at 50 ºC did not induce spectral changes associated with hydrogenation of the -$COCH_3$ ligand. Instead, the presence of H_2 resulted in the reduction of the carbonyl group to yield a formyl group, Ru-CO → Ru-COH. This indicates that the carbonyl group can be reduced to a formyl in the presence of hydrogen at low temperature, as has been previously proposed,[7,10] but also shows that the -$COCH_3$ ligand is stable, and its reduction requires alternative conditions. In experiments in liquid phase, no reaction was observed between the acetyl complex and an organic hydride (PMBIH). Thus, in processes that involve the hydrogenation of CO to ethanol on Ru complexes,[3] the CO insertion into a Ru-CH_3 unit is not the rate determining step in the catalytic process. For a conversion cycle similar to that displayed in Figure 1a, a renewable

electrophile must be identified to take the place of the stoichiometric trityl cation as well as a means to further reduce and release the acyl-derived ligand.

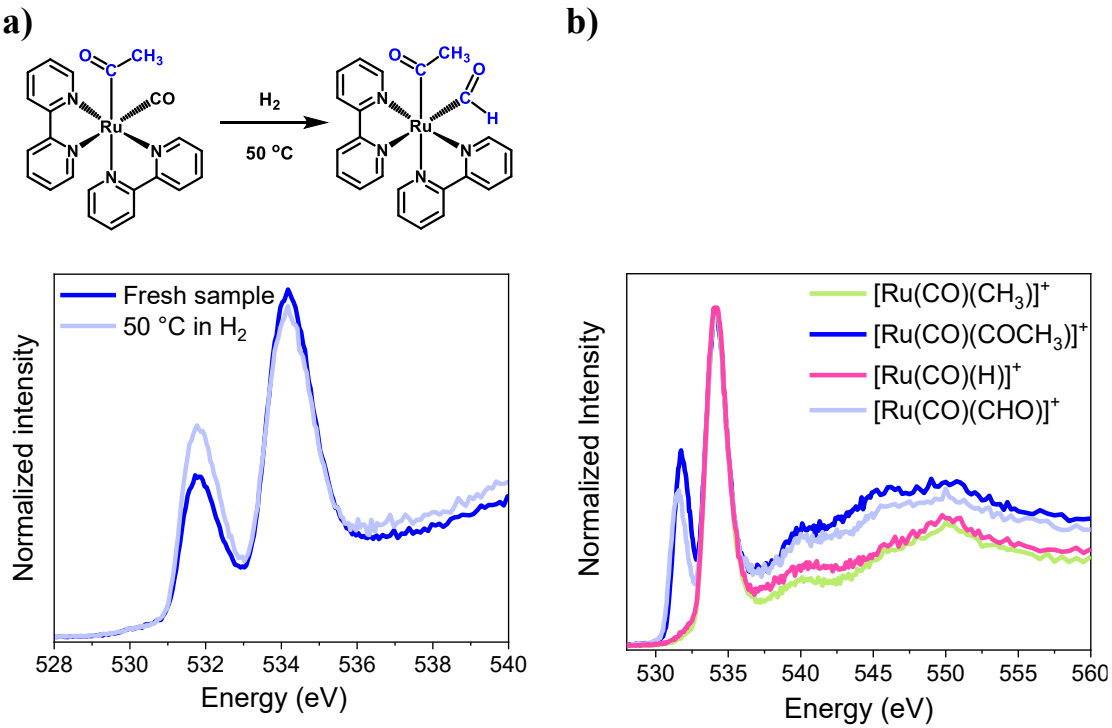

Figure 5. O K-edge XANES of a) $[Ru(bpy)_2(CO)(COCH_3)]^+$ under reaction conditions with 1.333 x 10^3 Pa (10 Torr) of H_2 at 50 °C, and b) $[Ru(bpy)_2(CO)(CH_3)]^+$, $[Ru(bpy)_2(CO)(COCH_3)]^+$, $Ru(bpy)_2(CO)(H)]^+$ and $[Ru(bpy)_2(CO)(CHO)]^+$.

In summary, we studied and compared a CO insertion reaction into a Ru-CH_3 bond of $[Ru(bpy)_2(CO)(CH_3)]^+$ in liquid and gas-solid media. In solutions of dichloromethane or acetonitrile, no insertion of CO into the Ru-CH_3 bond was seen even under high pressures of the gas (2.026 x 10^6 Pa; 20 atmospheres), probably due to site blocking by the solvent. XPS and XANES enabled us to examine the CO insertion and C─C coupling in gas-solid interactions. Our results show that spontaneous insertion of CO into a Ru-CH_3 bond of $[Ru(bpy)_2(CO)(CH_3)]^+$ occurs at 40-100 °C, and the process is accelerated by exposure to CO gas at 25-50 °C. Thus, the migratory insertion of CO and generation of C─C bonds at moderate temperatures is a relatively easy process, opening the door for the synthesis of ethanol and more energy dense liquids.

Acknowledgement

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Supporting Information

Experimental procedures, sample characterization with NMR and XPS.

Disclaimer

Certain commercial equipment, instruments, or materials are identified in this paper in order to specify the experimental procedure adequately, and do not represent an endorsement by the National Institute of Standards and Technology.

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