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Synthesis and Catalytic Applications of Heterobimetallic Carbene Complexes Obtained via Sequential Metalation of Two Bisazolium Salts

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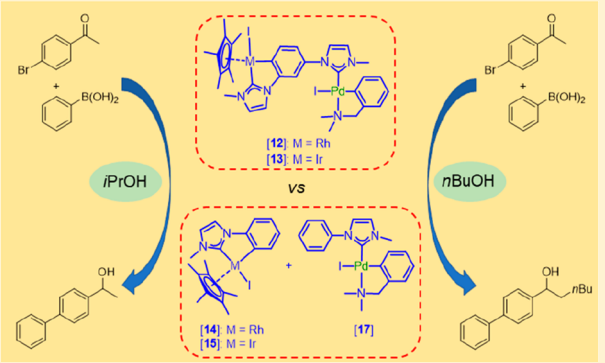
Supporting Information

ABSTRACT: A simple sequential metalation approach starting from the imidazolium/benzimidazolium salt **4**$(I)_2$ yielded the heterobimetallic Rh^{III}/M (M = Pd^{II}, Ir^{I}, Au^{I}, Ru^{II}) complexes [**6**]−[**9**]. Alternatively, a symmetrical 1,3-imidazolium substituted benzene was used for the preparation of the heterobimetallic M'/Pd^{II} (M′ = Rh^{III}, Ir^{III}) complexes [**12**] and [**13**]. The versatile stepwise approach used for the preparation of complexes [**6**]−[**9**] involved the deprotonation reaction of the bisazolium salt **4**$(I)_2$ in the presence of $[RhCp^*(Cl)_2]_2$ to afford the monometallic complex [**5**]I featuring a chelating coordinated bidentate C_{NHC}^C_{phenyl} ligand. Complex [**5**]I was reacted with Ag_2O to give a nonisolated Rh^{III}/Ag^{I} complex which in a subsequent transmetalation reaction yielded the heterobimetallic Rh^{III}/M bis-NHC complexes (M = Pd^{II} [**6**], Ir^{I} [**7**], Au^{I} [**8**], Ru^{II} [**9**]). Similarly, heterobimetallic M'/Pd^{II} bis-NHC complexes [**12**] (M′ = Rh^{III}) and [**13**] (M′ = Ir^{III}) have been prepared from a symmetrical bisazolium salt by generating first the monometallic M′ complexes followed by a transmetalation reaction of the *in situ* generated M'/Ag^{I} complexes with $[Pd(dmba)(\mu\text{-}Cl)]_2$. The Rh^{III}/Pd^{II} complexes [**6**] and [**12**] and the Ir^{III}/Pd^{II} complex [**13**] were used as catalysts for two orthogonal tandem reactions, namely, the Suzuki−Miyaura coupling/transfer hydrogenation and the Suzuki−Miyaura-coupling/α-alkylation of ketones. The catalytic activity of the heterobimetallic complexes was compared to mixtures of the related monometallic analogues [**14**]−[**17**], with the heterobimetallic complexes generally showing a higher catalytic activity. In addition, *n*BuOH was found to play a dual role as an alkylating and reducing agent in the Suzuki−Miyaura coupling/α-alkylation of ketones.



INTRODUCTION

Performing multiple reactions in a "one-pot" atom efficient scenario constitutes one of the most attractive targets for optimizing new catalytic transformations. Among one-pot reactions, orthogonal tandem catalysis is a process in which noninterfering, mechanistically distinct catalytic cycles are combined in order to facilitate the synthesis of organic molecules reducing both waste and time.[1] Polymetallic catalysis is based on the combined action of different metals in a chemical transformation.[2] Ultimately, the different catalysts must be compatible, meaning that they must accommodate the same reaction conditions and catalyst lifetimes over the whole sequence of catalytic transformations. If the two different metals are linked by a single-frame ligand, the close proximity between the metals may provide favorable conditions for the occurrence of improved catalytic properties.[3] This forms the basis for the recent significant interest in finding rational synthetic protocols for the preparation of heterometallic complexes.

We have contributed to the field of multimetallic catalysis by designing families of ditopic and tritopic N-heterocyclic carbene ligands (NHCs) for the preparation of heterometallic catalysts that were used in several orthogonal tandem processes.[3c,4] Among the combinations of metals that were studied, we found that heterometallic Ir/Pd or Rh/Pd complexes afforded highly versatile tandem catalysts, due to the large number of mechanistically distinct catalytic processes that could be combined.[4a,c,e] In particular, the combination of reactions involving the borrowing-hydrogen processes (catalyzed by Ir or Rh) with C−C coupling processes involving aryl halides (facilitated by Pd) constitute efficient one-pot methods

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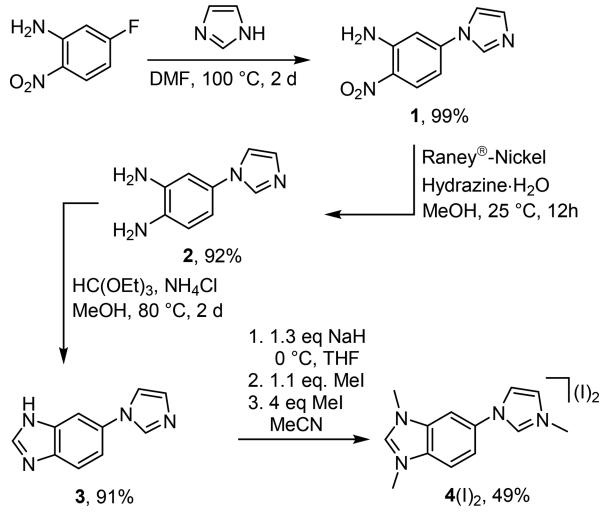
for the generation of complex organic molecules with potential pharmaceutical applications. Inspired by these results and aiming to find new effective methods for the preparation of NHC-based heterometallic homogeneous catalysts, we now report the synthesis of a family of M/Rh^{III} complexes (M = Pd^{II}, Ir^{I}, Au^{I}, and Ru^{II}) supported by a new benzimidazolylidene-imidazolylidene ligand. In addition, we describe two novel heterobimetallic Pd^{II}/M′ (M′ = Rh^{III}, Ir^{III}) complexes based on a benzene-bis(imidazolylidene) ligand. We also disclose the catalytic activity of various Pd^{II}/M (M = Rh^{III}, Ir^{III}) complexes in two different tandem transformations, namely the Suzuki−Miyaura coupling/transfer hydrogenation and Suzuki−Miyaura coupling/α-alkylation of *para*-bromoacetophenone.

RESULTS AND DISCUSSION

Synthesis and Characterization of New Complexes. For the synthesis of heterobimetallic complexes from a bis-NHC precursor, the benzimidazolium/imidazolium salt $\mathbf{4}(I)_2$ was prepared on the gram scale and in good yield following the multistep procedure depicted in Scheme 1.

Scheme 1. Synthesis of bis-NHC Ligand Precursor $\mathbf{4}(I)_2$

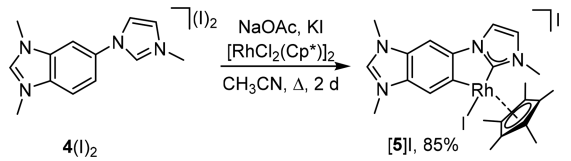


The synthesis of $\mathbf{4}(I)_2$ commenced with the preparation of **1** from 5-fluoro-2-nitroaniline and imidazole in 99% yield by a nucleophilic aromatic substitution. This was followed by reduction of the nitro group in **1** using hydrazine monohydrate and a catalytic amount of Raney nickel to give the diamine **2**. The benzimidazol moiety was constructed by condensation of the diamine **2** with ammonium chloride and triethyl orthoformate to give **3**. Finally, the triple N-alkylation was performed in a stepwise fashion. Deprotonation of the benzimidazole/imidazole derivative **3** with sodium hydride followed by the addition of methyl iodide resulted in the formation of di-NHC precursor $\mathbf{4}(I)_2$ in 49% yield.

Salt $\mathbf{4}(I)_2$ was fully characterized by NMR spectroscopy, mass spectrometry, and elemental analysis. In addition, an X-ray diffraction study confirmed the composition and molecular structure of $\mathbf{4}(I)_2$ (see the Supporting Information, Figure S23). Bisazolium salt $\mathbf{4}(I)_2$ was used as the starting material for the preparation of heterobimetallic bis-NHC complexes. These were prepared through the stepwise metalation of the NHC donors obtained by the sequential deprotonation of the azolium groups in $\mathbf{4}(I)_2$.

We first attempted the monometalation of $\mathbf{4}(I)_2$ by its reaction with 1 equiv of NaOAc as a base followed by the addition of 1 equiv of complexes $[MCl_2(Cp^*)]_2$ (M = Rh, Ir) and KI. KI was added to the reaction mixture in order to support the formation of only one halogen containing species. For M = Ir, this reaction led to a mixture of monometallic iridium complexes. However, for M = Rh only the monometalated complex [**5**]I was obtained. The metalation of $\mathbf{4}(I)_2$ with rhodium occurred selectively at the C2 position of the deprotonated imidazolium group leading via a subsequent orthometalation of the phenyl ring to the metallacycle found in [**5**]I (Scheme 2). The benzimidazolium

Scheme 2. Site-Selective Monometalation of Bisazolium Salt $\mathbf{4}(I)_2$



group stays intact. At this point we can only speculate about the reasons for the differences in reactivity observed for Ir^{III} and Rh^{III} in this monometalation. Rh−C_{NHC} bonds are known to be rather labile compared to the more inert Ir−C_{NHC} bonds.[5] Thus, it is reasonable to assume that any undesirable M−benzimidazolylidene complex can rearrange to the more stable C_{NHC}^C_{phenyl} chelate complex for M = Rh, while such a rearrangement is less likely for M = Ir. We therefore assume that the selective formation of monometalated rhodium chelate complex [**5**]I is favored, but only for metals forming reasonably labile M−C_{NHC} bonds such as rhodium (and not Ir^{III}) which can rearrange to the most stable complex.

Complex [**5**]I was obtained in a high yield of 85% and characterized by NMR spectroscopy, mass spectrometry, and elemental analysis. The ^{1}H NMR spectrum features the resonance for the benzimidazolium N−CH−N proton at δ = 9.44 ppm only slightly upfield from the equivalent resonance in $\mathbf{4}(I)_2$, while the resonance for an imidazolium N−CH−N proton was no longer detected. Clear evidence for the metalation by rhodium was provided by $^{13}C\{^1H\}$ NMR spectroscopy showing the resonances for the rhodium bound C_{NHC} and C_{phenyl} carbon atoms at δ = 180.3 ppm (d, $^1J_{C,Rh}$ = 54.2 Hz) and δ = 157.5 ppm (d, $^1J_{C,Rh}$ = 36.7 Hz), respectively.

The molecular structure of [**5**]I was determined by an X-ray diffraction study (Figure 1). Cation $[\mathbf{5}]^+$ adopts the classical piano-stool geometry. The rhodium center is coordinated by a bidentate, orthometalated *N*-phenyl substituted imidazolylidene ligand; a pentamethylcyclopentadienyl ligand; and an iodo ligand. The C_{NHC}^C_{phenyl} chelate ligand exhibits a rather small bite angle (angle C2−Rh−C8 78.01(19)°), leading to angles involving the iodo ligand (I−Rh−C2 91.70(15)° and I−Rh−C8 92.80(14)°) which are both larger than 90°. In accord with previous observations,[6] a smaller N−C−N angle (N1−C2−N3 105.4(5)°) was observed for the metalated diamino-heterocycle in comparison to the protonated one (N13−C14−N15 110.4(5)°). The Rh−C2 distance measures 1.993(5) Å and thus falls in the range previously reported for rhodacycle complexes bearing an C_{NHC}^C_{phenyl} chelate ligand.[7] The Rh−C2 distance, however, is significantly shorter than the Rh−C8 separation of 2.049(5) Å. This situation was previously suggested by $^{13}C\{^1H\}$ NMR spectroscopy where the longer

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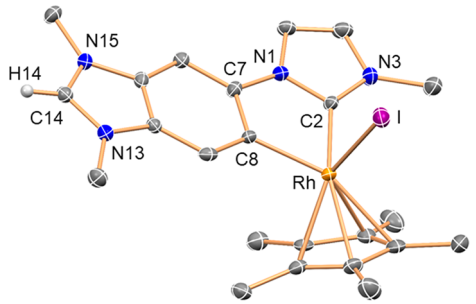
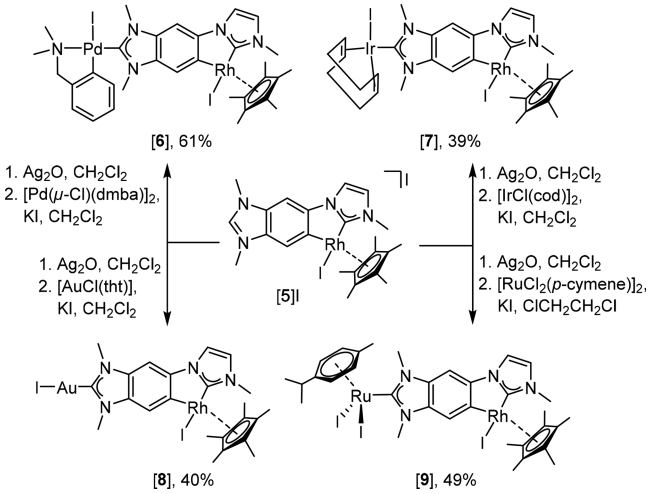


Figure 1. Molecular structure (50% displacement ellipsoids, hydrogen atoms except for H14 have been omitted for clarity) of complex cation $[5]^+$ in $[5]I{\cdot}2.5CH_2Cl_2$. The asymmetric unit contains two essentially identical equivalents of [5]I, only one of which is depicted. Selected bond distances (Å) and angles (deg): Rh−I 2.6903(5), Rh−C2 1.993(5), Rh−C8 2.049(5), range Rh−C_{Cp^*} 2.142(5)−2.269(5), N1−C2 1.352(6), N3−C2 1.341(6), N13−C14 1.332(7), N15−C14 1.339(7); I−Rh−C2 91.70(15), I−Rh−C8 92.80(14), C2−Rh−C8 78.01(19), N1−C2−N3 105.5(4), N13−C14−N15 110.4(5).

Rh−C8 separation leads to a smaller $^1J_{C,Rh}$ coupling constant of 36.7 Hz than the shorter Rh−C2 bond ($^1J_{C,Rh}$ = 54.2 Hz). The remaining bond distances and bond angles in [5]I fall in the range observed previously for related rhodium complexes.[7,8a]

Compound [5]I appears to be a useful starting material for the preparation of heterobimetallic complexes. It can act as a metalloligand and become metalated at the benzimidazolium site with a second metal. The rhodacycle in [5]I is stable enough to tolerate the deprotonation/metalation of the benzimidazolium group. Starting from [5]I, we have prepared the heterobimetallic Rh^{III}/M complexes [6]−[9] (M = Pd^{II}, Ir^{I}, Au^{I}, and Ru^{II}, Scheme 3) in moderate yields, which are most likely caused by the two reactions (reaction with Ag_2O followed by transmetalation) performed in a one-pot synthesis.

Scheme 3. Preparation of Heterobimetallic Complexes [6]−[9] from [5]I



The metalation of the benzimidazolim site in [5]I was accomplished by transmetalation of the metalloligand from the *in situ* generated Ag^{I}/Rh^{III}-bis-NHC complex to Pd^{II}, Ir^{I}, Au^{I}, and Ru^{II} complexes. The Ag^{I}/Rh^{III}-bis-NHC complex was obtained from [5]I and Ag_2O in dichloromethane. This complex was not isolated but used directly for the transmetalation reaction.

The Rh^{III}/Pd^{II} complex [6] was synthesized in 61% yield by transmetalation of the metalloligand from the Ag^{I}/Rh^{III}-bis-NHC complex to $[Pd(\mu\text{-}Cl)(dmba)]_2$ in dichloromethane (Scheme 3). Complex [6] was obtained as an air stable mixture of two isomeric complexes in the ratio 60:40. The NMR spectra feature two sets of resonances (see the Supporting Information, Figures S11 and S12) for the two atropisomers. For example, the C_{NHC} resonances were observed in the $^{13}C\{^1H\}$ NMR spectrum at δ = 181.9 ppm (d, $^1J_{C,Rh}$ = 54.6 Hz, C_{NHC}−Rh), δ = 181.3 ppm (C_{NHC}−Pd) for isomer A, and at δ = 181.6 ppm (C_{NHC}−Pd), δ = 180.0 ppm (d, $^1J_{C,Rh}$ = 54.7 Hz, C_{NHC}−Rh) for isomer B. The two different atropisomers apparently result from the hindered rotation about the Pd−C_{NHC} bond, which leads to two different orientations of the {Pd(dmba)I} moiety relative to the Rh(Cp*) moiety. Restricted rotation about the Pd−C_{NHC} bond in palladium complexes bearing the dmba ligand resulting in the formation of atropisomers has been observed multiple times and is rather common for such complexes.[9]

Similarly, complex [7] was prepared by transmetalation of the metalloligand from the *in situ* generated Ag^{I}/Rh^{III}-bis-NHC complex to $[IrCl(cod)]_2$ in dichloromethane in 39% yield. No isomeric complexes were observed in the case of [7]. The $^{13}C\{^1H\}$ NMR spectrum features the resonances for the Ir−C_{NHC} carbon atom at δ = 188.4 ppm and for the Rh−C_{NHC} carbon atom at δ = 182.1 ppm (d, $^1J_{C,Rh}$ = 54.7 Hz).

Crystals of composition $[7]{\cdot}CH_2Cl_2$ were obtained by vapor diffusion of diethyl ether into a solution of [7] in dichloromethane. The molecular structure of the heterodinuclear complex (Figure 2) features a hexacoordinate Rh^{III} and a square-planar, tetracoordinate Ir^{I} atom. The metric parameters of the complex fragment containing the rhodium atom do not differ significantly from those found in the mononuclear complex [5]I, indicating that the second metalation does not affect the bond parameters involving the rhodium atom. Metalation of the benzimidazolium site, however, changes the metric parameters within the affected diaminoheterocycle significantly. In accord with previous observations,[6] the N−C−N angle of the iridium−metalated benzimidazolylidene shrinks to 106.0(5)° from 110.4(5)° in the benzimidazolium

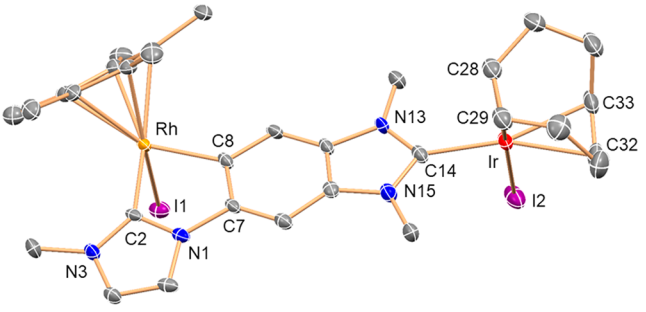


Figure 2. Molecular structure (50% displacement ellipsoids, hydrogen atoms have been omitted for clarity) of complex [7]. Selected bond distances (Å) and angles (deg): Ir−I2 2.6515(5), Ir−C14 2.024(5), Ir−C28 2.113(7), Ir−C29 2.102(6), Ir−C32 2.203(6), Ir−C33 2.189(6), Rh−I1 2.6865(5), Rh−C2 1.992(5), Rh2−C8 2.038(5), range Rh−C_{Cp^*} 2.153(5)−2.268(6); I2−Ir−C14 89.09(15), I1−Rh−C2 90.18(15), I1−Rh−C8 90.15(15), C2−Rh−C8 78.2(2), N1−C2−N3 104.7(4), N13−C14−N15 106.0(5).

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unit of [5]I. The bite angle of the bidentate C_{NHC}^C_{phenyl} ligand measures 78.2(2)° and is thus very similar to the equivalent bite angle in [5]I. The Ir−C_{cod} bond distances *trans* to the NHC ligand (Ir−C32 2.203(6) Å, Ir−C33 2.189(6) Å) are significantly longer than the Ir−C_{cod} bond distances *trans* to the iodo ligand (Ir−C28 2.113(7) Å, Ir−C29 2.102(6) Å) in accord with a long C28−C29 bond of 1.439(10) Å and a shorter C32−C33 bond of 1.399(10) Å. This is most likely due to the anionic iodo ligand being a better donor than the NHC ligand.

Reaction of [5]I with Ag_2O followed by transmetalation with [AuCl(tht)] yielded the heterobimetallic Au^I/Rh^{III} complex [8] (Scheme 3). This complex was characterized by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy, mass spectrometry, and elemental analysis. The $^{13}C\{^1H\}$ NMR spectrum of [8] features the characteristic resonances for the C_{NHC}−Au carbon atom at δ = 185.7 ppm and for the C_{NHC}−Rh carbon atom at δ = 182.7 ppm (d, $^1J_{C,Rh}$ = 54.7 Hz). The latter resonance is almost unchanged when compared to the equivalent resonances in [5]I and [7].

Crystals of [8]·1.25CH_2Cl_2 were obtained by vapor diffusion of diethyl ether into a CH_2Cl_2 solution of [8]. The structure analysis (Figure 3) shows the rhodium atom coordinated the

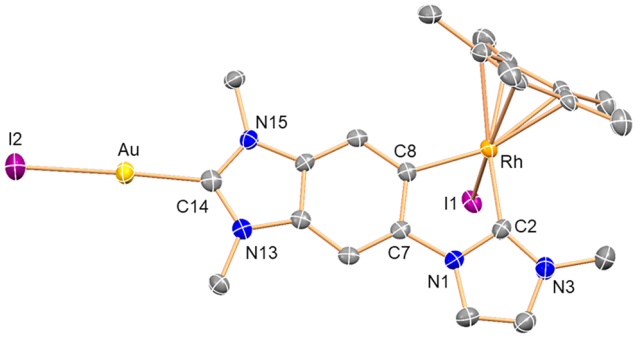

Figure 3. Molecular structure (50% displacement ellipsoids, hydrogen atoms have been omitted for clarity) of [8]. The asymmetric unit contains two essentially identical molecules of [8], only one of which is depicted, and 2.5 CH_2Cl_2 molecules. Selected bond distances (Å) and angles (deg): Au−I2 2.5309(4), Au−C14 1.988(5), Rh−I 2.6923(5), Rh−C2 2.003(5), Rh−C8 2.051(5), range Rh−C_{Cp^*} 2.158(6)−2.261(5); I2−Au−C14 173.34(15), I1−Rh−C2 86.61(14), I1−Rh−C8 88.73(13), C2−Rh−C8 78.3(2), N1−C2−N3 104.7(4), N13−C14−N15 106.2(4).

same fashion as previously observed for [5]I and [7]. The gold atom is coordinated almost linearly (angle I2−Au−C14 173.34(15)°). All other metric parameters in [8] compare well to equivalent parameters in [7]. The bonds involving the gold atom fall in the range previously reported for related gold(I) complexes.[10]

Finally, complex [5]I was metalated at the benzimidazolium site with ruthenium(II) by reacting the monometallic complex [5]I with Ag_2O followed by transmetalation with [$RuCl_2$(*p*-cymene)]$_2$ in 1,2-dichloroethane (Scheme 3). ^1H and $^{13}C\{^1H\}$ NMR spectroscopy indicate the formation of the heterobimetallic complex [9]. Formation of [9] was confirmed by an X-ray diffraction analysis (Figure 4) showing the two metals coordinated in a piano-stool geometry. The bond parameters are unspectacular, and the {Rh(Cp*)(NHC)I} moiety in [9] is essentially unchanged when compared to the same moiety in [7] and [8].

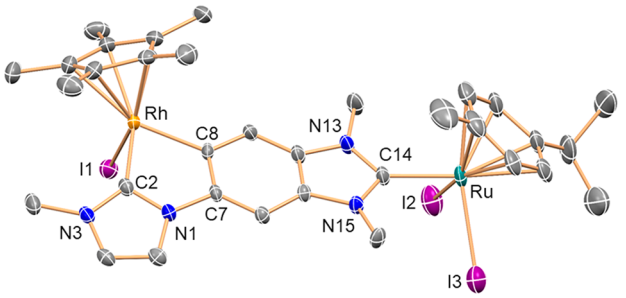

Figure 4. Molecular structure (50% displacement ellipsoids, hydrogen atoms have been omitted for clarity) of complex [9]. Selected bond distances (Å) and angles (deg): Rh−I1 2.6878(7), Rh−C2 1.998(7), Rh−C8 2.060(6), range Rh−C_{Cp^*} 2.154(7)−2.260(7), Ru−I2 2.7282(9), Ru−I3 2.7583(9), Ru−C14 2.074(7); I1−Rh−C2 92.6(2), I1−Rh−C8 93.6(3), C2−Rh−C8 77.5(3), I2−Ru−I3 82.84(3), I2−Ru−C14 97.9(2), I3−Ru−C14 86.3(2), N1−C2−N3 104.9(6), N13−C14−N15 105.0(5).

The preparation of complexes [6]−[9] illustrates the suitability of the bisazolium salt **4**$(I)_2$ for the preparation of a variety of heterobimetallic complexes. The coordination of the three different metals (Ir^I, Au^I, and Ru^{II}) to the monometallic complex[5]I has little influence on the metric parameters of the {Rh(Cp*)(NHC)I} moiety in the resulting heterobimetallic complexes as illustrated by the almost unchanged Rh−C_{NHC} (1.993(5) in [5]I, 1.992(5) in [7], 2.003(5) in [8], and 1.998(7) Å in [9]) and Rh−C_{phenyl} distances (2.049(5) in [5]I, 2.038(5) in [7], 2.051(5) in [8], and 2.060(6) Å in [9]).

Next, we wanted to test the applicability of the heterobimetallic complexes in orthogonal tandem catalysis. We thought that complexes of type [6] would be perfect to start this investigation given our previous experience in designing tandem processes for the Ir/Pd and Rh/Pd couples.[4a,b,b,e] In order to expand the number of Ir/Pd and Rh/Pd catalysts used and aiming to perform a more detailed comparative study, we also prepared two additional heterobimetallic M^{III}/Pd^{II} (M = Rh, Ir) complexes based on a benzene-bridged bis-imidazolylidene ligand. As shown in Scheme 4, complexes [12] and [13] were prepared from the monometallic M^{III} complexes [10] and [11], which recently have been described.[8a]

The second metalation of the metalloligands [11] and [12] with Pd^{II} was achieved by transmetalation of the *in situ* generated Ag^I/M^{III}-NHC (M = Rh, Ir) complexes, generated by the addition of Ag_2O to [10] and [11], respectively, with [PdCl(dmba)]$_2$. The new complexes were characterized by NMR spectroscopy, mass spectrometry, and elemental analysis. The NMR spectra of complexes [12] and [13] display double signal sets for all resonances (Figures S19−S22) indicative of the formation of two atropisomers. These are present in ratios of 55:45 [12] and 52:48 [13], respectively. The existence of the two atropisomers is a consequence of the restricted rotation about the C_{phenyl}−N_{NHC} bond of the imidazolylidene donor bound to Pd^{II}. Formation of similar atropisomers has been observed for complex [6] and for additional palladium NHC complexes bearing the dmba ligand.[9]

Catalytic Studies. The heterobimetallic Pd/M (M = Ir, Rh) complexes [6], [12], and [13] were tested in two different catalytic tandem transformations. These were the Suzuki−Miyaura coupling/transfer hydrogenation and the Suzuki−Miyaura coupling/α-alkylation of *para*-bromoacetophenone. In

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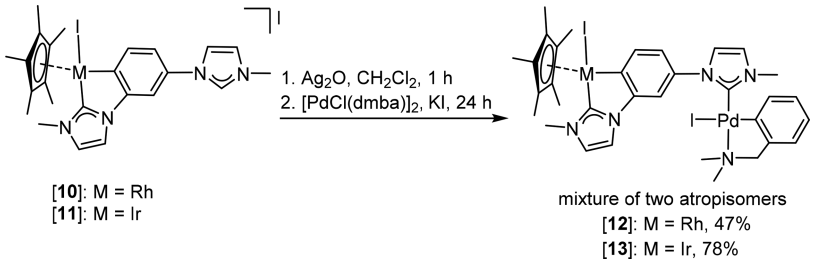
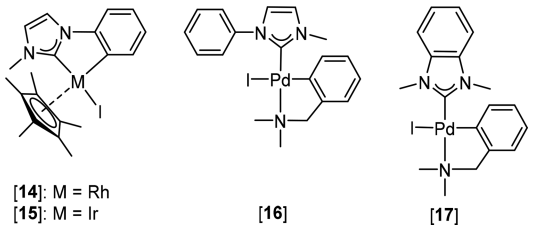
Scheme 4. Preparation of Heterobimetallic M^{III}/Pd^{II} Complexes [12] and [13]



order to determine if the heterobimetallic nature of the complexes would generate any benefits compared to the activity provided by mixtures of monometallic analogs, we also prepared the known complexes [**14**],[11] [**15**],[12] [**16**],[9a] and [**17**][9a] (Scheme 5) using described synthetic procedures.

Scheme 5. Monometallic Complexes Prepared for Comparative Catalytic Studies



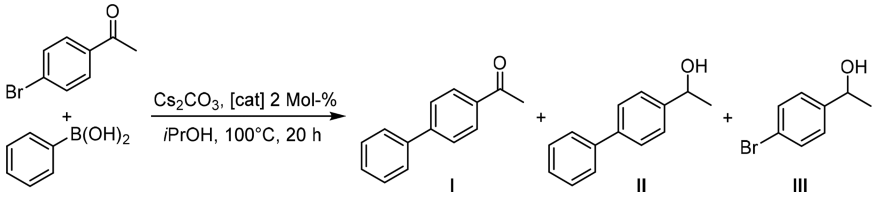
These monometallic complexes feature virtually the same stereoelectronic properties as the corresponding complex fragments in complexes [**6**], [**12**], and [**13**].

First, we evaluated the activity of three mixtures containing the monometallic complexes in the catalytic Suzuki coupling/transfer hydrogenation of *p*-bromoacetophenone in isopropyl alcohol (Table 1, entries 1−3) under standard reaction conditions.[4a] The reaction mixture containing complexes [**14**] + [**16**] (entry 2) produced compound **II** in high yield (84%). Compound **II** resulted from the Suzuki−Miyaura C−C coupling and the reduction of the ketone to an alcohol, indicating that the combination of a rhodium and a palladium catalyst is very effective in this tandem reaction. The mixtures containing [**14**] + [**17**] and [**15**] + [**16**] were less effective, indicating that the optimum combination of catalysts for promoting the tandem reaction involves the use of the rhodium catalyst (rather than iridium) and the imidazolylidene (rather than the benzimidazolylidene) palladium catalyst.

Next, the performance of the three heterobimetallic complexes [**6**], [**12**], and [**13**] (entries 4−6) was evaluated for the same process. The catalytic activity observed for the heterobimetallic complexes [**12**] and [**13**] was comparable to that displayed by the most active mixture [**14**] + [**16**](entry 2) and superior to that shown by [**6**]. Interestingly, the Pd^{II}/Ir^{III} complex [**13**] (entry 6) showed somewhat higher activity than the corresponding mixture [**15**] + [**16**] of two monometallic complexes (entry 3). Finally, a blank reaction carried out in the absence of any catalyst afforded only the hydrogenated reaction product **III** in 54% yield.

In order to get further insight into the catalytic process, the time-dependent reaction profile of the Suzuki−Miyaura coupling/transfer hydrogenation of *p*-bromoacetophenone was studied (Figure 5). The reaction was carried out in 2-propanol in the presence of Cs_2CO_3 at 100 °C using 2 mol % of the most active catalyst [**13**]. As can be seen from the reaction profile, the consumption of the *p*-bromoacetophenone is accompanied by the immediate formation of **I**. The subsequent reduction of the ketone affords the corresponding alcohol derivative **II** in 84% yield after 24 h. The reaction profile also shows that the palladium catalyzed C−C coupling between the acetophenone and the boronic acid occurs almost instantaneously. The reduction of the ketone, however, is a

Table 1. Catalytic Suzuki Coupling/Transfer Hydrogenation of *p*-Bromoacetophenone in Isopropyl Alcohol[a]



entry	catalyst	time h	conversion %	yield %[b] I	II	III
1	[**14**] + [**17**]	20	98	36	62	0
2	[**14**] + [**16**]	20	99	15	84	0
3	[**15**] + [**16**]	20	98	25	73	0
4	[**6**]	20	99	46	53	0
5	[**12**]	20	99	17	82	0
6	[**13**]	20	99	15	84	0
7	none	20	70	0	0	54

[a]Reaction conditions: 0.36 mmol of *p*-bromoacetophenone, 0.54 mmol of phenylboronic acid, 1.08 mmol of Cs_2CO_3, 2 mL of 2-propanol (as reagent and solvent), 2 mol % catalyst loading, 100 °C, 20 h. [b]Yields were determined by GC using anisole (0.36 mmol) as internal standard.

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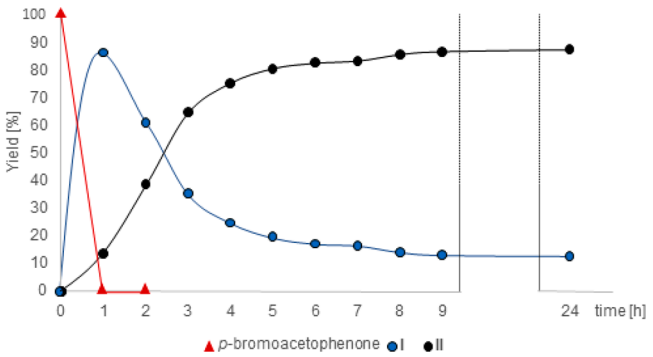


Figure 5. Time-dependent reaction profile of the Suzuki–Miyaura coupling/transfer hydrogenation in 2-propanol using catalyst [**13**]. Reaction conditions: 0.36 mmol of *p*-bromoacetophenone, 0.54 mmol of phenylboronic acid, 1.08 mmol of Cs_2CO_3, 2 mL of 2-propanol (as reagent and solvent), 2 mol % catalyst loading, 100 °C, 20 h. Yields were determined by GC using anisole (0.36 mmol) as an internal standard.

much slower process and constitutes the rate-determining step of the overall reaction. This situation also accounts for the observation that no direct reduction of *p*-bromoacetophenone to the alcohol **III** was observed in the presence of any catalyst (Table 1).

In view of the results obtained for the Suzuki–Miyaura coupling/transfer hydrogenation reaction, we next decided to explore the performance of the heterobimetallic catalysts in the Suzuki–Miyaura coupling/α-alkylation of *p*-bromoacetophenone.[4a] This model reaction has straightforward applications, since the resulting biphenyl substituted ketones are known to behave as nonsteroidal inhibitors of 5α-reductase, the enzyme that catalyzes the conversion of testosterones to dihydrotestosterone.[13]

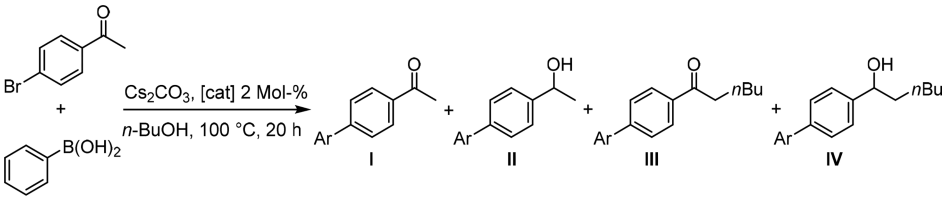
We initially tested the activity of mixtures of [**14**] + [**16**] and [**15**] + [**16**] (Table 2, entries 1 and 2), using a 2 mol % catalyst loading in the presence of Cs_2CO_3 and *n*-butyl alcohol both as a solvent and as an alkylating reagent. Although full conversion was observed for both mixtures, only a small amount of the alkylated biphenyl ketone **III** was obtained together with a negligible amount of the biphenyl alkylated alcohol **IV** (entries 1 and 2). A blank experiment was carried out in the absence of any catalyst (entry 3). While 54% conversion was detected in this experiment, a mixture of decomposition products was obtained, and none of the compounds **I**–**IV** was detected. We then evaluated the performance of the heterobimetallic complexes [**12**] and [**13**] (entries 4 and 5). Of these, the heterobimetallic Pd^{II}/Rh^{III} complex [**12**] produced 24% of **III** and 40% of the alcohol **IV** (entry 4), while the Pd^{II}/Ir^{III} complex [**13**] produced 37% of **III** and 13% of **IV** (entry 5). These results indicate that both heterobimetallic complexes are significantly more active than the respective mixtures of the monometallic analogues and also showed that the heterobimetallic catalysts are more active in the reduction of the ketone to the alcohol.

At this point, it should be mentioned that the alkylation of the ketone to give **III** and subsequently alcohol **IV** proceeds via the well-accepted steps for an α-alkylation process[14] followed by reduction of the ketone by transfer hydrogenation.[15] This reaction sequence involves (*i*) hydrogen transfer from *n*-butanol to iridium to give the aldehyde and the iridium–hydride complex, (*ii*) base-catalyzed condensation between the resulting butanal and the ketone to give the α,β-unsaturated ketone, (*iii*) selective hydrogenation of the α,β-unsaturated ketone to form ketone **III**, and (*iv*) reduction of **III** by an iridium dihydride, again generated by reaction of the catalyst and *n*-butanol. Obviously, the overall process implies that butanal is produced in the reaction sequence, although we were unable to detect it.

In order to confirm that the reaction was homogeneously catalyzed and that the activity of the catalysts was not due to the formation of metal nanoparticles generated by decomposition of the heterobimetallic complex, we carried out the same reaction using catalyst [**12**] in the presence of a drop of mercury (entry 6). We observed that both, the activity and selectivity of the process was quasi-identical compared to the performance in the absence of mercury (compare to entry 4), and therefore the contribution of heterogeneous nanoparticles to the catalytic process can be discarded.

The time dependent reaction profile of the Suzuki–Miyaura coupling/α-alkylation is depicted in Figure 6. The reaction was carried out in *n*-butyl alcohol in the presence of Cs_2CO_3 at 100

Table 2. Suzuki–Miyaura Coupling/α-Alkylation in *n*-Butyl Alcohol[a]



				yield %[b]			
entry	catalyst	time h	conversion %	I	II	III	IV
1	[**14**] + [**16**]	20	99	0	14	21	6
2	[**15**] + [**16**]	20	99	11	23	12	5
3	none	20	54	0	0	0	0
4	[**12**]	20	99	6	12	24	40
5	[**13**]	20	99	4	8	37	13
6[c]	[**12**]	20	99	6	11	20	38

[a]Reaction conditions: 0.36 mmol of *p*-bromoacetophenone, 0.54 mmol of phenylboronic acid, 1.08 mmol of Cs_2CO_3, 2 mL of *n*-butanol (as reagent and solvent), 2 mol % catalyst loading, 100 °C, 20 h. [b]Yields were determined by GC using anisole (0.36 mmol) as an internal standard. [c]The reaction was performed in the presence of a drop of mercury.

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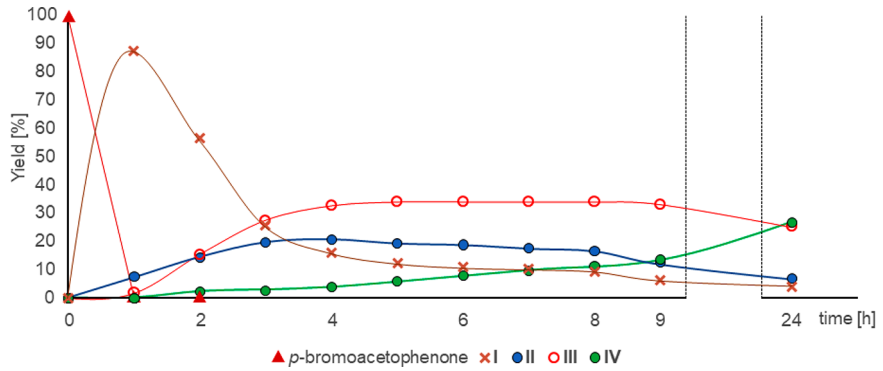


Figure 6. Time-dependent reaction profile of the Suzuki–Miyaura coupling/α-alkylation in *n*-butyl alcohol with catalyst [**12**]. Reaction conditions: 0.36 mmol of *p*-bromoacetophenone, 0.54 mmol of phenylboronic acid, 1.08 mmol of Cs_2CO_3, 2 mL of *n*-butanol (as reagent and solvent), 2 mol % catalyst loading, 100 °C, 20 h. Yields were determined by GC using anisole (0.36 mmol) as an internal standard under aerobic conditions.

°C using 2 mol % of catalyst [**12**]. As can be seen from the profile, the consumption of *p*-bromoacetophenone proceeds rapidly with concurrent formation of **I**, indicating that the palladium catalyzed C–C coupling is faster than the rhodium-catalyzed borrowing hydrogen processes. The formation of compounds **II** and **IV** occurs at a similar rate, as both involve the borrowing-hydrogen processes with a common rate-determining step. The formation of **IV** as the major product is only completed after 20 h of reaction time.

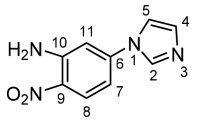
CONCLUSIONS

In summary, we have used bisazolium salts for the preparation of a variety of heterobimetallic complexes with the metal combinations Rh/Ru, Rh/Ir, Rh/Au, Rh/Pd, and Ir/Pd. The easy-to-prepare bisazolium salts together with the high-yield syntheses of the metal complexes illustrate that this methodology can be used for the preparation of a much larger library of heterobimetallic complexes. The Rh/Pd and the Ir/Pd complexes prepared were tested as catalysts in two orthogonal tandem reactions, namely, the palladium catalyzed Suzuki–Miyaura coupling/transfer hydrogenation and the Suzuki–Miyaura coupling/α-alkylation of ketones. Although the activity of the heterobimetallic catalysts was not superior compared to that found for related catalysts reported by us[4a] and others,[8b] two important results emerged from our study: (*i*) in general, the activity of the heterobimetallic complexes was superior to the activity shown by mixtures of the related monometallic analogues, suggesting that catalytic additivity or cooperativity may play an important role in the process, and (*ii*) *n*-BuOH was found to play a dual action as an alkylating and reducing agent, thus constituting a novelty in this type of process for which *i*PrOH is often needed in order to reduce the ketone to alcohol. The reasons for the higher activity of the heterobimetallic complexes compared to mixtures of monometallic ones remain elusive and are subject to speculations, as is the case with related reactions described in the literature.

EXPERIMENTAL SECTION

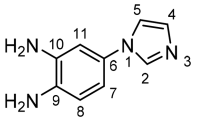
General Procedures. All manipulations were carried out under an argon atmosphere unless stated otherwise. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded at 298 K on Bruker AVANCE I 400 and Bruker AVANCE III 400 spectrometers. Chemical shifts (δ) are expressed in parts per million downfield from tetramethylsilane using the residual protonated solvent as an internal standard. Coupling constants are expressed in Hertz. For the assignment of the NMR resonances, see the numbering in the molecular plots. Mass spectra were obtained with Reflex IV MALDI TOF (Bruker) and Orbitrap LTQ XL (Thermo Scientific, ESI) spectrometers. Elemental analyses were carried out with an Elementar Vario EL III CHNS analyzer. The metal precursors $[RhCp^*(Cl)_2]_2$,[16] $[IrCp^*(Cl)_2]_2$,[16] [AuCl(tht)-Cl],[10] $[Ir(cod)Cl]_2$,[17] $[Pd(dmba)(\mu\text{-}Cl)]_2$,[9a] and $[Ru(p\text{-cymene})\text{-}Cl_2]_2$[18] were prepared according to literature procedures.

Synthesis of 5-(1H-Imidazol-1-yl)-2-nitroaniline ***1****.* A sample of 5-fluoro-2-nitroaniline (5.00 g, 32.0 mmol) and imidazol (8.72 g, 128.1



mmol) were dissolved in DMF (40 mL), and the mixture was stirred at 100 °C for 2 days. The solution was then allowed to cool to ambient temperature, and H_2O (100 mL) was added. A yellow precipitate formed, which was isolated by filtration, washed with H_2O (2 × 100 mL), and dried *in vacuo* to give **1** as a yellow solid. Yield: 6.52 g (31.9 mmol, 99%). ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 8.27 (s, 1H, H2), 8.09 (d, $^3J_{H,H}$ = 9.3 Hz, 1H, H8), 7.68 (s, 1H, H4/5), 7.53 (s, 2H, NH_2), 7.19 (d, $^4J_{H,H}$ = 2.4 Hz, 1H, H11), 7.15 (s, 1H, H4/5), 6.95 (dd, $^3J_{H,H}$ = 9.3 Hz, $^4J_{H,H}$ = 2.4 Hz, 1H, H7). ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): δ (ppm) 147.0 (C9), 141.8 (C10), 135.5 (C2), 130.5 (C8), 128.6 (C6), 127.8 (C11), 117.5 (C7), 108.1 (C4/5), 107.8 (C4/5). MS (EI, 20 eV): *m*/*z* (%) 204 (100, [**1**]$^+$). HRMS (ESI, positive ions): *m*/*z* (%) 205.0722 (100, calculated for [**1**+H]$^+$, 205.0726), 227.0542 (50, calculated for [**1** + Na]$^+$, 227.0545). MS (MALDI-TOF, matrix DHB): *m*/*z* (%) 205 (100, [**1**+H]$^+$). Anal. Calcd for **1**: C, 52.93; H, 3.95; N, 27.44. Found: C, 52.22; H, 3.90; N, 27.16.

Synthesis of 4-(1H-Imidazol-1-yl)benzene-1,2-diamine ***2****.* Compound **1** (4.67 g, 22.9 mmol) and hydrazine monohydrate (4.44 mL,



91.5 mmol) were dissolved in MeOH (50 mL). The yellow solution was cooled to 0 °C, and a catalytic amount of Raney nickel was added dropwise. The dark suspension was stirred at ambient temperature for 12 h. The suspension was then filtered through Celite leading to a colorless solution. The solvent was removed to yield a white solid. Yield: 3.68 g (21.1 mmol, 92%). ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 7.88 (s, 1H, H2), 7.39 (s, 1H, H4/5), 7.01 (s, 1H, H4/5), 6.67 (d, $^4J_{H,H}$ = 2.2 Hz, 1H, H11), 6.60–6.57 (m, 2H, H7/8), 4.77 (s, 2H, NH_2), 4.64 (s, 2H, NH_2). ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): δ (ppm) 135.8 (s, C9/10), 135.2 (C-2), 134.2 (s, C9/10), 128.9 (C8), 127.6 (C6), 118.3 (C11), 114.2 (C7), 109.6 (C4/5), 107.0 (C4/5). MS (EI, 20 eV): *m*/*z* (%) 174 (100, [**2**]$^+$). HRMS (ESI, positive ions): *m*/*z* (%) 175.0976 (100, calculated for [**2** + H]$^+$, 175.0984),

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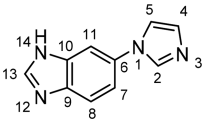
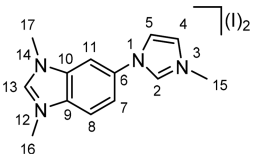
197.0799 (30, calculated for $[2+Na]^+$, 197.0803). MS (MALDI-TOF, matrix DHB): m/z (%) 175 (100, $[2 + H]^+$). Anal. Calcd for **2**: C, 62.05; H, 5.79; N, 32.16. Found: C, 61.74; H, 5.81; N, 31.94

Synthesis of 6-(1H-Imidazol-1-yl)-1H-benzo[d]imidazole ***3***. Diamine **2** (3.68 g, 21.1 mmol), ammonium chloride (226 mg, 4.2 mmol)



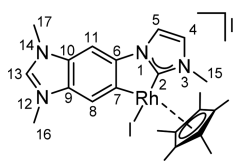
and triethyl orthoformate (5.25 mL, 31.7 mmol) were dissolved in MeOH (40 mL), and the mixture was heated to reflux for 2 days. After cooling to ambient temperature, all volatiles were removed *in vacuo*. The residue was dissolved in H_2O (20 mL), and the solution was extracted with EtOAc (10 × 80 mL). The combined organic extracts were dried over $MgSO_4$, and the solvent was removed *in vacuo* to give **3** as a red solid. Yield: 3.56 g (19.3 mmol, 91%). ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 12.68 (br, 1H, NH), 8.29 (s, 1H, H2), 8.16 (s, 1H, H13), 7.84 (s br, 1H, H11), 7.73 (s, 1H, H4/5), 7.71 (d, $^3J_{H,H}$ = 8.7 Hz, 1H, H8), 7.43 (dd, $^3J_{H,H}$ = 8.7 Hz, $^4J_{H,H}$ = 2.0 Hz, 1H, H7), 7.10 (s, 1H, H4/5). ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): δ (ppm) 143.6 (C13), 135.9 (C2), 131.8 (br), 129.5, 119.8 (br), 118.8, 115.7 (br), 112.4 (br), 111.1 (br), 104.2 (br). MS (EI, 20 eV): m/z (%) 184 (100, $[3]^+$). HRMS (ESI, positive ions): m/z (%) 185.0819 (80, calculated for $[3 + H]^+$, 185.0827), 207.0639 (100, calculated for $[3 + Na]^+$, 207.0647). MS (MALDI-TOF, matrix DHB): m/z (%) 185 (100, $[3+H]^+$). Anal. Calcd for **3**: C, 65.21; H, 4.38; N, 30.42. Found: C, 65.11; H, 4.50; N, 30.05.

Synthesis of [N-(6′-(1′, 3′-Dimethylbenzimidazolyl)-N′-methyl]-imidazoliumdiiodide ***4***$(I)_2$. To a solution of compound **3** (3.56 g,



19.3 mmol) in dry THF (40 mL) was added sodium hydride (60% dispersion in mineral oil, 1.00 g, 25.1 mmol) at 0 °C. The reaction mixture was then stirred at ambient temperature until the gas evolution had ceased. Subsequently, methyl iodide (1.33 mL, 21.3 mmol) was added dropwise, and the suspension was stirred for 12 h. All volatiles were then removed *in vacuo*. Acetonitrile (50 mL) and methyl iodide (4.81 mL, 77.2 mmol) were added to the residue, and the solution was heated under reflux for 2 days. The resulting precipitate was isolated by filtration, washed with a small amount of acetonitrile, and dried *in vacuo*. The bisazolium salt **4**$(I)_2$ was obtained as an off-white solid. Yield: 4.54 g (9.42 mmol, 49%). ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 9.97 (s, 1H, H2), 9.86 (s, 1H, H13), 8.65 (d, $^4J_{H,H}$ = 2.1 Hz, 1H, H11), 8.44 (s, 1H, H5), 8.35 (d, $^3J_{H,H}$ = 8.9 Hz, 1H, H8), 8.12 (dd, $^3J_{H,H}$ = 8.9 Hz, $^4J_{H,H}$ = 2.1 Hz, 1H, H7), 8.05 (s, 1H, H4), 4.18 (s, 3H, H16/17), 4.15 (s, 3H, H16/17), 4.01 (s, 3H, H15). ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): δ (ppm) 145.5 (C13), 136.5 (C2), 132.7 (C6), 131.7 (C9), 131.9 (C10), 124.5 (C4), 121.2 (C5), 120.2 (C7), 115.4 (C8), 107.7 (C11), 36.3 (C15), 33.8 (C16/17), 33.7 (C16/17). HRMS (ESI, positive ions): m/z (%) 355.0434 (100, calculated for $[4 + I]^+$, 355.0420). Anal. Calcd for **4**(I_2): C, 32.39; H, 3.35; N, 11.62. Found: C, 31.98; H, 3.37; N, 11.54.

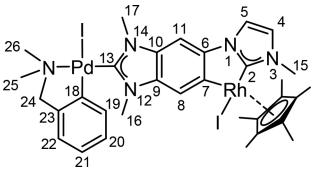
Synthesis of [5]I. To a mixture of **4**$(I)_2$ (96 mg, 0.20 mmol), NaOAc (66 mg, 0.8 mmol), KI (133 mg, 0.8 mmol), and



$[Rh(Cp^*)Cl_2]_2$(30.9 mg, 0.05 mmol) was added acetonitrile (40 mL). The red suspension was heated to reflux for 2 days. The resulting yellow suspension was filtered through Celite, and the filtrate was brought to dryness under reduced pressure. The yellow residue was purified by chromatography (silica gel, CH_2Cl_2/MeOH, 6:1) to give compound [**5**]I as an orange, hygroscopic solid. Yield: 61 mg (0.085 mmol, 85%). ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 9.44 (s, 1H, H13), 8.22 (d, $^3J_{H,H}$ = 2.1 Hz, 1H, H5), 8.18 (s, 1H, H11), 7.90 (s, 1H, H8), 7.61 (d, $^3J_{H,H}$ = 2.1 Hz, 1H, H4), 4.10 (s, 3H, H16/17), 4.04 (s, 3H, H16/17), 3.84 (s, 3H, H15), 1.82 (s, 15H, Cp*-CH_3). ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): δ (ppm) 180.3 (d, $^1J_{C,Rh}$ = 54.2 Hz, C2), 157.5 (d, $^1J_{C,Rh}$ = 36.7 Hz, C7), 144.9 (s, C6), 128.8 (s, C9/10), 128.6 (s, C9/10), 124.4 (s, C4), 120.4 (s, C8), 115.9 (s, C5), 97.9 (d, $^1J_{C,Rh}$ = 4.8 Hz, Cp*-C), 95.4 (s, C11), 37.4 (s, C15), 33.0 (s, C16/17), 32.8 (s, C16/17), 10.1 (s, Cp*-CH_3). HRMS (ESI, positive ions): m/z (%) 591.0485 (100, calculated for $[5]^+$, 591.0492). MS (MALDI-TOF, matrix DHB): m/z (%) 591 (100, $[5]^+$). Anal. Calcd for [**5**]I·H_2O: C, 37.52; H, 4.24; N, 7.61. Found: C, 37.57; H, 4.16; N, 7.43.

General Procedure for the Synthesis of Complexes [6]–[8]. To a mixture of the monometallic complex [**5**]I (72 mg, 0.10 mmol) and Ag_2O (23 mg, 0.10 mmol) was added CH_2Cl_2 (15 mL). The reaction mixture was stirred at ambient temperature for 24 h under exclusion of light. Subsequently, the second metal precursor ($[Pd(\mu\text{-}Cl)(dmba)]_2$, 28 mg, 0.05 mmol or $[Ir(\mu\text{-}Cl)(cod)]_2$, 34 mg, 0.05 mmol, or [AuCl(tht)], 32 mg, 0.10 mmol) and KI (166 mg, 1.0 mmol) were added, and the reaction mixture was stirred for an additional 24 h. The resulting suspensions were filtered through Celite, and the solvent of the filtrate was removed under reduced pressure.

Complex [6]. Analytically pure [**6**] was obtained as an isomer mixture by column chromatography on aluminum oxide/CH_2Cl_2.



Yield: 58 mg (0.061 mmol, 61%). Isomer A (60%), ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.71 (s, 1H, H8), 7.47 (d, $^3J_{H,H}$ = 2.1 Hz, 1H, H5), 7.15 (s, 1H, H11), 7.02 (d, $^3J_{H,H}$ = 2.1 Hz, 1H, H4), 7.06–6.99 (m, 1H, H22), 6.99–6.92 (m, 1H, H21), 6.72–6.67 (m, 1H, H20), 5.94–5.87 (m, 1H, H19), 4.13 (s, 3H, H16), 4.07 (s, 3H, H17), 4.02–4.00 (m, 1H, H24), 3.96 (s, 1H, H24), 3.90 (s, 3H, H15), 3.01 (s, 3H, H25/26), 2.99 (s, 3H, H25/26), 1.87 (s, 15H, Cp*-CH_3). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ (ppm) 181.9 (d, $^1J_{C,Rh}$ = 54.6 Hz, C2), 181.3 (s, C13), 152.9 (s, C18), 150.7 (d, $^1J_{C,Rh}$ = 36.1 Hz, C7), 148.4 (s, C23), 141.2 (s, C6), 134.9 (s, C19), 133.0 (s, C9), 132.1 (s, C10), 125.8 (s, C20), 124.1 (s, C21), 122.6 (s, C4), 122.4 (s, C22), 118.9 (s, C8), 115.2 (s, C5), 98.1 (d, $^1J_{C,Rh}$ = 4.9 Hz, Cp*-C), 93.2 (s, C11), 71.9 (s, C24), 52.2 (s, C25/26), 51.9 (s, C25/26), 38.0 (s, C15), 35.5 (s, C17), 35.3 (s, C16), 10.6 (s, Cp*-CH_3). Isomer B (40%), ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.69 (s, 1H, H8), 7.27 (s, 1H, H11), 7.22 (d, $^3J_{H,H}$ = 2.1 Hz, 1H, H5), 7.06–6.99 (m, 1H, H22), 6.99–6.92 (m, 1H, H21), 6.72–6.67 (m, 1H, H20), 6.67 (d, $^3J_{H,H}$ = 2.1 Hz, 1H, H4), 5.94–5.87 (m, 1H, H19), 4.17 (s, 3H, H16), 4.04 (s, 3H, H17), 3.98 (s, 2H, H24), 3.93 (s, 3H, H15), 3.01 (s, 3H, H25/26), 2.99 (s, 3H, H25/26), 1.85 (s, 15H, Cp*-CH_3). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ (ppm) 181.6 (s, C13), 180.0 (d, $^2J_{C,Rh}$ = 54.7 Hz, C2), 153.4 (s, C18), 150.5 (d, $^2J_{C,Rh}$ = 35.9 Hz, C7), 148.7 (s, C23), 141.5 (s, C6), 134.6 (s, C19), 132.7 (s, C9), 132.1 (s, C10), 125.4 (s, C20), 124.0 (s, C21), 122.5 (s, C22), 122.2 (s, C4), 118.2 (s, C8), 115.4 (s, C5), 98.0 (d, $^2J_{C,Rh}$ = 4.8 Hz, Cp*-C), 94.4 (s, C11), 71.9 (s, C24), 52.1 (s, C25/26), 52.1 (s, C25/26), 38.4 (s, C15), 35.5 (s, C16), 35.3 (s, C17), 10.6 (s, Cp*-CH_3). HRMS (ESI, positive ions): m/z (%) 830.0424 (45, calculated for $[6–I]^+$, 830.0431), 979.9371 (10, calculated for $[6+Na]^+$, 979.9373). MS (MALDI-TOF, matrix DHB): m/z (%) 830 (100, $[6–I]^+$). Anal.

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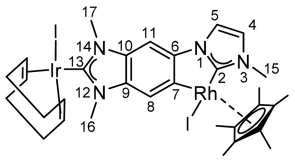
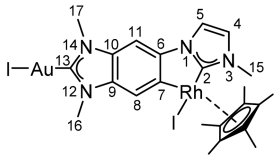
Calcd for [**6**]·CH_2Cl_2: C, 38.01; H, 4.06; N,6.72. Found: C, 38.33; H, 4.07; N, 6.35.

Complex [7]. Analytically pure [7] was obtained by extraction of the raw product with Et_2O (3 × 20 mL) and subsequent removal of



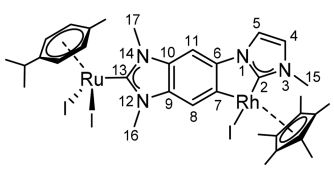
the solvent from the extract *in vacuo*. Yield: 40 mg (0.039 mmol, 39%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.60 (s, 1H, H8), 7.44 (d, $^3J_{H,H}$ = 2.1 Hz, 1H, H5), 7.04 (s, 1H, H11), 7.02 (d, $^3J_{H,H}$ = 2.1 Hz, 1H, H4), 4.89−4.83 (m, 2H, cod-CH), 4.08 (s, 3H, H16), 4.03 (s, 3H, H17), 3.91 (s, 3H, H15), 3.04−2.89 (m, 2H, cod-CH), 2.32−2.07 (m, 4H, cod-CH_2), 1.88 (s, 15H, Cp*-CH_3), 1.86−1.80 (m, 2H, cod-CH_2), 1.46−1.40 (m, 2H, cod-CH_2). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ (ppm) 188.4 (s, C13), 182.1 (d, $^1J_{C,Rh}$ = 54.7 Hz, C2), 150.3 (d, $^1J_{C,Rh}$ = 36.1 Hz, C7), 140.7 (s, C6), 133.7 (s, C9), 132.7 (s, C10), 122.6 (s, C4), 118.5 (s, C8), 115.0 (s, C5), 98.1 (d, $^1J_{C,Rh}$ = 4.4 Hz, Cp*-C), 92.8 (s, C11), 84.0 (s, cod-CH), 84.0 (s, cod-CH), 55.5 (s, cod-CH), 55.3 (s, cod-CH), 38.0 (s, C15), 34.1 (s, C16/17), 34.1 (s, C16/17), 33.0 (s, cod-CH_2), 33.0 (s, cod-CH_2), 30.3 (s, cod-CH_2), 30.3 (s, cod-CH_2), 10.6 (s, Cp*-CH_3). MS (MALDI-TOF, matrix DHB): *m*/*z* (%) 891 (20, [7−I]$^+$). Anal. Calcd for [7]·H_2O: C, 35.95; H, 4.09; N, 5.41. Found: C, 35.45; H, 3.85; N, 4.99.

Complex [8]. Analytically pure [**8**] was obtained by column chromatography on silica gel/CH_2Cl_2. Yield: 34 mg, 0.04 mmol, 40%.



^{1}H NMR (400 MHz, CD_2Cl_2): δ (ppm) 7.74 (s, 1H, H11), 7.56 (d, $^3J_{H,H}$ = 2.1 Hz, 1H, H5), 7.23 (s, 1H, H8), 7.12 (d, $^3J_{H,H}$ = 2.1 Hz, 1H, H4), 4.05 (s, 3H, H16/17), 3.98 (s, 3H, H16/17), 3.90 (s, 3H, H15), 1.85 (s, 15H, Cp*-CH_3). ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2): δ (ppm) 185.7 (s, C13), 182.7 (d, $^1J_{C,Rh}$ = 54.7 Hz, C2), 154.7 (d, $^1J_{C,Rh}$ = 36.2 Hz, C7), 143.6 (s, C6), 131.7 (d, $^3J_{C,Rh}$ = 2.0 Hz, C9), 130.9 (s, C10), 123.6 (s, C4), 120.4 (s, C8), 115.6 (s, C5), 98.6 (d, $^1J_{C,Rh}$ = 4.7 Hz, Cp*-C), 94.2 (s, C11), 38.4 (s, C15), 35.0 (s, C16/17), 35.0 (s, C16/17), 10.1 (s, Cp*-CH_3). HRMS (ESI, positive ions): *m*/*z* (%) 936.9026 (30, calculated for [**8** + Na]$^+$, 936.9022), 952.8760 (90, calculated for [**8** + K]$^+$, 952.8761), 1377.0490 (100, calculated for [2[**8**]−Au−2I]$^+$, 1377.0493). MS (MALDI-TOF, matrix DCTB): *m*/*z* (%) 787 (75, [**8**−I]$^+$), 1377 (39, [2[**8**]−Au−2I]$^+$). Anal. Calcd for [**8**]: C, 30.22; H, 3.09; N, 6.13. Found: C, 29.90; H, 2.99; N, 5.90.

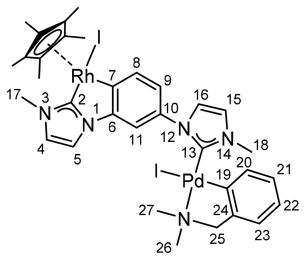
Synthesis of Complex [9]. To a mixture of complex [**5**]I (72 mg, 0.1 mmol) and Ag_2O (23 mg, 0.1 mmol) was added 1,2-



dichloroethane (15 mL). The reaction mixture was stirred at ambient temperature for 24 h under exclusion of light. Subsequently, [$RuCl_2$(*p*-cymene)]$_2$ (31 mg, 0.05 mmol) and KI (166 mg, 1.0 mmol) were added, and the reaction mixture was heated to 60 °C for 24 h. The suspension was filtered through Celite, and the filtrate was concentrated to 2 mL. The addition of 15 mL of Et_2O resulted in the formation of a precipitate. The precipitate was isolated by filtration, washed with Et_2O, and dried *in vacuo*. Yield: 53 mg (0.049 mmol, 49%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.88 (s, 1H, H8), 7.49 (s, 1H, H5), 7.07 (s, 1H, H4), 7.07 (s, 1H, H11), 5.73−5.62 (m, 2H, *p*-Cym-CH), 5.25−5.14 (m, 2H, *p*-Cym-CH), 4.27 (s, 3H, H16), 4.19 (s, 3H, H17), 3.92 (s, 3H, H15), 3.40−3.23 (m, 1H, *p*-Cym-C*H*(CH_3)$_2$), 1.94 (s, 3H, *p*-Cym-CH_3), 1.84 (s, 15H, Cp*-CH_3), 1.31 (s, 3H, *p*-Cym-CH−C*H*$_3$), 1.30 (s, 3H, *p*-Cym-CH-C*H*$_3$). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ (ppm) 182.4 (d, $^1J_{C,Rh}$ = 51.5 Hz, C2), 181.7 (s, C13), 151.9 (d, $^1J_{C,Rh}$ = 35.9 Hz, C7), 141.6 (s, C6), 133.9 (s, C9), 133.0 (s, C10), 122.7 (s, C4), 119.0 (s, C8), 115.2 (s, C5), 111.1 (s, *p*-Cym-C_q), 99.4 (s, *p*-Cym-C_q), 98.2 (d, $^1J_{C,Rh}$ = 4.8 Hz, Cp*-C), 92.9 (s, C11), 87.2 (s, *p*-Cym-CH), 87.1 (s, *p*-Cym-CH), 83.0 (s, *p*-Cym-CH), 82.8 (s, *p*-Cym-CH), 41.6 (s, C16), 41.6 (s, C17), 38.0 (s, C15), 31.7 (s, *p*-Cym-C*H*(CH_3)$_2$), 23.0 (s, *p*-Cym-CH-CH_3), 22.9 (s, *p*-Cym-CH-CH_3), 19.2 (s, *p*-Cym-CH_3), 10.5 (s, Cp*-CH_3). HRMS (ESI, positive ions): *m*/*z* (%) 952.9605 (10, calculated for [[**9**]−I]$^+$, 952.9607). MS (MALDI-TOF, matrix DCTB): *m*/*z* (%) 861 (53, [[**9**]+Cl−2I]$^+$), 953 (100, [[**9**]−I]$^+$). Anal. Calcd for [**9**]·2H_2O: C, 35.53; H, 4.16; N, 5.02. Found: C, 35.46; H, 3.78; N, 4.99.

General Procedure for the Synthesis of Complexes [12] and [13]. The monometallic complexes [**10**] and [**11**] were prepared according to published procedures.[8a] Samples of complexes [**10**] (60.3 mg, 0.1 mmol) or [**11**] (69.3 mg, 0.1 mmol) and Ag_2O (13.9 mg, 0.06 mmol) were suspended in CH_2Cl_2 (5 mL) and stirred for 1 h at ambient temperature under exclusion of light. After filtration through Celite, the filtrate was added to a solution of ([Pd(*μ*-Cl)(dmba)]$_2$ (27.6 mg, 0.05 mmol) and KI (166 mg, 1.00 mmol) in CH_2Cl_2 (5 mL). The reaction mixture was stirred for an additional 24 h. The suspension was filtered through Celite, and the filtrate was evaporated to dryness.

Complex [12]. Analytically pure [**12**] was obtained as an isomer mixture by column chromatography on aluminum oxide using



CH_2Cl_2/MeOH (6:1). Yield: 45.4 mg (0.047 mmol, 47%). Isomer A (55%), ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.54 (d, $^4J_{H,H}$ = 2.2 Hz, 1H, H11), 7.61 (d, $^3J_{H,H}$ = 2.1 Hz, 1H, H5), 7.59 (d, $^3J_{H,H}$ = 8.0 Hz, 1H, H8), 7.29 (d, $^3J_{H,H}$ = 1.9 Hz, 1H, H16), 7.09 (d, $^3J_{H,H}$ = 1.9 Hz, 1H, H15), 7.01−6.94 (m, 2H, H4/H9), 6.89−6.80 (m, 2H, H22/H23), 6.73−6.66 (m, 1H, H21), 5.87 (d, $^3J_{H,H}$ = 7.5 Hz, 1H, H20), 4.01 (s, 3H, H18), 3.88 (s, 3H, H17), 3.81 (d, $^2J_{H,H}$ = 13.9 Hz, 1H, H25), 3.54 (d, $^2J_{H,H}$ = 13.9 Hz, 1H, H25), 2.88 (s, 3H, H26), 2.66 (s, 3H, H27), 1.72 (s, 15H, Cp*-CH_3). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ (ppm) 182.5 (d, $^1J_{C,Rh}$ = 55.5 Hz, C2), 172.1 (s, C13), 157.0 (d, $^1J_{C,Rh}$ = 35.0 Hz, C7), 152.8 (s, C19), 147.7 (s, C24), 144.9 (s, C6), 138.2 (s, C8), 135.8 (s, C10), 134.7 (s, C20), 125.2 (s, C21), 123.5 (s, C22), 122.5 (s, C15), 122.5 (s, C4), 121.8 (s, C23), 121.8 (s, C16), 120.1 (d, $^3J_{C,Rh}$ = 1.2 Hz, C9), 115.8 (s, C5), 109.7 (s, C11), 97.8 (d, $^1J_{C,Rh}$ = 4.8 Hz, Cp*-C), 71.7 (s, C25), 52.2 (s, C26), 51.8 (s, C27), 39.1 (s, C18), 37.8 (s, C17), 10.3 (s, Cp*-CH_3). Isomer B (45%), ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.45 (d, $^4J_{H,H}$ = 2.2 Hz, 1H, H11), 7.65 (d, $^3J_{H,H}$ = 8.0 Hz, 1H, H8), 7.54 (d, $^3J_{H,H}$ = 2.1 Hz, 1H, H5), 7.27 (d, $^3J_{H,H}$ = 1.9 Hz, 1H, H16), 7.10 (d, $^3J_{H,H}$ = 1.9 Hz, 1H, H15), 7.01−6.94 (m, 1H, H9), 6.95 (d, $^3J_{H,H}$ = 2.1 Hz, 1H, H4), 6.89−6.80 (m, 2H, H22/H23), 6.73−6.66 (m, 1H, H21), 5.81 (d, $^3J_{H,H}$ = 7.5 Hz, 1H, H20), 4.01 (s, 3H, H18), 3.87 (s, 3H, H17), 3.68 (s, 2H, H25), 2.82 (s, 3H, H26), 2.62 (s, 3H, H27), 1.83 (s, 15H, Cp*-CH_3). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ (ppm) 182.2 (d, $^1J_{C,Rh}$ = 55.1 Hz, C2), 172.6 (s, C13), 156.6 (d, $^1J_{C,Rh}$ = 35.4 Hz, C7), 152.9 (s, C19), 148.2 (s, C24), 145.2 (s, C6), 138.3 (s, C8), 135.7 (s, C10), 134.2 (s, C20), 125.4 (s, C21), 123.8 (s, C22), 122.4 (s, C15), 122.3 (s, C4), 122.2 (s, C23), 122.2 (s, C16), 120.0 (d, $^3J_{C,Rh}$ = 1.2 Hz, C9), 115.8 (s, C5), 109.8 (s, C11), 97.8 (d, $^1J_{C,Rh}$ =

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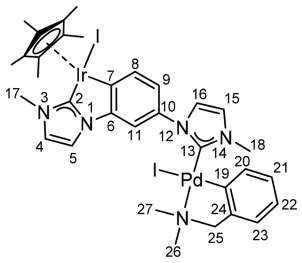
4.8 Hz, Cp*-C), 71.6 (s, C25), 52.3 (s, C27), 51.9 (s, C26), 39.0 (s, C18), 37.8 (s, C17), 10.2 (s, Cp*-CH_3). HRMS (ESI, positive ions): m/z (%) 842.0429 (100, calculated for $[[\mathbf{12}]-I]^+$ 842.0431). Anal. Calcd for $[\mathbf{12}]\cdot 2CH_2Cl_2$: C, 36.88; H, 3.89; N, 6.15. Found: C, 37.03; H, 3.86; N, 5.92.

Complex [13]. Analytically pure [**13**] was obtained as an isomer mixture by column chromatography on aluminum oxide using



CH_2Cl_2/MeOH (6:1). Yield: 83 mg (0.078 mmol, 78%). Isomer A (52%), ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.52 (d, $^4J_{H,H}$ = 2.2 Hz, 1H, H11), 7.52 (d, $^3J_{H,H}$ = 2.1 Hz, 1H, H5), 7.52 (d, $^3J_{H,H}$ = 8.0 Hz, 1H, H8), 7.28 (d, $^3J_{H,H}$ = 1.9 Hz, 1H, H16), 7.08 (d, $^3J_{H,H}$ = 1.9 Hz, 1H, H15), 7.00−6.92 (m, 2H, H4/H9), 6.88−6.79 (m, 2H, H22/H23), 6.74−6.64 (m, 1H, H21), 5.87 (d, $^3J_{H,H}$ = 7.5 Hz, H20), 4.00 (s, 3H, H18), 3.85 (s, 3H, H17), 3.78 (d, $^2J_{H,H}$ = 13.8 Hz, 1H, H25), 3.54 (d, $^2J_{H,H}$ = 13.8 Hz, 1H, H25), 2.87 (s, 3H, H27), 2.64 (s, 3H, H26), 1.78 (s, 15H, Cp*-CH_3). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ (ppm) 172.0 (C13), 163.9 (C2), 152.9 (C19), 147.8 (C24), 145.7 (C6), 140.0 (C7), 136.9 (C8), 135.0 (C10), 134.7 (C20), 125.2 (C21), 123.5 (C22), 122.4 (C15), 121.9 (C16), 121.7 (C23), 121.6 (C4), 120.6 (C9), 115.3 (C5), 109.2 (C11), 91.4 (Cp*-C), 71.6 (C25), 52.2 (C27), 51.7 (C26), 39.0 (C18), 37.5 (C17), 10.1 (Cp*-CH_3). Isomer B (48%), ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.45 (d, $^4J_{H,H}$ = 2.2 Hz, 1H, H11), 7.58 (d, $^3J_{H,H}$ = 8.0 Hz, 1H, H8), 7.47 (d, $^3J_{H,H}$ = 2.1 Hz, 1H, H5), 7.27−7.26 (m 1H, H16), 7.09 (d, $^3J_{H,H}$ = 1.9 Hz, 1H, H15), 7.00−6.92 (m, 2H, H4/H9), 6.88−6.79 (m, 2H, H22/H23), 6.74−6.64 (m, 1H, H21), 5.80 (d, $^3J_{H,H}$ = 7.5 Hz, H20), 4.00 (s, 3H, H18), 3.84 (s, 3H, H17), 3.67 (s, 2H, H25), 2.80 (s, 3H, H26), 2.62 (s, 3H, H27), 1.88 (s, 15H, Cp*-CH_3). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ (ppm) 172.5 (C13), 163.6 (C2), 152.9 (C19), 148.1 (C24), 146.0 (C6), 139.7 (C7), 137.0 (C8), 135.0 (C10), 134.1 (C20), 125.3 (C21), 123.7 (C22), 122.3 (C15), 122.1 (C16), 122.1 (C23), 121.6 (C4), 120.4 (C9), 115.3 (C5), 109.4 (C11), 91.5 (Cp*-C), 71.6 (C25), 52.3 (C27), 51.8 (C26), 38.9 (C18), 37.5 (C17), 10.2 (Cp*-CH_3). HRMS (ESI, positive ions): m/z (%) 932.0988 (100, calculated for $[[\mathbf{13}]-I]^+$, 932.0997). Anal. Calcd for $[\mathbf{13}]\cdot 0.5CH_2Cl_2$: C, 36.52; H, 3.75; N, 6.36. Found: C, 36.19; H, 3.40; N, 6.41.

X-ray Crystallography. Single crystals of $[\mathbf{5}]I\cdot 2.5CH_2Cl_2$, $[\mathbf{7}]\cdot CH_2Cl_2$, $[\mathbf{8}]\cdot 1.25CH_2Cl_2$, and [**9**] were analyzed by X-ray diffraction (for crystallographic data of $\mathbf{4}(I)_2$, see the Supporting Information). X-ray diffraction data were collected at T = 100(2) K with a Bruker AXS APEX II CCD diffractometer equipped with a microsource using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Semiempirical multiscan absorption corrections were applied to all data sets.[19] Structure solutions were found with SHELXT (intrinsic phasing)[20a] and were refined with SHELXL[20b] against $|F^2|$ of all data using first isotropic and later anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were added to the structure models on calculated positions.

Crystal Data for [5]I·2.5CH$_2$Cl$_2$. Crystals suitable for an X-ray diffraction study were obtained by slow diffusion of diethyl ether into a concentrated solution of [**5**]I in dichloromethane. Formula $C_{25.5}H_{34}N_4Cl_5I_2Rh$, M = 930.52, orange needles, 0.40 × 0.07 × 0.07 mm^3, monoclinic, space group $P2_1/c$, a = 16.2748(6), b = 16.5838(6), c = 24.5442(9) Å, β = 92.699(2)°, V = 6617.1(4) Å^3, Z = 8, ρ_{calcd} = 1.868 g·cm^{-3}, μ = 2.809 mm^{-1}, 174 490 intensities measured in the range 3.0° ≤ 2Θ ≤ 61.2°, 20 246 independent intensities (R_{int} = 0.0788), 15 205 observed intensities [$I \geq 2\sigma(I)$], semiempirical absorption correction (0.566 ≤ T ≤ 0.746), refinement of 693 parameters against all $|F^2|$ with anisotropic thermal parameters for all non-hydrogen atoms and hydrogen atoms on calculated positions, R = 0.0546, wR = 0.1359 [$I \geq 2\sigma(I)$], R = 0.0789, wR = 0.1555 (all data). The asymmetric unit contains two formula units of [**5**]I and five molecules of CH_2Cl_2.

Crystal Data for [7]·CH$_2$Cl$_2$. Crystals suitable for an X-ray diffraction study were obtained by slow diffusion of diethyl ether into a concentrated solution of [**7**] in dichloromethane. Formula $C_{32}H_{42}N_4Cl_2I_2IrRh$, M = 1102.50, orange plates, 0.08 × 0.05 × 0.05 mm^3, triclinic, space group $P\bar{1}$, a = 10.7952(2), b = 11.3055(2), c = 14.3625(2) Å, α = 82.6630(10), β = 89.3780(10)°, γ = 88.1930(10), V = 1737.62(5) Å^3, Z = 2, ρ_{calcd} = 2.107 g·cm^{-3}, μ = 6.259 mm^{-1}, 51 322 intensities measured in the range 3.8° ≤ 2Θ ≤ 61.1°, 10 606 independent intensities (R_{int} = 0.0495), 8448 observed intensities [$I \geq 2\sigma(I)$], semiempirical absorption correction (0.656 ≤ T ≤ 0.746), refinement of 399 parameters against all $|F^2|$ with anisotropic thermal parameters for all non-hydrogen atoms and hydrogen atoms on calculated positions, R = 0.0454, wR = 0.1097 [$I \geq 2\sigma(I)$], R = 0.0627, wR = 0.1196 (all data). The asymmetric unit contains one formula unit of [**7**]·CH_2Cl_2.

Crystal Data for [8]·1.25CH$_2$Cl$_2$. Crystals suitable for an X-ray diffraction study were obtained by slow diffusion of diethyl ether into a concentrated solution of [**8**] in dichloromethane. Formula $C_{24.25}H_{30.5}N_4Cl_{2.5}I_2AuRh$, M = 1020.33, orange needles, 0.32 × 0.06 × 0.06 mm^3, monoclinic, space group $P2_1/n$, a = 15.6991(3), b = 13.6300(3), c = 28.3902(6) Å, β = 98.7790(10)°, V = 6003.7(2) Å^3, Z = 8, ρ_{calcd} = 2.258 g·cm^{-3}, μ = 7.731 mm^{-1}, 161 167 intensities measured in the range 4.7° ≤ 2Θ ≤ 59.4°, 16 968 independent intensities (R_{int} = 0.0610), 13 686 observed intensities [$I \geq 2\sigma(I)$], semiempirical absorption correction (0.504 ≤ T ≤ 0.746), refinement of 656 parameters against all $|F^2|$ with anisotropic thermal parameters for all non-hydrogen atoms and hydrogen atoms on calculated positions, R = 0.0362, wR = 0.0794 [$I \geq 2\sigma(I)$], R = 0.0528, wR = 0.0865 (all data). The asymmetric unit contains two formula units of [**8**] and 2.5 molecules of CH_2Cl_2. One of the CH_2Cl_2 molecules is located about a crystallographic inversion center between two asymmetric units.

Crystal Data for Complex [9]. Crystals suitable for an X-ray diffraction study were obtained by slow diffusion of diethyl ether into a concentrated solution of [**9**] in dichloromethane. Formula $C_{33}H_{42}N_4I_3RhRu$, M = 1079.38, red block, 0.10 × 0.09 × 0.06 mm^3, monoclinic, space group $P2_1/c$, a = 15.4517(2), b = 15.9094(2), c = 15.1420(2) Å, β = 105.1560(10)°, V = 3592.84(8) Å^3, Z = 4, ρ_{calcd} = 1.995 g·cm^{-3}, μ = 3.485 mm^{-1}, 37 908 intensities measured in the range 2.7° ≤ 2Θ ≤ 58.5°, 9760 independent intensities (R_{int} = 0.0425), 7388 observed intensities [$I \geq 2\sigma(I)$], semiempirical absorption correction (0.671 ≤ T ≤ 0.799), refinement of 390 parameters against all $|F^2|$ with anisotropic thermal parameters for all non-hydrogen atoms and hydrogen atoms on calculated positions, R = 0.0567, wR = 0.1657 [$I \geq 2\sigma(I)$], R = 0.0781, wR = 0.1837 (all data). The asymmetric unit contains one formula unit of [**9**].

Catalytic Suzuki Coupling/Transfer Hydrogenation Studies. In a Schlenk tube containing a stirring bar were placed *p*-bromoacetophenone (71.7 mg, 0.36 mmol), phenylboronic acid (67.1 mg, 0.54 mmol), Cs_2CO_3 (351.9 mg, 1.08 mmol), catalyst (2 mol %, 0.0072 mmol), and anisole (internal reference, 38.9 mg, 0.36 mmol). The mixture was dissolved in 2-propanol (2 mL, used as reagent and solvent). The tube was sealed, and the reaction mixture was stirred at 100 °C under inert conditions for the given reaction time. The products (yields) were determined with a GC-2010 (Shimadzu) gas chromatograph equipped with a FID and a Teknokroma (TRB5, 30 m, 0.25 × 0.25 mm) column.

Catalytic Suzuki−Miyaura Coupling/α-Alkylation in *n*-Butyl Alcohol. In a Schlenk tube containing a stirring bar were placed *p*-bromoacetophenone (71.7 mg, 0.36 mmol), phenylboronic acid (67.1 mg, 0.54 mmol), Cs_2CO_3 (351.9 mg, 1.08 mmol), catalyst (2 mol %, 0.0072 mmol), and anisole (internal reference, 38.9 mg, 0.36 mmol). The mixture was dissolved in *n*-butanol (2 mL, used as reagent and solvent). The tube was sealed, and the reaction mixture was stirred at 100 °C under aerobic conditions for the given reaction time. The

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products (yields) were determined with a GC-2010 (Shimadzu) gas chromatograph equipped with a FID and a Teknokroma (TRB5, 30 m, 0.25 × 0.25 mm) column.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.9b00120.

Crystallographic data for $4(I)_2$ and spectra of all new complexes (PDF)

Accession Codes

CCDC 1897003−1897007 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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