

Ir^{III}/Au^I and Rh^{III}/Au^I Heterobimetallic Complexes as Catalysts for the Coupling of Nitrobenzene and Benzylic Alcohol

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Supporting Information

ABSTRACT: Two simple bisimidazolium salts derived from *m*- or p-bisimidazolebenzenes have been used as ligand precursors for the preparation of a series of heterobimetallic Rh^{III}/Au^I and Ir^{III}/Au^I complexes. All complexes have been fully characterized, and the molecular structures of selected derivatives have been determined by X-ray diffraction studies. These analyses showed that, regardless of the ligand used, the direct coordination environment of the metals is composed of identical donors (M^{III}: C_{NHC} , C_{benzene} , η^5 -Cp*, and I⁻; Au^I: C_{NHC} and I⁻) and is rather similar in the heterobimetallic complexes. The catalytic activity of the heterobimetallic complexes in the coupling of nitrobenzene with benzylic alcohol has been investigated. In all cases, the performance observed for the heterobimetallic complexes was superior to that shown by mixtures of homometallic M^{III}/Au^I complexes, suggesting a cooperative effect between the



two metal centers. In addition and in spite of the similarity of the donor groups of the two bis-NHC ligands used, the slightly different relative orientation of the two metals in the heterobimetallic complexes also plays a role in the catalytic conversion observed.

INTRODUCTION

Nitrogen-containing compounds are abundant in natural products, and many of them show an interesting biological and medical activity.¹ However, the construction of C-N bonds requires harsh reaction conditions or the use of expensive catalysts. Finding ways for the production of nitrogen-containing compounds using inexpensive starting materials and mild reaction conditions is still a major challenge for synthetic chemists.² Given that nitro compounds are inexpensive and easily available, the reductive coupling of alcohols and nitroarenes for the construction of C-N bonds through a metalcatalyzed tandem reaction involving transfer hydrogenation is highly desirable. Often, tandem processes involving at least one C-N bond formation step can generate structurally complex nitrogen-containing molecules. In addition, the use of one-pot multistep reactions is arguably the most efficient method for the production of nitrogen-containing compounds, since these processes avoid the need of isolation or purification of intermediates. One-pot reactions involving multiple catalytic processes facilitated by one catalyst can be an interesting alternative to multistep protocols.³ A close proximity between the catalytic active sites (the metals) often provides favorable conditions for the occurrence of an enhanced catalytic activity.⁴ This proximity can result from the use of catalysts with metal-metal interactions or by designing suitable ligands for multimetallic catalysts.⁵

We became interested in the preparation of NHC-based heterometallic complexes.⁶ In most cases, these complexes were obtained by the stepwise metalation of suitable ligand precursors, but some recent reports describe the convenient preparation of heterometallic complexes by a single-step siteselective metalation of the polycarbene ligands.⁷ Many of the heterometallic complexes prepared by us were used for tandem catalytic processes, and we often found that these catalysts outperformed the activity exhibited by mixtures of the related homometallic catalysts.^{5a,6e,k} With regard to the construction of C-N bonds, we have prepared an Ir^{III}/Pd^{II} catalyst for the generation of a variety of functionalized imines from nitroarenes and primary alcohols.^{6g} The multistep reaction involved the reduction of the nitroarene to an amine with the concomitant oxidation of the alcohol to an aldehyde followed by the condensation of the aldehyde and the amine to form the imine. We also observed that the combination of Ir^{III} and Au^I in a heterometallic catalyst produced important benefits in the reduction of nitroarenes with benzyl alcohol to produce N-benzylideneaniline.^{6h} The catalytic benefits resulting from the introduction of the gold(I) metal center into heterobimetallic catalysts can be related to the enhanced catalytic activity provided by organogold complexes when combined

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Scheme 1. Stepwise Preparation of M^{III}/Au^I Heterobimetallic Complexes



with palladium,⁸ iron,⁹ nickel,¹⁰ and rhodium¹¹ and serve as examples for dual catalysis.

On the basis of these previous results, we now describe the preparation of a new series of Rh^{III}/Au^{I} and Ir^{III}/Au^{I} complexes which we used as catalysts for the preparation of amines from the reaction of nitrobenzene and benzyl alcohol. We also describe evidence for dual catalytic action provided by the two different metals in the heterobimetallic complexes.

RESULTS AND DISCUSSION

Synthesis and Characterization of New Complexes. We hypothesized that two simple bisimidazolium salts such as 1^{12} and 2^{13} (Scheme 1) might constitute useful ligand precursors for the preparation of new heterometallic complexes. Due to their structural similarity, the bisimidazolium salts should also afford structurally related complexes which might exhibit different catalytic properties. The different relative orientation of the imidazolium units attached to the central benzene ring may provide a simple way for modulating the distance between two metal centers, while maintaining the basic steric and electronic properties of the ligand. The preparation of the M^{III}/Au^{I} (M = Rh, Ir) heterobimetallic complexes was achieved by the stepwise procedure displayed in Scheme 1. First, the monometallic Rh^{III} and Ir^{III} complexes [3]-[6] were prepared by the *in situ* deprotonation of the bisimidazolium salts with a mixture of cesium carbonate and sodium acetate in the presence of $[MCp*Cl_2]_2$ (M = Rh, Ir) and potassium iodine. All four complexes were obtained in very good yields (83-91%) and were characterized by NMR spectroscopy, mass spectrometry, and elemental analysis.

The monometallic complexes [3]-[6] were subsequently used as precursors for the preparation of the Rh^{III}/Au^I and Ir^{III}/Au^I heterobimetallic complexes [7]-[10]. The coordination of the second NHC donor to Au^I was achieved by transmetalation of the *in situ* preformed M^{III}/Ag^I-NHC complexes with [AuCl(tht)] (tht = tetrahydrothiophene) in CH₂Cl₂ at room temperature. The silver(I)-NHC complexes were generated by addition of Ag₂O to the metalloproligands [3]-[6]. Complexes [7]-[10] were obtained as air-stable compounds in yields ranging from 21 to 56%. Details regarding the characterization of complexes [3]-[10] can be found in the Experimental Section. The molecular structures of the monometallic complexes [3], [4], and [5] were determined by X-ray diffraction studies. The molecular structure of [3] is shown in Figure 1 (ORTEP diagrams of [4] and [5] are depicted in the Supporting Information).



Figure 1. Molecular structure (50% displacement ellipsoids) of complex [3] in [3]·MeCN. Hydrogen atoms (except H14) and the iodide counterion have been omitted for clarity. Selected bond distances (Å) and angles (deg): Rh–I 2.6940(4), Rh–C2 2.015(4), Rh–C12 2.031(4); I–Rh–C2 85.58(12), I–Rh–C12 90.58(12), C2–Rh–C12 78.20(17), N1–C2–N3 105.5(4), N13–C14–N15 108.7(4).

Complex [3] exhibits a *pseudo*-piano-stool geometry with the orthometalated phenyl-substituted imidazolylidene ligand and the iodo ligand forming the legs. The orthometalated phenyl ring contains an additional methylimidazolium substituent at the *p*-position relative to the metalated imidazolylidene. The cationic charge of the complex is balanced by the presence of an iodide counteranion. The Rh– $C_{\rm NHC}$ distance measures 2.015(4) Å and is unexceptional, as are the other molecular parameters.

Single crystals of the heterobimetallic complexes [7] and [8] suitable for X-ray diffraction studies were obtained by vapor diffusion of diethyl ether into saturated acetonitrile solutions of the complexes. Their molecular structures are depicted in Figure 2. These are very similar and confirm the coordination of the M^{III} center (M = Rh, Ir) by one NHC ligand and the orthometalation of the M^{III} center through the central phenyl ring. This leaves the M^{III} center in a *pseudo*-piano-stool coordination geometry composed of a Cp* ligand, a C_{NHC}^C_{phenyl} chelate ligand, and a iodo ligand. The Au^I center is coordinated



Figure 2. Molecular structures of [7] in [7]· $0.5Et_2O$ ·MeCN (top) and [8] in [8]· $0.5Et_2O$ ·MeCN (bottom, 50% displacement ellipsoids). Hydrogen atoms and the iodo counterions have been omitted for clarity. The asymmetric unit of both compounds contains two essentially identical molecules, one of which is depicted. Selected bond distances (Å) and angles (deg) for [7] [[8]]: M–I2 2.6664(17) [2.6819(4)], M–C9 2.048(17) [2.055(5)], M–C14 1.988(17) [1.996(5)], Au–I1 2.5493(15) [2.5512(4)], Au–C2 2.034(19) [1.997(6)]; I2–M–C9 92.8(4) [91.41(13)], I2–M–C14 85.1(5) [85.05(14)], C9–M–C14 77.1(7) [77.9(2)], I1–Au1–C2 176.5(6) [176.17(16)], N1–C2–N3 107.9(16) [105.2(5)], N13–C14–N15 104.1(15) [104.6(4)]. The asymmetric unit contains two formula units for both compounds, one of which is shown.

by the second imidazolylidene donor, with an iodo donor completing the linear arrangement about this metal center. The bond lengths and angles around the rhodium or iridium centers fall within the expected range, $(Rh-C_{NHC} = 1.988(17) \text{ Å}$, $Ir-C_{NHC} = 1.996(5) \text{ Å}$). The Au- C_{NHC} bond distances measure 2.034(19) Å for [7] and 1.997(6) Å for [8].

Catalytic Studies. The heterobimetallic complexes [7]-[10] were tested in the catalytic coupling between nitrobenzene and benzyl alcohol. The reduction of nitroarenes normally involves the use of molecular hydrogen and Pd/C. This catalytic system is very active in the hydrogenation of many functional groups, but the main drawback is the lack of chemoselectivity. The mechanism of reduction of nitrobenzene leading to aniline is known to involve various intermediates;¹⁴ thus, an effective new catalyst must not only generate the products in high yield, but it should also be highly selective to give only one product. For comparative purposes, we also tested the activity of mixtures of monometallic complexes. To this end, we prepared complexes [11]–[13] featuring the metal centers in a stereoelectronic environment similar to that observed in the dinuclear complexes [7]–[10] (Scheme 2).





The catalytic reactions were carried out using nitrobenzene and benzyl alcohol (which also acted as solvent) in the presence of Cs_2CO_3 at 100 °C with a 0.5 mol % catalyst loading. From the results shown in Table 1, it can be concluded that

Table 1. Catalytic Tandem Condensation of Nitrobenzene with Benzyl Alcohol and Imine Reduction^{a,b}



^{*a*}The reaction produces benzaldehyde as a necessary side-product. Reaction conditions: 0.3 mmol of nitrobenzene, 1 mL of benzyl alcohol, 0.3 mmol of Cs_2CO_3 , 0.5% catalyst loading, 100 °C, 22 h. ^{*b*}Yields were determined by GC using anisol (0.3 mmol) as an internal standard. ^{*c*}0.25 mol % catalyst loading. ^{*d*}0.1 mol % catalyst loading. ^{*e*}The reaction was conducted in the presence of a drop of mercury.

the outcome of the reaction is highly dependent on the catalyst used in the reaction. First, we observe that the mixture of monometallic complexes [11]/[13] and [12]/[13] (entries 1 and 2) afforded moderate yields of the imine III with yields slightly over 55%. This result is interesting when compared with the activity shown by the monometallic complexes [12] and [13] alone (entries 3 and 4), for which we observed that the iridium(III) complex [12] produced moderate amounts of the imine, while the Au^{I} complex [13] mainly yielded the azoxy (I) and azo (II) reaction intermediates. This latter product mixture is about the same as what was obtained in the absence of a catalyst (entry 5). The results obtained with the monometallic complexes indicate that the M^{III} complexes alone are not efficient in the coupling between the nitroarene and the primary alcohol, but the combination of the Ir^{III} and Au^I catalysts is beneficial when compared to the activity of the M^{III} complex alone. This result is also in agreement with our previous findings showing the dual action of Ir^{III} and Au^I for the same process.^{6h}

When comparing the performance of the heterobimetallic catalysts, we observe that the type of ligand used for the construction of these complexes has important ramifications for their catalytic conversions. The conversions obtained with Rh^{III}/Au¹ catalysts [7] and [9] (entries 6 and 8) are identical; however, [7] yields N-benzylideneaniline (III) as the major product, while [9] catalyzes the formation of the benzylphenylamine (IV) as the major product. Comparison of the Ir^{III}/Au^{I} catalysts [8] and [10] (entries 7 and 9) reveals a higher total conversion of [10] and similarly to the couple [7] and [9]catalyst [8] (para-bis-NHC) produces imine (III) as the major product, while [10] (*meta*-bis-NHC) produces the amine (IV) in an excellent yield of 82%. Given that the coordination environments and donors for both metal centers M^{III} (M = Rh, Ir) and Au^{I} are identical in catalysts [7]-[10], we believe that the differences in selectivity observed for either [7] and [8] (imine III as the major product) or [9] and [10] (amine IV as the major product) may be ascribed to electronic differences arising from the different bridging ligands.

Given the high activity of [10] in the production of the amine IV, the catalyst loading was reduced from the initial 0.5 mol % to 0.25 and 0.1 mol %. For these lower catalyst loadings, the production of the amine was reduced to 51 and 43%, respectively, although the conversion (related to the consumption of substrates) was complete in all cases. The mercury-drop test was performed in order to test if the process is homogeneously catalyzed.¹⁵ The comparison of the results (entries 9 and 12) indicates that the addition of the mercury drop has a small (but not negligible) influence on the percentage of conversion, with the yield of the amine IV dropping from 82 to 55%. This would indicate that the reduction of the imine is affected by the addition of the mercury drop. We assume that [10] can decompose to yield small gold nanoparticles, a process that should not affect the overall outcome of the process much, given the known activity of gold nanoparticles in the reduction of imines to amines.¹

In order to get some insight into the mechanism of the catalytic conversion, we decided to study the time-dependent reaction profile of the coupling between nitrobenzene and benzaldehyde (Figure 3). The reaction was carried out in



Figure 3. Time-dependent reaction profile of the reduction of nitroarene with catalyst [10]. Reagents and conditions: nitrobenzene (0.3 mmol), benzyl alcohol (as solvent and reagent, 1 mL), Cs_2CO_3 (0.3 mmol), anisole (as internal reference, 0.3 mmol), 100 °C, aerobic conditions. Yields were determined by GC analysis.

benzyl alcohol in the presence of Cs_2CO_3 at 100 °C using 0.5 mol % of [10]. As can be seen from the profile, the consumption of nitrobenzene proceeds concomitant with the formation of the imine and with negligible formation of the azo and azoxy intermediates which remain as minor products of

the reaction all along the profile. As soon as the imine is produced in a significant amount, the formation of the amine becomes evident, although the rate of reduction of the imine is clearly lower than the rate of reduction of nitrobenzene. This observation is rather logical if we take into account that imines are rather inert to reduction.

CONCLUSIONS

In summary, we have prepared a series of Rh^{III}/Au^I and Ir^{III}/Au^I heterobimetallic complexes by using two simple bisimidazolium salts as bis-NHC ligand precursors. The structural analysis of the new complexes shows that, regardless of the ligand used, the individual coordination environments and the donors bound to the two metals (M^{III} and Au^I) are very similar. The catalytic properties of the heterobimetallic complexes were tested in the coupling of nitrobenzene and benzyl alcohol. From the results obtained, we can conclude that (i) the cooperation of the two metals (M^{III} and Au^I) is supported by the fact that mixtures of homometallic M^{III}/Au^I complexes provide better results than the use of the individual monometallic complexes alone, (ii) the use of the heterobimetallic complexes affords better results than the use of mixtures of the related monometallic catalysts, particularly with the complexes derived from the meta-bis-NHC ligands, and (iii) in spite of the similar coordination environment at the metal centers provided by the two bis-NHC ligands used, the complexes of the meta-bis-NHC ligands ([9] and [10]) outperform the complexes of the para-bis-NHC ligands ([7] and [8]) regarding the production of the amine IV. Our study provides a new example for the benefits associated with the use of heterobimetallic complexes in facilitating complex organic transformations. However, at this time, our study is mostly phenomenological and the elucidation of the actual reaction mechanism and the parameters associated with it require further research.

EXPERIMENTAL SECTION

1. General Procedures. All reagents and solvents were used as received without further purification. ¹H and ¹³C{¹H} NMR spectra were recorded at 298 K on Bruker AVANCE I 400 and Bruker AVANCE III 400 spectrometers. Chemical shifts (δ) are expressed in ppm downfield from tetramethylsilane using the residual protonated solvent as an internal standard. Coupling constants are expressed in Hertz. Mass spectra were obtained with Reflex IV MALDI TOF (Bruker) and Orbitrap LTQ XL (Thermo Scientific, ESI) spectrometers. High resolution mass spectra (HRMS) were recorded on a Q-TOF Premier mass spectrometer (Waters) with an electrospray source operating in the V-mode. Elemental analyzes were carried out with an Elementar Vario EL III or a TruSpec Micro Series elemental analyzer. The two bisimidazolium salts 1 and 2 (Scheme 1) were synthesized according to reported procedures.^{12,13} The metal precursors [RhCp*(Cl)₂]₂,¹⁷ [IrCp*(Cl)₂]₂,¹⁷ and [AuCl(tht)]¹⁸ and the monometallic NHC complexes [11],¹⁹ [12],²⁰ and [13]¹⁸ were prepared according to literature procedures.

2. Synthesis of Complexes [3]–[6]. One of the ligand precursors 1 or 2 (0.20 mmol, 2.00 equiv), Cs_2CO_3 (0.15 mmol, 1.50 equiv), NaOAc (0.40 mmol, 4.00 equiv), $[MCp^*(Cl)_2]_2$ (M = Rh, Ir) (0.050 mmol, 0.50 equiv), and KI (0.60 mmol, 6.00 equiv) were dissolved in MeCN (30 mL). The reaction mixture was heated under reflux for 3 h and then allowed to cool down to ambient temperature. The obtained suspension was filtered through Celite, and the filtrate was brought to dryness *in vacuo*. The crude solid product was purified by column chromatography on silica (eluent: $CH_2Cl_2:MeOH = 6:1$) to give the desired complex as air and moisture stable solid.

2.1. Characterization of Complex [3].



Yield: 66.1 mg, 0.091 mmol, 91%. ¹H NMR (400 MHz, DMSO- d_6): δ (ppm) = 9.62 (s, 1H, H13), 8.21 (t, ${}^{3}J_{H,H}$ = 1.8 Hz, 1H, H16), 8.13 (d, ${}^{3}J_{HH}$ = 2.1 Hz, 1H, H5), 7.95 (t, ${}^{3}J_{H,H}$ = 1.8 Hz, 1H, H15), 7.77 (d, ${}^{4}J_{H,H}$ = 2.3 Hz, 1H, H10), 7.65 (d, ${}^{3}J_{H,H}$ = 8.3 Hz, 1H, H7), 7.56 (d, ${}^{3}J_{H,H}$ = 8.3 Hz, 1H, H7), 7.56 (d, ${}^{3}J_{H,H}$ = 2.1 Hz, 1H, H4), 7.31 (dd, ${}^{3}J_{HH}$ = 8.3 Hz, ${}^{4}J_{HH}$ = 2.3 Hz, 1H, H8), 3.97 (s, 3H, N–CH₃), 3.83 (s, 3H, N–CH₃), 1.82 (s, 15H, CH₃–Cp*). ¹³C{¹H} NMR (101 MHz, DMSO- d_6): δ (ppm) = 180.4 (d, ${}^{1}J_{C,Rh}$ = 54.4 Hz, C2), 160.3 (d, ${}^{1}J_{C,Rh}$ = 36.6 Hz, C11), 147.1 (s, C6), 135.3 (s, C10), 130.8 (s, C13), 130.1 (d, ${}^{3}J_{C,Rh}$ = 1.6 Hz, C9), 124.1 (s, C4), 124.0 (s, C16), 121.2 (s, C8), 116.3 (s, C5), 115.9 (s, C15), 111.4 (s, C7), 97.7 (d, ${}^{1}J_{C,Rh}$ = 4.7 Hz, C_q–Cp*), 37.3 (s, N–CH₃), 36.0 (s, N–CH₃), 10.1 (s, CH₃–Cp*). HR-MS (ESI, positive ions): m/z (%) = 603.0483 (100) (calculated for [3–I]⁺ 603.0492). MS (MALDI-TOF, matrix DCTB): m/z (%) = 603 (100) [3–I]⁺. Anal. Calcd for [3]-H₂O: C, 38.52; H, 4.18; N, 7.49. Found: C, 38.34; H, 4.16; N, 7.29.

2.2. Characterization of Complex [4].



Yield: 68.0 mg, 0.083 mmol, 83%. ¹H NMR (400 MHz, DMSO- d_6): δ (ppm) = 9.61 (s, 1H, H13), 8.20 (t, ${}^{3}J_{\rm H,\rm H}$ = 1.8 Hz, 1H, H16), 8.05 (d, ${}^{3}J_{\rm H,\rm H}$ = 2.2 Hz, 1H, H5), 7.94 (d, ${}^{3}J_{\rm H,\rm H}$ = 1.8 Hz, 1H, H15), 7.72–7.62 (m, 2H, H7, H10), 7.54 (d, ${}^{3}J_{\rm H,\rm H}$ = 2.1 Hz, 1H, H4), 7.23 (dd, ${}^{3}J_{\rm H,\rm H}$ = 8.3 Hz, ${}^{4}J_{\rm H,\rm H}$ = 2.4 Hz, 1H, H8), 3.97 (s, 3H, N–CH₃), 3.83 (s, 3H, N–CH₃), 1.88 (s, 15H, CH₃–Cp*). ¹³C{¹H} NMR (101 MHz, DMSO- d_6): δ (ppm) = 162.3 (s, C2), 147.8 (s, C6), 142.9 (s, C11), 135.3 (s, C10), 130.5 (s, C9), 129.7 (s, C13), 124.1 (s, C16), 123.0 (s, C4), 121.2 (s, C8), 115.4 (s, C5), 115.4 (s, C15) 111.0 (s, C7), 91.5 (s, C_q–Cp*), 37.0 (s, N–CH₃), 36.0 (s, N–CH₃), 9.9 (s, CH₃–Cp*). HR-MS (ESI, positive ions): m/z (%) = 693.1056 (100) (calculated for [4–I]⁺ 693.1066). MS (MALDI-TOF, matrix DCTB): m/z (%) = 693 (100) [4–I]⁺. Anal. Calcd for [4]: C, 35.17; H, 3.57; N, 6.84. Found: C, 34.91; H, 3.44; N, 6.77.

2.3. Characterization of Complex [5].



Yield: 65.5 mg, 0.090 mmol, 90%. ¹H NMR (400 MHz, DMSO- d_6): δ (ppm) = 9.73 (t, ${}^{3}J_{H,H} = 1.7$ Hz, 1H, H13), 8.26 (t, ${}^{3}J_{H,H} = 1.7$ Hz, 1H, H16), 8.06 (d, ${}^{3}J_{H,H} = 2.1$ Hz, 1H, H5), 7.96 (t, ${}^{3}J_{H,H} = 1.7$ Hz, 1H, H15), 7.90 (d, ${}^{4}J_{H,H} = 2.4$ Hz, 1H, H11), 7.79 (d, ${}^{3}J_{H,H} = 8.1$ Hz, 1H, H8), 7.58 (d, ${}^{3}J_{H,H} = 2.1$ Hz, 1H, H4), 7.28 (dd, ${}^{3}J_{H,H} = 8.1$ Hz, ${}^{4}J_{H,H} = 2.4$ Hz, 1H, H4), 7.28 (dd, ${}^{3}J_{H,H} = 8.1$ Hz, ${}^{4}J_{H,H} = 2.4$ Hz, 1H, H9), 3.97 (s, 3H, N–CH₃), 3.84 (s, 3H, N–CH₃), 1.81 (s, 15H, CH₃–Cp*). ${}^{13}C{}^{1}H$ NMR (101 MHz, DMSO- d_6): δ (ppm) = 181.0 (d, ${}^{1}J_{C,Rh} = 54.7$ Hz, C2), 160.1 (d, ${}^{1}J_{C,Rh} = 36.1$ Hz, C7), 147.4 (s, C6), 139.2 (s, C8), 135.3 (s, C13), 130.1 (s, C10), 124.1 (s, C15), 124.1 (s, C4), 121.0 (s, C16), 116.4 (s, C9), 115.6 (s, C5), 104.7 (s, C11), 97.7 (d, ${}^{1}J_{C,Rh} = 4.8$ Hz, C_q –Cp*), 37.4 (s, N–CH₃), 36.1 (s, N–CH₃), 10.1 (s, CH₃–Cp*). HR-MS (ESI, positive ions): m/z (%) = 603.0487 (100) (calculated for [5–I]⁺ 603.0492). MS (MALDI-TOF, matrix DCTB): m/z (%) = 603 (100) [5–I]⁺. Anal. Calcd for [5]·H₂O: C, 38.52; H, 4.18; N, 7.49. Found: C, 38.49; H, 3.90; N, 7.10.





Yield: 72.0 mg, 0.088 mmol, 88%. ¹H NMR (400 MHz, DMSO-*d*₆): δ (ppm) = 9.71 (t, ³*J*_{H,H} = 1.7 Hz, 1H, H13), 8.25 (t, ³*J*_{H,H} = 1.7 Hz, 1H, H16), 7.97 (d, ³*J*_{H,H} = 2.1 Hz, 1H, H5), 7.95 (t, ³*J*_{H,H} = 1.7 Hz, 1H, H15), 7.91 (d, ⁴*J*_{H,H} = 2.4 Hz, 1H, H11), 7.73 (d, ³*J*_{H,H} = 8.1 Hz, 1H, H8), 7.56 (d, ³*J*_{H,H} = 2.4 Hz, 1H, H11), 7.73 (d, ³*J*_{H,H} = 8.1 Hz, 1H, H8), 7.56 (d, ³*J*_{H,H} = 2.1 Hz, 1H, H4), 7.21 (dd, ³*J*_{H,H} = 8.1 Hz, ⁴*J*_{H,H} = 2.4 Hz, 1H, H9), 3.96 (s, 3H, N–CH₃), 3.84 (s, 3H, N–CH₃), 1.87 (s, 15H, CH₃–Cp*). ¹³C{¹H} NMR (101 MHz, DMSO-*d*₆): δ (ppm) = 162.8 (s, C2), 147.4 (s, C7), 143.0 (s, C6), 137.9 (s, C8), 135.2 (s, C13), 129.3 (s, C10), 124.1 (s, C15), 123.1 (s, C4), 121.0 (s, C16), 117.0 (s, C9), 115.1 (s, C5), 104.3 (s, C11), 91.5 (s, C_q–Cp*), 37.1 (s, N–CH₃), 36.0 (s, N–CH₃), 9.9 (s, CH₃–Cp*). HR-MS (ESI, positive ions): *m/z* (%) = 693.1062 (100) (calculated for [6–I]⁺ 693.1066). MS (MALDI-TOF, matrix DCTB): *m/z* (%) = 693 (100) [6–I]⁺. Anal. Calcd for [6]: C, 35.17; H, 3.57; N, 6.84. Found: C, 34.88; H, 3.44; N, 6.71.

3. Synthesis and Characterization of Complexes [7]–[10]. To a mixture of one of the monometallic complexes [3]-[6] (0.08 mmol, 1.00 equiv) and Ag₂O (0.05 mmol, 0.60 equiv) was added CH₂Cl₂ (10 mL). The reaction mixture was stirred at room temperature under exclusion of light for 1 h, and the resulting dark suspension was filtered through a pad of Celite. A clear filtrate was obtained. To this was added upon stirring at ambient temperature [AuCl(tht)] (0.08 mmol, 1.00 equiv) and KI (1.2 mmol, 15.00 equiv). Immediately, the formation of a white precipitate was observed. The suspension was stirred for 18 h at room temperature and subsequently filtered through a small pad of Celite. After removal of the volatiles, the crude product was purified by column chromatography on silica (eluent CH₂Cl₂) to give the desired complex as an air and moisture stable solid. Further purification can be achieved by recrystallization from CH₂Cl₂/Et₂O.

3.1. Characterization of Complex [7].



Yield: 16.0 mg, 0.017 mmol, 21%. ¹H NMR (400 MHz, CD₂Cl₂): δ (ppm) = 7.78–7.76 (m, 1H, H10), 7.49 (d, ³J_{HH} = 2.1 Hz, 1H, H5), 7.34–7.30 (m, 1H, H8), 7.26 (d, ³J_{HH} = 2.1 Hz, H7), 7.23 (d, ³J_{HH} = 2.1 Hz, 1H, H16), 7.14–7.08 (m, 2H, H4, H15), 3.95 (s, 3H, N–CH₃), 3.89 (s, 3H, N–CH₃), 1.89 (s, 15H, CH₃–Cp*). ¹³C{¹H} NMR (101 MHz, CD₂Cl₂): δ (ppm) = 182.9 (d, ¹J_{RhC} = 54.5 Hz, C2), 181.0 (s, C13), 160.2 (d, ¹J_{RhC} = 36.2 Hz, C11), 146.9 (s, C6), 135.4 (s, C10), 135.3 (d, ³J_{C,Rh} = 1.8 Hz, C9), 123.3 (s, C16), 122.9 (C4), 121.8 (s, C15), 120.0 (s, C8), 115.6 (d, ³J_{C,Rh} = 1.4 Hz, C5), 111.0 (d, ³J_{C,Rh} = 1.4 Hz, C7), 98.6 (d, ¹J_{C,Rh} = 5.0 Hz, C_q–Cp*), 38.4 (s, N–CH₃), 38.3 (s, N–CH₃), 11.2 (s, CH₃–Cp*). HR-MS (ESI, positive ions): *m/z* (%) = 1401.0511 (100) (calculated for [2·7–Aul₂]⁺ 1401.0493). MS (MALDI-TOF, matrix DCTB): *m/z* (%) = 799 (25) [7–I]⁺; 1401 (100) [2·7–Aul₂]⁺. Anal. Calcd for [7]. CH₂Cl₂: *C*, 29.70; H, 2.99; N, 5.54. Found: C, 29.53; H, 2.87; N, 5.40.





Yield: 28.4 mg, 0.028 mmol, 34%. ¹H NMR (400 MHz, CD₂Cl₂): δ (ppm) = 7.72 (d, ⁴ $J_{H,H}$ = 2.3 Hz, 1H, H10), 7.42 (d, ³ $J_{H,H}$ = 2.1 Hz, 1H, H5), 7.29 (d, ³ $J_{H,H}$ = 8.2 Hz, 1H, H7), 7.25 (d, ³ $J_{H,H}$ = 1.8 Hz, 1H, H16), 7.15 (dd, ³ $J_{H,H}$ = 8.2 Hz, ⁴ $J_{H,H}$ = 2.3 Hz, 1H, H8), 7.11–7.05 (m, 2H, H4, H15), 3.95 (s, 3H, N–CH₃), 3.88 (s, 3H, N–CH₃), 1.94 (s, 15H, CH₃–Cp^{*}). ¹³C{¹H} NMR (101 MHz, CD₂Cl₂): δ (ppm) = 181.0 (s, C13), 164.7 (s, C2), 147.7 (s, C6), 143.2 (s, C11), 135.9 (s, C9), 134.3 (s, C10), 123.0 (s, C16), 122.4 (s, C4), 121.8 (s, C15), 119.1 (s, C8), 115.2 (s, C5), 110.6 (s, C7), 92.4 (s, C_q–Cp^{*}), 38.4 (s, N–CH₃), 38.0 (s, N–CH₃), 11.0 (s, CH₃–Cp^{*}). HR-MS (ESI, positive ions): m/z (%) = 1579.1635 (100) (calculated for [2·8–AuI₂]⁺ 1579.1620). MS (MALDI-TOF, matrix DCTB): m/z (%) = 889 (100) [8–I]⁺; 1581 (56) [2·8–AuI₂]⁺. Anal. Calcd for [8]·CH₂Cl₂·Et₂O): C, 29.65; H, 3.43; N, 4.77. Found: C, 29.47; H, 3.03; N, 4.97.

3.3. Characterization of Complex [9].



Yield: 17.2 mg, 0.021 mmol, 26%. The NMR spectra of complex [9] feature two sets of resonances caused by ligand redistribution at the gold atoms in solution (formation of NHC-Au-NHC complexes with a AuI₂ counterion). This type of redistribution at Au^I has been observed multiple times in the past with the same consequences for the NMR spectra.²¹ If resolved, we report the resonances for the complex [9] and those for the NHC-Au-NHC complexes obtained by ligand redistribution. ¹H NMR (400 MHz, CD_2Cl_2): δ (ppm) = 7.93-7.72 (m, 6H), 7.32-7.02 (m, 8H), 3.91 (s, br, 6H, 2 × N-CH₃ for two compounds), 3.48 and 3.45 (s, 3H each, N-CH₃ for two compounds), 1.87 and 1.86 (s, br, 15H each, $2 \times CH_3 - Cp^*$ for two compounds). ¹³C{¹H} NMR (101 MHz, CD₂Cl₂): δ (ppm) = 183.5 (br, C13 and C13'), 182.7 (d, ${}^{1}J_{C,Rh}$ = 55.0 Hz, C2), 182.7 (d, ${}^{1}J_{C,Rh}$ = 55.2 Hz, C2'), 159.6 (d, ${}^{1}J_{C,Rh}$ = 35.5 Hz, C7), 159.5 (d, ${}^{1}J_{C,Rh}$ = 35.2 Hz, C7'), 146.4 (s, C6), 146.4 (s, C6'), 139.2 (s, C8), 139.2 (s, C8'), 134.9 (s, C10), 134.9 (s, C10'), 123.6 (s, C15), 123.6 (s, C15'), 122.9 (s, C4), 122.9 (s, C4'), 122.6 (s, C16), 122.6 (s, C16'), 120.4 (s, C9), 120.4 (s, C9'), 116.4 (s, C5), 115.3 (s, C5'), 108.5 (s, C11), 108.5 (s, C11'), 98.3 (d, ${}^{1}J_{C,Rh}$ = 4.9 Hz, C_q-Cp*), 98.3 (d, ${}^{1}J_{C,Rh}$ = 4.9 Hz, C_q-Cp*), 38.9 (s, N-CH₃), 38.9 (s, N-CH₃'), 38.2 (s, N-CH₃), 38.2 (s, N-CH₃'), 10.6 (s, CH₃-Cp*), 10.6 (s, CH₃-Cp*'). HR-MS (ESI, positive ions): m/z (%) = 1401.0491 (100) (calculated for $[2.9-AuI_2]^+$ 1401.0493). MS (MALDI-TOF, matrix DCTB): m/z (%) = 799 (10) [9–I]⁺, 1401 (60) [2·9–AuI₂]⁺. Anal. Calcd for 9 CH₂Cl₂: C, 29.70; H, 2.99; N, 5.54. Found: C, 29.68, H, 2.81; N, 5.47.

3.4. Characterization of Complex [10].



The NMR spectra of complex [10] feature two sets of resonances caused by ligand redistribution at the gold atoms in solution (formation of NHC–Au–NHC complexes with a AuI₂ counterion). This type of redistribution at Au^I has been observed multiple times in the past with the same consequences for the NMR spectra.²¹ If resolved, we report the resonances for the complex [10] and those for the NHC–Au–NHC complexes obtained by ligand redistribution. Yield: 46 mg, 0.045 mmol, 56%. ¹H NMR (400 MHz, CD₂Cl₂): δ (ppm) = 7.81–7.69 (m, 6H), 7.32–7.27 (m, 2H), 7.19–7.08 (m, 6H), 3.89 (s, br, 6H, 2 × N–CH₃ for two compounds), 3.49 and

3.46 (s, 3H each, 2 × N–CH₃ for two compounds), 1.92 and 1.91 (s, br, 15H each, 2 × CH₃–Cp* for two compounds). ¹³C{¹H} NMR (101 MHz, CD₂Cl₂): δ (ppm) = 183.5 (br, C13 and C13'), 164.6 (s, C2), 164.5 (s, C2'), 147.3 (s, C6), 147.2 (s, C6'), 142.7 (s, C7), 142.6 (s, C7'), 138.1 (s, C8), 138.0 (s, C8'), 134.1 (s, C10), 134.1 (s, C10'), 122.9 (s, C15), 122.8 (s, C15'), 122.7 (s, C4), 122.7 (s, C4'), 122.6 (s, C16), 122.6 (s, C16'), 121.0 (s, C9), 120.9 (s, C9'), 115.8 (s, C5), 115.7 (s, C5'), 108.0 (s, C11), 107.9 (s, C11'), 92.1 (s, 2 × C_q–Cp*), 38.9 (s, N–CH₃), 38.8 (s, N–CH₃'), 37.9 (s, 2 × N–CH₃), 10.3 (s, 2 × CH₃–Cp*). HR-MS (ESI, positive ions): *m/z* (%) = 1579.1621 (100) (calculated for [2·10–AuI₂]⁺ 1579.1620). MS (MALDI-TOF, matrix DCTB): *m/z* (%) = 1579 (100) [2·10–AuI₂]⁺. Anal. Calcd for 10·CH₂Cl₂: C, 27.29; H, 2.75; N, 5.09. Found: C, 27.45; H, 2.82; N, 4.89.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.8b00642.

Spectra of the new complex, crystallographic data, and details of the catalytic studies (PDF)

Accession Codes

CCDC 1858122–1858126 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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