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Intramolecular Oxidation of the Alcohol Functionalities in Hydroxyalkyl-N-Heterocyclic Carbene Complexes of Iridium and Rhodium

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Abstract: A series of hydroxyalkyl-functionalized imidazolium salts have been coordinated to Rh and Ir to afford the corresponding MCp*–(NHC) (Cp* = pentamethylcyclopentadienyl) complexes. The reactivity of the new complexes has been studied with special attention to the transformations that deal with the alcohol functionality. The metal-mediated intramolecular transformations allowed the formation of several products that resulted from the oxidation of the alcohols to aldehydes and esters. All the new complexes have been fully characterized, and the crystal structures of the most representative complexes have been resolved.

Keywords: alcohols · carbene ligands · iridium · oxidation · rhodium

Introduction

N-Heterocyclic carbenes (NHCs) are now widely used in the design of homogeneous catalysts.[1] Among the features that make NHCs a very interesting class of ligands are the easy access to their ligand precursors (mostly azolium salts), the strength of the M–NHC bond, and their strong electron-donating character. Most azolium salts are easy-to-make compounds that allow the design of NHC ligands with tuned stereoelectronic properties,[2] and the library of known N-heterocyclic carbene ligands now covers an extraordinary wide set of architectures that is far from being fully explored.

Imidazolylidenes are often obtained from the corresponding imidazolium salts. Imidazolium salts are very easy to functionalize, often by simple reactions that allow the introduction of a manifold of N-substituents (or wingtips),[3] many of which can possess functional groups that can be activated or transformed by the metal in the course of their coordination reactions.

Some 'Cp*Ir' (Cp* = pentamethylcyclopentadienyl) complexes are known to be very active in the homogeneously catalyzed transformations of alcohols,[4] including their oxidation to aldehydes,[5,6] esterification,[7,8] β alkylation with primary alcohols[9,10] and coupling with amines,[10–12] among many other processes, most of them following the seminal works carried out by Fujita and Yamaguchi et al.[5,12,13]

We have also been interested in the application of 'Cp*Ir-(NHC)' complexes in catalytic reactions that involve the use of alcohols.[14] Because we are interested in experimentally studying the reaction mechanisms that involve the oxidation of alcohols by Ir^{III} complexes, we thought that using N-heterocyclic carbenes with alcohol substituents at the NHC wingtips might shed some light into the reaction pathways that govern the processes. The introduction of the alcohol functionality close to the active metal center might help produce the activation of the alcohol through a chelate-assisted process, and the transformed products are forced to remain attached to the metal, thus allowing for their complete characterization and facilitating the study of their reactivity through further subsequent reactions. Although most alcohol-functionalized imidazolium salts afford NHC-alkoxide chelate complexes,[15] some examples are known in which the alcohol functionalities remain untouched[16,17] and can undergo further reactions promoted by the metal center.[17] In this work we describe the reactivity of $[\{MCp^*Cl_2\}_2]$ (M = Ir, Rh) with a series of alcohol-functionalized azolium salts, and the characterization of the reaction products that resulting from the coordination of the NHC ligands to the metal centers and the subsequent activation of the alcohol functionalities. The step-by-step oxidation of the NHC wingtip allowed for the isolation of the corresponding alcohol, carbonyl, carboxylate, and ester-functionalized NHC–metal complexes.

Results and Discussion

The reaction of 1-(2-hydroxyethyl)-3-methylimidazolium iodide with $[\{IrCp^*Cl_2\}_2]$ in the presence of Ag_2O and KI in methanol at room temperature allows the formation of the 'Cp*Ir(NHC)' complex **1** in moderate yield. A similar complex, but with a hydroxypropyl wingtip can be obtained if the reaction is carried out with 1-(2-hydroxypropyl)-3-methylimidazolium bromide, but for this precursor the coordination is more efficient when carried out in refluxing acetoni-

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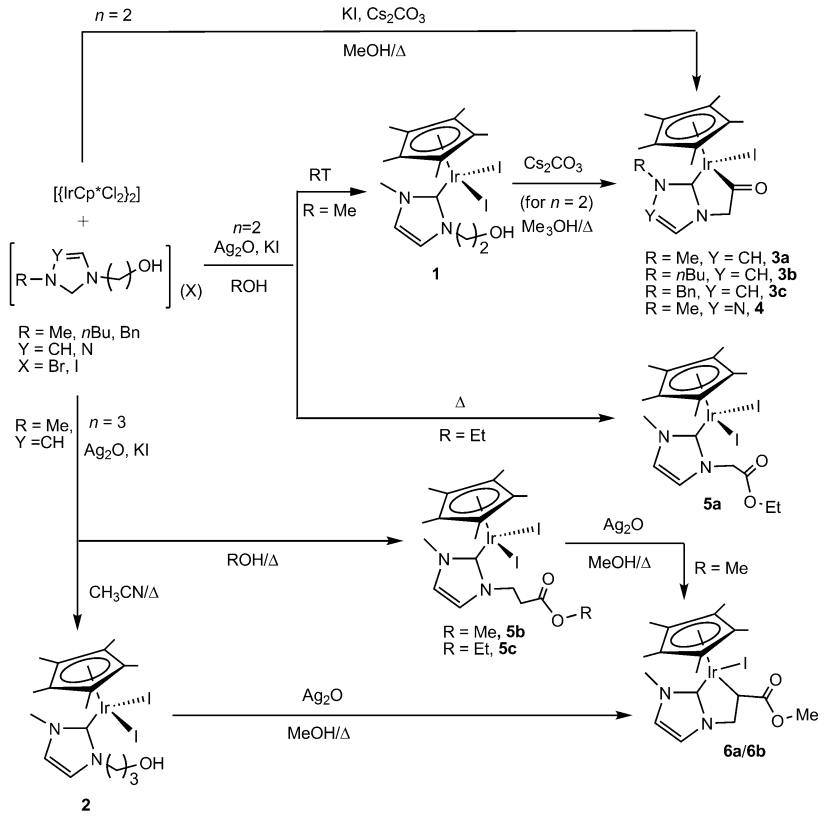


Scheme 1.

trile (complex **2** in Scheme 1). These two complexes have in common the presence of an alcohol substituent at the NHC wingtip, so the intramolecular transformations of this functionality can be studied. For example, in the presence of Cs_2CO_3 in methanol heated at reflux, compound **1** affords the cyclometalated complex **3a**. Complex **3a** can also be obtained by direct reaction of 1-(2-hydroxyethyl)-3-methylimidazolium iodide with $[\{IrCp^*Cl_2\}_2]$ in methanol heated at reflux in the presence of Cs_2CO_3 (Scheme 1).

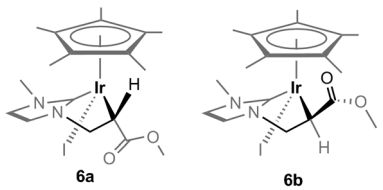
We wanted to study the factors that influence the cyclometalation of the NHC-alcohol ligand, so we decided to check the effects of the N wingtip, the metal, and the azolylidene ring in the process. For the reactions carried out with $[\{IrCp^*Cl_2\}_2]$ and the hydroxyethyl-substituted azolium salts with *n*Bu and Bn (Bn = benzyl) wingtips, we observed that the reactions performed in the presence of Cs_2CO_3 afforded the NHC-acyl cyclometalated species **3a**, **3b**, and **3c**. This result is interesting because it illustrates the high tendency of the hydroxyethyl group ($n=2$ in Scheme 1) to afford the cyclometalated acyl group in the presence of the base, even when the N–Bn group is present. In previous works,[18] we demonstrated the high tendency of the N–Bn groups at 'Cp*Ir(NHC)' complexes to undergo *ortho*-metalation of the phenyl ring, so in this new case the oxidation of the alcohol and the cyclometalation of the resulting aldehyde is preferred over the *ortho*-metalation of the phenyl ring. The use of a triazolium salt in the reaction with $[\{IrCp^*Cl_2\}_2]$ allows the isolation of the triazolylidene complex **4**. We thought that the use of the weaker electron-donating triazolylidene ligand might have some influence on the reactivity of the N wingtip of the ligand, but it actually gave access to the same cyclometalated species with a similar tendency. All these reactions illustrate the high tendency of the N-hydroxyethyl group to undergo oxidation and cyclometalation in the presence of a weak base. The formation of **3** and **4** can also be achieved when a nonalcoholic solvent such as acetonitrile is used, thereby affording the final products with similar yields. However, we observed that the preparation of **1** cannot be achieved in acetonitrile.

All these complexes were characterized by NMR spectroscopy, mass spectrometry, and elemental analysis. The most representative signals in the ^{1}H NMR spectra of the cyclometalated complexes **3**–**4**, are those due to the diastereotopic protons of the N–CH_2 group, which appear as two doublets ($^2J(H,H)\approx16$ Hz) between $\delta=3.5$ and 3.7 ppm. The ^{13}C NMR spectra shows the corresponding signals due to the Ir–$C_{carbene}$ carbon atoms ($\delta=162$–166 ppm), and the ones assigned to the metalated carbonyl carbon ($\delta=221$–224 ppm). It has to be noted that most of the complexes described here are obtained in low yields. This is due to the generation of mixtures of complexes in most of the reactions, thus implying that the reaction products were purified by column chromatography, with the concomitant purification loss.

When the reaction between 1-(2-hydroxyethyl)-3-methylimidazolium iodide and $[\{IrCp^*Cl_2\}_2]$ is carried out in the presence of Ag_2O in ethanol heated at reflux, the oxidation of the alcohol to the corresponding methyl ester is produced and complex **5a** is formed. Similarly, when the reaction is carried out in alcohol (methanol or ethanol) heated at reflux with the N-hydroxypropyl-substituted imidazolium salt ($n=3$, Scheme 1), we observed the products that resulted from the oxidation of the hydroxyl group to a methyl (**5b**) or ethyl (**5c**) ester. For all the reactions performed with the N-hydroxypropyl-substituted imidazolium salt ($n=3$), we did not observe the formation of the NHC-acyl cyclometalated species. This observation may imply that the generation of the cyclometalated complexes **3**–**4** is favored by the formation of a five-membered ring, compared to the six-membered ring that should be formed if the N-hydroxypropyl group reacted in a similar way. The ^{1}H NMR spectrum of

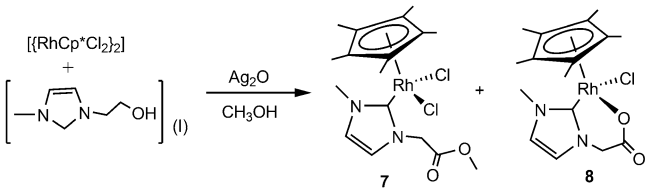
5a shows the doublets due to the diastereotopic protons at the methylene group of the ester branch ($\delta = 5.96$, 4.83 ppm), and the resonances due to the ethylene group ($\delta = 4.25$ and 1.32 ppm). The ^{13}C NMR spectrum of **5a** shows its most significant signals at $\delta = 169.2$ ppm due to the carbon at the carbonyl group and $\delta = 159.9$ ppm due to the metalated carbene carbon. The NMR spectra of **5b** and **5c** are qualitatively similar, with the main difference being the signals due to the methyl or ethyl group at the ester. The ^1H NMR spectrum of **5b** shows the signals assigned to the diastereotopic protons at the two methylene groups of the ester wingtips ($\delta = 5.20$, 3.83, 3.22, and 2.87 ppm), and the two resonances due to the protons at the two existing methyl groups ($\delta = 3.73$ and 3.83 ppm for NCH_3 and OCH_3, respectively). The ^{13}C NMR spectrum of **5b** displays the resonances due to the carbonyl carbon ($\delta = 172.3$ ppm) and the metalated carbene carbon ($\delta = 152.2$ ppm). The ^{13}C NMR spectrum of **5c** shows the signal due to the carbonyl carbon at $\delta = 171.8$ ppm and metalated carbene carbon at $\delta =$ 152.3 ppm. Metal complexes with ester-functionalized NHC ligands have been previously reported, but they all were obtained from preformed imidazolium salts with ester functionalities.[19] In our case, the formation of the ester is a consequence of the reactivity of the N-hydroxyalkyl group.

Interestingly, complexes **2** and **5b** in methanol heated at reflux in the presence of Ag_2O undergo cyclometalation to afford compound **6**. This complex has two stereogenic centers, one at the Ir center and other at the metalated CH carbon. This implies that four enantiomers are expected in the reaction mixture, with two pairs of diastereomers (**6a**/**6b**) being clearly differentiated by NMR spectroscopy and showing a 60:40 (**6a**:**6b**) molar ratio according to the integrals of the ^1H NMR spectrum of the mixture. Unfortunately, we could not separate both diastereomers by the ordinary purification methods (column chromatography or crystallization). However, we were lucky to selectively obtain single crystals of **6a**, the molecular structure of which is discussed below. We believe that the steric factors govern the different stability of both diastereomers, thus justifying that **6a** is always the major product obtained. In this regard, the two possible orientations of the ester branch relative to the metal center may determine the stability of the two species. For the isomer with the hydrogen of the stereogenic metalated carbon that points toward the bulky Cp* ligand (**6a**), a lower steric hindrance is expected than the isomer with the ester branch close to the Cp* ring (**6b**). These two possible orientations are depicted in Scheme 2, in which a fixed chiral conformation at the metal has been taken.



Scheme 2.

To compare the reactivity of rhodium and iridium with our alcohol-functionalized NHCs, we carried out the reaction between 1-(2-hydroxyethyl)-3-methylimidazolium iodide and $[\{RhCp^*Cl_2\}_2]$ in the presence of Ag_2O and under the same reaction conditions as those described above. The reaction afforded two different compounds that could be separated and purified by column chromatography. Both compounds resulted from the overoxidation of the alcohol to an ester (**7**) and a carboxylate (**8**). The carboxylate-functionalized NHC ligand in complex **8** chelates the metal through the carbene and one oxygen atom (Scheme 3).



Scheme 3.

The ^1H NMR spectrum of complex **7** shows the two doublets due to the diastereotopic protons at the N-methylene group at $\delta = 6.35$ and 4.78 ppm. The presence of the methyl group at the ester is confirmed by the signal at $\delta = 4.04$ ppm. The ^{13}C NMR spectrum shows the resonance assigned to the carbene carbon at $\delta = 171.8$ ppm ($^1J(Rh,C) = 57$ Hz), and to the carbonyl of the ester at $\delta = 170.5$ ppm. The ^1H NMR spectrum of **8** shows the two doublets due to the diastereotopic protons of the methylene group of the carboxylate at $\delta = 4.58$ and 4.48 ppm. The ^{13}C NMR spectrum displays the two most representative signals at $\delta = 174.6$ and 169.1 (doublet, $^1J(Rh,C) = 53$ Hz), due to the carbonyl group and the metalated carbene carbon, respectively.

We were able to grow single crystals of the representative complexes **1**, **2**, **3b**, **5b**, **6a**, and **7**, so their molecular structures were confirmed by X-ray diffraction analyses. We also obtained single crystals of complex **8**. Although the X-ray diffractometry studies did not allow us to obtain a molecular structure of enough quality for publication, it allowed us to confirm its proposed geometry and the chelating nature of the NHC-carboxylate ligand (a molecular diagram is available in the Supporting Information).

The molecular structures of **1** and **2** (Figure 1 and Figure 2, respectively) confirm the expected three-legged piano-stool geometry of both complexes. Both structures are very similar, with the only difference being that **1** contains a 2-hydroxyethyl N-substituent at the NHC ligand instead of the 3-hydroxypropyl group of complex **2**. The distances of the $Ir-C_{carbene}$ bonds are 2.056(9) Å (for **1**) and 2.066(10) Å (for **2**). All other distances and angles are in the expected range.

The molecular structure of complex **3b** (Figure 3) consists of an Ir^{III} center with a chelating imidazolylidene-acyl ligand, which forms a five-membered iridacycle. A Cp* ligand and an iodide ligand complete the coordination

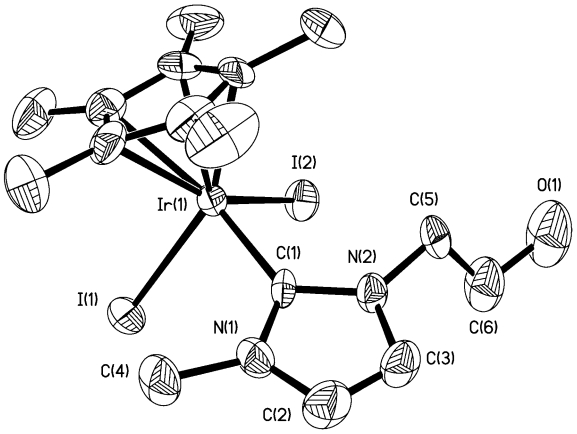


Figure 1. Molecular diagram of **1** (ellipsoids at 50% probability). All hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Ir(1)–I(1) 2.7359(8), Ir(1)–I(2) 2.7230(8), Ir(1)–C(1) 2.056 (9), Ir(1)–Cp*(centroid) 1.841; I(2)-Ir(1)-I(1) 85.63(3), I(1)-Ir(1)-C(1) 92.7(3), I(2)-Ir(1)-C(1) 96.2(3).

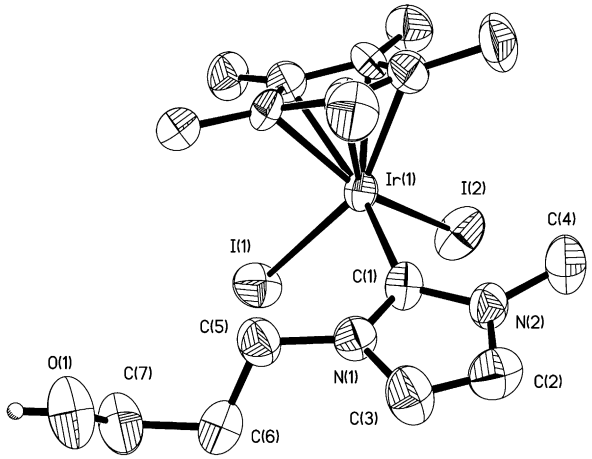


Figure 2. Molecular diagram of **2** (ellipsoids at 50% probability). All hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Ir(1)–I(1) 2.7359(8), Ir(1)–I(2) 2.7169(9), Ir(1)–C(1) 2.066(10), Ir(1)–Cp*(centroid) 1.826; I(2)-Ir(1)-I(1) 85.21(3), I(1)-Ir(1)-C(1) 94.8(3), I(2)-Ir(1)-C(1) 92.7(3).

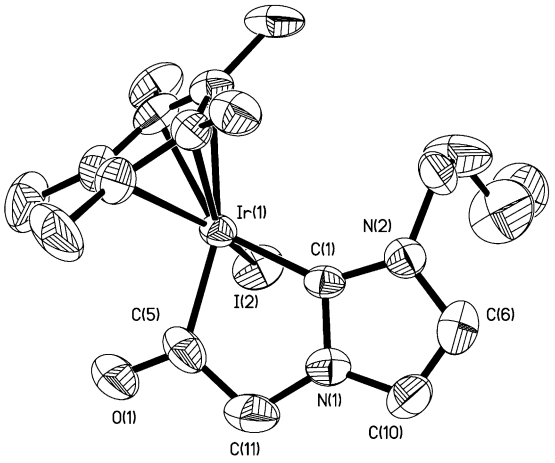


Figure 3. Molecular diagram of **3b** (ellipsoids at 50% probability). All hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Ir(1)–I(2) 2.6971(8), Ir(1)–C(1) 1.995(10), Ir(1)–C(5) 2.017(12), Ir(1)–Cp*(centroid) 1.891; C(1)-Ir(1)-I(2) 88.2(3), C(5)-Ir(1)-I(2) 86.2(3), C(1)-Ir(1)-C(5) 78.7(4).

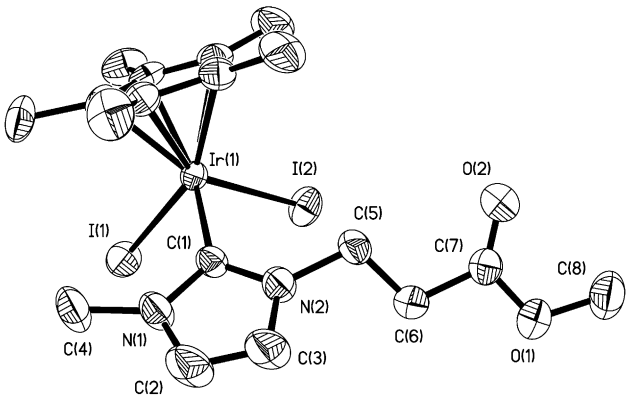


Figure 4. Molecular diagram of **5b** (ellipsoids at 50% probability). All hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Ir(1)–I(1) 2.7344(4), Ir(1)–I(2) 2.7118(5), Ir(1)–C(1) 2.050(4), Ir(1)–Cp*(centroid) 1.833; I(2)-Ir(1)-I(1) 85.483(11), I(2)-Ir(1)-C(1) 94.6(1), I(1)-Ir(1)-C(1) 93.1(1).

sphere about the metal. The Ir–$C_{carbene}$ bond length is 1.995(1) Å, slightly shorter than the rest of the Ir–$C_{carbene}$ distances of the complexes reported in this work but similar to other 'Cp*Ir(NHC)' complexes in which the NHC ligand is chelated.[18] The Ir–C(O) bond length is 2.017(12) Å, and the chelate bite angle is 78.7(4)°.

Complex **5b** (Figure 4) contains an imidazolylidene with a methoxy-carbonyl-ethyl wingtip. Two iodides and a Cp* ring complete the coordination sphere about the iridium center. The Ir–$C_{carbene}$ bond length is 2.050(4) Å. All other distances and angles are unexceptional.

The molecular structure of complex **6a** (Figure 5) confirms that the cyclometalation of the NHC-ester ligand has occurred with the formation of a five-membered iridacycle. The Cp* ring and a iodine complete the coordination sphere about the metal center. The molecule contains a stereogenic center at the metal and at the metalated CH carbon. The unit cell contains the racemic mixture of the $S_{Ir}R_C$ and $R_{Ir}S_C$ enantiomers. The chelate bite angle is 77.9°. The Ir–C bond lengths are 1.999(3) Å for the carbene and 2.152(3) Å for the CH metalated group.

The molecular structure of the rhodium complex **7** (Figure 6) confirms the esterification of the N wingtip, as observed by the presence of a methoxy-carbonyl-methyl group. The Rh–$C_{carbene}$ bond length is 2.064(3) Å, and all other distances and angles lie in the expected range.

The reactions that we have described in this paper illustrate the step-by-step oxidation of alcohols to esters or carboxylates, with the isolation of most of the stable intermediates. A possible mechanism that justifies the formation of all the reactions products is depicted in Scheme 4. According to this scheme, the first step of the reaction implies the deprotonation of the hydroxyalkyl to form a chelating NHC-alk-

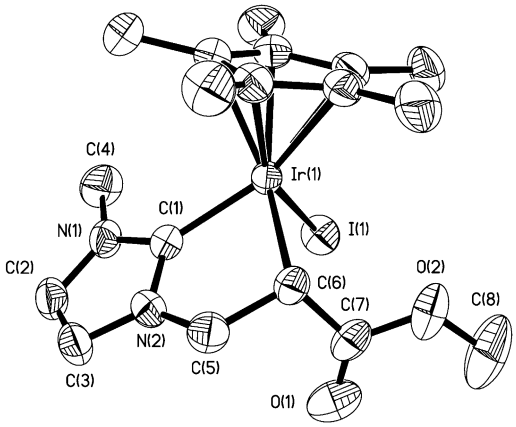


Figure 5. Molecular diagram of **6a**, only the $S_{Ir}R_C$ enantiomer is represented for clarity (ellipsoids at 50% probability). All hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Ir(1)–I(1) 2.7317(3), Ir(1)–C(1) 1.999(3), Ir(1)–C(6) 2.152(3), Ir(1)–Cp*-(centroid) 1.846; I(1)-Ir(1)-C(1) 90.06(9), I(1)-Ir(1)-C(6) 98.04(9), C(1)-Ir(1)-C(6) 77.9(1).

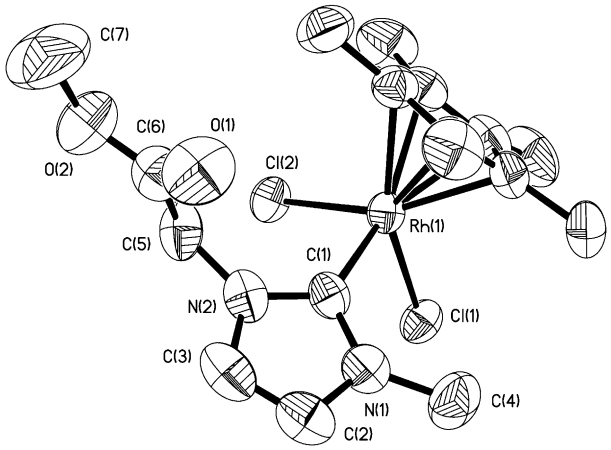
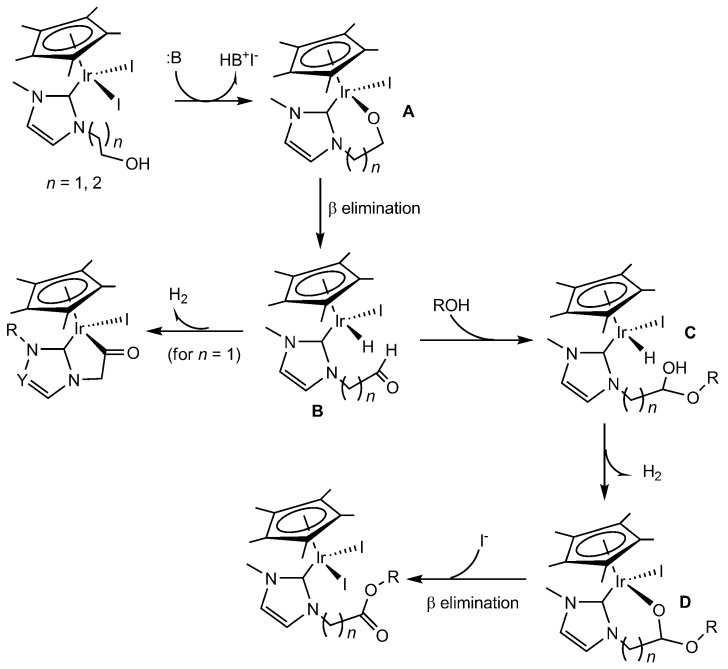


Figure 6. Molecular diagram of **7** (ellipsoids at 50% probability). All hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Rh(1)–Cl(1) 2.4271(12), Rh(1)–Cl(2) 2.4087(10), Rh(1)–C(1) 2.064(3), Rh(1)–Cp*(centroid) 1.812; Cl(2)-Rh(1)-Cl(1) 87.55(3), Cl(1)-Rh(1)-C(1) 90.32(9), Cl(2)-Rh(1)-C (1) 93.90(9).

oxide **A**. The β elimination of **A** generates the aldehydic intermediate **B**, which, depending on the number of methylene groups, affords the cyclometalated NHC-acyllated complex or reacts with an alcohol to yield the hemiacetal **C**. The release of hydrogen from **C** may lead to the chelating species **D**, which forms the final ester by β elimination and substitution of the resulting hydride with iodide, which has been present in the reaction medium since the first step of the process.

The first step of the process is supported by the number of chelated NHC-alkoxides that are generally formed by the reaction of hydroxyalkyl-imidazolium salts with metals in the presence of a base.[15] The formation of the aldehyde (**B**) and further cyclometalation justify the oxidation of the alcohol without the need of oxidizing the metal to an Ir^V state, which is in accordance with recently published mechanisms proposed for the oxidation of alcohols by 'Cp*Ir' complexes.[20] The formation of the final cyclometalated NHC-acyl compound is favored by the formation of the five-membered iridacycle when $n=1$ (Scheme 4). The reaction of the intermediate **B** with the alcohol recalls the mechanism proposed for the iridium-catalyzed Tishchenko reactions of aldehydes with alcohols to form esters,[8,21] in which a hemiacetal (**C**) is formed and further dehydrogenated by the iridium center to form the final product. This overall process is a base-induced reaction, as seen by the first step of the reaction mechanism. In our case, Ag_2O should play the role of the base[22] in the transformation of **2** into **5** and in the formation of the rhodium species **7** and **8**.



Scheme 4.

For the formation of the NHC-carboxylate rhodium complex **8**, we believe that a reasonable explanation may imply the presence of water in the basic reaction medium. An OH^- group might coordinate the metal in the rhodium analogue of **B**, and then the aldehyde inserts the C=O into the Rh–OH to form the resulting

carboxylate, as recently described by Tejel and co-workers for Rh^{III} complexes.[23]

Conclusion

In summary, we have used a series of hydroxyalkyl–imidazolium salts for the preparation of alcohol-functionalized iridium and rhodium complexes. The study of the reactivity of these complexes allowed us to obtain most of the reaction intermediates that lead to the final ester-functionalized NHC complexes. The identity of most products has been confirmed by means of X-ray diffractometry. Although many works have been published in which different reaction mechanisms for this processes are proposed, we have given a method for the step-by-step detection of most reaction intermediates. The reactions and products described in this work might shed some light on the mechanism that governs the important catalytic oxidation of alcohols.

Experimental Section

General: Ligand precursors and $[\{IrCp^*Cl_2\}_2]$[24] were prepared according to literature procedures. All subsequent synthesis were performed in air using reagent-grade solvents, which were used as received. All other reagents are commercially available and were used as received from commercial suppliers. NMR spectra were recorded using Varian Innova 300 and 500 MHz spectrometers, with $CDCl_3$, CD_3OD, and $[D_6]$acetone as solvents (Merk and Aldrich). Elemental analyses were carried out using an EA 1108 CHNS-O Carlo Erba analyzer. Electrospray mass spectra (ESI-MS) were recorded using a Micromass Quatro LC instrument, and nitrogen was employed as drying and nebulizing gas. HRMS were recorded using a Q-TOF premier mass spectrometer with an electrospray source (Waters, Manchester, UK), and nitrogen was employed as drying and cone gas. A solution of leucine enkephalin (*m*/*z* 556.2771) was employed as standard.

1-(2-Hydroxyethyl)-3-methylimidazolium iodide: *N*-Methylimidazole (242.7 μL, 3.04 mmol) and 2-iodoethanol (237.4 μL, 3.04 mmol) were heated at 100 °C for 4 h in a sealed Pyrex tube. After this time, the reaction mixture was cooled to room temperature and the resulting brown oil was washed twice with diethyl ether (2×5 mL). Yield: 754 mg (98%); ^{1}H NMR (300 MHz, CD_3OD, 303 K): δ = 8.98 (s, 1H; NC*H*N), 7.66 (s, 1H; C$H_{imidazole}$), 7.60 (s, 1H; C$H_{imidazole}$), 4.34 (t, ^3J(H,H) = 5 Hz, 2H; CH_2OH), 3.97 (s, 3H; CH_3N), 3.90 ppm (t, ^3J(H,H) = 5 Hz, 2H; CH_2N); ^{13}C{^{1}H} NMR (75 MHz, CD_3OD, 303 K): δ = 136.9 (s; NCHN), 123.5, 122.8 (s; *C*H$_{imidazole}$), 59.8 (s; *C*H$_2$OH), 52.1 (s; *C*H$_3$N), 36.1 ppm (s; *C*H$_2$N); HRMS: *m*/*z*: calcd for $C_6H_{11}ON_2I$ $[M]^+$: 127.0871; found: 127.0867.

1-(3-Hydroxypropyl)-3-methylimidazolium bromide: *N*-Methylimidazole (242.7 μL, 3.04 mmol) and 3-bromopropanol (266.1 μL, 3.04 mmol) were heated at 100 °C for 4 h in a sealed Pyrex tube. After this time, the reaction mixture was cooled to room temperature and the resulting yellow oil was washed twice with diethyl ether (2×5 mL). Yield: 641 mg (95%); ^{1}H NMR (300 MHz, CD_3OD, 303 K): δ = 9.00 (s, 1H; NC*H*N), 7.68 (s, 1H; C$H_{imidazole}$), 7.62 (s, 1H; C$H_{imidazole}$), 4.38 (t, ^3J(H,H) = 7 Hz, 2H; CH_2OH), 3.98 (s, 3H; CH_3N), 3.62 (t, ^3J(H,H) = 7 Hz, 2H; CH_2N), 2.12 ppm (q, ^3J(H,H) = 7 Hz, 2H; CH$_2$CH_2CH$_2$); ^{13}C{^{1}H} NMR (75 MHz, CD_3OD, 303 K): δ = 136.8 (s; NCHN), 123.6, 122.5 (s; *C*H$_{imidazole}$), 57.6 (s; *C*H$_2$OH), 46.7 (s; *C*H$_3$N), 35.5 (s; *C*H$_2$N), 32.3 ppm (s; CH$_2$*C*H$_2$CH$_2$); HRMS: *m*/*z*: calcd for $C_7H_{13}ON_2Br$ $[M]^+$: 141.1028; found: 141.1026.

1-(2-Hydroxyethyl)-3-butylimidazolium iodide: *N*-Butylimidazole (264.5 μL, 2.01 mmol) and 2-iodoethanol (157.0 μL, 2.01 mmol) were heated at 100 °C for 4 h in a sealed Pyrex tube. After this time, the reaction mixture was cooled to room temperature and the resulting brown oil was washed twice with diethyl ether (2×5 mL). Yield: 572 mg (96%); ^{1}H NMR (300 MHz, CD_3OD, 303 K): δ = 9.04 (s, 1H; NC*H*N), 7.67 (s, 2H; C$H_{imidazole}$), 4.54 (t, ^3J(H,H) = 4 Hz, 2H; CH_2OH), 4.26 (t, ^3J(H,H) = 7.5 Hz, 2H; CH_2N), 3.89 (t, ^3J(H,H) = 4 Hz, 2H; CH_2N), 1.90 (q, ^3J(H,H) = 7.5 Hz, 2H; CH$_2$CH_2CH$_2$), 1.41 (s, ^3J(H,H) = 7.5 Hz, 2H; CH$_3$CH_2CH$_2$), 0.99 ppm (t, ^3J(H,H) = 7.5 Hz, 2H; CH_3); ^{13}C{^{1}H} NMR (75 MHz, [D$_6$]acetone, 303 K): δ = 136.5 (s; NCHN), 123.1, 122.3 (s; *C*H$_{imidazole}$), 59.6 (s; *C*H$_2$OH), 52.1 (s; *C*H$_2$N), 49.3 (s; *C*H$_2$N), 31.9, 19.2 (s; *C*H$_2$), 13.0 ppm (s; *C*H$_3$). HRMS: *m*/*z*: calcd for $C_9H_{17}ON_2I$ $[M]^+$: 169.1341; found: 169.1340.

1-(2-Hydroxyethyl)-3-methyltriazolium iodide: *N*-Methyltriazole (227.3 μL, 3.08 mmol) and 2-iodoethanol (240.3 μL, 3.08 mmol) were heated at 100 °C for 4 h in a sealed Pyrex tube. After this time, the reaction mixture was cooled to room temperature and the resulting reddish oil was washed twice with diethyl ether (2×5 mL). Yield: 754 mg (96%); ^{1}H NMR (300 MHz, CD_3OD, 303 K): δ = 9.95 (s, 1H; NC*H*N), 8.96 (s, 1H; C$H_{triazole}$), 4.43 (t, ^3J(H,H) = 5 Hz, 2H; CH_2OH), 4.16 (s, 3H; CH_3N), 3.93 ppm (t, ^3J(H,H) = 5 Hz, 2H; CH_2N); ^{13}C{^{1}H} NMR (75 MHz, [D$_6$]acetone, 303 K): δ = 144.8 (s; NCHN), 143.2 (s; *C*H$_{triazole}$), 59.1 (s; *C*H$_2$OH), 50.9 (s; *C*H$_3$), 39.7 ppm (s; *C*H$_2$N); HRMS: *m*/*z*: calcd for $C_5H_{10}ON_3I$ $[M]^+$: 128.0824; found: 128.0823.

1-(2-Hydroxyethyl)-3-benzylimidazolium iodide: *N*-Benzylimidazole (250 mg, 1.58 mmol) and 2-iodoethanol (123.4 μL, 1.58 mmol) were heated at 100 °C for 4 h in a sealed Pyrex tube. After this time, the reaction mixture was cooled to room temperature and the resulting yellow oil was washed twice with dichloromethane (2×5 mL). Yield: 506 mg (97%); ^{1}H NMR (300 MHz, CD_3OD, 303 K): δ = 7.66 (s, 1H; C$H_{imidazole}$), 7.62 (s, 1H; C$H_{imidazole}$), 7.44 (m, 5H; CH_{phenyl}), 5.45 (s, 2H; CH_2Ph), 4.32 (t, ^3J(H,H) = 3 Hz, 2H; CH_2OH), 3.88 ppm (t, ^3J(H,H) = 3 Hz, 2H; CH_2N). The signal of NCHN and the OH are not observed for H/D exchange with the deuterated solvent; ^{13}C{^{1}H} NMR (75 MHz, CD_3OD, 303 K): δ = 137.4 (s; NCHN), 133.9 (s; C_{phenyl}), 129.1, 128.9, 128.7, 128.6, 128.1 (s; *C*H$_{phenyl}$), 123.3, 122.1 (s; *C*H$_{imidazole}$), 59.7 (s; *C*H$_2$OH), 52.8 (s; *C*H$_2$N), 52.1 ppm (s; *C*H$_2$N); HRMS: *m*/*z*: calcd for $C_{12}H_{15}ON_2I$ $[M]^+$: 203.1184; found: 203.1180.

Compound 1: A mixture of Ag_2O (58.2 mg, 0.25 mmol) and 1-(2-hydroxyethyl)-3-methylimidazolium iodide (63.8 mg, 0.25 mmol) was stirred in MeOH (10 mL) at room temperature for 2 h in the absence of light. After this time, the mixture was filtered through Celite. $[\{IrCp^*Cl_2\}_2]$ (100 mg, 0.125 mmol) and KI (250 mg, 1.51 mmol) were added, and the mixture stirred at room temperature for 2 h. The reaction mixture was filtered, and the solvent was removed under reduced pressure. The resulting solid was purified by chromatographic column. Elution with CH_2Cl_2/acetone (97:3) afforded an orange band that contained compound **1**. Further elution with CH_2Cl_2/acetone (9:1) afforded the separation of a yellow band that contained compound **3a** (yield: 10%). Compound **1** was obtained as an orange solid by precipitation from CH_2Cl_2/hexane. Yield: 44 mg (25%). Crystals suitable for X-ray diffraction were obtained by slow diffusion of hexane into a concentrated solution of **1** in CH_2Cl_2. ^{1}H NMR (300 MHz, $CDCl_3$, 303 K): δ = 7.25 (d, ^3J(H,H) = 2 Hz, 1H; C$H_{imidazole}$), 6.96 (d, ^3J(H,H) = 2 Hz, 1H; C$H_{imidazole}$), 5.15 (m, 1H; CH$_2$CH_2OH), 4.04–3.97 (br, 5H; NCH_3, NCH_2CH$_2$), 3.77 (m, 1H; CH_2CH$_2$OH), 2.37–2.02 (br, 1H; O*H*), 1.79 ppm (s, 15H; C$_5$(CH_3)$_5$); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 303 K): δ = 151.2 (s; Ir–NC*N*), 123.8 (s; *C*H$_{imidazole}$), 122.0 (s; *C*H$_{imidazole}$), 90.1 (s; *C*$_5$(CH$_3$)$_5$), 62.6 (s; *C*H$_2$OH), 54.2 (s; *C*H$_3$N), 43.5 (s; *C*H$_2$N), 10.5 ppm (s; C$_5$(*C*H$_3$)$_5$); ESI-MS (20 V, CH$_3$OH): *m*/*z*: 581.0 $[M-I]^+$; elemental analysis calcd (%) for $C_{16}H_{25}ON_2I_2Ir$: C 27.17, H 3.56, N 3.96; found: C 27.06, H 3.61, N 4.00.

Compound 2: A mixture of Ag_2O (58.2 mg, 0.25 mmol) and 1-(3-hydroxypropyl)-3-methylimidazolium bromide (55.5 mg, 0.25 mmol) was stirred in CH_3CN (10 mL) at room temperature for 2 h in the absence of light. After this time, the mixture was filtered through Celite. $[\{IrCp^*Cl_2\}_2]$ (100 mg, 0.125 mmol) and KI (250 mg, 1.51 mmol) were added, and the mixture was heated under reflux conditions for 2 h. After cooling, the mixture was filtered and the solvent was removed at reduced pressure. The resulting solid was purified by chromatographic column. Elution

with CH_2Cl_2/acetone (97:3) afforded an orange band that contained compound **2**. Compound **2** was obtained as an orange solid by precipitation from CH_2Cl_2/hexane. Yield: 43% yield (78 mg). Crystals suitable for X-ray diffraction were obtained by slow diffusion of hexane into a concentrated solution of **2** in CH_2Cl_2. ^{1}H NMR (300 MHz, $CDCl_3$, 303 K): $\delta =$ 7.05 (d, ^3J(H,H) = 2 Hz, 1H; C$H_{\text{imidazole}}$), 6.98 (d, ^3J(H,H) = 2 Hz, 1H; C$H_{\text{imidazole}}$), 5.09 (td, ^2J(H,H) = 4 Hz, ^3J(H,H) = 12 Hz, 1H; CH_2CH_2OH), 4.00 (s, 3H; NCH_3), 3.75 (m, 2H; NCH_2CH$_2$), 3.66 (td, ^2J(H,H) = 4 Hz, ^3J(H,H) = 12 Hz, 1H; CH_2CH_2OH), 2.60–2.45 (br, 1H; OH), 2.01 (m, 2H; $CH_2CH_2CH_2$), 1.81 ppm (s, 15H; $C_5(CH_3)_5$); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 303 K): $\delta =$ 151.6 (s; Ir–NCN), 124.1 (s; C$H_{\text{imidazole}}$), 121.9 (s; C$H_{\text{imidazole}}$), 90.3 (s; $C_5(CH_3)_5$), 60.5 (s; CH_2OH), 51.1 (s; CH_3N), 43.8 (s; CH_2N), 34.2 (s; $CH_2CH_2CH_2$), 10.8 ppm (s; $C_5(CH_3)_5$); ESI-MS (20 V, CH_3OH): m/z: 595.0 $[M-I]^+$; elemental analysis calcd (%) for $C_{17}H_{27}ON_2I_2Ir$: C 28.30, H 3.77, N 3.88; found: 28.42, H 3.80, N 3.84.

Compound 3a: 1-(2-Hydroxyethyl)-3-methylimidazolium iodide (63.8 mg, 0.25 mmol), [{IrCp*Cl$_2$}$_2$] (100 mg, 0.125 mmol), Cs_2CO_3 (491 mg, 1.51 mmol), and KI (250 mg, 1.51 mmol) were heated at 85 °C in MeOH (15 mL) for 5 h in a 25 mL flask. The reaction mixture was cooled to room temperature and filtered. The volatiles were removed under reduced pressure. The crude solid was purified by chromatographic column. Elution with CH_2Cl_2/acetone (9:1) separated a yellow band that contained compound **3a**. Compound **3a** was obtained as a yellow solid by precipitation from CH_2Cl_2/hexane. Yield: 43 mg (30%); ^{1}H NMR (300 MHz, $CDCl_3$, 303 K): $\delta =$ 7.08 (d, ^3J(H,H) = 2 Hz, 1H; C$H_{\text{imidazole}}$), 6.86 (d, ^3J(H,H) = 2 Hz, 1H; C$H_{\text{imidazole}}$), 3.79 (s, 3H; CH_3N), 3.58 (AB, ^2J(A,B) = 16 Hz, 1H; NCH_2CO), 3.51 (AB, ^2J(A,B) = 16 Hz, 1H; NCH_2CO), 1.92 ppm (s, 15H; $C_5(CH_3)_5$); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 303 K): $\delta =$ 223.5 (s; Ir–CO), 162.4 (s; Ir–NCN), 122.6 (s; C$H_{\text{imidazole}}$), 116.6 (s; C$H_{\text{imidazole}}$), 94.8 (s; $C_5(CH_3)_5$), 72.2 (s; NCH_2CO), 37.9 (s; CH_3N), 10.1 ppm (s; $C_5(CH_3)_5$); IR (CH_2Cl_2): $\tilde{\nu} = 1628\ cm^{-1}$ (ν_{CO}); HRMS: m/z: calcd for $C_{16}H_{22}ON_2IIrH$ $[M+H]^+$: 580.0438; found: 580.0436; elemental analysis calcd (%) for $C_{16}H_{22}ON_2IIr$: C 33.28, H 3.84, N 4.85; found: C 33.29, H 3.92, N 4.70.

Compound 3a from 1: Compound **1** (20 mg, 0.03 mmol) was dissolved in $CDCl_3$ in a J. Youngs re-sealable NMR spectroscopy tube. Cs_2CO_3 (29 mg, 0.09 mmol) was added to this solution, and the resulting mixture was heated at 65 °C for 3 h. Conversion of compound **1** into compound **3a** was monitored by ^{1}H NMR spectroscopy.

Compound 3b: 1-(2-Hydroxyethyl)-3-butylimidazolium iodide (74.3 mg, 0.25 mmol), [{IrCp*Cl$_2$}$_2$] (100 mg, 0.125 mmol), Cs_2CO_3 (491 mg, 1.51 mmol), and KI (250 mg, 1.51 mmol) were heated at 85 °C in MeOH (15 mL) for 5 h in a 25 mL flask. The reaction mixture was cooled to room temperature and filtered. The volatiles were removed under reduced pressure. The crude solid was purified by chromatographic column. Elution with CH_2Cl_2/acetone (9:1) separated a yellow band that contained compound **3b**. Compound **3b** was obtained as a yellow solid by precipitation from CH_2Cl_2/Et_2O. Yield: 53 mg (28%). Crystals suitable for X-ray diffraction were obtained by slow diffusion of Et_2O into a concentrated solution of **3b** in CH_2Cl_2. ^{1}H NMR (300 MHz, $CDCl_3$, 303 K): $\delta =$ 7.09 (s, 1H; C$H_{\text{imidazole}}$), 6.89 (s, 1H; C$H_{\text{imidazole}}$), 4.12 (m, 1H; CH_2N), 3.95 (m, 1H; CH_2N), 3.58 (AB, ^2J(A,B) = 15 Hz, 1H; NCH_2CO), 3.52 (AB, ^2J(A,B) = 15 Hz, 1H; NCH_2CO), 1.92 (s, 15H; $C_5(CH_3)_5$),1.46 (m, 2H; CH_2), 1.60 (m, 2H; CH_2), 0.90 ppm (m, 3H; CH_3); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 303 K): $\delta =$ 222.9 (s; Ir–CO), 164.7 (s; Ir–NCN), 120.4 (s; C$H_{\text{imidazole}}$), 116.4 (s; C$H_{\text{imidazole}}$), 94.6 (s; $C_5(CH_3)_5$), 71.7 (s; NCH_2CO), 50.6 (s; CH_2N), 32.5, 20.2 (s; CH_2), 13.9 (s; CH_3), 9.9 ppm (s; $C_5(CH_3)_5$); IR (CH_2Cl_2): $\tilde{\nu} = 1635\ cm^{-1}$ (ν_{CO}); ESI-MS (20 V, CH_3OH): m/z: 621.0 $[M+H]^+$; HRMS: m/z: calcd for $C_{19}H_{28}ON_2IIr$ $[M+H]^+$: 621.0955; found: 621.0961; elemental analysis calcd (%) for $C_{19}H_{28}ON_2IIr$: C 36.83, H 4.56, N 4.52; found: C 36.78, H 4.50, N 4.49.

Compound 3c: 1-(2-Hydroxyethyl)-3-benzylimidazolium iodide (82.9 mg, 0.25 mmol), [{IrCp*Cl$_2$}$_2$] (100 mg, 0.12 mmol), Cs_2CO_3 (491 mg, 1.51 mmol), and KI (250 mg, 1.51 mmol) were heated at 85 °C in MeOH (15 mL) for 16 h in a 25 mL flask. The reaction mixture was cooled to room temperature and filtered. The volatiles were removed under reduced pressure. The crude solid was purified by chromatographic column. Elution with CH_2Cl_2/acetone (9:1) separated a yellow band that contained compound **3c**. Compound **3c** was obtained as a yellow solid by precipitation from CH_2Cl_2/hexane. Yield: 41 mg (25%); ^{1}H NMR (300 MHz, $CDCl_3$, 303 K): $\delta =$ 7.45–7.35 (m, 5H; CH_{benzyl}), 7.07 (d, ^3J(H,H) = 1.2 Hz, 1H; C$H_{\text{imidazole}}$), 6.61 (d, ^3J(H,H) = 1.2 Hz, 1H; C$H_{\text{imidazole}}$), 5.44 (d, ^2J(H,H) = 9 Hz, 1H; C$H_{2\text{benzyl}}$), 5.13 (d, ^2J(H,H) = 9 Hz, 1H; C$H_{2\text{benzyl}}$), 3.64 (AB, ^2J(A,B) = 10 Hz, 1H; NCH_2CO), 3.57 (AB, ^2J(A,B) = 10 Hz, 1H; NCH_2CO), 1.90 ppm (s, 15H; $C_5(CH_3)_5$); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 303 K): $\delta =$ 222.5 (s; Ir–CO), 163.1 (s; Ir–NCN), 134.8 (s; C_{benzyl}), 128.6 (s; C$H_{\text{imidazole}}$), 128.4 (s; C$H_{\text{imidazole}}$), 129.7, 128.3, 122.1, 121.0, 117.3 (s; CH_{benzyl}), 94.4 (s; $C_5(CH_3)_5$), 71.8 (s; NCH_2CO), 54.0 (s; C$H_{2\text{benzyl}}$), 10.1 ppm (s; $C_5(CH_3)_5$); HRMS: m/z: calcd for $C_{16}H_{22}ON_2IIrH$ $[M+H]^+$: 655.0798; found: 655.0795; m/z: calcd for $C_{16}H_{22}ON_2IIrNa$ $[M+Na]^+$: 677.0618; found: 677.0610; elemental analysis calcd (%) for $C_{22}H_{26}ON_2IIr$: C 40.43, H 4.01, N 4.29; found C 40.48, H 3.98, N 4.25.

Compound 4: 1-(2-Hydroxyethyl)-3-methyltriazolium iodide (32.1 mg, 0.25 mmol), [{IrCp*Cl$_2$}$_2$] (100 mg, 0.12 mmol), Cs_2CO_3 (491 mg, 1.51 mmol) and KI (250.1 mg, 1.51 mmol) were heated at 85 °C in MeOH (15 mL) for 16 h in a 25 mL flask. The reaction mixture was cooled to room temperature and filtered. The volatiles were removed under reduced pressure. The crude solid was purified by chromatographic column. Elution with CH_2Cl_2/acetone (9:1) separated a yellow band that contained compound **4**. Compound **4** was obtained as a yellow solid by precipitation from CH_2Cl_2/hexane. Yield: 36 mg (25%); ^{1}H NMR (300 MHz, $CDCl_3$, 303 K): $\delta =$ 8.08 (s, 1H; CH_{triazole}), 3.99 (s, 3H; NCH_3), 3.62 (AB, ^2J(A,B) = 16 Hz, 1H; NCH_2CO), 3.57 (AB, ^2J(A,B) = 16 Hz, 1H; NCH_2CO), 1.93 ppm (s, 15H; $C_5(CH_3)_5$); ^{13}C{^{1}H} ppm (75 MHz, $CDCl_3$, 303 K): $\delta =$ 220.9 (s; Ir–CO), 166.5 (s; Ir–NCN), 137.5 (CH_{triazole}), 95.3 (s; $C_5(CH_3)_5$), 68.3 (s; NCH_2CO), 38.8 (CH_3N), 9.5 ppm (s; $C_5(CH_3)_5$); HRMS: m/z: calcd for $C_{15}H_{21}ON_3IIrH$ $[M+H]^+$: 580.0438; found: 580.0436; elemental analysis calcd (%) for $C_{15}H_{21}ON_3IIr$: C 31.14, H 3.66, N 7.26; found: C 31.10, H 3.70, N 7.22.

Compound 5a: A mixture of Ag_2O (58.2 mg, 0.25 mmol) and 1-(3-hydroxypropyl)-3-methylimidazolium bromide (55.5 mg, 0.25 mmol) was stirred in EtOH (10 mL) at room temperature for 2 h in the absence of light. After this time, the mixture was filtered through Celite. [{IrCp*Cl$_2$}$_2$] (100 mg, 0.125 mmol) and KI (250 mg, 1.51 mmol) were added, and the mixture was heated under reflux conditions for 3 h. After cooling, the mixture was filtered and the solvent was removed at reduced pressure. The resulting solid was purified by chromatographic column. Elution with CH_2Cl_2 afforded an orange band that contained unreacted [{IrCp*Cl$_2$}$_2$] and a red band that contained compound **5a**. Further elution with CH_2Cl_2/acetone (9:1) separated a yellow band that contained compound **3a** in 10% yield. Compound **5a** was obtained as a red solid by precipitation from CH_2Cl_2/hexane. Yield: 15% yield (28 mg). ^{1}H NMR (300 MHz, $CDCl_3$, 303 K): $\delta =$ 7.01 (d, ^3J(H,H) = 2 Hz, 1H; C$H_{\text{imidazole}}$), 6.97 (d, ^3J(H,H) = 2 Hz, 1H; C$H_{\text{imidazole}}$), 5.96 (d, ^2J(H,H) = 18 Hz, 1H; NCH_2CO), 4.83 (d, ^2J(H,H) = 18 Hz, 1H; NCH_2CO), 4.25 (q, ^3J(H,H) = 7 Hz, 2H; CH_2O), 3.99 (s, 3H; NCH_3), 1.83 (s, 15H; $C_5(CH_3)_5$), 1.32 ppm (t, ^3J(H,H) = 7 Hz, 3H; CH_2CH_3); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 303 K): $\delta =$ 169.2 (s; CH_2CO), 159.9 (s; Ir–NCN), 125.5 (s; C$H_{\text{imidazole}}$), 123.4 (s; C$H_{\text{imidazole}}$), 90.4 (s; $C_5(CH_3)_5$), 61.9 (s; CH_2), 56.8 (s; CH_2), 43.5 (s; NCH_3), 14.4 (s; CH_2CH_3), 10.5 ppm (s; $C_5(CH_3)_5$); ESI-MS (20 V, CH_3OH): m/z: 623.0 $[M-I]^+$; elemental analysis calcd (%) for $C_{18}H_{27}O_2N_2I_2Ir$: C 28.85, H 3.63, N 3.74; found: C 28.92, H 3.60, N 3.71.

Compound 5b: A mixture of Ag_2O (58.2 mg, 0.25 mmol) and 1-(3-hydroxypropyl)-3-methylimidazolium bromide (55.5 mg, 0.25 mmol) was stirred in MeOH (10 mL) at room temperature for 2 h in the absence of light. After this time, the mixture was filtered through Celite. [{IrCp*Cl$_2$}$_2$] (100 mg, 0.125 mmol) and KI (250 mg, 1.51 mmol) were added, and the mixture was heated under reflux conditions for 3 h. After cooling, the mixture was filtered, and the solvent was removed at reduced pressure. The resulting solid was purified by chromatographic column. Elution with CH_2Cl_2 afforded an orange band that contained unreacted [{IrCp*Cl$_2$}$_2$] and a red band that contained compound **5b**. Compound **5b** was obtained as a red solid by precipitation from CH_2Cl_2/hexane. Yield: 34% yield (65 mg). Crystals suitable for X-ray diffraction were obtained by slow diffusion of hexane into a concentrated solution

of **5b** in CH_2Cl_2. ^{1}H NMR (300 MHz, $CDCl_3$, 303 K): $\delta = 7.09$ (s, 1H; C$H_{imidazole}$), 6.96 (s, 1H; C$H_{imidazole}$), 5.20 (m, 1H; CH_2CO), 4.00–3.83 (br, 1H; CH_2CO and 3H; OCH_3), 3.73 (s, 3H; NCH_3), 3.22 (m, 1H; NCH_2), 2.87 (m, 1H; NCH_2), 1.82 ppm (s, 15H; $C_5(CH_3)_5$); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 303 K): $\delta = 172.3$ (s; CH_2CO), 152.2 (s; Ir–N*C*N), 124.1 (s; *C*H$_{imidazole}$), 121.6 (s; *C*H$_{imidazole}$), 90.2 (s; $C_5(CH_3)_5$), 52.1 (s; O*C*H$_3$), 48.9 (s; N*C*H$_2$), 43.7 (s; N*C*H$_3$), 36.8 (s; *C*H$_2$CO), 10.6 ppm (s; $C_5(CH_3)_5$); ESI-MS (20 V, CH_3OH): m/z: 623.0 $[M-I]^+$; elemental analysis calcd (%) for $C_{18}H_{27}O_2N_2I_2Ir$: C 28.85, H 3.63, N 3.74; found: C 28.80, H 3.66, N 3.80.

Compound 5c: A mixture of Ag_2O (58.2 mg, 0.25 mmol) and 1-(3-hydroxypropyl)-3-methylimidazolium bromide (55.5 mg, 0.25 mmol) was stirred in EtOH (10 mL) at room temperature for 2 h in the absence of light. After this time, the mixture was filtered through Celite. $[\{IrCp^*Cl_2\}_2]$ (100 mg, 0.125 mmol) and KI (250 mg, 1.51 mmol) were added, and the mixture was heated under reflux conditions for 3 h. After cooling, the mixture was filtered, and the solvent was removed at reduced pressure. The resulting solid was purified by chromatographic column. Elution with CH_2Cl_2 afforded an orange band that contained unreacted $[\{IrCp^*Cl_2\}_2]$ and a red band that contained compound **5c**. Compound **5c** was obtained as a red solid by precipitation from CH_2Cl_2/hexane. Yield: 20% yield (38 mg); ^{1}H NMR (300 MHz, $CDCl_3$, 303 K): $\delta = 7.10$ (s, 1H; C$H_{imidazole}$), 6.95 (s, 1H; C$H_{imidazole}$), 5.20 (m, 2H; CH_2), 4.18 (q, ^3J(H,H) = 7 Hz, 2H; CH_2O), 3.99 (s, 3H; NCH_3), 3.20 (m, 1H; CH_2), 2.83 (m, 1H; CH_2), 1.82 (s, 15H; $C_5(CH_3)_5$), 1.01 ppm (t, ^3J(H,H) = 7 Hz, 3H; CH_2CH_3); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 303 K): $\delta = 171.8$ (s; CH_2CO), 152.3 (s; Ir–N*C*N), 124.0 (s; *C*H$_{imidazole}$), 121.6 (s; *C*H$_{imidazole}$), 90.1 (s; $C_5(CH_3)_5$), 61.0 (s; *C*H$_2$), 48.9 (s; *C*H$_2$), 43.6 (s; *C*H$_3$), 37.1 (s; *C*H$_2$), 14.3 (s; *C*H$_3$), 10.5 ppm (s; $C_5(CH_3)_5$); ESI-MS (20 V, CH_3OH): m/z: 637.2 $[M-I]^+$; elemental analysis calcd (%) for $C_{19}H_{29}O_2N_2I_2Ir$: C 29.89, H 3.83, N 3.67; found: C 29.99, H 3.78, N 3.70.

Compounds 6a and 6b: A mixture of **2** (40 mg, 0.055 mmol) and Ag_2O (12.8 mg, 0.055 mmol) was heated under reflux conditions in MeOH (10 mL) for 3 h. After this time, the mixture was filtered through Celite, and the solvent was removed at reduced pressure. The resulting solid was purified by chromatographic column. Elution with CH_2Cl_2/acetone (98:2) afforded a yellow band. Precipitation from CH_2Cl_2/hexane afforded a yellow solid as a mixture of **6a** and **6b** in a ratio 60:40. Yield: 80% (28 mg). Crystallization by slow diffusion of Et_2O into a concentrated solution of the mixture **6a** and **6b** in CH_2Cl_2 afforded suitable crystals for X-ray diffraction of **6a**. For **6a**: ^{1}H NMR (500 MHz, $CDCl_3$, 303 K): $\delta =$ 6.90 (d, ^3J(H,H) = 2 Hz, 1H; C$H_{imidazole}$), 6.81 (d, ^3J(H,H) = 2 Hz, 1H; C$H_{imidazole}$), 4.31 (m, 1H; CH_2), 4.15 (dd, ^2J(H,H) = 12 Hz, ^3J(H,H) = 2 Hz, 1H; C*H*), 3.68 (s, 3H; CH_3), 3.66 (m, 1H; CH_2), 3.56 (s, 3H; CH_3), 1.91 ppm (s, 15H; $C_5(CH_3)_5$); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 303 K): $\delta =$ 184.0 (s; *C*O), 158.5 (s; Ir–N*C*N), 122.0 (s; *C*H$_{imidazole}$), 117.5 (s; *C*H$_{imidazole}$), 89.6 (s; $C_5(CH_3)_5$), 53.0 (s; NCH$_2$), 50.4 (s; *C*H$_3$), 38.0 (s; *C*H$_3$), 18.4 (s; *C*H), 10.0 ppm (s; $C_5(CH_3)_5$); HRMS: m/z: calcd for $C_{18}H_{26}O_2N_2IIr$ $[M-I]^+$: 493.1600; found: 493.1597; elemental analysis calcd (%) for $C_{18}H_{26}O_2N_2IIr$: C 34.78, H 4.22, N 4.51; found: C 34.83, H 4.18, N 4.56. For **6b**: ^{1}H NMR (500 MHz, $CDCl_3$, 303 K): $\delta = 6.95$ (d, ^3J(H,H) = 2 Hz, 1H; C$H_{imidazole}$), 6.82 (d, ^3J(H,H) = 2 Hz, 1H; C$H_{imidazole}$), 5.01 (dd, ^2J(H,H) = 12 Hz, ^3J(H,H) = 6 Hz, 1H; C*H*), 4.30 (m, 1H; CH_2), 3.96 (dd, ^2J(H,H) = 12 Hz, ^3J(H,H) = 6 Hz, 1H; CH_2), 3.75 (s, 3H; CH_3), 3.69 (s, 3H; CH_3), 1.79 ppm (s, 15H; $C_5(CH_3)_5$); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 303 K): $\delta = 181.4$ (s; *C*O), 159.5 (s; Ir–N*C*N), 122.2 (s; *C*H$_{imidazole}$), 117.6 (s; *C*H$_{imidazole}$), 89.3 (s; $C_5(CH_3)_5$), 54.9 (s; *C*H$_2$), 50.6 (s; *C*H$_3$), 37.9 (s; *C*H$_3$), 18.6 (s; *C*H), 9.3 ppm (s; $C_5(CH_3)_5$).

Compounds 7 and 8: A mixture of Ag_2O (58.2 mg, 0.32 mmol) and 1-(2-hydroxyethyl)-3-methylimidazolium iodide (82.4 mg, 0.32 mmol) was stirred in MeOH (10 mL) at room temperature for 2 h in the absence of light. After this time, the mixture was filtered through Celite. $[\{RhCp^*Cl_2\}_2]$ (100 mg, 0.16 mmol) was added, and the mixture heated under reflux conditions for 3 h. After cooling, the mixture was filtered and the solvent was removed at reduced pressure. The resulting solid was purified by chromatographic column. Elution with CH_2Cl_2/acetone (1:1) afforded an red band that contained compound **7**. Compound **7** was obtained as a red solid by precipitation from CH_2Cl_2/hexane. Yield: 25% yield (35 mg). Further elution with acetone afforded an orange band that contained compound **8**. Compound **8** was obtained as an orange solid by precipitation from CH_2Cl_2/hexane. Yield: 15% yield (20 mg). Crystals of **7** suitable for X-ray diffraction were obtained by slow diffusion of hexane into a concentrated solution of the complex in CH_2Cl_2. For **7**: ^{1}H NMR (300 MHz, $CDCl_3$, 303 K): $\delta = 7.04$ (s, 1H; C$H_{imidazole}$), 7.00 (s, 1H; C$H_{imidazole}$), 6.35 (d, ^2J(H,H) = 17 Hz, 1H; NCH_2CO), 4.78 (d, ^2J(H,H) = 17 Hz, 1H; NCH_2CO), 4.04 (s, 3H; OCH_3), 3.79 (s, 3H; NCH_3), 1.61 ppm (s, 15H; $C_5(CH_3)_5$); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 303 K): $\delta =$ 171.8 (d, ^1J(C,Rh) = 57 Hz; Rh–N*C*N), 170.5 (s; *C*O), 124.5 (s; *C*H$_{imidazole}$), 124.4 (s; *C*H$_{imidazole}$), 96.7 (d, ^1J(C,Rh) = 7 Hz; $C_5(CH_3)_5$), 52.6 (s; OCH$_3$), 39.4 (s; NCH$_2$CO), 31.0 (s; NCH$_3$), 9.4 ppm (s; $C_5(CH_3)_5$); ESI-MS (20 V, CH_3OH): m/z: 427.1 $[M-Cl]^+$; elemental analysis calcd (%) for $C_{17}H_{25}O_2N_2RhCl_2$ (**7**): C 44.08, H 5.44, N 6.05; found: C 44.12, H 5.40, N 6.10. For **8**: ^{1}H NMR (300 MHz, $CDCl_3$, 303 K): $\delta = 7.04$ (s, 1H; C$H_{imidazole}$), 7.02 (s, 1H; C$H_{imidazole}$), 4.58 (AB, ^2J(A,B) = 17 Hz, 1H; NCH_2CO), 4.48 (AB, ^2J(A,B) = 17 Hz, 1H; NCH_2CO), 3.88 (s, 3H; NCH_3), 1.66 ppm (s, 15H; $C_5(CH_3)_5$); ^{13}C{^{1}H} NMR (75 MHz, CD_3OD, 303 K): $\delta = 174.6$ (s; NCH$_2$*C*O), 169.1 (d, ^1J(C,Rh) = 53 Hz; Rh–N*C*N), 124.6 (s; *C*H$_{imidazole}$), 124.3 (s; *C*H$_{imidazole}$), 98.2 (d, ^1J(C,Rh) = 7 Hz; $C_5(CH_3)_5$), 53.9 (s; NCH$_2$CO), 40.8 (s; NCH$_3$), 10.2 ppm (s; $C_5(CH_3)_5$); ESI-MS (25 V, CH_3OH): m/z: 376.9 $[M-Cl]^+$; elemental analysis calcd (%) for $C_{16}H_{22}O_2N_2RhCl$ (**7**): C 46.56, H 5.37, N 6.79; found: C 46.61, H 5.43, N 6.86.

X-ray diffraction studies: Crystals for X-ray diffraction of **1**, **2**, **3b**, **5b**, and **7** were obtained by slow diffusion of hexane into a concentrated solution of the compounds in CH_2Cl_2. Crystals for X-ray diffraction of **6a** were obtained by slow diffusion of ether into a concentrated solution of the mixture **6a** and **6b** in CH_2Cl_2. Data collection was performed at room temperature using a Siemens Smart CCD diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). The diffraction frames were integrated using the SAINT package.[25]

Space-group assignment was based on systematic absences, *E* statistics, and successful refinement of the structures. The structure was solved by direct methods with the aid of successive difference Fourier maps and refined using the SHELXTL 6.1 software package.[26] All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were assigned to ideal positions and refined using a rigid model.

CCDC-821846 (**1**), 821847 (**2**), 821848 (**3b**), 821849 (**5b**), 821850 (**6a**), and 821851 (**7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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