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Arene–Ruthenium(II) and –Iridium(III) Complexes with "Click"-Based Pyridyl-triazoles, Bis-triazoles, and Chelating Abnormal Carbenes: Applications in Catalytic Transfer Hydrogenation of Nitrobenzene

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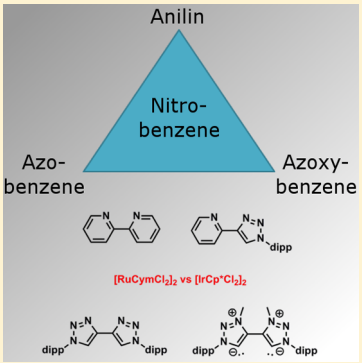
Supporting Information

ABSTRACT: The complexes $[(Cym)Ru(\mathbf{L})Cl]PF_6$, **2**–**4**, and $[Cp^*Ir(\mathbf{L})Cl]PF_6$, **6**–**8** (Cym = *p*-cymene, Cp* = pentamethylcyclopentadienyl), with **L** = "click"-derived pyridyl-triazol, bis-triazole, or bis-abnormal carbene, were synthesized and spectroscopically characterized. Structural elucidation of the complexes shows a half-sandwich, piano-stool type of coordination around the metal centers and a delocalized situation within the triazolylidene rings. All the complexes were tested for their catalytic efficiency in the transfer hydrogenation of nitrobenzenes, and the results were compared with their 2,2′-bipyridine (bpy) Ru counterpart **1** and Ir counterpart **5**. Remarkably, the nature of the final catalytic product is strongly dependent on the chosen metal center, with aniline being preferentially formed with the Ru complexes and azobenzenes with the Ir complexes. Judicious selection of catalyst and reaction conditions also facilitates the isolation of azoxybenzene. To the best of our knowledge, this is a rare example of a homogeneous catalytic synthesis of azobenzene from nitrobenzene. The influence of ligand substitution, metal substitution, and temperature variation on catalytic activity and selectivity has been investigated, whereby a systematic variation of the ligands from bpy, to pyridyl-triazole, to bis-triazole, to bis-abnormal carbene has been carried out. We also present a mechanistic investigation for this transformation with the aim of understanding reaction behavior.



INTRODUCTION

The Cu(I)-catalyzed [3+2] cycloaddition reaction between azides and alkynes, the best "click" reaction reported to date, has turned into a power house for synthetic chemists.[1] The resulting 1,2,3-triazoles in various forms have found extensive use as ligands in recent years in coordination and organometallic chemistry.[2] Metal complexes derived from such ligands have been utilized for investigating electron transfer[3] and magnetic properties,[4] as well as in homogeneous catalysis.[5] The ease of methylation of the triazoles, and their subsequent deprotonation to generate triazolylidene-based abnormal N-heterocyclic carbenes (*a*NHC),[6] has opened up another vibrant field of research.[7] These ligands, which have also been labeled as mesoionic carbenes (MIC),[8] have mainly found use in homogeneous catalysis in the last years.[9] N-Heterocyclic carbenes (NHC) occupy a special place in the toolbox of chemists dealing with homogeneous catalysis, and the potent nature of the metal complexes of these ligands has been reported for a variety of catalytic chemical transformation.[10] Although NHCs have primarily been utilized as ligands in homogeneous catalysis, other fascinating properties of these compounds have also been emerging in recent years,[11] with their redox-active behavior being one of them.[12]

The most extensively used bis-chelating "click" ligand in the literature has been the pyridyl-triazole ones,[2c,d] with reports on the bis-triazole ligands being rather limited.[3f,13] On the triazolylidene front, almost all efforts have concentrated on the monodentate triazolylidenes,[7] with only a handful of reports being present on potentially chelating bis-triazolylidenes.[14] Out of those, only one was actually shown to function as a chelating ligand.[14a]

Anilines and azobenzenes are important precursors and intermediates for various industrially useful chemicals.[15] Hence, benign and catalytic ways of generating anilines is an important chemical goal. Catalytic transfer hydrogenation provides an excellent method for the hydrogenation of multiple bonds.[16] One advantage of this method over the direct use of H_2 for hydrogenation reactions is the ability of transfer hydrogenation reactions to function without the need for gases at high pressures. The elucidation of the mechanism of catalytic action is the best way to improve catalytic activity and, hence, develop better catalysts. Inspired by a recent report on the catalytic activity of Cym-ruthenium complexes with polypyridine ligands (Cym = *p*-cymene) in the transfer hydrogenation of nitroarenes to anilines,[17] and by our own interest in developing a systematic correlation between bipyridine (bpy, $\mathbf{L^1}$), pyridyl-triazole, bis-triazole, and bis-triazolylidene ligands,[3d−f] we ventured into the present project.

In the following we present metal complexes with the ligands $\mathbf{L^1}$–$\mathbf{L^4}$ (Figure 1) coordinated to [Ru(Cym)Cl] (**1**–**4**) and to [Ir(Cp*)Cl] (**5**–**8**, Cp* = pentamethylcyclopentadienyl). **1** and **5** are literature-reported compounds and have been resynthesized here for comparison purposes.[18a,b] Structural

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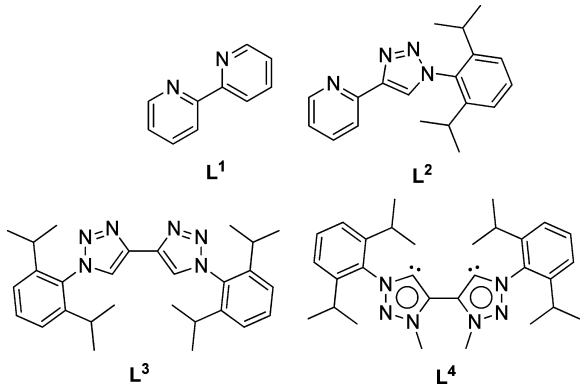


Figure 1. Ligands used in this work.

characterization of the ligands and the complexes is presented. The use of these complexes as (pre)catalysts for the transfer hydrogenation of nitroarenes in the presence of ^{i}PrOH is presented. The influence of changing the metal atom (Ru(II) vs Ir(III)), the ligand donor properties, and the reaction conditions on the catalytic efficiency and product distribution is probed. Mechanistic insights into the catalytic reactions are provided below as well.

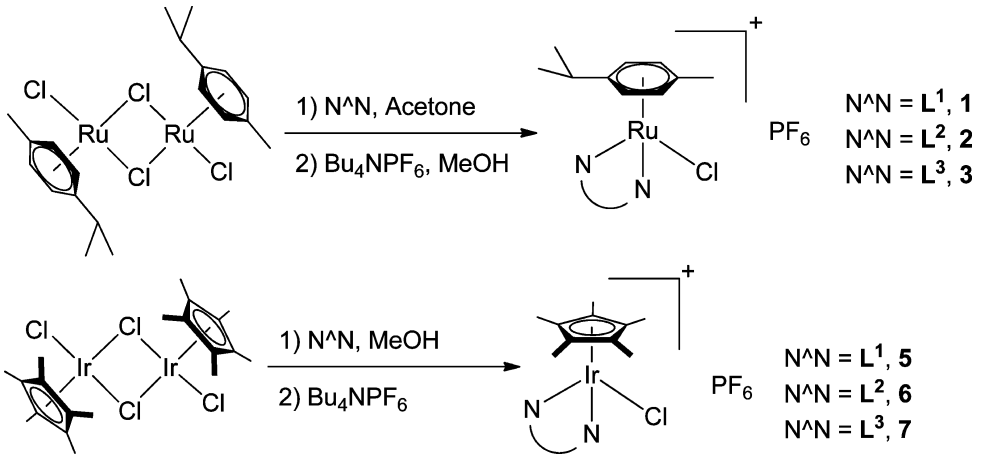
RESULTS AND DISCUSSION

Synthesis and Characterization of Ligands and Complexes. The ligands L^2–L^4 were chosen with the same substituent, 2,6-diisopropylphenyl (dipp), on the triazole rings. This was done to keep all electronic factors other than ligand donor atoms the same in the ligands. Furthermore, the bulky dipp substituents are expected to provide steric protection at the metal center during catalysis. The ligand L^2 was reported by us previously.[3f,5e] For the present work, we used a new synthetic route, developed in our group, that uses Cu(I) complexes of *a*NHCs as catalysts for the "click" reaction (see Experimental Section).[9j] This route delivered L^2 in excellent yields. The ligand L^3 has been reported before by Bertrand et al.[14] We have synthesized it via a route published by Fletcher et al. for the synthesis of bis-triazole ligands.[13b] This route uses 1,4-bis(trimethylsilyl)-1,3-butadiyne as the dialkyne source. Methylation of L^3 with Meerwein's salt delivered $L^4[BF_4]_2$ in excellent yields, which served as a precursor for the generation of the chelating *a*NHC L^4 (see discussion below). The identity and purity of the ligands were established by ^{1}H and ^{13}C NMR spectroscopy and elemental analysis. In their ^{1}H NMR spectra, the ligands L^2, L^3, and $L^4[BF_4]_2$ display a characteristic singlet for the C–H proton of the triazole or triazolium rings at low fields (see Experimental Section).

The complexes **2**, **3**, **6**, and **7** were synthesized by the reactions of the chloro-bridged dimeric metal precursors with the corresponding nitrogen-donating ligands either in acetone (for the Ru complexes) or in methanol (for the Ir complexes). Salt metathesis with Bu_4NPF_6 followed by washing with methanol and diethyl ether delivered the complexes in excellent yields (Schemes 1 and 2). The complexes were characterized by NMR spectroscopy, mass spectrometry, and elemental analysis (see Experimental Section). The complexes **4** and **8**, with the chelating *a*NHC ligand L^4, were synthesized via the trans-metalation route with Ag_2O. The silver complex was first generated by the reaction of $L^4[BF_4]_2$ with Ag_2O in the presence of a chloride source in the dark. The thus generated silver complex was reacted with the chloro-bridged dimeric metal precursors. Salt metathesis with KPF_6 resulted in the generation of the metal complexes in good yields (Scheme 2). The complexes were characterized by ^{1}H and ^{13}C NMR spectroscopy, elemental analyses, and mass spectrometry. Disappearance of the C–H signal of the triazolium ring in the ^{1}H NMR spectrum of the complexes was a first indication of the formation of the carbene complexes. The molecular peak for the cationic part of the complexes (without PF_6^-) was observed in the ESI spectrum. The carbene-C signal for **4** and **8** was observed at 179.2 and 154.5 ppm, respectively, in their ^{13}C NMR spectrum. The signals corresponding to the Cym group in **4** were broadened at room temperature, possibly due to the formation of rotamers and fast interconversion between them. On heating the sample to 80 °C, sharp "normal" NMR signals were observed for **4**, indicating the existence of only one rotamer at that temperature.

X-ray Crystal Structures of Ligands and Complexes. Single crystals of L^3 suitable for X-ray diffraction were grown by slow evaporation of a concentrated diethyl ether solution at room temperature. L^3 crystallizes in the monoclinic $P2(1)/n$ space group (Table S1). The bond lengths within the triazole rings in L^3 are consistent with previous reports[3d–f] and exhibit a central short N1–N3 bond with a distance of 1.305(1) Å flanked by two longer bonds with bond lengths of N3–N5 = 1.352(2) Å and N1–C3 = 1.362(2) Å. The same situation is

Scheme 1. Synthesis of Complexes with Nitrogen-Donor Ligands



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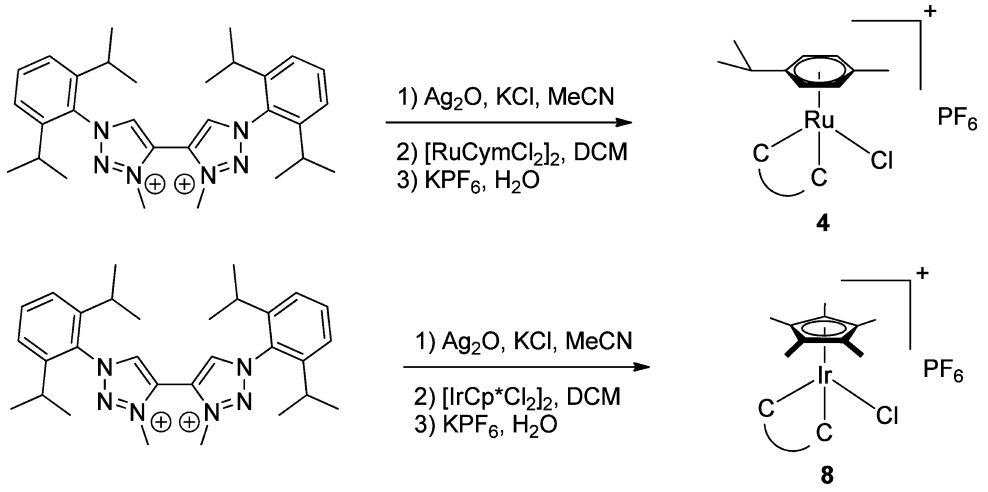
Scheme 2. Synthesis of Complexes with *a*NHC-Donor Ligands



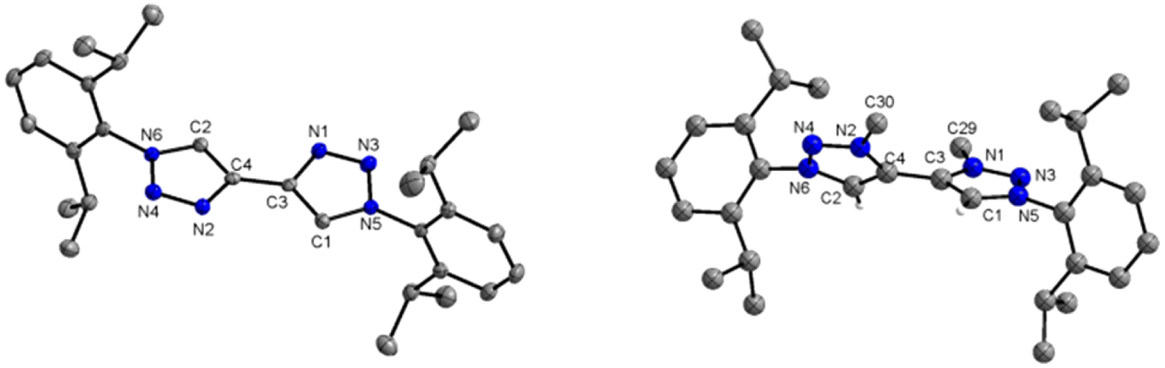


Figure 2. ORTEP plot of L^3 (left) and $L^4[OTf]_2$ (right). All ellipsoids are drawn at 50% probability. Hydrogen atoms (except for C−H of the triazolium ring in $L^4[OTf]_2$) and counterions are omitted for clarity.

observed in the second triazole ring of L^3 as well (Table S2). The two triazole rings in L^3 are oriented *anti* to each other (Figure 2) and are almost coplanar, with a dihedral angle of 9.01(7)° between them. The dipp substituents on the triazole rings in L^3 are perpendicular to the triazole rings, showing dihedral angles of 89.89(6)° and 88.47(7)° with respect to the triazole planes.

Attempts at crystallization of $L^4[BF_4]_2$ unfortunately did not result in suitable single crystals. Hence we resorted to anion exchange and generated the triflate salt $L^4[OTf]_2$ by using a reported synthetic route.[14a] Gratifyingly, slow diffusion of diethyl ether in a concentrated solution of dichloromethane resulted in the formation of suitable single crystals of $L^4[OTf]_2$. $L^4[OTf]_2$ crystallizes in the monoclinic space group $P2(1)/n$ (Table S1). Methylation of the triazole rings leads to a more delocalized situation within the triazolium rings as compared to the neutral triazole rings in L^3. This can be seen from the N1−N3 and N3−N5 bond distances in $L^4[BF_4]_2$ which are 1.321(8) and 1.319(8) Å, respectively; the corresponding distances in L^3 are 1.305(1) and 1.352(2) Å, respectively (Table S2). Furthermore, the triazolium rings are now no longer coplanar, as seen from the dihedral angle of 50.9(3)° between them. The dipp substituents are almost perpendicular to the triazolium rings, exhibiting a dihedral angles of 79.3(3)° and 84.4(3)°, respectively.

Single crystals of the complexes **2**−**4** and **6**−**8** as solvates were obtained for X-ray diffraction studies (see Experimental Section). The crystallographic details are given in Table S1. All the complexes display the expected half-sandwich three-legged piano-stool type of coordination around the metal centers (Figure 3). The Cym ligand in **2**−**4** is bound to the Ru(II) center in a η^6 mode, and the Cp* ligand in **6**−**8** is coordinated to the Ir(III) center in a η^5 mode. The Ru−N and Ru−Cl distances in **2** and **3** and the Ir−N and Ir−Cl distances in **6** and **7** are in the expected range (Table S2).[13c,e] The bond localization within the triazole ring, as observed in L^3, is maintained in the complexes **2**, **3**, **6**, and **7**. For the complexes **2** and **6** with mixed-donor ligands, the Ru1−N1 and Ir1−N1 distances to the triazole N-donor of 2.072(2) and 2.071(2) Å, respectively, are shorter than the Ru−N2 and Ir−N2 distances of 2.113(2) and 2.122(2) Å, respectively, to the pyridine N-donors. The Ru−N1(triazole) and Ir1−N1(triazole) distances in the complexes **3** and **7** with bis-triazole ligands are however longer than the corresponding metal-N(triazole) distances in **2** and **6** (Table S2). Hence, the shorter metal−N(triazole) distances compared to the metal−N(pyridine) distances in **2** and **6** are probably a result of the geometrical conformation of the mixed-donor ligands and not necessarily related to better donor properties of the triazole-N donors, as compared to the pyridine-N donors. Coordination of metal centers to the triazole rings in **2**, **3**, **6**, and **7** leads to an opening up of the angles C4−N2−N4 and C3−N1−N3. This is apparent in the larger values of these angles in the metal complexes, as compared to the free ligand L^3.

In **4** and **8**, the Ru and Ir centers are bonded through the triazolylidene C atoms of the ligand L^4. The Ru1−C1 distance

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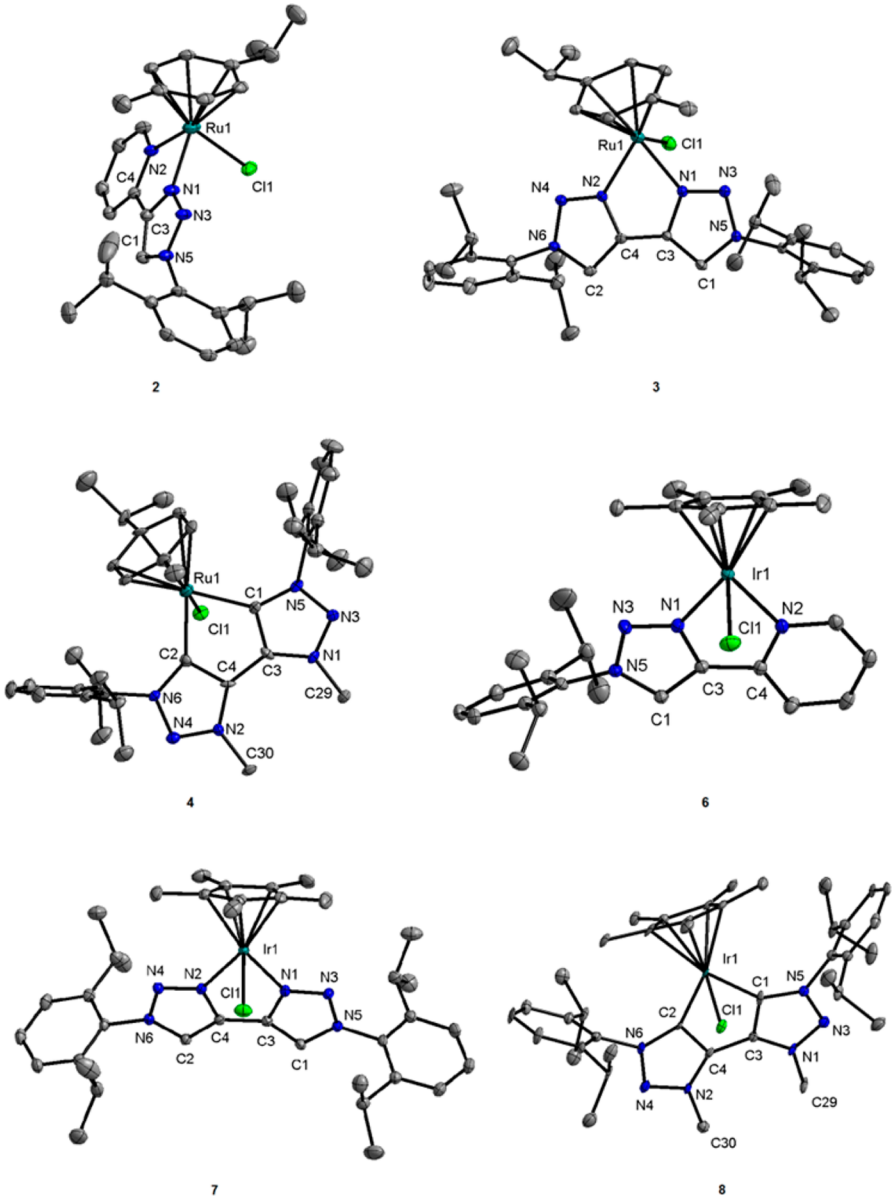

Figure 3. ORTEP plots of **2**, **3** (top), **4**, **6** (middle), and **7**, **8** (bottom). All ellipsoids are drawn at 50% probability. Hydrogen atoms, counterions, and solvent molecules are omitted for clarity.

of 2.059(6) Å in **4** and the Ir1−C1 distance of 2.081(6) Å in **8** are in the expected range for distances between Ru or Ir centers and NHC or *a*NHC carbon atoms.[7b,c] Deprotonation of C1 and coordination of the metal centers through the C1 and C2 atoms of L^4 (Figure 3) leads to a shrinking of the respective angles around the C1 and C2 atoms. This is apparent in the smaller C3−C1−N5 and C4−C2−N6 angles in **4** and **8** as compared to the ligand precursors L^3 and $L^4[BF_4]_2$. Just as in the free ligands, the dipp substituents are perpendicular to the triazole or triazolylidene rings in all the ruthenium and iridium complexes. The distances between the centroid of Cym and the Ru center are 1.677(1), 1.670(1), and 1.727(1) Å respectively for **2**, **3**, and **4**. The corresponding distance between the centroid of Cp* and the Ir center are 1.771(1), 1.765(1), and 1.841(1) Å for **6**, **7**, and **8**, respectively. Hence it is seen that for the complexes **4** and **8**, with the *a*NHC ligands, the metal centers are farther away from the arene rings as compared to the complexes with the nitrogen-donor ligands. This is most likely due to the larger steric repulsion between the dipp substituents and the arene rings in **4** and **8**, where the dipp substituents are closer to the metal center as compared to **2**, **3** or **6**, **7** (Figure 3).

Catalytic Transfer Hydrogenation of Nitrobenzene. Anilines and azobenzenes are valuable chemicals for basic research and for the industry.[15] Anilines appear as intermediates for various chemicals that are useful for the pharmaceutical industry.[15a,b] Recently, an efficient catalytic route for the transfer hydrogenation of nitroarenes to anilines, by using Ru-Cym in combination with polypyridine ligands as catalyst, was reported.[17] Certain hints at the reaction mechanism were also presented in that report. Inspired by that work, we wanted to check the influence of the variation of ligand donicity on the catalytic efficiency of the corresponding metal complexes. The complexes presented above, with a systematic variation of the "click"-derived ligands, present an ideal platform for testing such effects. Development of efficient

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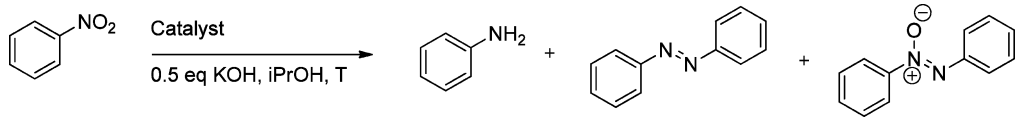
Scheme 3. Conversion of Nitrobenzene to Various Products Using the Conditions Shown in Tables 1 and 2



catalysts for the synthesis of useful chemicals and the understanding of the reaction mechanisms of such catalytic processes are highly important goals in contemporary chemistry.

For testing the complexes for their catalytic ability in the transfer hydrogenation of nitrobenzene, an initial screening was carried out with 1.5 mol % of the complexes and 0.5 equivalent of KOH in 2-propanol at 80 °C (Scheme 3). The catalytic screening showed us that the final products of catalysis were strongly dependent on the metal center present in the catalyst (Ru or Ir). Whereas the use of the Ru(II) complexes **1**–**4** as (pre)catalysts delivered various amounts of aniline and azoxybenzene as the final products, the Ir(III) complexes **5**–**8** delivered a mixture of aniline, azobenzene, and azoxybenzene as the final products (with various amounts of unreacted nitrobenzene, Table 1). Under identical conditions, and in the absence of a catalyst, 70% unreacted nitrobenzene was recovered, and aniline, azobenzene, and azoxybenzene were formed in amounts of 6%, 7%, and 17%, respectively. From this initial screening, it was clear that the Ru(II) complex **2** is the best catalyst for converting nitrobenzene to aniline, and the Ir(III) complex **7** is the best catalyst for producing azobenzene from nitrobenzene. Under the same conditions complex **8** delivered the best yield for azoxybenzene. Hence the rest of the investigations were carried out with **2** and **7** as (pre)catalysts.

Table 1. Product Distribution on Using the Various (Pre)catalysts for the Reaction Shown in Scheme 3[a]

	nitrobenzene (recovered)	aniline	azobenzene	azoxybenzene
1	46	29	0	25
2	16	50	2	32
3	34	30	0	36
4	37	26	0	37
5	0	21	41	38
6	2	22	40	36
7	0	9	68	23
8	21	9	3	67

[a]Reaction conditions: 1.5 mol % catalyst loading, 0.5 equiv of KOH, ^{i}PrOH, 80 °C, 24 h.

We were next interested in finding the optimum reaction conditions for the functioning of our best (pre)catalysts. In order to do this, both the temperature of the reaction and the catalyst loading were varied. While using 1.5 mol % of the Ru(II) complex **2** as a (pre)catalyst, increasing the temperature from 80 °C to 100 °C resulted in an increase in aniline formation from 50% of the total products to 56% of the total products (Scheme 3 and Table 2). The increase in the amount of aniline formation at higher temperatures corresponded with a decrease in the amount of azoxybenzene formation. Increasing the amount of the (pre)catalyst to 5 mol % resulted in a drastic improvement in catalytic activity. The best results were obtained with 5 mol % of **2** at 100 °C. Under those conditions, a complete conversion of nitrobenzene to aniline was observed (Table 2). The use of excess amounts of ligands was not necessary for high catalytic activity. For the Ir(III) complex **7**, an increase in the temperature from 80 °C to 100 °C by keeping catalyst loading at 1.5 mol % resulted in an increase in the amount of aniline formation (Table 2). The increase in the amount of aniline came at the expense of azobenzene and azoxybenzene, whose formation was negligible at higher temperatures. Increasing the amount of catalytic loading to 5 mol % by setting the temperature at 80 °C showed more conversion to aniline at the expense of azoxybenzene as compared to 1.5 mol % catalyst loading at the same temperature (Table 2). On using 5 mol % of **7** at 100 °C, the amount of aniline formed was seen to increase at the expense of azobenzene (Table 2). Hence while using **7** as a (pre)catalyst, an increase in temperature and catalytic loading leads to a decrease in the formation of azoxybenzene and an increase in the formation of aniline and azobenzene by various amounts.

Having established the best conditions for catalytic performance and having observed the differences in product distribution under various temperatures and reaction conditions, we next turned to the mechanism of action of this catalytic process. At this point, a couple of published works were extremely useful for our interpretation. The first of these is the work on the transfer hydrogenation of nitrobenzene with Ru-Cym complexes of polypyridines as mentioned above.[17] The second paper deals with the metal-induced conversion of nitrosobenzene to azoxybenzene.[19] This contribution is of particular relevance to us, as we observe the formation of azoxybenzene under certain conditions with our catalysts. On the basis of this knowledge, a catalytic mechanism as shown in Scheme 4 can be formulated.

On the basis of previous literature reports, it can be assumed that the metal complexes presented here would get converted

Table 2. Product Distribution on Using 2 or 7 as (Pre)catalysts under Various Conditions for the Reaction Shown in Scheme 3[a]

catalyst	loading (mol %)	temp (°C)	nitro-benzene (recovered)	aniline	azobenzene	azoxybenzene
2	1.5	100	23	56	2	19
2	5	80	10	75	0	15
2	5	100	0	100	0	0
7	1.5	100	0	50	49	1
7	5	80	0	26	74	0
7	5	100	0	45	55	0

[a]Reaction conditions: 0.5 equiv of KOH, ^{i}PrOH, 24 h.

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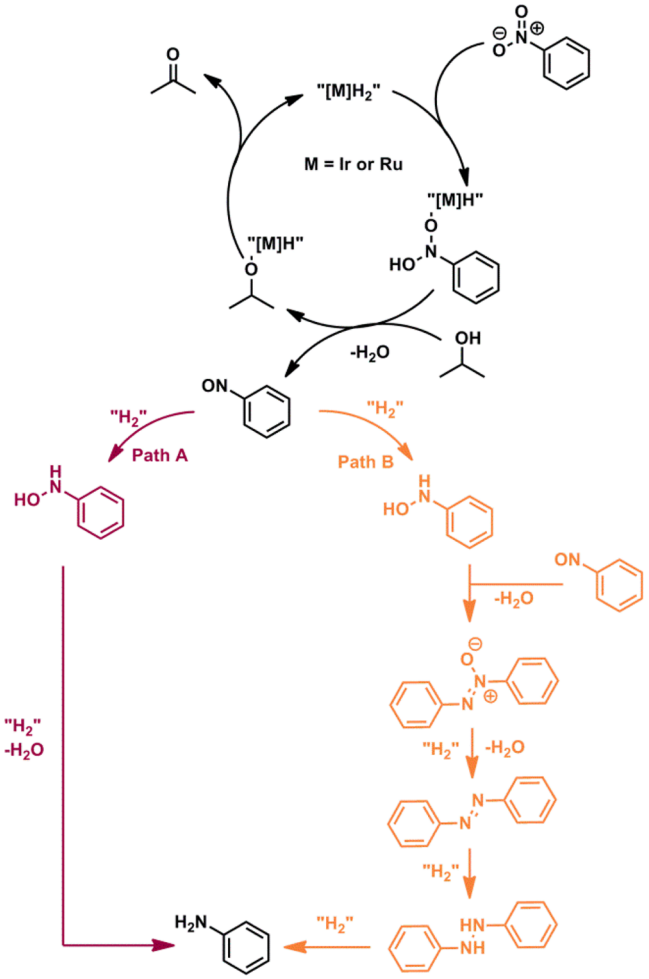
Scheme 4. Postulated Mechanism of the Catalysts in the Transfer Hydrogenation of Nitrobenzene[a]



[a]"H_2" refers to a transfer hydrogenation process.[20]

to hydrides "[M]H_2" in the presence of KOH in 2-propanol (Scheme 4).[17,21] A hydride signal at −14.46 ppm was observed for **7** by performing the reaction under catalytic conditions without substrate (Figure S1). These hydrides are the starting points in the catalytic cycle. Insertion of nitrobenzene into the M−H bond and the elimination of H_2O (with participation of 2-propanol) results in the formation of nitrosobenzene. Once formed, the nitrosobenzene can follow two different pathways to deliver aniline. Whereas path A proceeds through *N*-phenylhydroxyamine and its direct conversion to aniline, path B proceeds through an azoxybenzene intermediate, which gets converted to azobenzene, before being finally converted to aniline (Scheme 4). In order to test this mechanism, we carried out additional catalytic experiments starting with two different substrates, nitrosobenzene and azobenzene, which appear as intermediates in the catalytic cycle. On starting with nitrosobenzene as a substrate and using 1.5 mol % of the Ru(II) complex **2** as a (pre)catalyst at 80 °C, a mixture of aniline, azobenzene, and azoxybenzene was obtained as products, with the major amount (59%) of the products being azoxybenzene (Scheme 5, Table 3). On increasingly the catalyst loading to 5 mol % and the temperature to 100 °C, a 93% conversion to aniline was observed, with the rest of the 7% being azoxybenzene. On using the Ir(III) complex **7** as a (pre)catalyst

Scheme 5. Conversion of Nitrosobenzene to Various Products by Using 2 or 7 as (Pre)catalysts

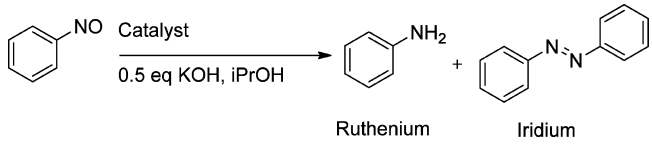


Table 3. Product Distribution on Using 2 or 7 as (Pre)catalysts under Various Conditions for the Reaction Shown in Scheme 5

catalyst	loading (mol %)	temp (°C)	aniline	azobenzene	azoxybenzene
2	1.5	80	18	23	59
7	1.5	80	17	83	0
2	5	100	93	0	7
7	5	80	44	56	0

and nitrosobenzene as a substrate, a conversion to 44% aniline and 56% azobenzene was observed with 5 mol % of the catalyst at 100 °C (Table 3). These results are identical to the catalytic results obtained while starting from nitrobenzene, hence pointing to the participation of nitrosobenzene in the catalytic cycle.

On using azobenzene as a substrate, the Ru(II) precatalyst **2** delivered a quantitative conversion to aniline with a 5 mol % catalyst loading at 100 °C (Scheme 6, Table 4). The Ir(III) complex **7** on the other hand showed no conversion of azobenzene to any products with 1.5 mol % catalyst loading at 80 °C. On increasing the catalyst loading to 5 mol %, at a temperature of 80 °C a 40% conversion to aniline was observed, with the rest of azobenzene remaining unreacted. These results match well with the results obtained while starting with nitrobenzene as a substrate, thus also indicating the involvement of azobenzene in the catalytic cycle.

In order to determine the relevance of path A or B with the Ru- and Ir-containing catalysts, a time-dependence of the product formation under catalytic conditions was carried out with **2** and **8** with nitrobenzene as the substrate. By using 5 mol % of **2** and a temperature of 80 °C, a conversion to about 70% aniline is observed. Additionally, the formation of a small amount of azoxybenzene is also seen (Figure 4). While the amount of azoxybenzene formed remains constant after a period of about 15 h, the increase in the formation of aniline correlates well with the decrease in the amount of nitrobenzene. No amount of azobenzene was detected during this conversion. These observations clearly establish the preference of path A (Scheme 4) for aniline formation with the ruthenium complex **2**.

On using 5 mol % of **8** at 100 °C, a time-dependence of product formation as shown in Figure 5 is observed. As can be seen from Figure 5, we followed the reaction for about 8 days. The first product obtained is azoxybenzene. At the same time small amounts of azobenzene and aniline are already detectable. Azobenzene production then immediately increases as soon as most of the nitrobenzene is consumed. At the same time the amount of azoxybenzene decreases again and is almost fully consumed as soon as azobenzene reaches its top concentration in the solution. When no more azoxybenzene is available for reduction and the concentration of azobenzene has reached its top value, the production of aniline increases dramatically at the expense of the amount of azobenzene. These observations

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Scheme 6. Conversion of Azobenzene to Various Products by Using 2 or 7 as (Pre)catalysts

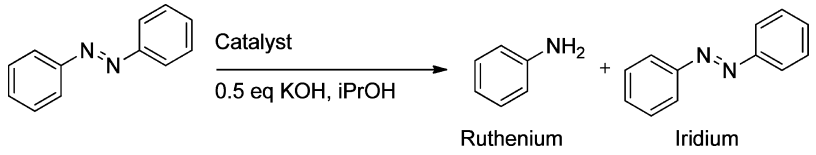

Table 4. Product Distribution on Using 2 or 7 as (Pre)catalysts under Various Conditions for the Reaction Shown in Scheme 6

catalyst	loading (mol %)	temp (°C)	aniline	azobenzene	azoxybenzene
2	1.5	80	36	64	0
7	1.5	80	0	100	0
2	5	100	99	1	0
7	5	80	40	60	0

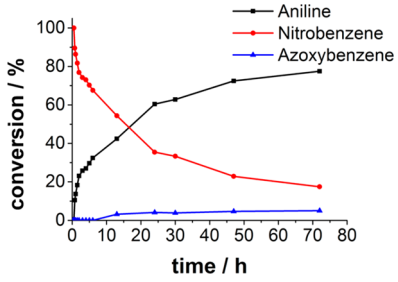

Figure 4. Time-dependence of product formation starting from nitrobenzene with 5 mol % of **2** at 80 °C.

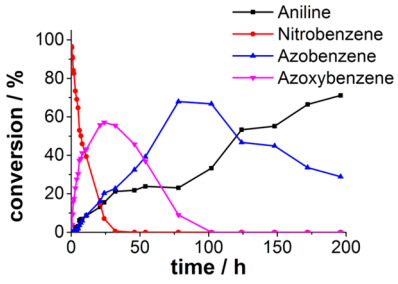

Figure 5. Time-dependence of product formation starting from nitrobenzene with 5 mol % of **8** at 100 °C.

clearly indicate the preference of path B (Scheme 4) for the iridium complex **8**.

Some generalizations can be made from the various control reactions that have been carried out. The Ru(II) complexes (with triazole donors as ligands) are highly efficient in catalytically reducing nitrobenzene to aniline, whereas the Ir(III) complexes are efficient in generating azobenzene. Lower catalyst loading and comparatively lower temperatures are the best conditions for generating azoxybenzene, with the bis-*a*NHC-containing Ir(III) complex **8** being the most efficient catalyst for generating azoxybenzene (Table 1). The preference for path A or B in the catalytic cycle (Scheme 4) seems to depend on the rate of direct conversion of *N*-phenylhydroxyamine to aniline. The Ru(II) catalysts seem to react preferentially through path A. For the Ir(III) catalysts, the direct conversion of *N*-phenylhydroxyamine to aniline is less efficient, and hence path B predominates with the Ir(III) catalysts with azobenzene being the main product of nitrobenzene reduction in those cases.

CONCLUSIONS

In conclusion, we have presented here a total of six new complexes of Ru(II) and Ir(III) with "click"-derived ligands. All of the complexes have been structurally characterized. In addition, we have compared the catalytic properties of those complexes with their bpy analogues. The donor properties of the ligands have been varied through the symmetric chelating bpy-N donors, to asymmetric chelating pyridyl-triazole-N donors, to symmetric bis-triazole-N donors, and finally to symmetric bis-*a*NHC-C donors. In doing so, we have also presented the crystal structures of **4** and **8**, which are only the second examples of metal complexes with a bidentate *a*NHC ligand of the triazolylidene type acting as a chelate to a metal center.[14a] Catalytic transfer hydrogenation of nitrobenzene with these complexes as (pre)catalysts presents some interesting trends. The catalysts with the bpy ligands delivered the worst results. Gratifyingly, the preferential reduction of nitrobenzene to either aniline, or azobenzene, or azoxybenzene could be controlled by varying the temperature, catalyst loading, the type of metal center, or the nature of the ligands. Thus, complex **8**, with a bis-*a*NHC ligand, delivers the largest amount of azoxybenzene on catalytic reduction of nitrobenzene. The Ru(II) complexes with the triazole-N donor containing ligands at high catalytic loading and high temperatures show a complete reduction of nitrobenzene to aniline. The Ir(III) complexes with the nitrogen-donor ligands on the other hand display a propensity to preferentially deliver azobenzene as the reduction product of nitrobenzene. Mechanistic investigations have been used to provide a rationale for this product distribution.

This is a rare case where the reduction product of nitrobenzene can be controlled by tuning the catalyst and reaction conditions. We also note that out of all the recent mechanisms discussed in the literature for the catalytic reduction of nitrobenzene under homogeneous conditions,[17,20] ours is the one where the role and formation of nitrosobenzene, *N*-phenylhydroxyamine, azoxybenzene, azobenzene, and aniline have been discussed and probed with relevant experiments. Our results here show the power of the "click" method in generating new ligands for organometallic chemistry and homogeneous catalysis. Furthermore, we have also shown the beauty of ligand variation on generating product selectivity in catalysis. In view of the importance of aniline, azobenzene, and azoxybenzene as useful chemical products, it will be intriguing to see if selectivity of the catalysts can be further improved by rational ligand tuning. Work in that direction is currently being pursued in our laboratories.

EXPERIMENTAL SECTION

Materials and Physical Methods. $[RuCymCl_2]_2$ and $[IrCp^*Cl_2]_2$ are commercially available. All commercially available reagents were used as supplied. The solvents used for metal complex synthesis were dried and distilled under argon and degassed by common techniques prior to use. ^1H and ^{13}C NMR spectra were recorded on a Bruker AC 250 spectrometer or a Jeol ECS 400 spectrometer. Elemental analyses

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were performed by the Perkin-Elmer Analyzer 240 and a Elementar Vario EL III. Mass spectrometry was performed on an Agilent 6210 ESI-TOF. GC-MS analysis was performed on a Varian Saturn 2100C (column: Varian factory four capillary column VF-5 ms; method: 50 to 250 °C, heating rate 20 K/min).

Synthesis of Ligands. *1-(2,6-Diisopropylphenyl)-4-(2-pyridyl)-1,2,3-triazole (L²).* This ligand has been reported in the literature by following a different synthetic route.[3f,5e] For the present work **L²** was synthesized following the standard click procedure by Hohloch et al.[9j] 2-Pyridylacetylene (1 equiv, 3 mmol, 309 mg) and 2,6-diisopropylphenyl azide (1 equiv, 3 mmol, 609 mg) were mixed in a small vial, and copper(I) iodide (0.01 equiv, 0.03 mmol, 6 mg), potassium *tert*-butoxide (0.02 equiv, 0.06 mmol, 6 mg), and 3-methyl-1-(2-(methylthio)phenyl)-4-phenyl-1,2,3-triazolium iodide (0.01 equiv, 0.03 mmol, 11 mg) were added. After a short time the mixture evolved heat and solidified. The crude products were purified by flash silica gel column chromatography using dichloromethane first, followed by dichloromethane/methanol (9:1), giving the corresponding ligand as off-white powders in good yields of 90%. ^{1}H NMR (400 MHz, $CDCl_3$; 25 °C, TMS): δ (ppm) 8.62−8.58 (m, 1H); 8.32−8.28 (m, 2H); 8.22 (s, 1H); 7.84−7.78 (m, 1H); 7.52−7.48 (m, 1H); 7.31−7.22 (m, 3H); 2.32 (hept, J = 7.2 Hz, 2H); 1.16−1.11 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) 150.3; 149.6; 148.2; 146.1; 137.1; 133.2; 131.0; 125.0; 123.9; 123.1; 120.5; 28.5; 24.3; 24.1. MS (ESI): m/z found 329.1747, calcd 329.1737 $[C_{19}H_{22}N_4 + Na]^+$. Anal. Calcd (%) for $[C_{19}H_{22}N_4]$: C 74.48, H 7.24, N 18.29. Found: C 74.32, H 8.63, N 17.56. Mp: 112−114 °C.

1,1′-Bis(2,6-diisophenyl)-4,4′-bis(1,2,3-triazole) (L³). An alternate synthetic route for this ligand has been reported in the literature.[14a] For the present work, **L³** was synthesized using a standard procedure reported by Fletcher et al.[13b] Copper sulfate pentahydrate (0.4 equiv, 1.2 mmol, 300 mg), sodium ascorbate (0.8 equiv, 2.4 mmol, 480 mg), and potassium carbonate (2 equiv, 6 mmol, 830 mg) were mixed in a flask. Afterward 30 mL of *tert*-butanol was added followed by 2,6-diisopropylphenyl azide (2 equiv, 6 mmol, 1.220 g) and 1,4-bis(trimethylsilyl)-1,3-butadiyne (1 equiv, 3 mmol, 582 mg). To the mixture were added 30 mL of water and 3 mL of pyridine. The mixture was capped and stirred at room temperature for up to 3 days. After the reaction, the mixture was diluted with dichloromethane (150 mL) and extracted with 5% ammonia solution in water five times (each washing 50 mL). The organic layers were separated and dried over sodium sulfate (40 g), and the solvents were evaporated under reduced pressure, leaving an off-white to brown product in excellent yields of 95% (0.285 mmol, 1.29 g). ^{1}H NMR (250 MHz, $CDCl_3$; 25 °C, TMS): δ (ppm) 8.23 (s, 2H); 7.51 (t, J = 7.5 Hz, 2H); 7.31 (d, J = 7.75 Hz, 4H); 2.34 (hept, J = 6.75 Hz, 4H); 1.16 (d, J = 7.75 Hz, 24H). ^{13}C NMR (60 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) 146.1; 139.8; 132.9; 131.0; 123.9; 123.6; 28.4; 24.3; 24.1. MS (ESI): m/z found 457.3066, calcd 457.3074 $[C_{28}H_{36}N_6 + H]^+$. Anal. Calcd (%) for $[C_{28}H_{36}N_6]$: C 73.65, H 7.95, N 18.40. Found: C 72.72, H 8.80, N 17.45. Mp: 266−268 °C.

1,1′-Bis(2,6-diisopropylphenyl)-3,3′-dimethyl-[4,4′-bis(1,2,3-triazole)]-3,3′-diium Ditetrafluoroborate (L⁴[BF₄]₂). **L³** (1 equiv, 1 mmol, 0.456 g) was dissolved in dichloromethane (15 mL) under an inert gas atmosphere, and Meerwein's salt (2.5 equiv, 2.5 mmol, 372 mg) was added to the solution. The reaction mixture was then stirred for 3 days at room temperature. After that, the crude mixture was slowly poured into diethyl ether (200 mL), and the white precipitate was filtered off and washed with diethyl ether several times. The product was obtained as a white fluffy solid in a yield of 94% (0.94 mmol, 0.620 g). ^{1}H NMR (250 MHz, DMSO-d_6; 25 °C, TMS): δ (ppm) 10.21 (s, 2H); 7.83−7.74 (m, 2H); 7.64−7.58 (m, 4H); 4.51 (s, 6H); 2.31 (hept, J = 6.75 Hz, 4H); 1.23 (d, J = 675 Hz, 12H); 1.16 (d, J = 6.75 Hz, 12H). ^{13}C NMR (60 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) 145.1; 134.2; 133.2; 130.2; 128.9; 125.0; 28.0; 23.9; 23.5. MS (ESI): m/z found 573.3480, calcd 573.3500 $[C_{30}H_{42}N_6B_1F_4]^+$. Anal. Calcd (%) for $[C_{30}H_{42}N_6B_2F_8 + 0.2CH_2Cl_2]$: C 52.91, H 6.25, N 12.20. Found: C 52.69, H 6.35, N 12.29. Mp: 298−300 °C.

Synthesis of Complexes with N^N Ligands. *General Procedure.* The corresponding metal dimer (1 equiv, 0.1 mmol) and the corresponding ligand (2 equiv, 0.2 mmol) were mixed in 15 mL of solvent (acetone for the ruthenium(II) complexes, methanol for the iridium(III) complexes) and stirred under an inert gas atmosphere overnight. Afterward the solvents were removed under high vacuum, and methanol (5 mL) and tetrabutylammonium hexafluorophosphate (4 equiv, 0.4 mmol, 155 mg) were added. The mixture was stirred until yellow solids started to precipitate. The yellow solids were collected by filtration and washed several times with methanol first, followed by diethyl ether, and dried under air to give the desired product in good to moderate yields from 75% to 90%.

Chloro(p-cymene)(2,2′-bipyridine)ruthenium(II) Hexafluorophoshate (1). Even though this compound is literature known,[18a] we synthesized it here following the general procedure stated above by using $[RuCymCl_2]_2$ (60 mg) and **L¹** (31 mg). Yield: 89% (0.178 mmol, 102 mg). ^{1}H NMR (400 MHz, $(CD_3)_2CO$; 25 °C, TMS): δ (ppm) 9.60−9.56 (m, 2H); 8.61−8.56 (m, 2H); 8.32−8.27 (m, 2H); 7.81−7.76 (m, 2H); 6.21 (d, J = 6.4 Hz, 2H); 5.96 (d, J = 6.4 Hz, 2H); 2.75 (hept, J = 6.8 Hz, 1H); 2.28 (s, 3H); 1.06 (d, J = 6.8 Hz, 6H). MS (ESI): m/z found 427.0543, calcd 427.0515 $[C_{20}H_{22}N_2Cl_1Ru]^+$. Anal. Calcd (%) for $[C_{20}H_{22}N_2Cl_1RuP_1F_6]$: C 42.00, H 3.88, N 4.90. Found: C 42.21, H 3.49, N 4.68.

Chloro(p-cymene)(1-(2,6-diisopropylphenyl)-4-(2-pyridyl)-1,2,3-triazole)ruthenium(II) Hexafluorophoshate (2). Following the general procedure and using $[RuCymCl_2]_2$ (60 mg) and **L²** (61 mg). Yield: 84%, (0.168 mmol, 121 mg). ^{1}H NMR (400 MHz, CD_2Cl_2; 25 °C, TMS): δ (ppm) 9.24−9.21 (m, 1H); 8.42 (s, 1H); 8.11−8.05 (m, 1H); 8.02−7.98 (m, 1H); 7.65−7.58 (m, 2H); 7.42−7.35 (m, 2H); 5.90−5.87 (m, 1H); 5.83−5.80 (m, 1H); 5.71−5.68 (m, 1H); 5.62−5.59 (m, 1H); 2.78 (hept, J = 7.2 Hz, 1H); 2.30−2.21 (m, 4H); 2.08 (hept, J = 7.2 Hz, 1H); 1.26−1.19 (m, 9H); 1.12−1.06 (m, 9H). MS (ESI): m/z found 577.1694, calcd 577.1670 $[C_{29}H_{36}N_4Cl_1Ru]^+$. Anal. Calcd (%) for $[C_{29}H_{36}N_4Cl_1Ru_1P_1F_6]$: C 48.24, H 5.02, N 7.76. Found: C 48.26, H 5.41, N 7.36. Dec: 255 °C.

Chloro(p-cymene)(1,1′-bis(2,6-diisophenyl)-4,4′-bis(1,2,3-triazole))ruthenium(II) Hexafluorophoshate (3). Following the general procedure and using $[RuCymCl_2]_2$ (60 mg) and **L³** (91 mg). Yield: 79% (0.158 mmol, 138 mg). ^{1}H NMR (250 MHz, CD_2Cl_2; 25 °C, TMS): δ (ppm) 8.44 (s, 2H); 7.70−7.60 (m, 2H); 7.47−7.38 (m, 4H); 5.93−5.88 (m, 2H); 5.68−5.64 (m, 2H); 3.00 (hept, J = 6.75 Hz, 1H); 2.43 (hept, J = 7 Hz, 2H); 2.17 (hept, J = 6.75 Hz, 2H); 1.32−1.25 (m, 18H); 1.22−1.12 (m, 12H). MS (ESI): m/z found 727.2832, calcd 727.2830 $[C_{38}H_{50}N_6Cl_1Ru]^+$. Anal. Calcd (%) for $[C_{38}H_{50}N_6Cl_1RuP_1F_6]$: C 52.32, H 5.78, N 9.63. Found: C 51.83, H 6.36, N 9.10. Dec: 248 °C.

Chloro(pentamethylcyclopentadienyl)(2,2′-bipyridine)iridium(III) Hexafluorophoshate (5). Even though this compound is literature known,[18b] we synthesized it here following the general procedure stated above by using $[IrCp^*Cl_2]_2$ (80 mg) and **L¹** (30 mg). Yield: 92% (0.184 mmol, 122 mg). ^{1}H NMR (400 MHz, $(CD_3)_2CO$; 25 °C, TMS): δ (ppm) 9.13−9.10 (m, 2H); 8.73−8.69 (m, 2H); 8.37−8.30 (m, 2H); 7.93−7.87 (m, 2H); 1.76 (s, 15H). MS (ESI): m/z found 519.1172, calcd 519.1167 $[C_{20}H_{23}N_2Cl_1Ir]^+$. Anal. Calcd (%) for $[C_{20}H_{23}N_2Cl_1IrP_1F_6]$ C 36.17, H 3.49, N 4.22. Found: C 36.11, H 3.54, N 4.00.

Chloro(pentamethylcyclopentadienyl)(1-(2,6-diisopropylphenyl)-4-(2-pyridyl)-1,2,3-triazole)iridium(III) Hexafluorophoshate (6). Following the general procedure and using $[IrCp^*Cl_2]_2$ (80 mg) and **L²** (61 mg). Yield: 88% (0.176 mmol, 143 mg). ^{1}H NMR (400 MHz, $(CD_3)_2CO$; 25 °C, TMS): δ (ppm) 9.41 (s, 1H); 9.13−9.10 (m, 1H); 8.39−8.35 (m, 1H); 8.33−8.28 (m, 1H); 7.83−7.78 (m, 1H); 7.73−7.67 (m, 1H); 7.56−7.49 (m, 1H); 2.43 (hept, J = 6.8 Hz, 1H); 2.26 (hept, J = 6.8 Hz, 1H); 1.83 (s, 15H). MS (ESI): m/z found 669.2335, calcd 669.2341 $[C_{29}H_{37}N_4Cl_1Ir]^+$. Anal. Calcd (%) for $[C_{29}H_{37}N_4Cl_1IrP_1F_6]$: C 42.78, H 4.58, N 6.88. Found: C 42.87, H 4.96, N 6.76. Dec: 285 °C.

Chloro(1,1′-bis(2,6-diisophenyl)-4,4′-bis(1,2,3-triazole))iridium(III) Hexafluorophoshate (7). Following the general procedure and using $[IrCp^*Cl_2]_2$ (80 mg) and **L³** (91 mg). Yield: 96% (0.192 mmol, 185 mg). ^{1}H NMR (250 MHz, CD_2Cl_2; 25 °C, TMS): δ (ppm) 8.59 (s, 2H); 7.70−7.61 (m, 2H); 7.47−7.37 (m, 4H); 2.40 (hept, J = 7 Hz,

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1H); 2.23 (hept, J = 7 Hz, 1H); 1.83 (s, 15H); 1.32−1.13 (m, 24H). MS (ESI): m/z found 819.3475, calcd 819.3481 $[C_{38}H_{51}N_6Cl_1Ir]^+$. Anal. Calcd (%) for $[C_{38}H_{51}N_6Cl_1IrP_1F_6]$: C 47.32, H 5.33, N 8.71. Found: C 46.82, H 5.68, N 8.43. Mp: 232−234 °C.

Synthesis of Bis-carbene Complexes. *General Procedure.* Azolium salt $L^4[BF_4]_2$ (2 equiv, 0.2 mmol, 133 mg) was mixed under an inert gas atmosphere with potassium chloride (20 equiv, 2 mmol, 148 mg) and silver(I) oxide (7 equiv, 0.0007 mol, 162 mg) and dissolved in MeCN (10 mL). The mixture was stirred with exclusion from light for 2 days at room temperature. Afterward the solution was filtered through Celite, and the solvent was removed under high vacuum to give a white solid. The solids were dissolved in DCM (15 mL), and the corresponding metal dimer (1 equiv, 0.1 mmol) was added. The mixture was again stirred for 2 days excluded from light. Afterward the mixture was filtered through Celite to remove silver chloride formed in the reaction. The solvent was evaporated, the yellow solids were then dissolved in acetone (3 mL), potassium hexafluorophosphate (8 equiv, 0.8 mmol, 147 mg) was added, and the resulting mixture was stirred for 10 min under air. Afterward water was added (50 mL) slowly to guarantee slow precipitation of the desired complexes. The yellow solids were collected by filtration, washed with water several times, and dried under air to give the desired product in good yields of 78% and higher.

*Chloro(p-cymene)(1,1′-bis(2,6-diisopropylphenyl)-3,3′-dimethyl-4,4′-bis(1,2,3-triazol-5,5′-ylidene))ruthenium(II) Hexafluorophosphate (**4**).* Following the general procedure stated above and using $[RuCymCl_2]_2$ (60 mg). Yield: 78% (0.157 mmol, 141 mg). ^{1}H NMR (400 MHz, CD_2Cl_2; 25 °C, TMS): δ (ppm) 7.68−7.63 (m,2H); 7.47−7.43 (m, 4H); 4.65 (s, 6H); 4.57−4.45 (m, 4H); 3.20 (hept, J = 6.8 Hz, 2H); 2.33 (hept, J = 6.8 Hz, 2H); 1.95 (s, br, 1H);1.67 (s, 3H); 1.36 (d, J = 6.8 Hz, 6H); 1.24 (d, J = 6.8 Hz, 6H); 1.19 (d, J = 6.8 Hz, 6H); 0.89 (d, J = 6.8 Hz, 6H); 0.74 (d, J = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, CD_2Cl_2, 25 °C, TMS): δ (ppm) 179.2 (carbene-C), 147.2, 146.3, 139.4, 134.8, 132.0, 124.3, 123.8, 40.4, 31.3, 28.9, 28.0, 27.0, 25.5, 22.4, 21.6, 21.5, 18.6. MS (ESI): m/z found 755.3140, calcd 755.3144 $[C_{40}H_{54}N_6Cl_1Ru]^+$. Anal. Calcd (%) for $[C_{40}H_{54}N_6Cl_1Ru_1P_1F_6{\cdot}3H_2O]$: C 50.34, H 6.34, N 8.81. Found: C 50.93, H 6.27, N 8.68. Dec: 250 °C.

*Chloro(pentamethylcyclopentadienyl)(1,1′-bis(2,6-diisopropylphenyl)-3,3′-dimethyl-4,4′-bis(1,2,3-triazol-5,5′-ylidene))iridium(III) Hexafluorophosphate (**8**).* Following the general procedure stated above and using $[IrCp^*Cl_2]_2$ (80 mg). Yield: 84% (0.168 mmol, 167 mg). ^{1}H NMR (400 MHz, CD_2Cl_2; 25 °C, TMS): δ (ppm) 7.60−7.54 (m, 2H); 7.41−7.36 (m, 4H); 4.70 (s, 6H); 3.35 (hept, J = 6.8 Hz, 2H); 2.35 (hept, J = 6.8 Hz, 2H); 1.29 (d, J = 6.8 Hz, 6H); 1.25−1.19 (m, 12H); 1.17 (s, 15H); 0.89 (d, J = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, CD_2Cl_2, 25 °C, TMS): δ (ppm) 154.5 (carbene-C); 147.2; 146.9; 142.1; 135.3; 131.9; 124.5; 124.1; 92.4; 40.6; 29.1; 27.7; 27.1; 25.3; 21.6; 21.5; 9.41. MS (ESI): m/z found 847.3789, calcd 847.3795 $[C_{40}H_{55}N_6Cl_1Ir]^+$. Anal. Calcd (%) for $[C_{40}H_{55}N_6Cl_1Ir_1P_1F_6{\cdot}H_2O]$: C 47.49, H 5.78, N 8.31. Found: C 47.23, H 5.73, N 7.76. Mp: 243−245 °C.

X-ray Crystallography. Single crystals of L^3 were generated by a slow evaporation of a concentrated diethyl ether solution under ambient conditions, and those of $L^4[OTf]_2$ were obtained by slow diffusion of diethyl ether into a dichloromethane solution. Single crystals of **2**, **3**, **6**, **7**, and **8** were obtained by slow diffusion of hexane into a concentrated solution in dichloromethane at 8 °C. X-ray quality crystals of **4** were obtained by layering a concentrated solution of **4** in acetone with hexane at −20 °C. X-ray data were collected on a Bruker Smart AXS or a Bruker Kappa ApexII duo system. Data were collected at 100(2) K using graphite-monochromated Mo Kα radiation (λ_α = 0.71073 Å). The strategy for the data collection was evaluated by using the CrysAlisPro CCD or Smart software. The data were collected by the standard phi-omega scan techniques and were scaled and reduced using CrysAlisPro RED software or Saint+ software. The structures were solved by direct methods using SHELXS-97 and refined by full matrix least-squares with SHELXL-97, refining on F^2.[22] It was not possible to refine the hydrogen atoms of solvent molecules in some of the structures. CCDC 906188, 906189, 906908, 846893, 945122, 908392, 846889, and 911406 contain the cif files of L^3, $L^4[OTf]_2$, **2**, **3**, **4**, **6**, **7**, and **8**, respectively. These data can be obtained free of charge from www.ccdc.cam.ac.uk/data_requests/cif. The A-Alert in the checkCIF file of $L^4[OTf]_2$ is related to the disorder of the triflate anions.

General Procedure for Transfer Hydrogenation Catalysis. Nitrobenzene (123 mg), nitrosobenzene (107 mg), and azobenzene (182 mg) (each 1 mmol) were mixed under an inert gas atmosphere with KOH (0.5 equiv, 0.5 mmol, 28 mg) and the corresponding complex in a Schlenk tube, and the reaction mixture was dissolved in dry ^{i}PrOH (4 mL). The mixtures were heated at the assigned temperature for 24 h, cooled, filtered through a small pad of silica using ^{i}PrOH, and analyzed by GC-MS chromatography using hexadecane as an internal standard.

General Procedure for Time-Dependent Transfer Hydrogenation Experiments. Nitrobenzene (1 equiv, 61 mg, 0.5 mmol) was mixed under a nitrogen atmosphere with KOH (0.5 equiv, 14 mg, 0.25 mmol) and the corresponding complex, and this was dissolved in ^{i}PrOH (15 mL). The mixtures were stirred at the assigned temperature for 2−8 days. After certain times small aliquots were taken out of the reaction mixture to analyze the conversions by GC-MS using hexadecane as an internal standard.

General Procedure for Catalyst-Free Transfer Hydrogenations. Nitrobenzene (1 equiv, 61 mg, 0.5 mmol) was mixed under a nitrogen atmosphere with KOH (0.5 equiv, 14 mg, 0.25 mmol), and this was dissolved in ^{i}PrOH (4 mL). The mixtures were stirred at the assigned temperature for 24 h. After certain times small aliquots were taken out of the reaction mixture to analyze the conversions by GC-MS using hexadecane as an internal standard.

■ ASSOCIATED CONTENT

Supporting Information

Cif files and tables giving the crystallographic details, bond lengths, and bond angles for ligands and complexes. These data can be obtained 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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