Homo- and Heterodinuclear Complexes with Triazolyl-diylidene. An Easy Approach to Tandem Catalysts[⊥]

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The reaction of 1,2,4-trimethyltriazolium tetrafluoroborate ($[LH_2](BF_4)_2$) with several metal precursors provides a series of homo- and heterodimetallic compounds of Rh and Ir. The reaction of $[LH_2](BF_4)_2$ with $[Cp^*IrCl_2]_2$ in the presence of NaH in MeOH yields the monocarbene complex $[Cp^*Ir(LH)Cl_2](BF_4)$, which is a very convenient synthon to the preparation of heterodimetallic species through the deprotonation of the remaining NC*H*N group. Three crystal structures of dimetallic compounds of di-iridium(III), iridium(III)/iridium(I), and iridium(III)/rhodium(I) are described. The complexes obtained have been tested in a tandem catalytic reaction implying the consecutive oxidative cyclization of 2-aminophenyl ethyl alcohol and the alkylation of the resulting imidazole with a series of primary alcohols. The new catalysts show high activity in the overall reaction process, and the selectivity in the production of the bisindolylmethane or monoalkylated indole is tuned by changing the indole/alcohol molar ratio.

Introduction

One of the most important areas of interest in the field of homogeneous catalysis is the search for single catalysts to mediate two or more reactions that are fundamentally different in nature.[1,2] The advantages of this type of catalysts are evident, since they may be used in the design of series of reactions that can be sequentially linked, thus providing an important saving in solvents, catalyst, reaction workups, and time. When considering the use of a single catalyst in sequential tandem reactions, the most important limitation is that we have to look for compounds that are compatible with residual material from preceding steps (solvent, additives, other catalysts, byproduct, catalyst lifetime, etc.). In the search for the most suitable catalyst, we also have to take into account that the catalyst must be versatile enough to catalyze two or more reactions; the more different in nature, the more versatile the catalyst. For a single metal with a well-defined environment, the number of possible active reactions is limited to the well-known reactions for which the metal is effective. In the cases where series of different-in-nature reactions are pursued, multiple catalysts containing different metals can be used.[1]

Stability and versatility seem to be the most interesting properties if we aim to prepare a catalyst for a multistep process. N-Heterocyclic carbenes (NHCs), which emerged as one of the most promising types of ligands in the design of new catalysts, may fulfill these requirements since they provide stable metal complexes,[3,4] together with a large variety of possibilities in terms of topological architectures and coordination abilities to a wide range of metals in different oxidation states.[3,5] On many occasions NHCs have allowed coordination modes that were unknown for other traditional ligands, such as those described for benzobis(imidazolylidene)s, which show a facially opposed coordination to two metal fragments (Janus-head type).[6]

In the search for new ligands for the synthesis of discrete dimetallic compounds that may show enhanced catalytic performances, we recently used a triazolyl-diylidene[7] ligand (ditz) for the preparation of Ir, Rh,[8] and Ru[9] compounds (Scheme 1). Ditz allows the coordination of two metals that may be electronically connected through the azole ring. The use of this ligand in the preparation of ditopic tandem catalysts was one of our aims since we obtained the first Rh and Ir complexes.[8]

On the basis of these previous results we now describe a new methodology that allowed us to obtain heterometallic complexes using the ditz ligand. The method is based on the preparation of monocarbene-metal species that can give further metalation to a second metal unit, providing easy access to series of homo- and heterodimetallic species. The compounds obtained have been fully characterized, and their molecular structures are described. We also report the catalytic properties of our new

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[⊥] This article is dedicated to Prof. Robert H. Crabtree on the occasion of his 60th birthday.

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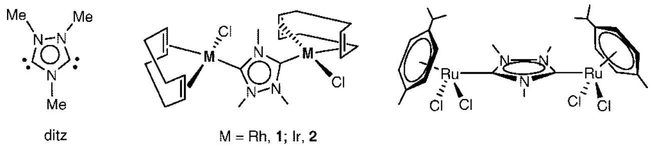
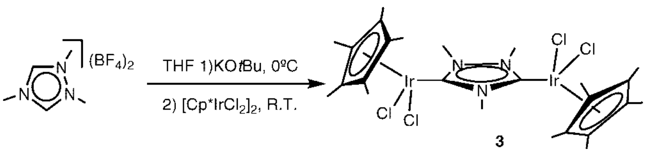
Scheme 1



ditz

M = Rh, **1**; Ir, **2**

Scheme 2



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complexes in the sequential oxidative cyclization of 2-aminophenyl ethyl alcohol and the alkylation of the resulting imidazole with a series of primary alcohols.

Results and Discussion

Synthesis and Characterization of Compounds. The reaction of 1,2,4-trimethyltriazolium tetrafluoroborate ([LH$_2$](BF$_4$)$_2$) with [Cp*IrCl$_2$]$_2$ in the presence of KO*t*Bu affords the dinuclear compound **3** in good yield (60%), as shown in Scheme 2. Compound **3** was characterized by NMR spectroscopy and mass spectrometry and gave satisfactory elemental analysis.

The ^{1}H NMR spectrum of **3** shows that the signal due to the two acidic HC*H*N protons has disappeared, thus providing the first evidence that the coordination has occurred. The resonances due to the methyl groups at δ 4.32 and 4.31, with a 1:2 ratio, suggest that the compound has a 2-fold symmetry. The ^{13}C NMR spectrum provides more direct evidence of the metalation, as seen by the signal at 168.9 ppm, assigned to the Ir$-$C$_{\text{carbene}}$. The dimetallic nature of the compound is confirmed by the data resulting from the electrospray mass spectrometry (ESI-MS), which shows a main peak at $m/z = 872.1$, due to $[\mathrm{M} - \mathrm{Cl}]^+$.

The preparation of the dinuclear Ir compound **3** confirms the high versatility of the ditz ligand and its easy handling. In order to improve the coordination applicability of the ligand, we tried to perform its single metalation to a monometallic fragment. The reaction of 1,2,4-trimethyltriazolium tetrafluoroborate ([LH$_2$](BF$_4$)$_2$) in methanol in the presence of an equimolecular amount of NaH affords the methanolic adduct [LH-MeOH]BF$_4$,[10] which could either be isolated or used *in situ*. The reaction of [LH-MeOH]BF$_4$ with the corresponding amount of [Cp*IrCl$_2$]$_2$ afforded the cationic compound **4**, in which the azole ligand is acting as a monocarbene (Scheme 3). Using the same procedure but adding [IrCl(cod)]$_2$ instead, we obtained compound **5**, which also shows the monocoordination of the carbene ligand. Compounds **4** and **5** were isolated and fully characterized by means of NMR spectroscopy and mass spectrometry. The ^{1}H NMR of **4** shows a singlet at δ 9.51, due to the only NC*H*N proton, with a relative integral of 1, compared to the three signals due to the methyl groups at 4.32, 4.18, and 4.13 ppm, thus indicating that only one of the two NC*H*N protons was lost upon coordination to the metal. The most relevant feature of the ^{13}C NMR spectrum is the signal at 169.0 ppm, which provides evidence of the metalation to the Ir(III) fragment.[11] The ^{1}H NMR of **5** shows the signal due to the NC*H*N proton at δ 9.36, and the ^{13}C NMR shows the resonance for the metalated carbene at 189.2, indicating the coordination to the Ir(I) fragment.

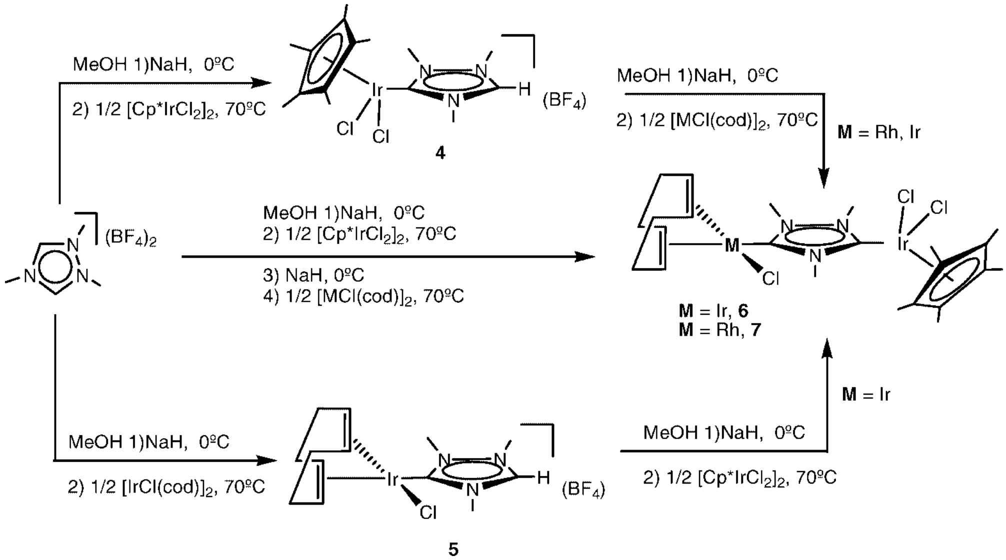
Both **4** and **5** are highly valuable synthons for the preparation of heterometallic dicarbene species, since a second CH bond at the azole ring can be activated to generate the second carbene. The reaction of **4** with [MCl(cod)]$_2$ (M = Rh, Ir) in the presence of NaH in MeOH affords the dimetallic species **6** (Ir$^{\text{III}}$/Ir$^{\text{I}}$) and **7** (Ir$^{\text{III}}$/Rh$^{\text{I}}$), two special cases of mixed-valence metal complexes (Scheme 3).

The reaction can also be performed by preparing and using **4** and **5** *in situ*, so that the stepwise metalation of the ligand provides directly the heterodimetallic compounds **6** and **7** (Scheme 3). This method is very convenient because it clearly simplifies the workups to the final products, together with a clear reduction of the amount of solvents used in the overall reaction and purification processes.

We also obtained compound **6** in high yield starting from **5**, by addition of [Cp*IrCl$_2$]$_2$ in the presence of NaH in MeOH. This alternative procedure to the preparation of **6** confirms the wide applicability of the stepwise metalation of 1,2,4-trimethyltriazolium, as a valuable way to prepare different homo- and heterodimetallic species.

The NMR spectra of compounds **6** and **7** clearly confirm the dicarbene nature of both species. The ^{1}H NMR spectra show the disappearance of the resonances due to the NC*H*N protons as a first indication that the double-metalation has occurred. The

Scheme 3



5

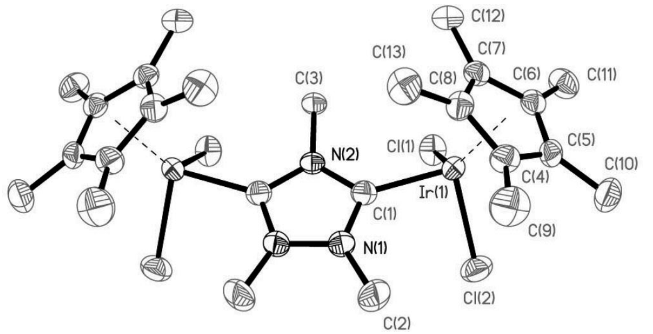


Figure 1. Molecular diagram of compound **3**. Hydrogen atoms and solvent (H_2O) have been omitted for clarity. Ellipsoids are at 50% probability. Selected bond distances (Å) and angles (deg): Ir(1)−C(1) 2.033(8), Ir(1)−Cl(1) 2.442(2), Ir(1)−Cl(2) 2.411(2), C(1)−Ir(1)−Cl(1) 91.5(2), C(1)−Ir(1)−Cl(2) 90.5(2), Cl(2)−Ir(1)−Cl(1) 85.31(8), N(1)−C(1)−Ir(1) 127.2(6), N(2)−C(1)−Ir(1) 129.1.

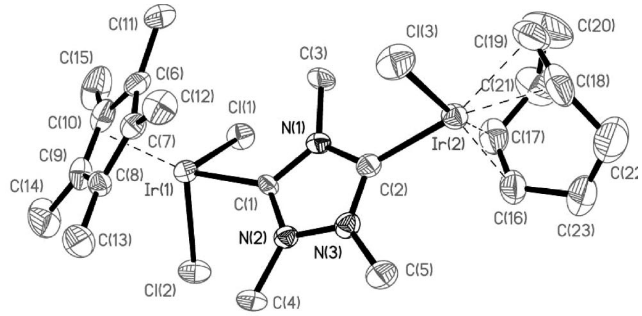


Figure 2. Molecular diagram of compound **6**. Hydrogen atoms and solvent (CH_2Cl_2) have been omitted for clarity. Ellipsoids are at 50% probability. Selected bond distances (Å) and angles (deg): Ir(1)−C(1) 2.023(7), Ir(2)−C(2) 2.006(7), Ir(1)−Cl(1) 2.4122(18), Ir(1)−Cl(2) 2.4180(19), Ir(2)−Cl(3) 2.3497(19), Ir(2)−C(16) 2.131(8), Ir(2)−C(17) 2.125(8), Ir(2)−C(20) 2.182(10), Ir(2)−C(21) 2.196(9), C(1)−Ir(1)−Cl(1) 91.69(19), C(1)−Ir(1)−Cl(2) 91.05(19), C(2)−Ir(2)−Cl(3) 87.11(19), N(1)−C(1)−Ir(1) 129.0(5), N(2)−C(1)−Ir(1) 127.9(5), N(1)−C(2)−Ir(2) 127.2(5), N(3)−C(2)−Ir(2) 129.3(5).

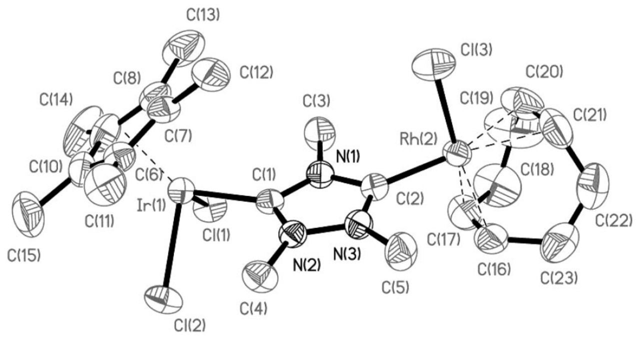


Figure 3. Molecular diagram of compound **7**. Hydrogen atoms and solvent (CH_2Cl_2) have been omitted for clarity. Ellipsoids are at 50% probability. Selected bond distances (Å) and angles (deg): Ir(1)−C(1) 2.032(4), Rh(2)−C(2) 2.006(4), Ir(1)−Cl(1) 2.4173(10), Ir(1)−Cl(2) 2.4198(11), Rh(2)−Cl(3) 2.3603(12), Rh(2)−C(16) 2.102(5), Rh(2)−C(17) 2.118(5), Rh(2)−C(20) 2.209(5), Rh(2)−C(21) 2.222(5), C(1)−Ir(1)−Cl(1) 91.58(11), C(1)−Ir(1)−Cl(2) 91.16(11), C(2)−Rh(2)−Cl(3) 86.12(12), N(1)−C(1)−Ir(1) 128.5(3), N(2)−C(1)−Ir(1) 127.7(3), N(1)−C(2)−Rh(2) 127.0(3), N(3)−C(2)−Rh(2) 128.9(3).

signals due to the cod and Cp* ligands are clearly observed in the spectra, and the three distinctive resonances due to the methyl groups indicate the asymmetry of the complex. The ^{13}C NMR spectra confirm that the metalation to the two metals has occurred, with two signals at 187.0 and 167.4 for **6** ($Ir^I-C_{carbene}$ and $Ir^{III}-C_{carbene}$, respectively) and at 191.6 (d, $^1J_{Rh-C} = 52.1$ Hz) and 167.3 for **7** ($Rh^I-C_{carbene}$ and $Ir^{III}-C_{carbene}$, respectively).

X-Ray Diffraction Studies. The molecular structures of **3**, **6**, and **7** were unambiguously confirmed by X-ray diffraction studies. The molecular diagrams are shown in Figures 1, 2, and 3, respectively.

The molecular structure of **3** consists of two fragments of Cp^*IrCl_2 connected by a triazolyl-diylidene bridge. The two metal fragments are disposed in a *syn* conformation, so there is a mirror plane perpendicular to the azole ring and containing the N(2) and C(3) atoms. The $Ir-C_{carbene}$ distance of 2.033 Å lies in the expected range for Cp*Ir(NHC) complexes.[11] The two iridium atoms are quasi-coplanar with the azole ring, with a small deviation of 2.8°, according to the corresponding torsion angle, Ir(1)−C(1)−N(1)−C(2). The distance between the two iridium atoms is 6.17 Å.

Compounds **6** and **7** are isostructural, despite the fact that **6** contains a IrCl(cod) fragment while **7** has RhCl(cod). The molecular structure of compound **6** consists of a Cp^*IrCl_2 moiety connected to IrCl(cod) by the triazolyl-diylidene ligand. The structure gives a unique opportunity to compare the bond distances to Ir(III) and Ir(I) by the same ligand within the same compound. These distances are 2.023 and 2.006 Å for the $Ir^{III}-C_{carbene}$ and $Ir^I-C_{carbene}$, respectively, thus showing a slightly shorter distance for the Ir^I-C bond. Although we are aware that the differences are within the experimental error, we believe that the shorter distance may be due to the more sterically released geometry in the square-planar part of the molecule than in the pseudotetrahedral fragment, thus allowing a closer approach of the ligand to the metal. The azole ring adopts an almost perpendicular orientation with respect to the coordination plane of the Ir^I metal fragment, as indicated by the torsion angles Cl(3)−Ir(2)−C(2)−N(3) and Cl(3)−Ir(2)−C(2)−N(1) of 90.8° and 86.9°, respectively. The distances of the Ir^I center to the carbons of the olefin *trans* to the carbene are longer than for the other olefin (*trans* $Ir-C_{olefin}$ 2.19, and *cis* $Ir-C_{olefin}$ 2.13, average distances) as a consequence of the high *trans* influence of the carbene ligand.

Compound **7** consists of a Cp^*IrCl_2 fragment connected to RhCl(cod) by the ligand ditz. Most structural parameters are similar to that shown by compound **6**, regarding angles and distances. Even the $M-C_{carbene}$ distances are very similar, 2.032 (M = Ir) and 2.006 Å (M = Rh).

Catalytic Studies. In order to test the catalytic activity of our new dimetallic compounds, we found it convenient to design a tandem process including two different catalytic reactions that would be catalyzed by M^I (M = Rh and Ir) and Ir^{III} complexes. This would help us to determine if the presence of the two different metal fragments in complexes **6** and **7** improves their catalytic applicability. As a model reaction we tested the consecutive cyclization of 2-aminophenyl ethyl alcohol (a reaction typically catalyzed by $[Cp^*IrCl_2]_2$)[12] and the alkylation of the resulting indole with a series of alcohols (catalyzed by

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Scheme 4

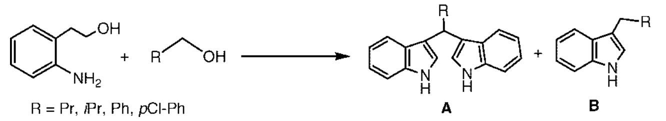

Table 1. Catalytic Tandem Cyclization/Alkylation of 2-Aminophenyl Ethyl Alcohol and Benzyl Alcohol[a]

entry	catalyst	time (h)	conversion (%)	**A**:**B**
1	**2**	7	>95	77:23
2	**3**	7	84	87:13
3	**6**	7	>95	90:10
4	**7**	20	30	50:50
5	$[Cp^*IrCl_2]_2$	7	>95	60:40
6	$[IrCl(cod)]_2$	7	58	70:30

[a] Reaction conditions: 0.25 mmol of amino alcohol, 0.25 mmol of benzyl alcohol, 0.5 mmol of KOH, 1 mol % catalyst, 0.3 mL of toluene. $T = 110$ °C. Conversions determined by ^{1}H NMR spectroscopy using ferrocene (0.025 mmol) as standard.

Ir,[13] Ru,[14] and In[15] compounds). 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.[16] Although there is a large list of articles describing the alkylation of indoles with ketones and aldehydes,[17,18] the number of works in which alcohols are used instead is scarce and recent, and most respond to the development of new catalytic processes implying transition metal complexes.[13–15,19] The one-pot tandem strategy to directly obtain alkylated indoles/bisindoles from the reaction of 2-aminophenyl ethyl alcohol and a series of alcohols (Scheme 4) is a challenging process because it will allow us to compare the different activities of our dimetallic catalysts in two different and consecutive processes and may also provide some interesting insights into the design of efficient methods for the preparation of imidazolyl-based complexes with a wider set of functionalizations. A very recent work by Grigg and co-workers studied for the first time this same reaction using $[Cp^*IrCl_2]_2$ as catalyst,[13] so we used their previous results as a reference to our new findings.

First we studied the activity in the reaction of the amino alcohol with benzylic alcohol of a wide set of catalysts, including the new complexes reported in this work (**3**, **6**, and **7**) together with other related compounds such as **2** (Scheme 1), $[Cp^*IrCl_2]_2$, and $[IrCl(cod)]_2$. This first set of data is displayed in Table 1 and allows us to compare our catalysts in terms of conversions and selectivities, since the bisindolylmethane (**A**) and the 3-alkylated (**B**) products are obtained in different ratios depending on the catalyst used. We did not observe any of the N-alkylated product under the reaction conditions used. Under the reaction conditions applied (equimolar amounts of alcohol and amino alcohol, catalyst loading of 1 mol %, toluene at 110 °C), a clear preference for the bisindolyl product **A** is observed for all catalysts except **7**, which yields an **A**:**B** ratio of 50:50. The catalyst containing the Ir^{III}/Ir^{I} couple (**6**) offers the best selectivity in the production of the bisindole **A**. In terms of conversions, the triazolyl-diylidene-bridged complexes **2** and **6** showed higher activity than **3** and **7**. The complex $[Cp^*IrCl_2]_2$ also showed a high activity toward the alkylated complexes, although it afforded a lower selectivity to **A**. These preliminary results show that the catalytic activity of all the complexes used cannot be assigned to any of the individual metal fragments that compose each dimetallic catalyst. For example, based on the high catalytic performances of **2** we should assume that the good results are due to the Ir^{I}(cod) fragment. This would be consistent with the good activities shown by **6**, which contains the $Ir^{I}(cod)/Cp^*Ir^{III}$ couple. The same argument can be applied to the Cp^*Ir^{III} fragment, by comparing the results obtained by **3** and **6**. However, the $Rh^{I}/CpIr^{III}$ compound **7** shows a very low activity, a result that contrasts with those shown by the other Cp^*Ir^{III}-containing complexes **3** and **6**.

Table 2. Catalytic Cyclization/Alkylation of 2-Aminophenyl Ethyl Alcohol with Different Primary Alcohols[a]

entry	catalyst	R	cat. load. (mol %)	time (h)	conversion (%)	**A**:**B**
1	**2**	Pr	1	20	61	100:0
2	**2**		0.1	12	10	100:0
3	**2**	Ph	1	7	>95	77:23
4	**2**		0.1	12	21	60:40
5	**2**	*p*Cl-Ph	1	7	>95	90:10
6	**2**		0.1	12	44	90:10
7	**2**	*i*Pr	1	36	15	100:0
8	**6**	Pr	1	20	>95	100:0
9	**6**		0.1	12	14	100:0
10	**6**	Ph	1	7	>95	90:10
11	**6**		0.1	12	50	90:10
12	**6**	*p*Cl-Ph	1	7	>95	80:20
13	**6**		0.1	12	45	80:20
14	**6**	*i*Pr	1	36	50	100:0
15	$[Cp^*IrCl_2]_2$	Pr	1	20	13	100:0
16	$[Cp^*IrCl_2]_2$	Ph	1	7	>95	60:40
17	$[Cp^*IrCl_2]_2$		0.1	20	40	70:30
18	$[Cp^*IrCl_2]_2$	*i*Pr	1	36	21	100:0

[a] Reaction conditions: 0.25 mmol of amino alcohol, 0.25 mmol of primary alcohol, 0.5 mmol of KOH, 0.3 mL of toluene. $T = 110$ °C. Conversions determined by ^{1}H NMR spectroscopy using ferrocene (0.025 mmol) as standard.

Since compounds **2**, **6**, and $[Cp^*IrCl_2]_2$ showed the best catalytic performances, they were tested using a wider range of primary alcohols. We also performed the reactions with a lower catalyst loading (0.1 mol %) in order to study in more detail the differences in catalytic activity of the compounds used. These data are shown in Table 2. According to these new data, it seems clear that all catalysts afford better activities when benzyl alcohols are used compared to the activity shown with *i*BuOH and *n*BuOH, in accordance with the previously reported data.[13] For a catalyst loading of 1 mol %, **6** is the most effective catalyst in terms of both conversions and selectivity, even achieving full conversion to the bisindolylmethane when *n*BuOH is used. Reducing the catalyst loading to 0.1 mol % results in a significant lowering of the catalytic productivity, although the conversions were still moderate (~50%) when catalyst **6** and the benzyl alcohols were used. Again, the significant differences between the catalytic performances of **2** and **6**, together with the data shown in Table 1 for compound **3**, support the idea

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Scheme 5

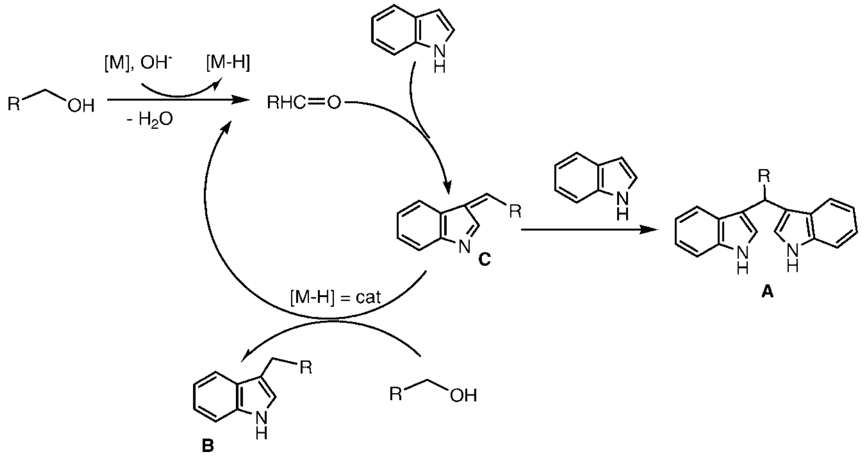

Table 3. Selectivity Dependence on Alcohol:Amino Alcohol Ratio[a]

entry	catalyst	amino alcohol:benzyl alcohol	**A**:**B**
1	**2**	1:1	100:0
2	**2**	1:5	50:50
3	**2**	1:10	0:100
4	**2**	1:20	0:100
5	**6**	1:1	100:0
6	**6**	1:5	60:40
7	**6**	1:10	0:100
8	**6**	1:20	0:100

[a] Reaction conditions: 0.25 mmol of amino alcohol, 0.5 mmol of KOH, 0.1 mol % catalyst, 0.3 mL of toluene. $T = 110$ °C, time 12 h. **A**:**B** ratios determined by ^{1}H NMR spectroscopy.

that there may be some catalytic cooperativity in catalyst **6**, since its activity cannot be regarded as the sum of the individual activities of the Cp*Ir^{III}Cl$_2$ and Ir^{I}Cl(cod) fragments.

According to the proposed mechanism for the alkylation of indole with alcohols,[13] the formation of the bisindolylmethane product (**A**, Scheme 4) arises from Michael addition of indole to the intermediate **C**. This intermediate can evolve to the monoalkylated species **B** after being hydrogenated by the alcohol in the presence of the base by a metal-mediated transfer hydrogenation process, as depicted in the mechanism shown in Scheme 5. The relative reaction rates leading to **A** and **B** from the intermediate **C** are responsible of the ratios in which the final products are obtained. Because the transfer hydrogenation is a relatively slow process, it is not surprising that **A** is the major compound obtained for the reaction conditions used. Since the alcohol is acting as both an alkylating agent and reductant, an excess of alcohol should favor the formation of the monoalkylated species **B**.

Table 3 shows the different product ratios upon variation of the amount of alcohol added when catalysts **2** and **6** were used. As can be seen, upon increasing the alcohol/amino alcohol molar ratios, an inversion of the selectivity is observed, so that the monoalkylated compound **B** is the only product obtained for alcohol/amino alcohol molar ratios higher than 10.

In order to discard that the activity of complex **6** may be due to the activity of a mixture **3** and **2** as a consequence of the disproportionation reaction of **6**, we decided to test the stability of the complex at high temperatures in different solvents. Long standing solutions (>2 h) of **6** in CDCl$_3$, toluene-d_8, and DMSO-d_6, at 80 and 110 °C, respectively, showed that the complex did not decompose, according to the NMR spectra recorded during and after the experiment. In principle, this stability test supports the idea that the dimetallic structure of the complex is maintained during the catalytic cycle, although we are aware that the experiment does not reproduce the conditions supported by the catalyst in the catalytic reaction.

Conclusions

In this work we have described the preparation of homo- and heterodimetallic M/Ir^{III} (M = Ir^{III}, Ir^I, Rh^I) complexes with a bridging triazolyl-diylidene ligand (ditz). Although we had previously described the coordination of this ligand to provide dimetallic compounds of Ir, Rh,[8] and Ru,[9] we now have widened its scope by presenting a convenient method to prepare asymmetric compounds containing two different metal fragments. If we take into account the high coordination versatility of NHCs, we can envisage that the sequential deprotonation of 1,2,4-trimethyltriazolium can provide a wide set of families of heterodimetallic complexes with interesting applications in the field of homogeneous catalysis.

The catalytic activities of our new compounds have been tested in a tandem reaction implying the oxidative cyclization of an amino alcohol to produce indole that is alkylated by a primary alcohol to selectively produce the 3-alkylated species or the bisindolylmethane compound. We performed a detailed study and proposed a mechanism that is slightly different from the previously proposed one.[13] Our results show not only that our compounds are highly effective for this tandem process but also that the heterometallic complexes show different activity than the homodimetallic species, in the sense that the activity of the heterometallic catalysts cannot be regarded as the sum of the individual components of the compound, thus implying that the connection of two different metal fragments through an aromatic bridging ligand may have important consequences in catalytic cooperativity.

Further investigations aiming to obtain a series of different metals coupled by the ditz ligand are underway. We believe that these studies will widen the scope of their catalytic applicabilities.

Experimental Section

General Procedures. [Cp*IrCl$_2$]$_2$,[20] 1,2,4-trimethyltriazolium tetrafluoroborate, [LH$_2$](BF$_4$)$_2$,[21] methanolic adduct [LH-MeO-H]BF$_4$,[10] and compounds **1** and **2**[8] were prepared according to

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Table 4. Crystallographic Data

	3	6	7
empirical formula	$(C_{25}H_{39}Cl_4Ir_2N_3)\cdot H_2O$	$(C_{23}H_{36}Cl_3Ir_2N_3)\cdot CH_2Cl_2$	$(C_{23}H_{36}Cl_3IrN_3Rh)\cdot CH_2Cl_2$
mol wt	925.79	930.22	840.93
radiation	Mo Kα (monochr); 0.71073 λ (Å)		
T (K)	298	293	298
cryst syst	orthorhombic	monoclinic	monoclinic
space group	*Pbcm*	$P2(1)/n$	$P2(1)/n$
a (Å)	8.4528(3)	12.5314(6)	12.5908(4)
b (Å)	15.0376(3)	15.3256(7)	15.2228(6)
c (Å)	23.8627(9)	16.6218(8)	16.6788(6)
α (deg)	90	90	90
β (deg)	90	106.6410(10)	106.8130(10)
γ (deg)	90	90	90
V (Å^3)	3033.2(2)	3058.5(3)	3060.13(19)
Z	4	4	4
D_{calcd} (Mg m^{-3})	2.023	2.020	1.825
μ(Mo Kα) (mm^{-1})	9.141	9.148	5.338
total, unique no. of rflns	16 412, 2733	20 703, 7015	20 994, 7028
R_{int}	0.0354	0.0560	0.0337
no. of params, restrictions	170, 0	315, 0	315, 0
R, R_w [$I > 2\sigma(I)$]	0.0297, 0.0807	0.0390, 0.0807	0.0267, 0.0680
GOF	1.183	1.027	1.034
min., max. resid dens (e Å^{-3})	−1.174, 1.985	−0.931, 1.021	−0.945, 1.341

literature procedures. All other reagents were used as received from commercial suppliers. NMR spectra were recorded on Varian Innova 300 and 500 MHz spectrometers, using $CDCl_3$, CD_3CN, and 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. Elemental analyses were carried out on a EuroEA3000 Eurovector analyzer.

Synthesis of 3. A mixture of 1,2,4-trimethyltriazolium tetrafluoroborate (43 mg, 0.15 mmol) and potassium *tert*-butoxide (51 mg, 0.45 mmol) was cooled to 0 °C in an ice bath. Freshly distilled THF (5 mL) was added, and the mixture was allowed to reach room temperature. To this suspension was added a solution of $[Cp^*IrCl_2]_2$ (120 mg, 0.15 mmol) in freshly distilled CH_2Cl_2 (5 mL). The mixture was stirred at room temperature for 1 h. Solvents were evaporated under reduced pressure, and the crude solid was redissolved in diethyl ether. The mixture was filtered through a pad of Celite, and after evaporation of the solvent, the crude solid was purified by column chromatography. The pure compound **3** was eluted with dichloromethane/acetone (8:2) and precipitated in a mixture of dichloromethane/diethyl ether to give an orange solid. Yield: 82 mg (60%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.32 (s, 3H, NCH_3), 4.31 (s, 6H, NCH_3), 1.67 (s, 15H, $C_5(CH_3)_5$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.9 (*C*-Ir carbene), 90.5 ($C_5(CH_3)_5$), 41.5 (NCH_3), 38.4 (NCH_3), 9.3 ($C_5(CH_3)_5$). Anal. Calcd for $C_{25}H_{39}Cl_4Ir_2N_3\cdot H_2O$: C, 32.43; H, 4.46; N, 4.54. Found: C, 32.32; H, 4.46; N, 4.55. Electrospray MS, cone 30 V (*m*/*z*, fragment): 872.1, [M − Cl]$^+$.

Synthesis of 4. Method a. A mixture of methanolic aduct [LH-MeOH]BF_4 (66 mg, 0.27 mmol) and $[Cp^*IrCl_2]_2$ (108 mg, 0.13 mmol) was refluxed in methanol (10 mL) for 2 h. Solvent removal afforded a mixture of compound **4** and an excess of $[Cp^*IrCl_2]_2$. The nonreacted $[Cp^*IrCl_2]_2$ was eliminated by fractional recrystallization in cold CH_3CN (2 × 15 mL). Compound **4** was obtained as an orange solid after precipitation in acetone/diethyl ether. Yield: 110 mg (69%).

Method b. A suspension of sodium hydride (60% in mineral oil, 17 mg, 0.42 mmol) in dry methanol was stirred at 0 °C under a nitrogen atmosphere until a clear solution of sodium methoxide was formed. 1,2,4-Trimethyltriazolium tetrafluoroborate (103 mg, 0.3 mmol) was added, and the mixture was stirred at room temperature for 1 h. After addition of $[Cp^*IrCl_2]_2$ (108 mg, 0.13 mmol) the mixture was refluxed at 70 °C for 2 h. The suspension was filtered and the solution concentrated under reduced pressure. Compound **4** was obtained as an orange solid after precipitation in acetone/diethyl ether. Yield: 136 mg (85%). ^{1}H NMR (500 MHz, CD_3CN): δ 9.51 (s, 1H, NC*H*N), 4.32 (s, 3H, NCH_3), 4.18 (s, 3H, NCH_3), 4.13 (s, 3H, NCH_3), 1.64 (s, 15H, $C_5(CH_3)_5$). ^{13}C NMR (75 MHz, DMSO-d_6): δ 169.0 (*C*-Ir carbene), 145.6 (N*C*HN), 90.8 ($C_5(CH_3)_5$), 38.0 (NCH_3), 37.5 (NCH_3), 37.1 (NCH_3), 8.8 ($C_5(CH_3)_5$). Anal. Calcd for $C_{15}H_{25}BCl_2F_4IrN_3$: C, 30.16; H, 4.22; N, 7.03. Found: C, 30.07; H, 4.20; N, 7.00. Electrospray MS, cone 20 V (*m*/*z*, fragment): 510.1, [M]$^+$.

Synthesis of 5. A suspension of sodium hydride (60% in mineral oil, 17 mg, 0.42 mmol) in dry methanol was stirred at 0 °C under a nitrogen atmosphere until a clear solution of sodium methoxide was formed. 1,2,4-Trimethyltriazolium tetrafluoroborate (103 mg, 0.3 mmol) was added, and the mixture was stirred at room temperature for 1 h. After addition of $[IrCl(cod)]_2$ (100 mg, 0.15 mmol) the mixture was refluxed at 70 °C for 2 h. The suspension was filtered and the solution concentrated under reduced pressure. Compound **5** was obtained as an orange-yellow oil. Yield: 140 mg (87%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.36 (s, 1H, NC*H*N), 4.85 (m, 2H, COD), 4.28 (s, 3H, CH_3), 4.1 (s, 6H, CH_3), 3.15 (m, 2H, COD), 2.27 (m, 5H, COD), 1.92 (m, 3H, COD), 1.76 (m, 3H, COD). ^{13}C NMR (75 MHz, $CDCl_3$): δ 189.2 (*C*-Ir carbene), 144.4 (N*C*HN), 91.9 (COD), 91.8 (COD), 55.3 (COD), 54.6 (COD), 37.9 (CH_3), 37 (CH_3), 36.9 (CH_3), 33.5 (COD), 33.4 (COD), 29.4 (COD). Electrospray MS, cone 20 V (*m*/*z*, fragment): 448, [M]$^+$.

Synthesis of 6. Method a. A suspension of sodium hydride (60% in mineral oil, 8 mg, 0.2 mmol) in dry methanol was stirred at 0 °C under a nitrogen atmosphere until a clear solution of sodium methoxide was formed. Compound **4** (111 mg, 0.17 mmol) was then added, and the mixture was stirred at room temperature for 30 min. After addition of $[IrCl(cod)]_2$ (50 mg, 0.074 mmol) the mixture was refluxed at 70 °C for 30 min. Solvent was evaporated under reduced pressure, and the crude solid was purified by column chromatography. Elution with dichloromethane/acetone (8:2) afforded compound **6**. Analytically pure material was obtained by precipitation from dichloromethane/hexanes as a yellow solid. Yield: 103 mg (82%).

Method b. A suspension of sodium hydride (60% in mineral oil, 26 mg, 0.6 mmol) in dry methanol was stirred at 0 °C under a nitrogen atmosphere until a clear solution of sodium methoxide was formed. Compound **5** (305 mg, 0.57 mmol) was then added, and the mixture was stirred at room temperature for 30 min. After addition of $[Cp^*IrCl_2]_2$ (200 mg, 0.25 mmol) the mixture was refluxed at 70 °C for 30 min. Solvent was evaporated under reduced pressure, and the crude solid was purified by column chromatography. Elution with dichloromethane/acetone (8:2) afforded compound **6**. Analytically pure material was obtained by precipitation from dichloromethane/hexanes as a yellow solid. Yield: 220 mg (52%).

Method c. A suspension of sodium hydride (60% in mineral oil, 16 mg, 0.4 mmol) in dry methanol was stirred at 0 °C under a nitrogen atmosphere until a clear solution of sodium methoxide was formed. 1,2,4-Trimethyltriazolium tetrafluoroborate (100 mg, 0.35 mmol) was then added, and the mixture was stirred at room temperature for 1 h. After addition of $[IrCl(cod)]_2$ (100 mg, 0.15 mmol) the mixture was refluxed at 70 °C for 90 min and subsequently cooled to room temperature and stirred for an additional 30 min.

Another solution of NaH (60% in mineral oil, 14 mg, 0.35 mmol) in methanol was prepared and added via cannula to the previous solution. The mixture was stirred for 1 h at room temperature. After addition of $[Cp^*IrCl_2]_2$ (100 mg, 0.12 mmol) the mixture was refluxed at 70 °C for 1 h. Solvent was evaporated under reduced pressure, and the crude solid was purified by column chromatography. Elution with dichloromethane/acetone (8:2) afforded compound **6**. Analytically pure material was obtained by precipitation from dichloromethane/hexanes as a yellow solid. Yield: 82 mg (40%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.77 (m, 2H, COD), 4.30 (s, 3H, NCH_3), 4.26 (s, 3H, NCH_3), 4.24 (s. 3H, NCH_3), 3.16 (m, 1H, COD), 2.95 (m, 1H, COD), 2.21 (m, 4H, COD), 1.84 (m, 2H, COD), 1.71 (m, 2H, COD), 1.66 (s, 15H, $C_5(CH_3)_5$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 187.0 (*C*-Ir^{I} carbene), 167.4 (*C*-Ir^{III} carbene), 90.4 ($C_5(CH_3)_5$), 89.1 (COD), 88.9 (COD), 53.7 (COD), 53.0 (COD), 40.6 (NCH_3), 37.2 (NCH_3), 36.8 (NCH_3), 33.7 (COD), 33.4 (COD), 29.5 (COD), 29.4 (COD), 9.3 ($C_5(CH_3)_5$). Anal. Calcd for $C_{23}H_{36}Cl_3Ir_2N_3 \cdot CH_2Cl_2$: C, 30.99; H, 4.12; N, 4.52. Found: C, 31.12; H, 4.13; N, 4.50. Electrospray MS, cone 25 V (*m*/*z*, fragment): 810, $[M - Cl]^+$

Synthesis of 7. Method a. A suspension of sodium hydride (60% in mineral oil, 13 mg, 0.32 mmol) in dry methanol was stirred at 0 °C under a nitrogen atmosphere until a clear solution of sodium methoxide was formed. Compound **4** (165 mg, 0.28 mmol) was then added, and the mixture was stirred at room temperature for 30 min. After addition of $[RhCl(cod)]_2$ (60 mg, 0.12 mmol) the mixture was refluxed at 70 °C for 30 min. Solvent was evaporated under reduced pressure, and the crude solid was purified by column chromatography. The pure compound **7** was eluted with dichloromethane/acetone (7:3) and precipitated in a mixture of dichloromethane/hexanes to give a pale yellow solid. Yield: 120 mg (66%).

Method b. A suspension of sodium hydride (60% in mineral oil, 22 mg, 0.54 mmol) in dry methanol was stirred at 0 °C under a nitrogen atmosphere until a clear solution of sodium methoxide was formed. 1,2,4-Trimethyltriazolium tetrafluoroborate (124 mg, 0.43 mmol) was then added, and the mixture was stirred at room temperature for 1 h. After addition of $[Cp^*IrCl_2]_2$ (150 mg, 0.18 mmol) the mixture was refluxed at 70 °C for 90 min and subsequently cooled to room temperature and stirred for an additional 30 min.

Another solution of NaH (60% in mineral oil, 15 mg, 0.37 mmol) in methanol was prepared and added via cannula to the previous solution. The mixture was stirred for 1 h at room temperature. After addition of $[RhCl(cod)]_2$ (70 mg, 0.14 mmol) the mixture was refluxed at 70 °C for 1 h. Solvent was evaporated under reduced pressure, and the crude solid was purified by column chromatography. The pure compound **7** was eluted with dichloromethane/acetone (7:3) and precipitated in a mixture of dichloromethane/hexanes to give a pale yellow solid. Yield: 115 mg (54%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.11 (m, 2H, COD), 4.42 (s, 6H, NCH_3), 4.21 (s, 3H, NCH_3), 3.19 (m, 1H, COD), 2.49 (m, 1H, COD), 2.40 (m, 4H, COD), 2.00 (m, 4H, COD), 1.66 (s, 15H, $C_5(CH_3)_5$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 191.6 (d, $^1J_{C-Rh} = 52.06$ Hz, *C*-Rh carbene), 167.3 (*C*-Ir carbene), 100 (d, $^1J_{C-Rh} = 7.1$ Hz, COD), 100.8 (d, $^1J_{C-Rh} = 6.8$ Hz, COD), 90.4 ($C_5(CH_3)_5$), 69.8 (d, $^1J_{C-Rh} = 9.1$ Hz, COD), 69.7 (d, $^1J_{C-Rh} = 8.8$ Hz, COD), 40.8 (NCH_3), 37.2 (NCH_3), 33.0 (COD), 32.8 (COD), 29.0 (COD), 28.9 (COD), 9.3 ($C_5(CH_3)_5$). Anal. Calcd for $C_{23}H_{36}N_3IrRhCl_3 \cdot CH_2Cl_2$: C, 34.28; H, 4.55; N, 5.00. Found: C, 34.20; H, 4.56; N, 4.99. Electrospray MS, cone 20 V (*m*/*z*, fragment): 720, $[M - Cl]^+$

Catalytic One-Pot Synthesis of 3-Substituted Indoles from 2-Aminophenyl Ethyl Alcohol and Primary Alcohols. General Procedure. A mixture of 2-aminophenyl ethyl alcohol (0.25 mmol), primary alcohol (0.25 mmol), catalyst (1 or 0.1 mol %), KOH (0.5 mmol), and toluene (0.3 mL) was combined in a thick-walled glass tube. The mixture was stirred at 110 °C. The reaction mixture was analyzed by ^{1}H NMR spectroscopy, and products were characterized according to previously reported spectroscopic data.[13,18,22] Ferrocene (0.025 mmol) was used in all cases as an internal standard.

X-Ray Diffraction Studies. Single crystals of **3**, **6**, and **7** were mounted on a glass fiber in a random orientation. Data collection was performed at room temperature on a Siemens Smart CCD diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) with a nominal crystal to detector distance of 4.0 cm. Space group assignment was based on systematic absences, E statistics, and successful refinement of the structures. The structure was solved by direct methods with the aid of successive difference Fourier maps and was refined using the SHELXTL 5.1 software package.[23] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned to ideal positions and refined using a riding model. Details of the data collection, cell dimensions, and structure refinement are given in Table 1. The diffraction frames were integrated using the SAINT package[24] and corrected for absorption with SADABS.[25]

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Supporting Information Available: X-ray crystallographic files in CIF format for the structure determinations of **3**, **6**, and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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