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Y-Shaped Tris-N-Heterocyclic-Carbene Ligand for the Preparation of Multifunctional Catalysts of Iridium, Rhodium, and Palladium

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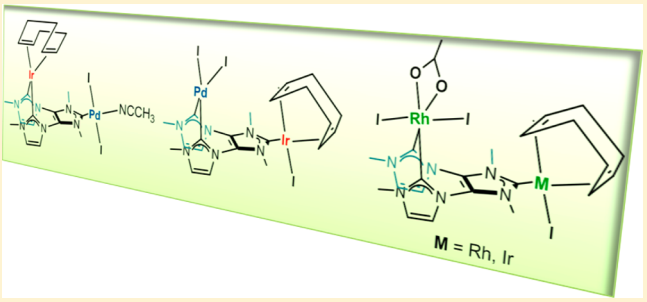
Supporting Information

ABSTRACT: A series of homo- and hetero-dimetallic complexes of Ir, Rh, and Pd have been obtained using our previously reported Y-shaped tris-NHC ligand. The new complexes can be obtained through the isolation of the corresponding monometallic intermediates (in which the ligand always coordinates in a chelating form) or by a one-pot stepwise synthetic protocol that avoids the isolation of the intermediate. The catalytic properties of the Ir−Pd complexes have been explored in two tandem processes: dehalogenation/transfer hydrogenation of haloacetophenones and Suzuki-coupling/transfer hydrogenation of *p*-bromoacetophenone. These two complexes have been also tested in two model reactions typically catalyzed by iridium (cyclization of 2-aminophenyl ethyl alcohol to yield indole) and palladium (acylation of bromobenzene with *n*-hexanal).



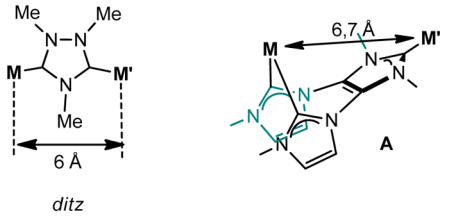
INTRODUCTION

Bimetallic catalysis by late transition metal complexes has recently emerged as an effective tool to promote organic transformations.[1] Bimetallic catalysts can display synergistic effects between the proximate metal centers, leading to improved reactivities and selectivities compared to their monometallic counterparts. In this regard, the search for multifunctional catalysts has promoted an increasing demand of ligands capable of combining several metal centers in a cooperative manner.[2] For the synthesis of well-defined dimetallic catalysts the choice of the ligand is of major importance, because the coordination environment determines the metal fragments that can be bound. Moreover, ligand effects such as flexibility, stereoelectronic properties, and metal−metal separation should determine the suitability of the bimetallic system for a specific catalytic process.[1e]

During the last five years, we have been working on the development of hetero-dimetallic catalysts for the tandem or sequential transformation of a substrate via two (or more) mechanistically distinct processes.[2,3] For the preparation of the bimetallic catalysts, we decided to use rigid NHC-based ligands, which may help to maintain a fixed metal−metal distance. Apart from the examples described below and reported by us, there is a small number of examples described in the literature of rigid NHC-based ligands that allow the coordination of two metals,[4] and only a very few have been used for the preparation of heterometallic complexes.[4f,g] In this regard, the use of 1,2,4-trimethyltriazol-di-ylidene (*ditz*, Chart 1),[5] as a bridging ligand for the preparation of homo- and hetero-dimetallic complexes, was extraordinarily useful in the development of a wide range of tandem catalytic reactions.[6] Although *ditz* constituted an excellent starting point for the development of catalysts with excellent applications in tandem catalysis, we thought that it may not be stable enough to endure the harsh conditions required for some catalytic reactions, and this also does not allow for the modification of its stereoelectronic properties. Within this context, we recently described a Y-shaped tris-NHC ligand potentially capable of coordinating two metals, affording two different coordination environments (**A**, Chart 1), while maintaining a short metal−metal separation.[7] We first coordinated **A** to palladium, envisaging that it would also offer the possibility to obtain hetero-dimetallic complexes, an issue that initially remained elusive to us.

We now describe the preparation of a series of homo- and hetero-dimetallic complexes of Pd, Ir, and Rh, together with the facile preparation of their monometallic intermediates. An exploratory study of the catalytic activity of the Ir−Pd complexes is also described and compared with our previously related results using the *ditz*-based complexes.[6b]

Chart 1. 1,2,4-Trimethyltriazol-di-ylidene (*ditz*) Ligand and the Y-Shaped Tris-NHC Ligand (A) Employed in This Work



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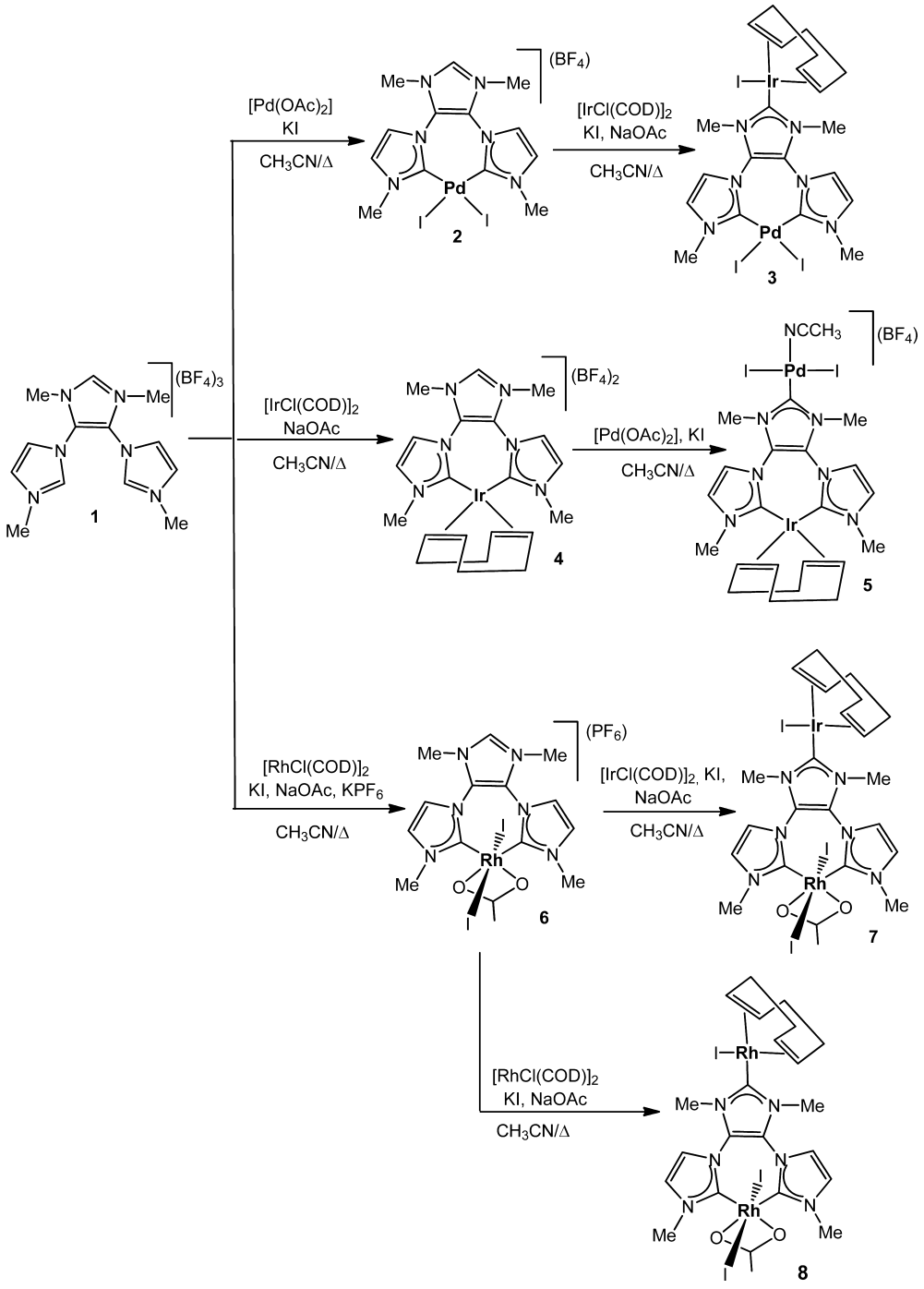
Scheme 1. Synthesis of Complexes 2 to 8



RESULTS AND DISCUSSION

The reactions of the triazolium salt **1**[7] with equimolecular amounts of $[Pd(OAc)_2]$ or $[MCl(COD)]_2$ (M = Rh or Ir) under the reaction conditions depicted in Scheme 1 afford the preparation of the monometallic complexes of Pd,[7] Ir, or Rh (**2**, **4**, and **6**, respectively, Scheme 1), in which the ligand coordinates to the metal in a chelating form. The iridium complex **4** was obtained in very good yield (83%), while the rhodium complex **6** could be obtained only in moderate-low yield (33%). Interestingly, complex **4** contains an Ir(I) center, as shown by the characteristic ^{13}C NMR resonance at 181.2 ppm due to the carbene carbon, while complex **6** contains a Rh(III) center, as suggested by the ^{13}C NMR doublet at 163 ppm ($^1J_{Rh-C}$ = 47.2 Hz), also attributed to the carbene carbon. It is important to mention that the coordination of the salt **1** to the rhodium source did not provide any clean reaction products in the absence of KI. However, when **1** was reacted with $[IrCl(COD)]_2$ under the same conditions depicted in Scheme 1, but with addition of KI, still the Ir(I) complex **4** was obtained. At this point we do not have a suitable explanation of the different outcome of the reactions when Ir or Rh sources were used. The fact that the coordination of **1** first proceeds via the chelating part of the ligand facilitates the design of sophisticated hetero-dimetallic complexes, by simply modifying the order of addition of the adequate metal sources. For example, the formation of an Ir−Pd hetero-dimetallic complex

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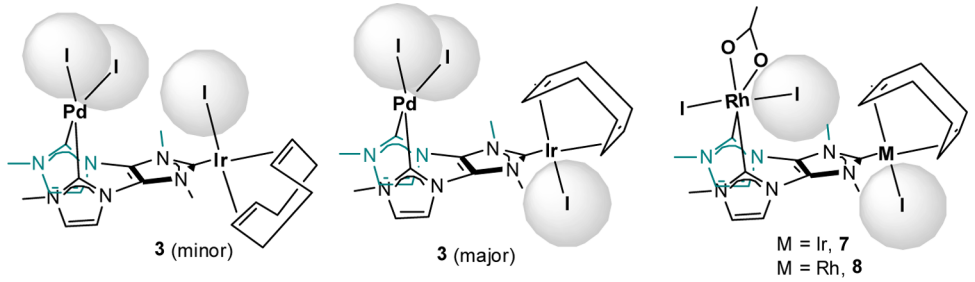
Chart 2. Representation of the Minor and Major Isomers of Complex 3 and the Observed Isomer for 7 and 8



can proceed from the reaction of either intermediate **2** or **4**, by adding $[IrCl(COD)]_2$ or $[Pd(OAc)_2]$, to afford **3** or **5**, respectively, under the reaction conditions shown in Scheme 1. Complex **3** has a chelate-palladium/monodentate-iridium NHC-based structure, while **5** has an inverted coordination of the ligand, with a chelate-iridium/monodentate-palladium structure. More interesting is the fact that both **3** and **5** can be obtained in a one-pot process without the isolation of the corresponding monometallic intermediates, by sequentially adding the desired metal sources and taking into account that the first metal added to the reaction vessel will be the one to coordinate in the chelate form. As will be discussed later, **3** and **5** (having the same two metals and the same bridging ligand) show distinct reactivity patterns, as a consequence of the two different coordination environments of the two metals.

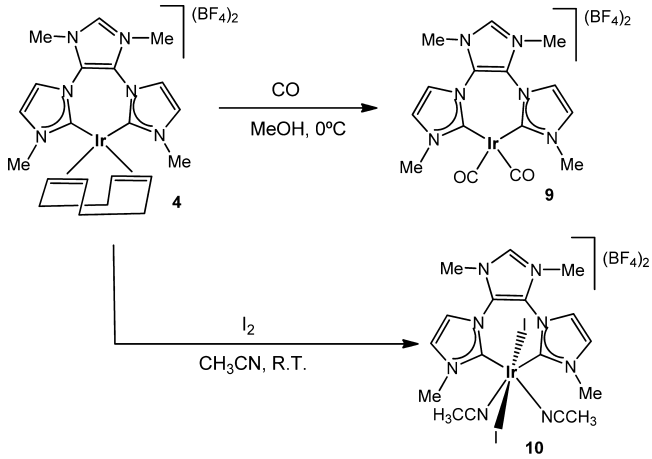
The Ir−Pd hetero-dimetallic complexes **3** and **5** were characterized by NMR and mass spectroscopy. The more representative NMR signals are those observed in the ^{13}C NMR spectra, at 178.8 and 166.0 ppm (**3**, Ir−$C_{carbene}$ and Pd−$C_{carbene}$, respectively) and 180.7 and 163.6 ppm (**5**, Ir−$C_{carbene}$ and Pd−$C_{carbene}$, respectively).

Starting from the rhodium complex **6**, the hetero-dimetallic Rh(III)/Ir(I) complex **7** and the mixed-valence Rh(I)/Rh(III) complex **8** can be obtained. Again, for the preparation of **7** and **8**, the isolation of the monometallic intermediate **6** can be circumvented if the complexes are obtained by a one-pot synthetic protocol implying the sequential addition of the two metal sources under the reaction conditions indicated in Scheme 1, thus greatly simplifying the experimental synthetic procedure. The ^{13}C NMR spectrum of **8** shows the two distinct resonances attributed to the carbene-carbon bound to Rh(I) (185.7 ppm, $^1J_{Rh-C}$ = 50.5 Hz) and Rh(III) (162.7 ppm, $^1J_{Rh-C}$ = 47.4 Hz), and in **7**, the signals due to the carbene-carbons bound to Ir(I) and Rh(III) appear at 182.3 and 163.1 ($^1J_{Rh-C}$ = 47.5 Hz) ppm, respectively.

It is interesting to point out that compound **3** is obtained as a mixture of two isomers (55:45 molar ratio) as a consequence of the restricted rotation around the Ir(I)−$C_{carbene}$ bond, due to the steric hindrance afforded by the presence of the bulky iodide ligand at the iridium center, and the two iodide ligands at the palladium coordination sphere. In principle, we have attributed the structure of the major rotamer to that in which the iodide ligands of the two metal centers are avoiding each other, yielding a more sterically relieved configuration (see Chart 2). A similar situation can be envisaged for complexes **7** and **8**, but in this case the octahedral coordination of the Rh(III) center is approaching one of the iodide ligands of the coordination sphere to the M(I) (M = Rh, Ir) fragment, thus avoiding the formation of the more sterically constrained rotamer in which the M(I)−I would be oriented close to the Rh(III)−I bond, as shown in Chart 2.

Apart from complexes **4** and **5**, which slowly decompose in the solid state at room temperature, all the other complexes are air stable. Complex **4** can be transformed into more stable monoiridium complexes by bubbling carbon monoxide to yield the biscarbonyl complex **9** or by oxidation with I_2 in acetonitrile to afford the Ir(III) complex **10** (Scheme 2).

Scheme 2. Synthesis of Complexes 9 and 10



The molecular structures of **3** and **8** were confirmed by means of X-ray diffraction studies. The molecular structure of **3** consists of a hetero-dimetallic complex of palladium and iridium in which the tris-NHC ligand is bridging the two metal centers in bis-chelating (Pd) and monodentate (Ir) forms (Figure 1). The bis-chelating palladium fragment completes its coordination sphere with two iodide ligands. The iridium fragment completes its pseudo-square-planar coordination sphere with a 1,5-cyclooctadiene (COD) and an iodide ligand. The molecular structure depicted in Figure 1 corresponds to that of the rotamer that we have assigned as the minor one for complex **3** (Chart 2), in which the three iodide ligands are pointing toward the same side of the molecule. The two coordination planes of the two metal fragments are in a quasi-perpendicular disposition (88.17°). The Pd−$C_{carbene}$ distances in the chelate fragment are 1.975(9) and 1.967(8) Å, and the Ir−$C_{carbene}$ distance is 2.032(9) Å. The chelating imidazolylidenes are at an angle of 61.5° with respect to the metal coordination plane. The coordination plane of the chelate palladium fragment is quasi-perpendicular with respect to the plane of the monocarbene azole ring that is coordinated to the iridium center (88.2°), a "chair angle" that is very similar to our previously reported dipalladium complex with the same tris-NHC ligand.[7] The through-space Ir−Pd distance is 6.76 Å.

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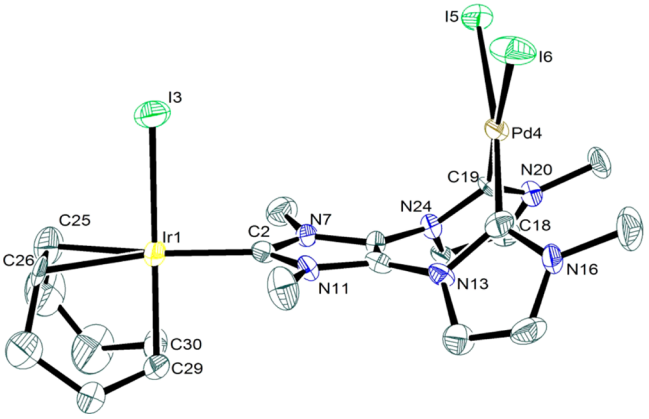

Figure 1. Molecular diagram of **3** (ellipsoids at 50% probability). All hydrogen atoms and solvent (CH_3CN) have been omitted for clarity. Selected bond distances (Å) and angles (deg): Ir(1)−C(2) 2.032(9), Ir(1)−I(3) 2.6664(7), Ir(1)−C(25) 2.157(10), Ir(1)−C(26) 2.191(9), Ir(1)−C(29) 2.112(9), Ir(1)−C(30) 2.108(9), Pd(4)−C(18) 1.975(9), Pd(4)−C(19) 1.967(8), Pd(4)−I(5) 2.6606(9), Pd(4)−I(6) 2.6347(9), C(2)−Ir(1)−I(3) 89.2(2), I(6)−Pd(4)−I(5) 95.97(3), C(19)−Pd(4)−C(18) 87.1(3).

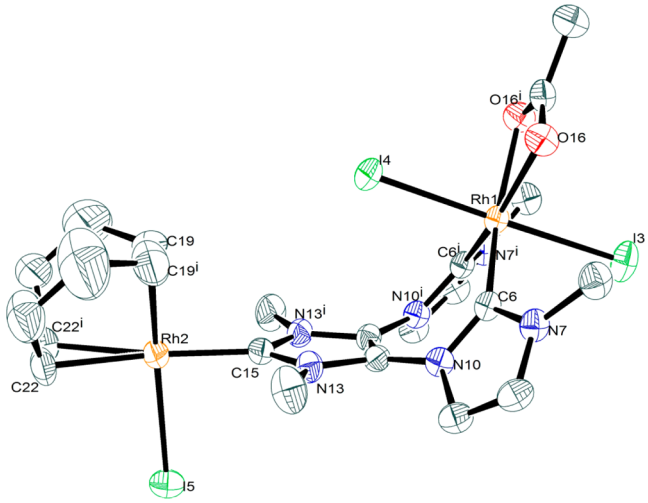

Figure 2. Molecular diagram of **8** (ellipsoids at 50% probability). All hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Rh(1)−C(6) 1.992(4), Rh(1)−I(4) 2.6435(6), Rh(1)−I(3) 2.6876(6), Rh(1)−O(16) 2.163(3), Rh(2)−C(15) 2.008(6), Rh(2)−I(5) 2.6513(6), Rh(2)−C(19) 2.102((5), Rh(2)−C(22) 2.209(5), I(4)−Rh(1)−I(3) 178.86(2), C(6)−Rh(1)−C(6′) 95.0, I(5)−Rh(2)−C(15) 86.86(17).

The molecular structure of **8** consists of a dimetallic Rh(I)−Rh(III) complex bound by the tris-NHC ligand (Figure 2). The bis-chelating part of the ligand binds to the Rh(III) center, while the monodentate part is bound to Rh(I). The pseudo-square-planar coordination sphere of the Rh(I) fragment is completed by an iodide and a COD ligand, while the pseudo-octahedral Rh(III) center completes its sphere with an acetate and two iodides in a relative *trans* disposition. The relative disposition of the ligands about the two metal fragments corresponds to the less hindered situation, with the iodide ligands of the two metals avoiding the steric interaction. The Rh(III)−$C_{carbene}$ distance is 1.992(4) Å, and the Rh(I)−$C_{carbene}$ distance is 2.008(6) Å. Due to the higher steric constraint about the Rh(III) octahedral fragment, the chelating imidazolylidenes are at an angle of 32.7° with respect to the meridional plane of metal fragment, a lower angle than the related one in **3** (61.5°). Interestingly, the chair angle (defined as the angle between the coordination plane of the chelate fragment and the plane of the monocarbene azole ring) is 108.2° (compare to 88.2° in **3**), thus implying that the ligand is flexible enough to afford a situation of minimum steric repulsion between the two metal coordination spheres. As a consequence, the distance between the two metals is slightly longer (7.003 Å) than the one shown in **3** (6.76 Å).

Because we wanted to test the catalytic capabilities of our complexes, we decided to use the Ir−Pd complexes **3** and **5** since the two metals contained in these two complexes display distinct catalytic properties. As we previously described,[6b] for the study of the catalytic properties of these complexes we considered that haloacetophenones should be excellent starting substrates because they combine a halide−aryl bond that can be activated by the palladium fragment and a C═O bond that can be transformed by the iridium center. We first studied a simple reaction consisting of the dehalogenation/transfer hydrogenation of 4-bromoacetophenone, because this reaction may allow us to compare the new results with those previously obtained by us with catalysts **11**−**15** (Chart 3).[6b] This simple model reaction was also recently used by other authors in the catalytic test of their hetero-dimetallic complex of Ir−Ni.[8]

The results for the dehalogenation/transfer hydrogenation of 4-bromoacetophenone in *i*PrOH in the presence of Cs_2CO_3 at 100 °C are shown in Table 1. For comparative purposes, our previously reported results for catalysts **11**−**15** are also shown (entries 8−11).[6b] As can be seen from the data shown, catalyst **5** gives better catalytic outcomes than **3**. The catalytic outcome of **5** compares well with our best previously reported Ir−Pd catalysts **12** and **13** (compare entry 5 with entries 9 and 10). Both **3** and **5** show better catalytic activities than the mixture of the two homo-dimetallic complexes **14** and **15** (entry 11). Interestingly, complex **5** affords full conversion to the final 1-phenylethanol when using a low catalyst loading of 1 mol %, although the time needed for the completion of the reaction was longer (48 h, entry 7).

In all cases, the reaction is very clean, and we did not observe the formation of any other products apart from **A**, **B**, and **C**. This gave us the opportunity to study the reaction time course (Figure 3), which has a similar profile to that previously reported,[6b] confirming that the debromination is faster than the reduction of the carbonyl group and that the transfer hydrogenation is accelerated at the point of maximum formation of acetophenone (**A**), 3 h, suggesting that the transfer hydrogenation is faster for acetophenone than for *p*-bromoacetophenone, in agreement with previously published results.[9]

On the basis of these results, we decided to extend our study to another tandem reaction combining the Suzuki coupling and transfer hydrogenation of 4-bromoacetophenone, since we already demonstrated the compatibility of these two catalytic processes.[6b] This model reaction has a straightforward application, because biphenyl-substituted ketones are known to behave as nonsteroidal inhibitors of 5α-reductase, the enzyme that catalyzes the conversion of testosterone to dihydrotestosterone.[10] Table 2 shows the most representative data for the Suzuki coupling of 4-bromoacetophenone with phenylboronic acid in a mixture of *i*PrOH and THF and includes the results provided by our previously reported catalyst **13** for comparison. As can be seen, **5** affords a good yield on

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Chart 3. Complexes Studied in the Different Catalytic Tests

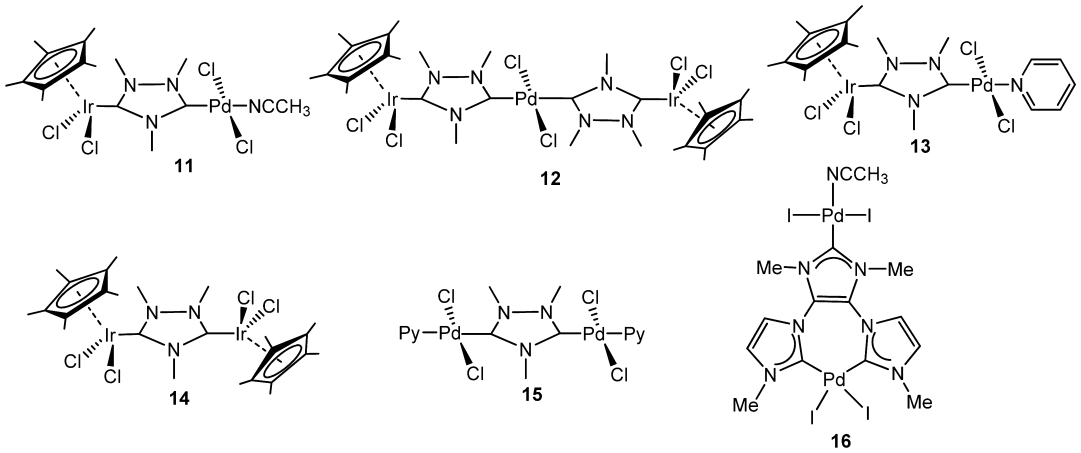
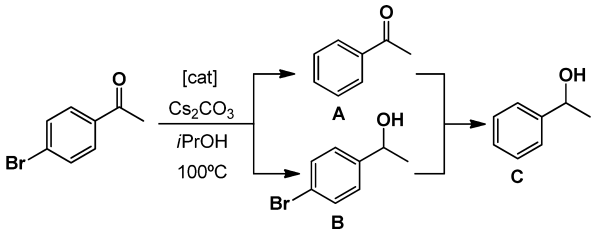


Table 1. Tandem Dehalogenation/Transfer Hydrogenation of 4-Bromoacetophenone[a]



entry	catalyst	cat. loading (mol %)	t (h)	**A** (%)[b]	**B** (%)[b]	**C** (%)[b]
1	**3**	2	20	70	9	21
2	**3**	2	48	51	8	41
3	**3**	1	20	89	5	6
4	**3**	1	48	82	5	13
5	**5**	2	20	1	0	99
6	**5**	1	20	55	3	42
7	**5**	1	48	0	0	99
8	**11**	2	20	22	0	75[d]
9	**12**	2	20	0	0	95[d]
10	**13**	2	20	0	0	99[d]
11[c]	**14** + **15**	1 + 1	20	72	0	25[d]

[a]Reaction conditions: 4-haloacetophenone (0.36 mmol), Cs_2CO_3 (0.43 mmol), anisole as internal reference (0.36 mmol), and 2 mL of 2-propanol. The solution was heated to 100 °C in aerobic conditions. [b]Yields determined by GC. [c]1 mol % of **14** + 1 mol % of **15**. [d]Data taken from ref 6b.

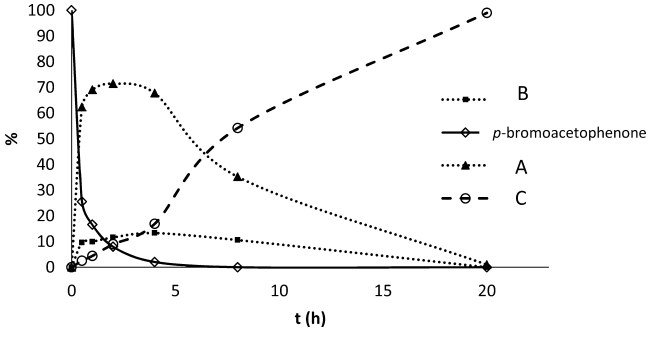


Figure 3. Time course of the transformation of 4-bromoacetophenone using 2 mol % of **5**.

product **E** after 24 h (72%, entry 5), although this result is worse than the one provided by **13** in terms of both product yield and completion time (entry 7). Again, the catalytic activity of **5** is much better than that shown by the mixture of the two homodimetallic complexes **14** and **15**, a result that confirms our previous finding that the use of one heterometallic catalyst usually renders better catalytic outcomes than the use of two homometallic catalysts.[6b,d,e]

In order to widen the applicability of the hetero-dimetallic complexes **3** and **5**, we decided to complement our study with two separate model reactions typically catalyzed by Ir and Pd. We tried to test the complexes in catalytic reactions with more mechanistically distinct cycles than those implied in the reactions shown before (transfer hydrogenation, dehalogenation of aryl halides, and Suzuki–Miyaura coupling). For the Ir-catalyzed process, we studied the cyclization of 2-aminophenyl ethyl alcohol.[6a,11] Because indole-based compounds are found in many natural products with pharmaceutical applications, new environmentally benign and efficient methods for indole synthesis and its functionalization continue to attract attention.[12] As can be seen from the data shown in Table 3, both iridium-containing complexes (**3** and **5**) afforded excellent yields in the formation of indole from 2-aminophenyl ethyl alcohol (entries 3 and 4), while the bis-palladium complex (**16**, Chart 3) showed a similar outcome to that achieved in the absence of catalyst, therefore implying that the catalytic activity attributed to the palladium complex **16** is negligible.

Complexes **3** and **5** also showed good activity in the acylation of bromobenzene with *n*-hexanal (Chart 4). The acylation of aryl halides with aldehydes, described by Xiao and co-workers,[13] allows the direct preparation of alkyl aryl ketones, avoiding the traditionally used Friedel–Crafts method, which involves hazardous reagents and does not work when electron-deficient arenes are used.[14] Despite the obvious interest in the reaction, the number of articles describing effective catalysts for this reaction is still very low.[15] Both **3** and **5** provided full conversion to the final product using a 2 mol % catalyst loading in DMF at 115 °C in 16 h. For comparative purposes we also checked the catalytic activity of the Ir–Rh complex **7** and confirmed that it showed negligible activity, therefore suggesting that the catalytic activity of **3** and **5** in this reaction is located at the palladium fragment of the bimetallic structures.

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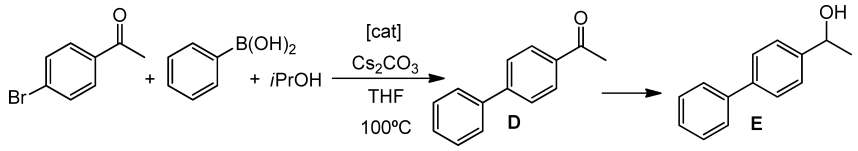
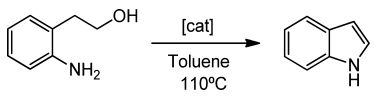
Table 2. Tandem Suzuki–Miyaura/Transfer Hydrogenationof 4-Bromoacetophenone[a]



entry	catalyst	t (h)	A (%)[b]	B (%)[b]	C (%)[b]	D (%)[b]	E (%)[b]
1	**5**	0.5	13	2	0	85	0
2	**5**	4	10	0	5	52	31
3	**5**	7	5	0	10	38	47
4	**5**	20	3	0	12	16	69
5	**5**	24	2	0	13	13	72
6	**13**	4	–	–	–	58	28[d]
7	**13**	7	–	–	–	2	88[d]
8[c]	**14** + **15**	4	–	–	–	55	5[d]

[a]Reaction conditions: 4-bromoacetophenone (0.36 mmol), phenylboronic acid (0.55 mmol), Cs_2CO_3 (1.08 mmol), anisole as internal reference (0.36 mmol), catalyst (2 mol %), 2 mL of *i*PrOH, and 2 mL of THF. The solution was heated at 100 °C. [b]Yields determined by GC. [c]1 mol % of **14** + 1 mol % of **15**. [d]Data taken from ref 6b.

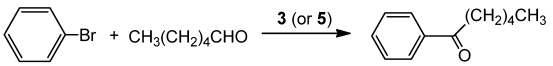
Table 3. Cyclization of 2-Aminophenyl Ethyl Alcohol[a]



entry	catalyst	cat. loading (%)	time (h)	indole (%)[b]
1	–	–	2	52
2	**16**	2	2	56
3	**3**	2	2	>99
4	**5**	2	2	>99

[a]Reaction conditions: 2-aminophenyl ethyl alcohol (0.25 mmol), KOH (0.5 mmol), anisole as internal reference (0.25 mmol), and 1 mL of toluene. The reaction mixture was stirred at 110 °C. [b]Yields determined by GC.

Chart 4. Acylation of Bromobenzene with *n*-Hexanal



Reaction Conditions: Bromobenzene (0.5 mmol), n-hexanal (0.6 mmol), pyrrolidine (1 mmol), TBAB (0.05 mmol), catalyst (2 mol%) in 2 mL of DMF and 4Å MS (1g). The reaction mixture was heated at 115°C.

CONCLUSIONS

In this work we have described the preparation of a series of mono- and bimetallic complexes of Ir, Rh, and Pd, using our previously reported Y-shaped tris-NHC ligand.[7] The ligand can bind to two different metals by a stepwise procedure in which the first step invariably implies coordination via the chelating side of the ligand, therefore facilitating the rational design of hetero-dimetallic complexes. All dimetallic complexes can be obtained via the isolation of their corresponding bis-chelate monometallic intermediates, although the stepwise one-pot synthesis also affords good yield to the final complexes, thus affording an important simplification of the experimental workups.

The two Ir–Pd hetero-dimetallic complexes **3** and **5** were tested in two different tandem processes, combining reactions that are typically catalyzed by Ir and Pd: dehalogenation/transfer hydrogenation of haloacetophenones and Suzuki-coupling/transfer hydrogenation of *p*-bromoacetophenone. Both complexes achieved excellent conversions to the final products and also showed better outcomes than the sum of related homodimetallic complexes, a fact that strengthens the idea that some catalytic cooperativity may be at play.[6b] We found that the activities shown are similar to those previously reported by us for our most active *ditz*-based heterometallic complex (**13**, Chart 3), but now we have the additional benefit provided by the simpler and higher yielding procedure to obtain **3** and **5**. Both complexes have also been tested in two model reactions typically catalyzed by iridium (cyclization of 2-aminophenyl ethyl alcohol to yield indole) and palladium (acylation of bromobenzene with *n*-hexanal), where they showed excellent catalytic activity, therefore illustrating the wide multifunctionality of these sophisticated (although easy-to-make) catalysts.

EXPERIMENTAL SECTION

General Procedures. Compounds **1** and **2** were prepared according to literature procedures.[7] All operations were carried out by using standard Schlenk techniques under a nitrogen atmosphere. All other reagents were used as received from commercial suppliers. NMR spectra were recorded on a Varian Innova 300 and 500 MHz, using $CDCl_3$, acetone-d_6, MeCN-d_3, or DMSO-d_6 as solvents. Electrospray mass spectra (ESI-MS) were recorded on a Micromass Quatro LC instrument; nitrogen was employed as drying and nebulizing gas. Exact mass analysis was realized using a Q-TOF premier mass spectrometer with electrospray source (Waters, Manchester, UK) operating at a resolution of ca. 16 000 (fwhm). Elemental analyses were carried out on a EuroEA3000 Eurovector analyzer. Infrared spectra (FTIR) were obtained on a Bruker EQUINOX 55 spectrometer with a spectra window of 4000–600 cm^{-1}.

Synthesis of Compound 3. A mixture of $[Pd(OAc)_2]$ (50 mg, 0.223 mmol), **1** (115.7 mg, 0.223 mmol), and KI (74.7 mg, 0.446 mmol) in acetonitrile was refluxed for 2 h under an inert atmosphere. $[IrCl(COD)]_2$ (74 mg, 0.11 mmol), NaOAc (24.6 mg, 0.3 mmol), and KI (74 mg, 0.446 mmol) were then added, and the resulting mixture was refluxed overnight. The solvent was removed under vacuum, and the crude solid was purified by column chromatography. Elution with a mixture 9:1 dichloromethane/acetone afforded the separation of a yellow band that contained compound **3**. Precipitation with a mixture of acetone/diethyl ether gave the desired product as a yellow solid. Yield: 70 mg, 30%. ^1H NMR (300 MHz, DMSO-d_6) for the minor isomer (45%): δ 8.20 (s, 2H, CH_{imid}), 7.72 (s, 2H, CH_{imid}), 4.68 (m, 2H, C*H*-COD), 3.85 (s, 12H, NCH_3), 2.98 (m, 2H, C*H*-COD), 2.16 (m, 4H, CH_2-COD), 1.47 (m, 4H, CH_2-COD); for the major isomer (55%): δ 8.11 (s, 2H, CH_{imid}), 7.74 (s, 2H, CH_{imid}), 4.68 (m, 2H, C*H*-COD), 3.89 (s, 12H, NCH_3), 3.35 (m, 2H, C*H*-COD), 2.16 (m, 4H,

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CH_2-COD), 1.78 (m, 4H, CH_2-COD). ^{13}C NMR (75 MHz, DMSO-d_6) for the minor isomer: δ 178.8 (Ir-$C_{carbene}$), 166.0 (Pd-$C_{carbene}$), 126.0 (CH_{imid}), 124.1 (C_q), 122.0 (CH_{imid}), 83.0 (CH-COD), 55.6 (CH-COD), 39.5 (NCH_3), 34.9 (NCH_3), 32.3 (CH_2−COD), 29.8 (CH_2-COD); for the major isomer: δ 178.1 (Ir-$C_{carbene}$), 167.5 (Pd-$C_{carbene}$), 126.0 (CH_{imid}), 122.7 (CH_{imid}), 122.1 (C_q), 82.4 (CH-COD), 55.4 (CH-COD), 39.7 (NCH_3), 35.2 (NCH_3), 32.4 (CH_2-COD), 29.9 (CH_2-COD). Anal. Calcd for $PdIrI_3N_6C_{21}H_{28}(2H_2O)$ (1079.85): C, 23.36; H, 3.00; N, 7.78. Found: C, 23.00; H, 3.27; N, 7.61. Electrospray MS (20 V, m/z): 958.2 $[M - I + MeCN]^+$, 917.2 $[M - I]^+$.

Synthesis of Compound 4. A mixture of compound **1** (78 mg, 0.149 mmol), $[IrCl(COD)]_2$ (50 mg, 0.0745 mmol), and NaOAc (49.2 mg, 0.6 mmol) in acetonitrile (15 mL) was refluxed for 1 h under an inert atmosphere. The mixture was then filtered at 0 °C. Removal of the volatiles afforded **4** as a red, air-sensitive solid. Yield: 90 mg, 83%. ^1H NMR (300 MHz, DMSO-d_6): δ 9.44 (s, 1H, NCHN), 8.00 (d, $^3J_{H-H}$ = 2.2 Hz, 2H, CH_{imid}), 7.73 (d, $^3J_{H-H}$ = 2.2 Hz, 2H, CH_{imid}), 4.34 (m, 2H, CH-COD), 4.07 (m, 2H, CH-COD), 4.00 (s, 6H, NCH_3), 3.82 (s, 6H, NCH_3), 2.31 (m, 4H, CH_2-COD), 1.75 (m, 4H, CH_2-COD). ^{13}C NMR (75 MHz, DMSO-d_6): δ 181.2 (Ir-$C_{carbene}$), 134.2 (C_q), 125.8 (NCHN), 123.9 (CH_{imid}), 121.7 (CH_{imid}), 80.3 (CH-COD), 75.8 (CH-COD), 37.4 (NCH_3), 34.1 (NCH_3), 30.6 (CH_2-COD), 30.5 (CH_2-COD). Satisfactory elemental analysis could not be obtained due to the low stability of the compound. Electrospray MS (15 V, m/z): 645.4 $[M + BF_4]^+$, 279.1 $[M]^{2+}$. Electrospray HR-MS (15 V, m/z): 645.2126 $[M + BF_4]^+$, 279.1038 $[M]^{2+}$.

Synthesis of Compound 5. A mixture of compound **1** (78 mg, 0.149 mmol), $[IrCl(COD)]_2$ (50 mg, 0.0745 mmol), and NaOAc (49.2 mg, 0.6 mmol) in acetonitrile (15 mL) was refluxed for 1 h under an inert atmosphere. $[Pd(OAc)_2]$ (33.7 mg, 0.149 mmol) and KI (100.6 mg, 0.6 mmol) were then added, and the reaction was refluxed for an additional 1 h. The mixture was filtered through a pad of Celite, and the solvent was removed under vacuum. The crude solid was purified by column chromatography. Elution with a 7:3 mixture of dichloromethane/acetone afforded the separation of an orange band that contained compound **5**. Precipitation with a mixture of acetone/diethyl ether gave the desired product as a brown, air-sensitive solid. Yield: 70 mg, 45%. ^1H NMR (300 MHz, DMSO-d_6): δ 8.07 (s, 2H, CH_{imid}), 7.67 (s, 2H, CH_{imid}), 4.27 (m, 2H, CH-COD), 3.93 (m, 2H, CH-COD), 3.88 (s, 6H, NCH_3), 3.80 (s, 6H, NCH_3), 2.30 (m, 2H, CH_2-COD), 2.09 (s, 3H, CH_3CN), 2.04 (m, 4H, CH_2-COD), 1.66 (m, 2H, CH_2-COD). ^{13}C NMR (75 MHz, DMSO-d_6): δ 180.7 (Ir-$C_{carbene}$), 163.6 (Pd-$C_{carbene}$), 125.4 (CH_{imid}), 124.3 (C_q), 122.0 (CH_{imid}), 79.3 (CH-COD), 75.1 (CH-COD), 37.2 (NCH_3), 36.2 (NCH_3), 30.7 (CH_2-COD), 30.4 (CH_2-COD), CH_3CN not observed. Satisfactory elemental analysis could not be obtained due to the low stability of the compound. Electrospray MS (20 V, m/z): 958.1 $[M]^+$, 917.1 $[M - MeCN]^+$. Electrospray HR-MS (20 V, m/z): 957.9382 $[M]^+$.

Synthesis of Compound 6. A mixture of compound **1** (105.4 mg, 0.203 mmol), $[RhCl(COD)]_2$ (50 mg, 0.1015 mmol), NaOAc (66.54 mg, 0.812 mmol), and KI (136.16 mg, 0.812 mmol) in acetonitrile (20 mL) was refluxed overnight under an inert atmosphere. Afterward, the solvent was removed under vacuum. The crude solid was purified by column chromatography. Elution with a mixture of acetone/KPF_6 afforded the desired compound as an orange solid. Yield: 55 mg, 33%. ^1H NMR (300 MHz, acetone-d_6): δ 9.32 (s, 1H, NCHN), 8.17 (d, $^3J_{H-H}$ = 2.2 Hz, 2H, CH_{imid}), 7.84 (d, $^3J_{H-H}$ = 2.2 Hz, 2H, CH_{imid}), 4.21 (s, 6H, NCH_3), 4.04 (s, 6H, NCH_3), 1.87 (s, 3H, $COOCH_3$). ^{13}C NMR (75 MHz, MeCN-d_3): δ 191.3 ($COOCH_3$), 163.0 (d, $^1J_{Rh-C}$ = 47.2 Hz, Rh-$C_{carbene}$), 136.3 (NCHN), 129.3 (CH_{imid}), 126.4 (C_q), 124.2 (CH_{imid}), 43.4 (NCH_3), 36.9 (NCH_3), 30.2 ($COOCH_3$). Anal. Calcd for $RhI_2O_2N_6C_{15}H_{20}PF_6(H_2O)_3$ (872.1): C, 20.66; H, 3.01; N, 9.64. Found: C, 20.77; H, 3.51; N, 9.23. Electrospray MS (20 V, m/z): 672.8 $[M]^+$.

Synthesis of Compound 7. A mixture of compound **1** (105.4 mg, 0.203 mmol), $[RhCl(COD)]_2$ (50 mg, 0.101 mmol), NaOAc (66.54 mg, 0.812 mmol), and KI (136.16 mg, 0.812 mmol) in acetonitrile (20 mL) was refluxed overnight under an inert atmosphere. Once at room temperature, $[IrCl(COD)]_2$ (68.14 mg, 0.101 mmol), NaOAc (25 mg, 0.3 mmol), and KI (68.1 mg, 0.406 mmol) were added, and the resulting mixture was refluxed for an additional 3 h. The solution was then filtered, and the solvent was removed under vacuum. The crude solid was purified by column chromatography. Elution with a 95:5 mixture of dichloromethane/acetone afforded the separation of an orange band that contained compound **7**. Precipitation with a mixture of dichloromethane/hexane gave the desired product as a brown solid. Yield: 72 mg, 32%. ^1H NMR (300 MHz, $CDCl_3$): δ 7.36 (d, $^3J_{H-H}$ = 2.2 Hz, 2H, CH_{imid}), 7.19 (d, $^3J_{H-H}$ = 2.2 Hz, 2H, CH_{imid}), 4.86 (m, 2H, CH-COD), 4.19 (s, 6H, NCH_3), 3.82 (s, 6H, NCH_3), 3.10 (m, 2H, CH-COD), 2.14 (m, 4H, CH_2-COD), 1.99 (s, 3H, $COOCH_3$), 1.82 (m, 4H, CH_2-COD). ^{13}C NMR (75 MHz, $CDCl_3$): δ 190.7 ($COOCH_3$), 182.3 (Ir-$C_{carbene}$), 163.1 (d, $^1J_{Rh-C}$ = 47.5 Hz, Rh-$C_{carbene}$), 126.3 (CH_{imid}), 124.8 (C_q), 122.1 (CH_{imid}), 84.9 (CH-COD), 57.5 (CH-COD), 42.9 (NCH_3), 36.7 (NCH_3), 32.7 (CH_2-COD), 31.1 ($COOCH_3$), 30.5 (CH_2−COD). Anal. Calcd for $RhIrI_3O_2N_6C_{23}H_{31}(CH_2Cl_2)_2$ (1269.22): C, 23.66; H, 2.78; N, 6.62. Found: C, 23.57; H, 2.53; N, 6.55. Electrospray MS (20 V, m/z): 1014 $[M - I + MeCN]^+$, 973.1 $[M - I]^+$.

Synthesis of Compound 8. A mixture of compound **1** (105.4 mg, 0.203 mmol), $[RhCl(COD)]_2$ (50 mg, 0.101 mmol), NaOAc (66.54 mg, 0.812 mmol), and KI (136.16 mg, 0.812 mmol) in acetonitrile (20 mL) was refluxed overnight under an inert atmosphere. Once at room temperature, $[RhCl(COD)]_2$ (50 mg, 0.101 mmol), NaOAc (33.3 mg, 0.406 mmol), and KI (68.1 mg, 0.406 mmol) were added, and the resulting mixture was refluxed for an additional 3 h. The solution was then filtered, and the solvent was removed under vacuum. The crude solid was purified by column chromatography. Elution with a 95:5 mixture of dichloromethane/acetone afforded the separation of a band that contained the desired product. After removal of the volatiles, **8** was isolated as a yellow solid. Yield: 68 mg, 33%. ^1H NMR (300 MHz, $CDCl_3$): δ 7.35 (s, 2H, CH_{imid}), 7.18 (d, 2H, CH_{imid}), 5.27 (m, 2H, CH-COD), 4.19 (s, 6H, NCH_3), 3.94 (s, 6H, NCH_3), 3.59 (m, 2H, CH-COD), 2.31 (m, 4H, CH_2-COD), 1.99 (s, 3H, $COOCH_3$), 1.84 (m, 4H, CH_2-COD). ^{13}C NMR (75 MHz, $CDCl_3$): δ 190.7 ($COOCH_3$), 185.7 (d, $^1J_{Rh-C}$ = 50.5 Hz, Rh-$C_{carbene}$), 162.7 (d, $^1J_{Rh-C}$ = 47.4 Hz, Rh-$C_{carbene}$), 126.3 (CH_{imid}), 124.9 (C_q), 122.1 (CH_{imid}), 98.0 (d, $^1J_{Rh-C}$ = 6.7 Hz, Rh-CH_{COD}), 74.3 (d, $^1J_{Rh-C}$ = 13.9 Hz, Rh-CH_{COD}), 42.9 (NCH_3), 37.3 (NCH_3), 32.2 (CH_2−COD), 29.7 (CH_2-COD), 25.1 ($COOCH_3$). Anal. Calcd for $Rh_2I_3O_2N_6C_{23}H_{31}$ (1010.06): C, 27.35; H, 3.09; N, 8.32. Found: C, 27.51; H, 3.21; N, 8.59. Electrospray MS (20 V, m/z): 923.9 $[M - I + MeCN]^+$, 882.9 $[M - I]^+$.

Synthesis of Compound 9. CO gas (1 atm, 10 mL/min) was passed through a solution of complex **4** (90 mg, 0.123 mmol) in methanol (15 mL) for 15 min at 0 °C. After this time, the solution was concentrated under reduced pressure. After addition of ether, a yellow solid precipitated. Yield: 77 mg, 92%. ^1H NMR (300 MHz, MeCN-d_3): δ 8.7 (s, 1H, NCHN), 7.6 (d, $^3J_{H-H}$ = 2.1 Hz, 2H, CH_{imid}), 7.5 (d, $^3J_{H-H}$ = 2.2 Hz, 2H, CH_{imid}), 3.9 (s, 6H, NCH_3), 3.9 (s, 6H, NCH_3). ^{13}C NMR (75 MHz, DMSO-d_6): δ 172.0 (Ir-$C_{carbene}$), 171.4 (Ir-CO), 135.5 (NCHN), 126.5 (CH_{imid}), 122.9 (CH_{imid}), 122.3 (C_q), 34.6 (NCH_3), 21.0 (NCH_3). Satisfactory elemental analysis could not be obtained due to the low stability of the compound. IR (KBr): 2079 ($\nu_{C\equiv O}$), 2017 ($\nu_{C\equiv O}$) cm^{-1}. Electrospray MS (20 V, m/z): 593.0 $[M + BF_4]^+$, 252.9 $[M]^{2+}$. Electrospray HR-MS (20 V, m/z): 593.1091 $[M + BF_4]^+$, 253.0516 $[M]^{2+}$.

Synthesis of Compound 10. A mixture of compound **1** (78 mg, 0.149 mmol), $[IrCl(COD)]_2$ (50 mg, 0.0745 mmol), and NaOAc (49.2 mg, 0.6 mmol) in acetonitrile (15 mL) was refluxed for 1 h under an inert atmosphere. Once at room temperature, I_2 (50.8 mg, 0.2 mmol) was added and the mixture was stirred for 3 h. The solution was then filtered, and volatiles were removed under vacuum. The crude solid was purified by column chromatography. Elution with a 1:1 mixture of dichloromethane/acetonitrile afforded the separation of a yellow band that contained compound **10**. Precipitation with a mixture of acetonitrile/diethyl ether gave the desired product as a yellow solid. Yield: 49 mg, 38%. ^1H NMR (300 MHz, MeCN-d_3): δ 8.69 (s, 1H, NCHN), 7.64 (d, $^3J_{H-H}$ = 2.3 Hz, 2H, CH_{imid}), 7.45 (d, $^3J_{H-H}$ = 2.3

Hz, 2H, CH_{imid}), 4.18 (s, 6H, NCH_3), 3.75 (s, 6H, NCH_3), 2.70 (s, 6H, CH_3CN). ^{13}C NMR (75 MHz, DMSO-d_6): δ 135.1 (Ir-$C_{carbene}$), 128.6 (C_q), 127.8 (NCHN), 124.4 (CH_{imid}), 122.7 (CH_{imid}), 118.0 (CH_3CN), 43.5 (NCH_3), 34.9 (NCH_3), 1.1 (CH_3CN). Anal. Calcd for $IrI_2N_8C_{17}H_{23}B_2F_8(Et_2O)_2$ (1107.31): C, 27.12; H, 3.91; N, 10.12. Found: C, 26.91; H, 4.23; N, 9.91. Electrospray MS (20 V, m/z): 393.1 $[M]^{2+}$, 352.0 $[M - 2MeCN]^{2+}$.

Catalytic Reactions: General Procedures. *Tandem Dehalogenation/Transfer Hydrogenation of 4-Bromoacetophenone.* In a typical run, a capped vessel containing a stirring bar was charged with 4-bromoacetophenone (0.36 mmol), Cs_2CO_3 (0.43 mmol), anisole as internal reference (0.36 mmol), catalyst (2% or 1% mmol), and 2 mL of 2-propanol. The reaction mixture was heated at 100 °C for the appropriate time. Reaction monitoring, yields, and conversions were determined by GC.

Suzuki–Miyaura Coupling/Transfer Hydrogenation. In a typical run, a capped vessel containing a stirring bar was charged with 4-bromoacetophenone (0.36 mmol), phenylboronic acid (0.55 mmol), Cs_2CO_3 (1.08 mmol), anisole as internal reference (0.36 mmol), catalyst (2% mmol), 2 mL of 2-propanol, and 2 mL of THF. The reaction mixture was heated at 100 °C for the appropriate time. Reaction monitoring, yields, and conversions were determined by GC.

Cyclization of 2-Aminophenyl Ethyl Alcohol. In a typical run, a capped vessel containing a stirring bar was charged with 2-aminophenyl ethyl alcohol (0.25 mmol), KOH (0.5 mmol), anisole as internal reference (0.25 mmol), catalyst (2% or 1% mmol), and 1 mL of toluene. The reaction mixture was heated at 110 °C for the appropriate time. Reaction monitoring, yields, and conversions were determined by GC.

Acylation of Bromobenzene with n-Hexanal. The catalyst (2% mol of **3** or **5**), TBAB (0.024 mmol), and 4 Å molecular sieves (0.5 g) were placed together in a thick-walled Schlenk tube fitted with a Teflon cap. The tube was evacuated and filled with nitrogen three times. Bromobenzene (0.24 mmol), *n*-hexanal (0.29 mmol), pyrrolidine (0.48 mmol), and dry *N,N*-dimethylformamide (DMF) (1 mL) were added. The reaction mixture was heated at 115 °C for 16 h. After cooling to room temperature, 8 mL of EtOAc was added, and the mixture was washed with H_2O (3 × 2.5 mL) to remove the DMF, dried over Na_2SO_4, and concentrated under vacuum. Conversions were determined by ^1H NMR spectroscopy.

X-ray Diffraction Studies. Diffraction data were collected on a Agilent SuperNova diffractometer equipped with an Atlas CCD detector using Mo Kα radiation (λ = 0.71073 Å). Single crystals were mounted on a MicroMount polymer tip (MiteGen) in a random orientation. Absorption corrections based on the multiscan method were applied.[16] The structures were solved by direct methods in SHELXS-97 and refined by the full-matrix method based on F^2 with the program SHELXL-97 using the OLEX software package.[17]

Crystal Data and Structure Refinement for Complex **3**. Crystals suitable for X-ray study of **3** were obtained by slow diffusion of diethyl ether into a concentrated solution of the complex in acetonitrile. Crystal system, monoclinic; space group, $P2_1$; a (Å), 13.2740(5); b (Å), 16.7105(4); c (Å), 14.4848(5); α (deg), 90.00; β (deg), 108.107(4); γ (deg), 90.00; Z, 4; independent reflections, 14702 [R(int) = 0.0476]; GOF, 1.026; final R indices [$I > 2\sigma(I)$], R_1 = 0.0430, wR_2 = 0.0525; min./max. resid dens (e Å^{-3}), −0.90 and 1.21.

Crystal Data and Structure Refinement for Complex **8**. Crystals suitable for X-ray study of **8** were obtained by slow diffusion of diethyl ether into a concentrated solution of the complex in chloroform. Crystal system, monoclinic; space group, $P2_1/m$; a (Å), 10.4283(3); b (Å), 12.2666(3); c (Å), 11.9217(3); α (deg), 90.00; β (deg), 96.174(2); γ (deg), 90.00; Z, 2; independent reflections, 4649 [R(int) = 0.0492]; GOF, 1.065; final R indices [$I > 2\sigma(I)$], R_1 = 0.0356, wR_2 = 0.0823; min./max. resid dens (e Å^{-3}), −1.10 and 1.29.

■ ASSOCIATED CONTENT

Supporting Information

Details of the catalytic experiments and the high-resolution mass spectra of compounds **4**, **5**, and **9** and X-ray diffraction data in the form of cif files of complexes **3** and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Shibasaki, Y.; Yamamoto, Y. *Multimetallic Catalysts in Organic Synthesis*; Wiley-VCH: Weinheim, 2004. (b) Perez-Temprano, M. H.; Casares, J. A.; Espinet, P. *Chem.—Eur. J.* **2012**, *18*, 1864. (c) Adams, R. D.; Cotton, F. A. *Catalysis by Di- and Polynuclear Metal Cluster Complexes*; Wiley-VCH: New York, 1998. (d) Shibasaki, M.; Sasai, H.; Arai, T. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1237. (e) van den Beuken, E. K.; Feringa, B. L. *Tetrahedron* **1998**, *54*, 12985. (f) Burke, A. J.; Marinho, V. R.; Furtado, O. M. R. *Curr. Org. Synth.* **2010**, *7*, 94. (g) Patil, N. T.; Shinde, V. S.; Gajula, B. *Org. Biol. Chem.* **2012**, *10*, 211.

(2) Lee, J. M.; Na, Y.; Han, H.; Chang, S. *Chem. Soc. Rev.* **2004**, *33*, 302.

(3) (a) Fogg, D. E.; dos Santos, E. N. *Coord. Chem. Rev.* **2004**, *248*, 2365. (b) Ajamian, A.; Gleason, J. L. *Angew. Chem., Int. Ed.* **2004**, *43*, 3754. (c) Wasilke, J. C.; Obrey, S. J.; Baker, R. T.; Bazan, G. C. *Chem. Rev.* **2005**, *105*, 1001.

(4) (a) Boydston, A. J.; Bielawski, C. W. *Dalton Trans.* **2006**, 4073. (b) Boydston, A. J.; Rice, J. D.; Sanderson, M. D.; Dykhno, O. L.; Bielawski, C. W. *Organometallics* **2006**, *25*, 6087. (c) Sanderson, M. D.; Kamplain, J. W.; Bielawski, C. W. *J. Am. Chem. Soc.* **2006**, *128*, 16514. (d) Tennyson, A. G.; Ono, R. J.; Hudnall, T. W.; Khramov, D. M.; Er, J. A. V.; Kamplain, J. W.; Lynch, V. M.; Sessler, J. L.; Bielawski, C. W. *Chem.—Eur. J.* **2010**, *16*, 304. (e) Mercs, L.; Neels, A.; Albrecht, M. *Dalton Trans.* **2008**, 5570. (f) Vujkovic, N.; Cesar, V.; Lugan, N.; Lavigne, G. *Chem.—Eur. J.* **2011**, *17*, 13151. (g) Ruiz, J.; Garcia, L.; Perandones, B. F.; Vivanco, M. *Angew. Chem., Int. Ed.* **2011**, *50*, 3010. (h) Rit, A.; Pape, T.; Hahn, F. E. *J. Am. Chem. Soc.* **2010**, *132*, 4572. (i) Prades, A.; Poyatos, M.; Mata, J. A.; Peris, E. *Angew. Chem., Int. Ed.* **2011**, *50*, 7666.

(5) (a) Mas-Marza, E.; Mata, J. A.; Peris, E. *Angew. Chem., Int. Ed.* **2007**, *46*, 3729. (b) Curphey, T. J.; Prasad, K. S. *J. Org. Chem.* **1972**, *37*, 2259. (c) Buron, C.; Stelzig, L.; Guerret, O.; Gornitzka, H.; Romanenko, V.; Bertrand, G. *J. Organomet. Chem.* **2002**, *664*, 70. (d) Guerret, O.; Sole, S.; Gornitzka, H.; Teichert, M.; Trinquier, G.; Bertrand, G. *J. Am. Chem. Soc.* **1997**, *119*, 6668. (e) Guerret, O.; Sole, S.; Gornitzka, H.; Trinquier, G.; Bertrand, G. *J. Organomet. Chem.* **2000**, *600*, 112.

(6) (a) Zanardi, A.; Corberan, R.; Mata, J. A.; Peris, E. *Organometallics* **2008**, *27*, 3570. (b) Zanardi, A.; Mata, J. A.; Peris, E. *J. Am. Chem. Soc.* **2009**, *131*, 14531. (c) Zanardi, A.; Mata, J. A.; Peris, E. *Organometallics* **2009**, *28*, 4335. (d) Zanardi, A.; Mata, J. A.; Peris, E. *Chem.—Eur. J.* **2010**, *16*, 13109. (e) Zanardi, A.; Mata, J. A.; Peris, E. *Chem.—Eur. J.* **2010**, *16*, 10502. (f) Sabater, S.; Mata, J. A.; Peris, E. *Chem.–Eur. J.* **2012**, *18*, DOI: 10.1002/chem.201103657.

(7) Gonell, S.; Poyatos, M.; Mata, J. A.; Peris, E. *Organometallics* **2011**, *30*, 5985.

(8) Zhong, R.; Wang, Y. N.; Guo, X. Q.; Chen, Z. X.; Hou, X. F. *Chem.—Eur. J* **2011**, *17*, 11041.
(9) Cuervo, D.; Gamasa, M. P.; Gimeno, J. *Chem.—Eur. J.* **2004**, *10*, 425.
(10) (a) McCarthy, A. R.; Hartmann, R. W.; Abell, A. D. *Bioorg. Med. Chem. Lett.* **2007**, *17*, 3603. (b) Picard, F.; Schulz, T.; Hartmann, R. W. *Bioorg. Med. Chem.* **2002**, *10*, 437.
(11) Fujita, K.; Yamamoto, K.; Yamaguchi, R. *Org. Lett.* **2002**, *4*, 2691.
(12) (a) Kuethe, J. T. *Chimia* **2006**, *60*, 543. (b) Humphrey, G. R.; Kuethe, J. T. *Chem. Rev.* **2006**, *106*, 2875.
(13) Ruan, J. W.; Saidi, O.; Iggo, J. A.; Xiao, J. L. *J. Am. Chem. Soc.* **2008**, *130*, 10510.
(14) Olah, G. A. *Friedel-Crafts Chemistry*; Wiley-Interscience: New York, 1973.
(15) (a) Colbon, P.; Ruan, J. W.; Purdie, M.; Xiao, J. L. *Org. Lett.* **2010**, *12*, 3670. (b) Alvarez-Bercedo, P.; Flores-Gaspar, A.; Correa, A.; Martin, R. *J. Am. Chem. Soc.* **2010**, *132*, 466.
(16) Clark, R. C.; Reid, J. S. *Acta Crystallogr. A* **1995**, *51*, 887.
(17) (a) Sheldrick, G. M. *Acta Crystallogr. A* **2008**, *64*, 112. (b) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Crystallogr.* **2009**, *42*, 339.