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Coordination Versatility of Pyridine-Functionalized N-Heterocyclic Carbenes: A Detailed Study of the Different Activation Procedures. Characterization of New Rh and Ir Compounds and Study of Their Catalytic Activity

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Three different reaction procedures for the coordination of *N*-*n*-butyl-*N*′-(2-pyridylmethyl)imidazolium salt have produced new N-heterocyclic complexes of Rh and Ir. The direct reaction of the imidazolium salt with $[IrCl(cod)]_2$ provides a NHC–Ir^{III}–H complex, while transmetalation from a silver–NHC complex and deprotonation with NEt_3 give new NHC complexes of M(I) and M(III) when reacting with $[MCl(cod)]_2$ or $[MCl(coe)_2]_2$ (M = Rh, Ir). The crystal structures of the biscarbene Rh(III) and Ir(III) complexes are described. The catalytic properties of the compounds obtained have been tested in the hydrosilylation of acetylenes, the cyclization of acetylenic carboxylic acids, and hydrogen transfer to ketones.

Introduction

The chemical versatility of N-heterocyclic carbenes has yielded a large number of new compounds with improved catalytic applications. Despite the design of NHC-based homogeneous catalysts being relatively recent, the interest in the area has increased so much that we can now find a large number of reviews regarding their preparation and catalytic properties.[1] The coordination of the NHC-ligand precursor to a metal fragment remains one of the most challenging matters of interest, since in many situations different activation forms can lead to different reaction products. Among the activation strategies that have been reported, we have preferentially used transmetalation from a silver−NHC complex, prepared from the direct reaction of an imidazolium precursor and Ag_2O,[2,3] and in situ deprotonation of an imidazolium salt with a weak base (i.e., NEt_3, NaOAc, and Cs_2CO_3).[4−8] Recently, we also found an example where C−H oxidative addition of an imidazolium salt provided a clean way to obtain a chelate bis-NHC-iridium-hydride.[9] While we showed that oxidative addition of an imidazolium salt could be used as an effective alternative method to obtain Rh− and Ir−NHC complexes, we limited our experiments to reactions which imply that

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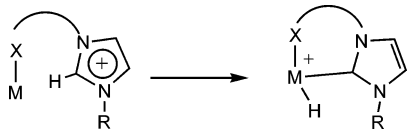
Scheme 1



bisimidazolium salts that had to be partially deprotonated with a weak base to facilitate that the second metalation (C−H oxidative addition) could be stabilized by the chelate coordination of the ligand. With this preliminary result in mind, we thought that, in the absence of a base, the C−H oxidative addition of an imidazolium salt could be facilitated in those cases where the NHC-ligand precursor contained another binding site that could assist the cyclometalation process (Scheme 1).

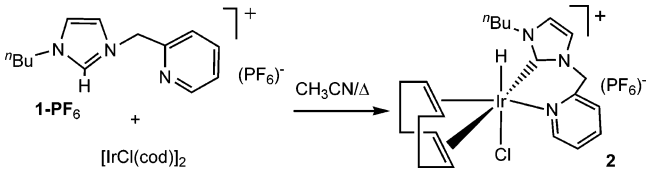
Pyridine-functionalized imidazolium salts have produced a series of interesting chelate transition metal complexes of Pd,[10,11] Ni,[12] Cu,[13] Rh,[14] and Ir.[14−16] Despite their apparent simple structures, pyridine-imidazolin-2-ylidene ligands have provided a large diversity of coordination modes, including "normal" and "abnormal" NHC bindings,[16] pyridine C−H agostic interactions,[14] and C−H oxidative addition of the pyridine[14] and imidazolium[10] rings. The type of coordination obtained depended on the activation method used, the metal precursor employed, and the presence of bulky substituents in the pyridine ring or the imidazolium wingtips.

We now report a new approach to different Rh and Ir complexes with the ligand *N*-*n*-butyl-*N*′-(2-pyridylmethyl)-imidazolin-2-ylidene. We were interested in determining if the different reaction conditions used in the coordination of the ligand would facilitate different reaction compounds, and hence, three different coordination procedures were used: (i) direct metalation by C−H oxidative addition of the imidazolium ring, (ii) transmetalation from a previously obtained silver carbene, and (iii) deprotonation of the imidazolium salt with NEt_3. We have observed that the type of compound obtained depends on the reaction procedure and on the type of activation of the imidazolium precursor. The compounds obtained have been fully characterized. The catalytic activity of some of these new compounds is also discussed.

Results and Discussion

(1) Preparation of the Compounds. Three different coordination strategies were used to coordinate the *N*-*n*-butyl-*N*′-(2-pyridylmethyl)imidazolium salts: oxidative addition of the imidazolium ring, transmetalation from a previously obtained silver carbene, and deprotonation of the imidazolium precursor with NEt_3.

Scheme 2



(a) C−H Oxidative Addition. We recently showed that C−H oxidative addition has to be considered to be a feasible method to form NHC complexes from azolium cations.[9] We thought that the presence of the pyridine ring in *N*-butyl-*N*′-(2-pyridylmethyl)imidazolium hexafluorophosphate, **1-PF$_6$**, would facilitate the C−H oxidative addition of the imidazolium ring by the formation of a chelate coordination, as depicted in Scheme 1. With this in mind, we decided to carry out a series of reactions of **1-PF$_6$** with Rh(I) and Ir(I) precursors, such as $[MCl(cod)]_2$ and $[M(cod)_2](BF_4)$ (M═Rh and Ir); the former gave better results. The reaction of $[RhCl(cod)]_2$ with **1-PF$_6$** in refluxing acetonitrile always yielded the original mixture, even when the reaction was carried out for long reaction times (one week). Modification of the reaction conditions (refluxing toluene, MeOH, $CHCl_3$, etc.), did not produce any of the desired products. The reaction was much more satisfactory when performed with $[IrCl(cod)]_2$. In the presence of **1-PF$_6$**, in refluxing acetonitrile, the desired H−Ir−NHC complex (**2**) was obtained in 2 h (Scheme 2).

Despite the yield in the preparation of **2** being high (∼70%, based on the ^{1}H NMR spectrum of the reaction mixture), we were unable to completely separate it from the reaction mixture, although almost spectroscopically pure samples of **2** were obtained by successive elimination of the oily residue generated in cold chloroform solutions. In any case, small amounts of unreacted **1-PF$_6$** accompanied **2** in all of the characterization experiments we carried out. Despite this unfavorable result, we were able to clearly identify this new NHC-Ir-hydride and assign the structure depicted in Scheme 2. We believe that a trans configuration of the H and Cl ligands is the most likely configuration in view of other similar NHC−Ir−H structures that we have recently reported.[9,17] The more interesting feature of the ^{1}H NMR is the signal from the hydride at −13.5 ppm. This chemical shift is similar to that shown for our previously reported NHC-Ir-hydride[9,17] compounds, for which the hydride is trans to the chlorine ligand. The signals from the imidazolylidene ring (7.4 and 6.9 ppm) and the pyridine ring (8.9, 7.9, 7.8, and 7.3 ppm) support the idea that the ligand is chelating with a normal coordination of the carbene fragment.[16] The two hydrogen atoms of the methylene linking group are diasterotopic because of the loss of symmetry of the ligand upon coordination. The ^{13}C{^{1}H} NMR of **2** shows a signal

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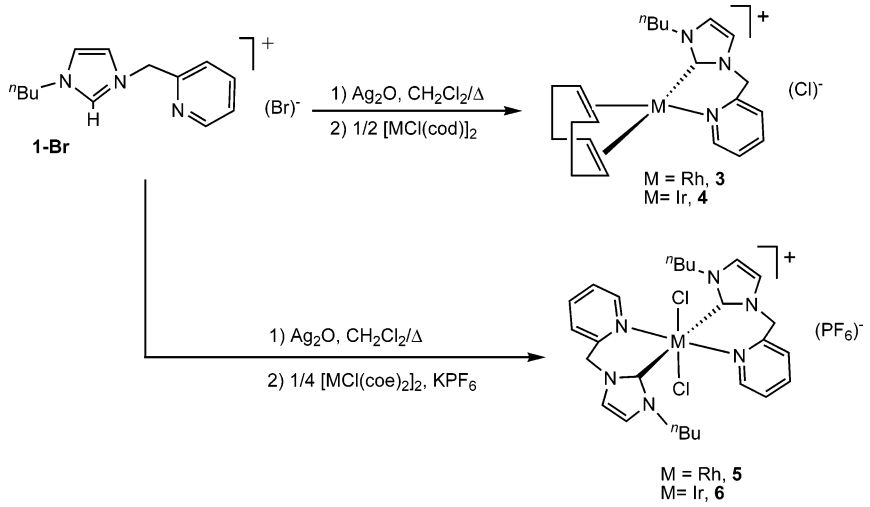
Scheme 3



at 154.6 ppm, corresponding to the metalated carbene, in the typical region for Ir(III)−NHC complexes.[9,14,18] Electrospray mass spectroscopy (ESI-MS) of the mixture containing **2** showed two peaks at *m*/*z* 552 ($\mathbf{2}^+$) and 516 ($\mathbf{2}^+-$HCl), together with a peak at 216 ($\mathbf{1}^+$) from the unreacted imidazolium ligand precursor.

As we have previously mentioned, we were not able to observe the same reactivity when rhodium(I) complexes were used as starting metal precursors. This result is not surprising if we take into account the previous results which show that the Rh(I) complexes are more inert to undergoing oxidative addition of C−H bonds.[9,14,17]

(b) Transmetalation from Silver Carbenes. Transmetalation from silver−NHC complexes has been shown to be an efficient method for the preparation of NHC complexes of transition metals.[19] The first step of this reaction involves the deprotonation of the imidazolium salt with silver oxide to form a silver−NHC species.[2,20] Although these complexes can be isolated, we used our NHC−silver complex in situ. The reaction yield depended on the imidazolium salt/metal molar ratio and on the starting metal complex used, as shown in Scheme 3.

When the reaction was carried out with a 1:1 (**1-Br**/M) molar ratio, complexes **3** (M = Rh) and **4** (M = Ir) were formed. The most significant feature of the spectroscopic data of compound **3** in the $^{13}C\{^1H\}$ NMR spectrum is the doublet from the metalated carbene at 183 ppm ($^1J_{Rh-C}$ = 51 Hz), in the usual range for other Rh(I)−NHC complexes.[4,6,8,21−23] The ^1H NMR spectrum shows diasterotopic protons for the CH_2 linker (δ = 6.0 and 5.7, $^2J_{H-H}$ = 15 Hz) which suggests that this group is out of the coordination plane of the molecule thus reducing its symmetry. Ir compound **4** shows spectroscopic features similar to those described for **3**. The $^{13}C\{^1H\}$ NMR spectrum shows a signal at 179 ppm from the metalated carbene, in the region where the Ir(I)−NHC carbenes appear.[8,17,21] Again, the ^1H NMR spectrum shows diasterotopic protons for the CH_2 linker (δ = 5.8 and 5.5, $^2J_{H-H}$ = 15 Hz), suggesting that this group is out of the coordination plane of the molecule. From the NMR spectroscopic data that we obtained, it is difficult to determine if the pyridine ring is coordinated to the metal or if we have a neutral mono-NHC complex with the pyridine unbound and the chlorine ligand completing the coordination sphere (mass spectroscopy and elemental analysis would not change for this new compound). A comparison with the NMR spectra of compounds **5** and **6** made us choose our proposed coordination mode. Positive ion ESI-MS analyses of isolated compounds **3** and **4** showed peaks at *m*/*z* 426 ($\mathbf{3}^+$) and 516 ($\mathbf{4}^+$).

Long standing of solutions of compounds **3** and **4** in chlorinated solvents (CH_2Cl_2, $CHCl_3$) resulted in the slow decomposition of the compounds, probably caused by processes involving the C−Cl oxidative addition of the solvent.

Compounds **5** (M = Rh, yield 60%) and **6** (M = Ir, yield 21%) were obtained from the reaction of **1-Br** with $[MCl(coe)_2]_2$ in a 2:1 (**1-Br**/M) molar ratio (Scheme 3). The reaction not only proceeded with the addition of two chelate ligands per metal unit but also oxidation to M(III) occurred. One of the main features of the ^1H NMR spectra of **5** and **6** is the absence of the cyclooctene (coe) ligand, indicating that this was lost during the reaction process. The signals corresponding to the protons of the pyridine-imidazolylidene rings suggest that both coordinated ligands are symmetry related. The signals from the CH_2 linker indicate that these are diasterotopic, thus indicating that both methylene bridging groups are out of the equatorial plane of the pseudo-octahedral molecule. The $^{13}C\{^1H\}$ NMR spectra of **5** and **6**, confirm the symmetrical disposition of the two chelate

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ligands. The signals for the metalated carbenes appear at 153 ($^1J_{Rh-C}$ = 53 Hz) and 156 ppm for **5** and **6**, respectively; these values lie in the usual range for other M(III)−NHC (M = Rh and Ir) complexes.[4,6,8,9,17,22]

For the reactions of imidazolium salts with metal complexes of Rh and Ir, we observed that, in certain cases, the metalation is accompanied by the oxidation of the metal from M(I) to M(III).[4,6,7,9,17,22] We recently justified this oxidation by the possible oxidative addition of the C−H bond of the imidazolium ring to the metal providing a NHC-M^{III}-hydride that could turn into NHC-M^{III}-X (X = halide) in the presence of an excess of halide.[9,17] For the reaction described in this work, this oxidation is difficult to interpret in terms of the oxidative addition of the imidazolium ring since the ligand is transferred to the metal from a previously prepared silver−NHC complex. We believe that the oxidation to the M(III) species can also be produced by the silver^{I}−NHC complex itself, thus implying that the silver complex would play a 2-fold role (i) in NHC transfer and (ii) as an oxidizing agent. The process would then imply that Ag^0 is produced during the last step of the reaction process, and in fact, some Ag^0 must be filtered off before purification of the final Rh and Ir complexes. In addition, a black mirror is formed in the reaction flask after the addition of the Rh and Ir complexes; this is obviously from the silver complex and not the Rh and Ir complexes because of obvious stoichiometric reasons (the yield of **5** is higher than 50%). In any case, the fact that the oxidation occurs under the mild conditions of this reaction process supports our previously reported observations that short linkers favor oxidation to M(III) when chelate imidazolylidene complexes are prepared.[4,6,17,22]

(c) Deprotonation with a Weak Base. In our previous works, we showed that deprotonation of an imidazolium salt with a weak base such as NEt_3 is an effective method for obtaining Rh− and Ir−NHC complexes.[4,6,9] Following the same procedure, we tried to coordinate the pyridine-imidazolium NHC precursor **1-Br** to $[M(cod)_2]BF_4$ (M = Rh and Ir) in the presence of NEt_3. Despite trying different reaction conditions and solvents, we always had mixtures of compounds difficult to characterize and separate. Our best results using this method were for the reactions carried out in refluxing acetonitrile, for which we obtained the M(III) complexes **5** and **6** in less than a 10% yield.

(2) Molecular Structure of 5 and 6. The molecular structures of **5** and **6** were unequivocally confirmed by means of single-crystal X-ray crystallography. Figure 1 shows the molecular structure of **5**, which is virtually identical to that of **6**. Both the Rh (in **5**) and Ir (in **6**) metal centers are in a pseudo-octahedral geometry with two chelate pyridine-imidazolin-2-ylidene ligands defining the equatorial plane and two chlorine ligands in a relative trans disposition. The pyridine-imidazolin-2-ylidene ligands are adopting an anti disposition with the carbene carbon atoms trans to the nitrogen of the pyridine rings. The M−C bond distances lie in the usual range for M^{III}−NHC complexes (av. 1.99 Å for **5** and av. 2.02 Å for **6**). The chelate−ligand bite angles are 85.0 and 86.2° for **5** and 84.8 and 85.2° for **6**. A number of interionic short CH···Cl and C−H···F contacts were detected in the crystal structures of both **5** and **6**, but these are most probably caused by crystal packing effects and should not affect to distances and angles in the molecules.

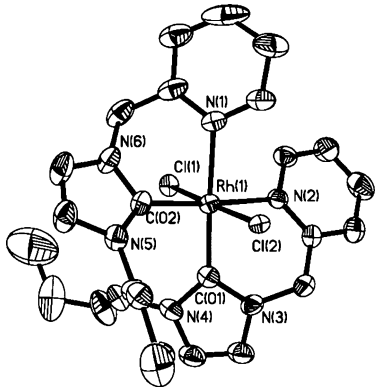

Figure 1. Molecular diagram of compound **5**. Hydrogen atoms and counteranions have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Rh(1)−C(01) = 1.981(7), Rh(1)−C(02) = 1.996(7), Rh(1)−N(1) = 2.166(6), Rh(1)−N(2) = 2.142(6), Rh(1)−Cl(1) = 2.4087(16), Rh(1)−Cl(2) = 2.4289(14), C(01)−Rh(1)−N(2) = 86.2(3), C(02)−Rh(1)−N(1) = 85.0(3), C(01)−Rh(1)−N(1) = 177.4(3), C(02)−Rh(1)−N(2) = 176.0(3).

(3) Catalytic Results. NHC complexes of Rh and Ir have been shown to be effective catalysts in a wide range of reactions. On the basis of the electronic and geometric properties of our newly obtained complexes, we found it appropriate to test them in reactions such as hydrosilylation of terminal alkynes, cyclization of acetylenic carboxylic acids, and hydrogen transfer from alcohols to ketones.

(a) Hydrosilylation of Alkynes. Hydrosilylation of multiple bonds represents a useful class of catalytic processes to functionalize organic molecules. Vinylsilanes, widely used intermediates for organic synthesis, could be efficiently prepared by transition metal-catalyzed addition of silanes to alkynes. Most of the recent efforts in the study of catalytic hydrosilylation concern the design of new and efficient catalysts which enable the preparation of both (*Z*)- and (*E*)-alkenylsilanes independently.[24,25] We thought that complexes **3** and **4** display all the structural and chemical requirements for this catalytic reaction and could throw some light to the reaction process.

Table 1 shows the catalytic results for the hydrosilylation of phenylacetylene with $HSiMe_2Ph$. The reactions were carried out in $CDCl_3$ at 60 °C and room temperature, with different catalyst loadings. Under these conditions, we also tried the hydrosilylation of 1-hexyne and we used $HSi(OEt)_3$ as hydrosilylating agent, but our compounds showed little activity with these substrates (data not shown in Table 1). Rhodium complex **3** is more active than iridium complex **4**. For the reactions studied, both catalysts used gave a mixture of the β-Z, β-E, and α-isomers, although the β-Z isomer

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Table 1. Catalytic Hydrosilylation of Alkynes Using Compound **3** and **4** as Catalysts[a]

entry	catalyst	cat. (mol %)	temp (°C)	time (h)	yield (100%)	E/Z/α
1	**3**	0.1	60	48	83	32/55/13
2		1	60	24	93	21/69/10
3		5	r.t	24	86	0/95/5
4	**4**	0.1	60	48	>99	48/34/18
5		1	60	24	60	24/62/14
6		5	RT	24	38	42/45/13

[a] Conditions: 0.077 mmol of alkyne (PhC≡CH), 0.085 mmol of silane ($HSiMe_2Ph$), and 0.1, 1, or 5 mol % of catalyst in 2 mL $CDCl_3$. Yields determined by ^1H NMR spectroscopy.

seems to be preferred. Only in the case of long reactions carried out with Ir complex **4** is the β-E isomer preferred (entry 4), probably because of a parallel process implying a β-E/β-Z isomerization, as we have previously reported.[4] Interestingly, this isomerization process seems to be minimized for the reactions carried out a room temperature, as observed for the very high selectivity obtained for the β-Z isomer when the hydrosilylation is performed at room temperature (entry 3). In most metal-catalyzed hydrosilylations, the selectivity is capriciously affected by factors such as the types of alkynes and silanes, the catalyst, the solvent, or the temperature. However, it has been reported that cationic Rh complexes catalyze the hydrosilylation of alkynes to give the β-*E*-vinyl-silanes as the major products, while neutral Rh complexes showed a higher preference to yield the β-Z isomers.[24,26,27] According to our results, it seems that our cationic compounds do not follow this tendency, so the cationic nature of the catalyst should not be considered to be a major contributor parameter toward the control of the stereochemistry of the process.

(b) Cyclization of 4-Pentynoic Acid and 5-Hexynoic Acid. The catalytic formation of five and six-membered ring systems containing oxygen is an important application in homogeneous catalysis given their essential relevance to the pharmaceutical industry. Several cationic Rh(I) complexes reportedly have shown good catalytic activity in this reaction.[28]

Catalytic cyclization was performed in an NMR tube containing 0.75 mL of acetonitrile-d_3 with a catalyst loading of 0.5 mol %. From the data shown in Table 2, we can conclude that the cyclization of 4-pentynoic acid is much more favorable than the cyclization of 5-hexynoic acid, as seen in other previously reported works.[21,28] From our results, we can conclude that our catalysts showed higher activity than complexes reported before, in terms of reaction rates and conversions achieved, even showing good activity at room temperature in the cyclization of 4-pentynoic acid.[28] As far as we know, compound **4** is the first Ir complex to show any catalytic activity in this type of reaction.

Table 2. Catalytic Cyclization of Acetylenic Carboxylic Acids Using Compounds **3** and **4** as Catalysts[a]

entry	substrate	catalyst	temp (°C)	time (h)	yield (%)
1	4-pentynoic acid	**3**	50	12	>99
2			RT	56	>99
3		**4**	50	12	>99
4	5-hexynoic acid		RT	96	>99
5		**3**	50	168	6
6		**4**	50	168	20

[a] Conditions: in an NMR tube, 1 mmol of substrate, 0.5 mol % of catalyst, 0.75 mL of acetonitrile-d_3 as solvent. Yields determined by ^1H NMR spectroscopy.

Table 3. Catalytic Transfer Hydrogenation Using Compounds **5** and **6** as Catalysts[a]

entry	substrate	cat. (mol %)	catalyst	time (h)	yield (%)
2	benzophenone	1[b]	**5**	10	>99
			6	2	>99
3		0.1[c]	**6**	72	90
4	acetophenone	1[b]	**5**	24	>90
5			**6**	3	>90
6		0.1[c]	**6**	50	>99

[a] Conditions: 10 mL of 0.1 M KOH in *i*-PrOH, reflux temperature 82 °C, *t*-BuOK (2 equiv vs catalyst); yields determined by ^1H NMR; TON = mol product/mol catalyst. [b] 0.2 mmol of substrate. [c] 2 mmol of substrate.

(c) Hydrogen Transfer. Complexes **5** and **6** catalyze the hydrogenation of the C═O groups of benzophenone and acetophenone via hydrogen transfer from *i*-PrOH/KOH at 82 °C. As shown from the data in Table 3, we can conclude that Ir complex **6** is a better catalyst than Rh complex **5** for this type of reaction. The hydrogenation of benzophenone is more effective than that shown for acetophenone under the same reaction conditions. In general, we have observed that our previously described NHC complexes of Rh are more active in the hydrogenation of aromatic ketones than they are for aliphatic ketones.[4,7]

Conclusions

With this work we have confirmed the chemical versatility of the ligand *N*-butyl-*N*′-(2-pyridylmethyl)imidazolin-2-ylidene. Starting from its imidazolium salt, we have described three different reaction procedures yielding electronically and structurally different compounds. More interestingly, we have shown that the direct reaction of *N*-butyl-*N*′-(2-pyridylmethyl)imidazolium hexafluorophosphate with $[IrCl(cod)]_2$ gives a new NHC-Ir^{III}-H compound by C−H oxidative addition of the imidazolium salt, thus implying that this method may also be used as a good procedure to obtain NHC complexes. We believe that the reaction is favored by the chelate effect provided by the ligand in the resulting compound. Although a previous theoretical study by Cavell, Yates, and co-workers proposed that this reaction should be possible for Rh compounds,[29] this is the first time that this type of activation was experimentally described for a metal other than low valent Ni, Pd,[30] and Pt[31] without using an

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external base. We believe that our results strongly suggest that C−H oxidative addition may be considered to be a useful method for the preparation of NHC-M-H complexes.

The compounds obtained have shown catalytic activity in reactions such as hydrosilylation of acetylenes, cyclization of acetylenic carboxylic acids, and hydrogen transfer to ketones, for which the preliminary studies showed the great potential of this type of compounds.

Experimental Section

NMR spectra were recorded on a Varian Innova 300 and 500 MHz instruments, using $CDCl_3$, acetone-d_6, acetonotrile-d_3, and DMSO-d_6. Elemental analyses were carried out in an EA 1108 CHNS−O Carlo Erba Analyzer. Electrospray mass spectra (ESI-MS) were recorded on a Micromass Quatro LC instrument; nitrogen was employed as the drying and nebulizing gas. The metal precursors $[RhCl(coe)_2]_2$[32] and $[IrCl(coe)_2]_2$[33] and the imidazolium salts **1-PF$_6$** and **1-Br**[16] were synthesized according to literature methods. All other reagents are commercially available and were used as received.

Synthesis of [*N*-*n*-butyl-*N*′-(2-pyridylmethyl)imidazole-2-ylidene](chloro)(hydrido)(1,5-cyclooactadiene)iridium(III) Hexafluorophosphate, 2. A mixture of $[IrCl(cod)]_2$ (100 mg, 0.15 mmol) and **1-PF$_6$** (107 mg, 0.30 mmol) was refluxed in CH_3CN (5 mL) for 120 min. The volatile components were removed under vacuum, and the crude solid was dissolved in CH_2Cl_2, precipitated with ether, and washed with cold $CHCl_3$. The yellow solid obtained was compound **2** and unreacted **1-PF$_6$** in a **2**/**1-PF$_6$** ratio of 7:3. ^{1}H NMR of compound **2** ($CDCl_3$, 500 MHz, COD and *n*-Bu signals omitted for clarity): δ 8.88 (d, 1H, $^3J_{H-H}$ = 5.5 Hz, H_{py}), 7.93 (t, 1H, $^3J_{H-H}$ = 7.5 Hz, H_{py}), 7.85 (d, 1H, $^3J_{H-H}$ = 7.5 Hz, H_{py}), 7.42 (d, 1H, $^3J_{H-H}$ = 2.1 Hz H_{imid}), 7.37 (t, 1H, $^3J_{H-H}$ = 7.0 Hz, H_{py}), 6.93 (d, 1H, $^3J_{H-H}$ = 2.1 Hz H_{imid}), 5.74 (d, 2H, $^2J_{H-H}$ = 16.5 Hz, $CH_{2linker}$), 5.57 (d, 2H, $^2J_{H-H}$ = 16.0 Hz, $CH_{2linker}$), −13.46 (s, 1H, Ir−H). ^{13}C{^{1}H} NMR (acetone-d_6, 125 MHz): δ 156.5 (C_{py}), 154.6 (C−Ir), 154.1 (C_{py}), 141.2 (C_{py}), 126.6 (C_{py}), 125.6 (C_{imid}), 122.8 (C_{py}), 122.3 (C_{imid}), 97.3 (CH_{COD}), 93.7 (CH_{COD}), 76.7 (CH_{COD}), 74.0 (CH_{COD}), 58.6 ($CH_{2linker}$), 49.4 ($CH_{2(n-Bu)}$), 34.4 (CH_{2COD}), 33.9 (CH_{2COD}), 31.8 ($CH_{2(n-Bu)}$), 26.9 (CH_{2COD}), 25.7 (CH_{2COD}), 19.8 ($CH_{2(n-Bu)}$), 13.3 ($CH_{3(n-Bu)}$). ESI-MS (cone 15 V, fragment): *m*/*z* 216 [**1**$^+$], 552 [M]$^+$, 516 [M − HCl]$^+$.

Synthesis of [*N*-*n*-butyl-*N*′-(2-pyridylmethyl)imidazole-2-ylidene](1,5-cyclooactadiene)rhodium(I) Chloride, 3. A mixture of Ag_2O (141 mg, 0.61 mmol) and **1-Br** (120 mg, 0.41 mmol) was refluxed in CH_2Cl_2 (10 mL) for 90 min. Then $[RhCl(cod)]_2$ (100 mg, 0.20 mmol) was added. The mixture was refluxed for 90 min and filtered through Celite, and the volatile components were removed under vacuum. The crude solid was redissolved in CH_2Cl_2, and the impurities were removed by precipitation with ether. The product was washed with cold ether and dried under vacuum. Yield: 132 mg (70%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.52 (d, 1H, $^3J_{H-H}$ = 4.5 Hz, H_{py}), 7.64 (t, 1H, $^3J_{H-H}$ = 7.2 Hz, H_{py}), 7.53 (d, 1H, $^3J_{H-H}$ = 7.5 Hz, H_{py}), 7.19 (m, 1H, H_{py}), 6.86 (s, 1H, H_{imid}), 6.81 (s, 1H, H_{imid}), 6.03 (d, 1H, $^2J_{H-H}$ = 15.5 Hz, $CH_{2linker}$), 5.72 (d, 1H, $^2J_{H-H}$ = 14.5 Hz, $CH_{2linker}$), 4.99 (m, 2H, CH_{COD}), 4.48 (t, 2H, $^3J_{H-H}$ = 7.2 Hz, $CH_{2(n-Bu)}$), 3.27 (m, 2H, CH_{COD}), 2.32 (m, 4H, CH_{2COD}), 1.92 (m, 4H, CH_{2COD}), 1.45 (m, 2H, $CH_{2(n-Bu)}$), 1.18 (m, 2H, $CH_{2(n-Bu)}$), 1.03 (t, 3H, $^3J_{H-H}$ = 7.2 Hz, $CH_{3(n-Bu)}$). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ 182.8 (d, $^1J_{C-Rh}$ = 51.2 Hz, C−Rh), 156.6 (C_{py}), 149.5 (C_{py}), 137.4 (C_{py}), 123.6 (C_{py}), 123.2 (C_{imid}), 121.2 (C_{py}), 120.9 (C_{imid}), 98.8 (CH_{COD}), 68.8 (d, $^1J_{C-Rh}$ = 15.8 Hz, CH_{COD}), 68.1 (d, $^1J_{Rh-C}$ = 13.4 Hz, CH_{COD}), 56.4 ($CH_{2linker}$), 50.8 ($CH_{2(n-Bu)}$), 33.1 (CH_{2COD}), 29.0 ($CH_{2(n-Bu)}$), 20.3 ($CH_{2(n-Bu)}$), 14.0 ($CH_{3(n-Bu)}$). Anal. Calcd for $C_{21}H_{29}RhN_3Cl$ (461.83): C, 54.61; H, 6.33; N, 9.10. Found: C, 54.20; H, 6.10; N, 9.05. ESI-MS (cone 40 V, fragment): *m*/*z* 426 [M]$^+$.

Synthesis of [*N*-*n*-butyl-*N*′-(2-pyridylmethyl)imidazole-2-ylidene](1,5-cyclooactadiene)iridium(I) Chloride, 4. A mixture of Ag_2O (103 mg, 0.44 mmol) and **1-Br** (88 mg, 0.30 mmol) was refluxed in CH_2Cl_2 (10 mL) for 90 min. Then $[IrCl(cod)]_2$ (100 mg, 0.15 mmol) was added. The mixture was refluxed for 90 min and filtered through Celite, and the volatile components were removed under vacuum. The crude solid was redissolved in CH_2Cl_2, and the impurities were removed by precipitation with ether. The product was washed with cold ether and dried under vacuum. Yield: 102 mg (62%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.53 (d, 1H, $^3J_{H-H}$ = 4.5 Hz, H_{py}), 7.62 (t, 1H, $^3J_{H-H}$ = 7.5 Hz, H_{py}), 7.45 (d, 1H, $^3J_{H-H}$ = 7.5 Hz, H_{py}), 7.17 (m, 1H, H_{py}), 6.90 (d, 1H, $^3J_{H-H}$ = 2.0 Hz, H_{imid}), 6.82 (d, 1H, $^3J_{H-H}$ = 1.5 Hz, H_{imid}), 5.84 (d, 1H, $^2J_{H-H}$ = 15.5 Hz, $CH_{2linker}$), 5.53 (d, 1H, $^2J_{H-H}$ = 14.5 Hz, $CH_{2linker}$), 4.40 (m, 2H, CH_{COD}), 4.34 (m, 2H, $CH_{2(n-Bu)}$), 2.89 (m, 2H, CH_{COD}), 2.18 (m, 4H, CH_{2COD}), 1.89 (m, 2H, $CH_{2(n-Bu)}$), 1.57 (m, 4H, CH_{2COD}), 1.41 (m, 2H, $CH_{2(n-Bu)}$), 0.96 (t, 3H, $^3J_{H-H}$ = 7.5 Hz, $CH_{3(n-Bu)}$). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 179.4 (C−Ir), 156.1 (C_{py}), 149.9 (C_{py}), 137.3 (C_{py}), 123.4 (C_{py}), 123.3 (C_{imid}), 120.9 (C_{py}), 120.5 (C_{imid}), 85.1 (CH_{COD}), 84.5 (CH_{COD}), 56.1 ($CH_{2linker}$), 51.1 (CH_{2COD}), 50.4 ($CH_{2(n-Bu)}$), 49.7 (CH_{2COD}), 34.2 (CH_{2COD}), 33.6 (CH_{2COD}), 33.2 ($CH_{2(n-Bu)}$), 20.2 ($CH_{2(n-Bu)}$), 14.0 ($CH_{3(n-Bu)}$). Anal. Calcd for $C_{21}H_{29}IrN_3Cl$ (550.5): C, 45.76; H, 5.30; N, 7.62. Found: C, 45.90; H, 5.45; N, 7.99. ESI-MS (cone 15 V, fragment): *m*/*z* 516 [M]$^+$.

Synthesis of *trans*-bis[*N*-*n*-butyl-*N*′-(2-pyridylmethyl)imidazole-2-ylidene]bis(chloride)rhodium(III) Hexafluorophosphate, 5. A mixture of Ag_2O (194 mg, 0.84 mmol) and **1-Br** (165 mg, 0.56 mmol) was refluxed in CH_2Cl_2 (10 mL) for 90 min. Then $[RhCl(coe)_2]_2$ (100 mg, 0.14 mmol) was added. The mixture was refluxed for 90 min and filtered through Celite, and the volatile components were removed under vacuum. The crude solid was redissolved in CH_2Cl_2 and purified by column chromatography. Elution with CH_2Cl_2/acetone (1:1) and KPF_6 resulted in the separation of a yellow band that contained compound **5**. Compound **5** was obtained as a yellow solid by precipitation with CH_2Cl_2/ether. Yield: 94 mg (60%). ^{1}H NMR (DMSO-d_6, 500 MHz): δ 8.62 (d, 2H, $^3J_{H-H}$ = 5.5 Hz, H_{py}), 8.14 (t, 2H, $^3J_{H-H}$ = 7.5 Hz, H_{py}), 7.85 (d, 2H, $^3J_{H-H}$ = 8.0 Hz, H_{py}), 7.74 (s, 2H, H_{imid}), 7.58 (m, 2H, H_{py}), 7.56 (s, 2H, H_{imid}), 6.97 (d, 2H, $^2J_{H-H}$ = 15.5 Hz, $CH_{2linker}$), 5.71 (d, 2H, $^2J_{H-H}$ = 15.5 Hz, $CH_{2linker}$), 3.90 (m, 2H, $CH_{2(n-Bu)}$), 3.78 (m, 2H, $CH_{2(n-Bu)}$), 1.87 (m, 2H, $CH_{2(n-Bu)}$), 1.69 (m, 2H, $CH_{2(n-Bu)}$), 1.24 (m, 2H, $CH_{2(n-Bu)}$), 1.14 (m, 2H, $CH_{2(n-Bu)}$), 0.75 (t, 6H, $^3J_{H-H}$ = 6.5 Hz, $CH_{3(n-Bu)}$). ^{13}C{^{1}H} NMR (DMSO-d_6, 75 MHz): δ 156.0 (C_{py}), 153.2 (d, $^1J_{C-Rh}$ = 53.0 Hz, C−Rh), 155.0 (C_{py}), 140.5 (C_{py}), 125.5 (C_{py}), 125.3 (C_{py}), 124.3 (C_{imid}), 122.3 (C_{imid}), 54.7 ($CH_{2linker}$), 49.7 ($CH_{2(n-Bu)}$), 32.5 ($CH_{2(n-Bu)}$), 19.8 ($CH_{2(n-Bu)}$), 13.0 ($CH_{3(n-Bu)}$). Anal. Calcd for $C_{26}H_{34}RhN_6Cl_2PF_6$ (749.36): C, 41.67; H, 4.57; N, 11.21. Found: C, 41.60; H, 5.1; N, 10.95. ESI-MS (cone 25 V, fragment): *m*/*z* 603.4 [M]$^+$.

Synthesis of *trans*-bis[*N*-*n*-butyl-*N*′-(2-pyridylmethyl)imidazole-2-ylidene]bis(chloride)iridium(III) Hexafluorophosphate, 6. A mixture of Ag_2O (155 mg, 0.67 mmol) and **1-Br** (132 mg, 0.45

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Table 4. Crystallographic Data of Compounds **5** and **6**

	5	**6**
empirical formula	$C_{26}H_{34}RhN_6Cl_2PF_6$	$C_{26}H_{34}IrN_6Cl_2PF_6$
fw	749.37	838.66
wavelength (Å)	0.71073	0.71073
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$
a (Å)	9.3390(4)	9.3595(4)
b (Å)	16.2845(7)	16.3229(7)
c (Å)	20.8177(9)	20.7536(10)
α (deg)	90.00	90.00
β (deg)	91.7260(10)	91.4450
γ (deg)	90.00	90.00
V (Å^3)	3164.5(2)	3169.6(2)
Z	4	4
D_{calcd} (Mg/m^3)	1.573	1.757
abs coeff (mm^{-1})	0.822	4.494
reflns collected	9562	5377
GOF on F^2	1.013	0.979
final R indices	R1 = 0.0855	R1 = 0.0551
[$I > 2\sigma(I)$]	wR2 = 0.2520	wR2 = 0.1274

mmol) was refluxed in CH_2Cl_2 (10 mL) for 90 min. Then [IrCl(coe)$_2$]$_2$ (100 mg, 0.11 mmol) was added. The mixture was refluxed for 90 min and filtered through Celite, and the volatile components were removed under vacuum. The crude solid was redissolved in CH_2Cl_2 and purified by column chromatography. Elution with CH_2Cl_2/acetone (1:1) and KPF_6 resulted in the separation of a yellow band that contained compound **6**. Compound **6** was obtained as a yellow solid by precipitation with CH_2Cl_2/ether. Yield: 40 mg (21%). ^{1}H NMR (acetone-d_6, 300 MHz): δ 8.58 (d, 2H, $^3J_{H-H}$ = 5.1 Hz, H_{py}), 8.20 (t, 2H, $^3J_{H-H}$ = 7.5 Hz, H_{py}), 7.91 (d, 2H, $^3J_{H-H}$ = 7.8 Hz, H_{py}), 7.71 (s, 2H, H_{imid}), 7.61 (t, 2H, $^3J_{H-H}$ = 6.5 Hz, H_{py}), 7.55 (s, 2H, H_{imid}), 6.99 (d, 2H, $^2J_{H-H}$ = 15.6 Hz, $CH_{2linker}$), 5.67 (d, 2H, $^2J_{H-H}$ = 15.6 Hz, $CH_{2linker}$), 3.96 (m, 2H, $CH_{2(n-Bu)}$), 3.80 (m, 2H, $CH_{2(n-Bu)}$), 1.86 (m, 2H, $CH_{2(n-Bu)}$), 1.71 (m, 2H, $CH_{2(n-Bu)}$), 1.30 (m, 2H, $CH_{2(n-Bu)}$), 1.21(m, 2H, $CH_{2(n-Bu)}$), 0.81 (t, 6H, $^3J_{H-H}$ = 7.2 Hz, $CH_{3(n-Bu)}$). ^{13}C{^{1}H} NMR (acetone-d_6, 75 MHz): δ 156.4 (C−Ir), 155.5 (C_{py}), 140.6 (C_{py}), 136.2 (C_{py}), 126.1 (C_{py}), 125.6(C_{py}), 123.4 (C_{imid}), 121.4 (C_{imid}), 54.4 ($CH_{2linker}$), 49.0 ($CH_{2(n-Bu)}$), 32.7 ($CH_{2(n-Bu)}$), 19.9 ($CH_{2(n-Bu)}$), 13.0 ($CH_{3(n-Bu)}$). Anal. Calcd for $C_{26}H_{34}IrN_6Cl_2PF_6$ (749.36): C, 37.23; H, 4.04; N, 10.02. Found: C, 37.21; H, 4.39; N, 9.65. ESI-MS (cone 25 V, fragment): m/z 693.5 [M]$^+$.

X-ray Diffraction Studies. Crystals for the X-ray diffraction of compounds **5** and **6** were obtained by slow diffusion of ether in a concentrated solution of each complex in CH_2Cl_2. Crystal Data are summarized in Table 3. Data collection was performed at room temperature on a Siemens Smart CCD diffractometer using graphite monochromated Mo Kα radiation (λ = 0.71073 Å). The diffraction frames were integrated using the SAINT package.

Space group assignment was based on systematic absences, E statistics, and successful refinement of the structures. The structures were solved by direct methods with the aid of successive difference Fourier maps and were refined using the SHELXTL 6.1 software package. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were assigned to ideal positions and refined using a riding model.

Hydrosilylation of 1-Alkynes with Silanes. General Procedure. In a 10 mL flask, PhC≡CH (0.077 mmol), $HSi(Me)_2Ph$ (0.085 mmol), and a catalytic amount of **3** or **4** (0.1 mol %, 7.7×10^{-5} mmol; 1%, 7.7×10^{-4}; 5%, 3.85×10^{-3}) were dissolved in $CDCl_3$ (2 mL). The mixture was kept at room temperature or 60 °C by immersion in a temperature-controlled oil bath. The progress of the reaction was monitored by ^{1}H NMR spectroscopy, according to the data of the products from the literature.[26]

Catalytic Cyclization of Acetylenic Carboxylic Acids. General Procedure. In a NMR tube, acetylenic carboxylic acid (4-pentynoic acid or 5-hexynoic acid, 1 mmol) and a catalytic amount of **3** or **4** (0,1 mol %) were dissolved in acetonotrile-d_3 (0.75 mL). The mixture was kept at room temperature or 50 °C by immersion in a temperature-controlled oil bath. The progress of the reaction was monitored by ^{1}H NMR spectroscopy, according to the data of the products from the literature.[28]

Hydrogen Transfer Catalysis. General Procedure. A mixture of the ketone (0.2 or 2 mmol), KOH (0.1 M in *i*-PrOH), catalyst **5** or **6** (1 or 0.1% mol vs substrate), and *t*-BuOK (2 equiv vs catalyst) were refluxed in 10 mL of *i*-PrOH. Aliquots were extracted from the reaction vessels and added to an NMR tube containing 0.5 mL of $CDCl_3$. Yields were determined by ^{1}H NMR spectroscopy.

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Supporting Information Available: Crystallographic data files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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