Synthesis and Reactivity of New Complexes of Rhodium and Iridium with Bis(dichloroimidazolylidene) Ligands. Electronic and Catalytic Implications of the Introduction of the Chloro Substituents in the NHC Rings

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The preparation of a new bis(dichloroimidazolylidene) ligand has provided chelate-N-heterocyclic complexes of Rh(I) and Ir(I), which have been fully characterized. The crystal structures of three of the new complexes are described. The study of the electronic properties of the new ligands was made on the basis of the ν(CO) stretching frequencies of the carbonyl derivatives, showing that the chloroimidazolylidene ligand is significantly less σ-donating than the related nonchlorinated analogue. This electronic modification of the ligand has important implications for the catalytic properties of the compounds obtained, as observed from enhanced activity shown in catalytic hydrosilylation of terminal acetylenes and cyclization of acetylenic carboxylic acids, compared to the complexes with the nonchlorinated NHC analogue ligand.

Introduction

One of the key steps in the preparation of selective and active catalysts is the design of ligands with tunable electronic and steric parameters. For the ubiquitous phosphine-based ligands, these parameters were quantified by Tolman,[1] in a work that had a major impact on the subsequent design of phosphine-based catalysts. For the more recently used N-heterocyclic-carbene ligands (NHCs), many efforts have been made in the design of compounds with different topologies,[2,3] including mono-,[2−4] bis-, and triscarbenes[3] with a wide variety of coordination modes, like bischelate, pincer,[3] and tripodal,[5−7] and even the possibility of introducing stereogenic centers for asymmetric catalyst design.[8] Despite the large versatility in coordination geometries and steric modifications that we can now find among NHC ligands, there is still a lack of studies concerning the modulation of their electronic effects. In general, NHC ligands are considered to be better σ-donors than phosphines,[9−12] and their basicity does not seem to be highly influenced by the modification of the nature of the N-substituents, as shown by a recent study by Nolan and co-workers.[11,12] This, in turn, means that, while we can easily modulate the steric properties of our NHC-based ligands, we still find it difficult to tune their electronic effects and, in any case, we will always increase the electron density of the metal when using NHCs compared with analogue complexes with phosphines. One of the more often used ways of modifying the electron density when employing NHCs is the use of saturated and unsaturated azole rings, the former traditionally considered as more electron-donating than the unsaturated ones, and implying significant differences in the catalytic properties of their complexes.[13] However, this common assumption was minimized by the recent theoretical studies by Yates,[14] who showed that the basicity of a series of NHCs had little to do with the saturated or unsaturated nature of the imidazole. Furthermore, the experimental data reported by Nolan[11] showed that unsaturated NHCs provided (little, but) more electron density to the metal than saturated ones. Substitution at the 4 and 5 positions of the imidazole ring was found to significantly

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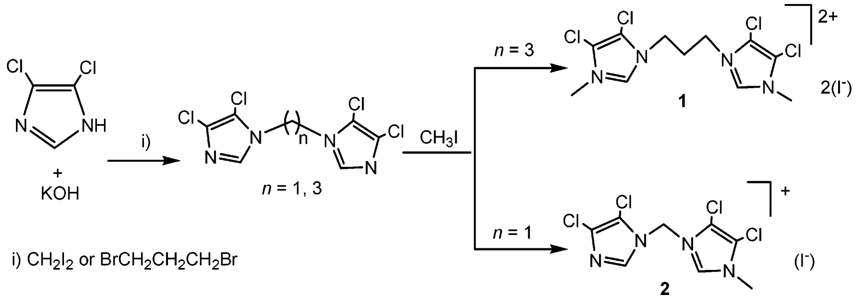
Scheme 1



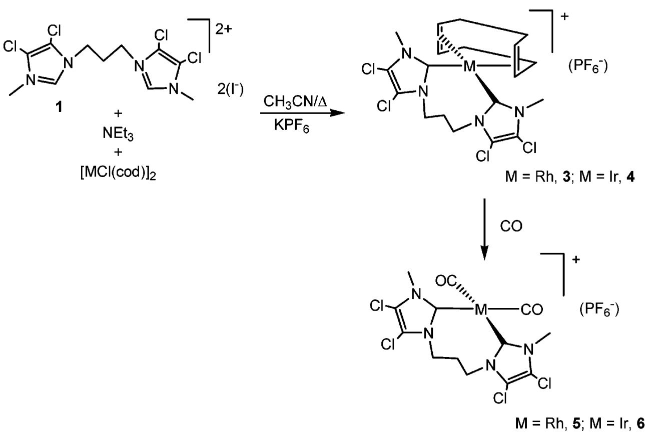
modify the basicity of the carbenes.[14] Chlorinated analogues of 1,3-dimesitylimidazole-2-ylidene (IMes) appeared to be less electron-donating ligands than the hydrogenated ones, as proved by calorimetric studies performed on the formation of Cp*RhCl(L) (L = imidazolylidene)[15] and on the U−O stretching frequencies of a series of uranyl complexes of the type $UO_2Cl_2L_2$.[16]

Taking all this into account and based on our previous experience, we now report a new type of bisimidazolylidene ligand with chlorine substituents in the 4 and 5 positions. The reactivity of this new ligand toward Rh and Ir has been studied, and a series of complexes have been fully characterized. The electronic properties of the new ligand have been compared to related nonchlorinated ligands, on the basis of the ν(CO) frequencies of the corresponding carbonyl complexes. The catalytic activity of the new compounds was tested in reactions such as hydrosilylation of terminal acetylenes and cyclization of acetylenic carboxylic acids, showing significant differences from the bis-(NHC) nonchlorinated analogues of Rh and Ir.

Results and Discussion

Synthesis of Compounds. The bisimidazolium ligand precursors were obtained according to the reaction depicted in Scheme 1. 4,5-Dichloroimidazole was deprotonated with KOH and then allowed to react with diiodomethane ($n = 1$) or 1,3-dibromopropane ($n = 3$). The corresponding bis(dichloroimidazole) compounds were reacted with CH_3I in order to afford the bismethylated complexes. While trimethylenebis(4,5-dichloroimidazole) readily afforded trimethylenebis((*N*-methyl)-4,5-dichloroimidazolium)diiodide, **1**, the analogue compound with a methylene bridge gave only the monomethylated monocationic compound, **2** (Scheme 1), in moderate yield (42%). In the preparation of **2** the reaction mixture was analyzed in order to check whether amounts of the dimethylated compounds could have been missed in the reaction workup, but all we found was unreacted starting compounds. This, in fact, may be a consequence of the lowering of the nucleophilic character of the nitrogen atoms of the imidazole rings by the introduction of the chlorine substituents. For the methylenebisimidazolium compound, the formation of the monocationic monomethylated species **2** results in a further reduction of the nucleophilic character of the nonmethylated nitrogen atom, thus avoiding the second methylation. The introduction of a longer connecting chain in the trimethylene species may reduce the inducting effect of the methylated azole over the nonmethylated one, thus facilitating a second methylation to afford the bismethylated dication **1**.

Scheme 2



The bis(dichloroimidazolium) compound **1** was used as NHC precursor in the synthesis of new Rh and Ir compounds. The reaction of **1** and $[MCl(cod)]_2$ (M = Rh, Ir) in the presence of NEt_3 afforded the corresponding bis(dichloroimidazolylidene) complexes **3** (M = Rh) and **4** (M = Ir) in moderate yield (25−45%) (Scheme 2). The most significant feature of the $^{13}C\{^1H\}$ NMR spectra of **3** and **4** is the signal at δ 182.8 ($^1J_{Rh-C} = 54.1$ Hz, **3**) and 178.1 (**4**) corresponding to the coordinated carbene-carbon atom, in the typical range where other bis-NHC complexes of Rh(I)[7,17,18] and Ir(I)[7] appear. The intensity of the signals of the carbon atoms of the imidazole ring is very low, because of the increase in the T_1 relaxation time upon replacement of hydrogen with chlorine. Reaction of **3** and **4** with carbon monoxide readily afforded the corresponding carbonyl compounds **5** (M = Rh) and **6** (M = Ir), by substitution of the COD ligand by CO. IR spectroscopy shows two strong bands in the carbonyl region, indicating a *cis* configuration. The $^{13}C\{^1H\}$ NMR spectra of **5** and **6** show the two signals due to the two different carbons directly bonded to the metal, doublets in the case of **5** (186.7 ppm, $^1J_{Rh-C} = 57.1$ Hz for Rh−*C*O, and 172.9 ppm, $^1J_{Rh-C} = 46.2$ Hz for $Rh-C_{carbene}$) and singlets in the case of the Ir complex **6** (180.5 ppm for Ir−*C*O; 168.5 ppm for $Ir-C_{carbene}$). All compounds **3**, **4**, **5**, and **6** were also analyzed by electrospray mass spectroscopy and elemental analysis.

Crystal Structure of 3, 5, and 6. Crystals suitable for X-diffraction were obtained by slow diffusion of hexanes into concentrated dichloromethane solutions of **3**, **5**, and **6**. The structure of compound **3** (Figure 1) shows the metal in a pseudo-square-planar geometry. The $Rh-C_{carbene}$ bond distances lie in the range where other bisimidazolylidene complexes of Rh appear [2.026(5), 2.050(5) Å],[10,17,19] thus meaning that the

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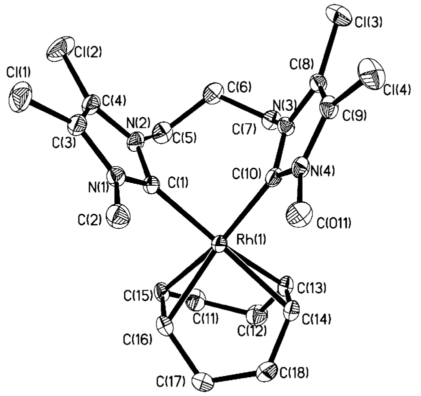


Figure 1. Molecular diagram of **3** with 30% anisotropic displacement ellipsoids. Hydrogen atoms and counterion (PF_6^-) are omitted for clarity. Selected bond distances (Å) and angles (deg): Rh(1)−C(1) 2.050(5), Rh(1)−C(10) 2.026(5), Rh(1)−C(13) 2.212(6), Rh(1)−C(14) 2.198(6), Rh(1)−C(15) 2.212(5), Rh(1)−C(16) 2.227(6), C(10)−Rh(1)−C(1) 83.6(2).

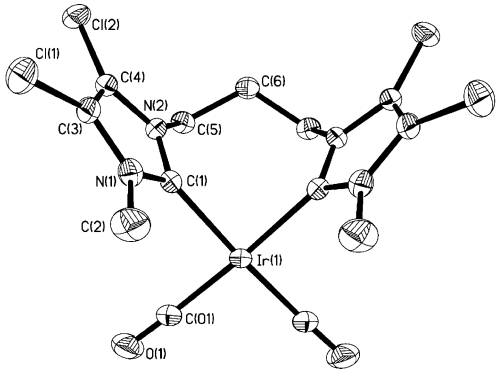
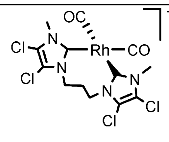
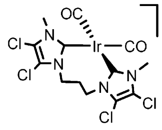
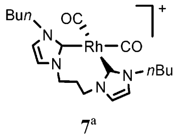
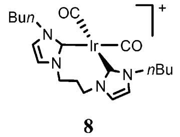
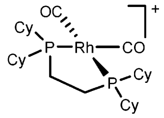
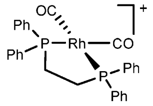


Figure 2. Molecular diagram of **6** with 30% anisotropic displacement ellipsoids. Hydrogen atoms and counterion (PF_6^-) are omitted for clarity. Selected bond distances (Å) and angles (deg): Ir(1)−C(1) 2.078(5), Ir(1)−C(01) 1.901(7), C(01)−O(1) 1.122(8), C(1)−Ir(1)−C(1) 85.7(3).

introduction of the chlorine atoms has little effect on the structural parameters of the molecule. The biscarbene bite angle is 83.6°, at a dihedral angle between the coordination plane of the complex and the NHC ring plane (α) of ca. 85.6°, thus implying a quasi-perpendicular disposition of the imidazolylidene rings with respect to the coordination plane of the molecule. The eight-membered ring containing the metal ion adopts a boat-chair conformation.

The molecular structure of compound **6** is shown in Figure 2. The pseudo-square-planar complex contains two carbonyl ligands in a *cis* disposition and a chelating bis(dichloroimidazolylidene) ligand. The Ir−$C_{carbene}$ bond distance is 2.078(5) Å, in the range of other chelate bisimidazolylidene complexes of Ir reported by us.[20,21] The bisimidazolylidene bite angle is 85.7(3)°, at a dihedral angle (α, defined by the NHC ring plane and the coordination plane of the molecule) of ca. 77.3°. The Ir−CO distance is 1.901(7) Å. The molecular structure of complex **5** was also confirmed by means of X-ray diffraction, but unfortunately the data do not fit the standards for publication (*R* factor too high). The data are available in the Supplementary Information in the form of a CIF file.

Table 1. Carbonyl Stretching Frequencies for $[M(L-L)(CO)_2]^+$ Compounds (measured in CH_2Cl_2)

Entry	Compound	ν(CO) (cm^{-1})	ν_{av}(CO) (cm^{-1})
1	 **5**	2030, 2088	2059
2	 **6**	2011, 2078	2044
3[a]	 **7**[a]	2006, 2075	2040
4	 **8**	1990, 2062	2026
5[b]	 **9**[b]	2027, 2086	2057
6[c]	 **10**[c]	2055, 2100	2078

[a]Data from ref 10. [b] Data from ref 22. [c] Data from refs 23, 24.

IR Spectroscopy Analysis. To obtain a direct comparison of the electronic factors governing our newly obtained ligands and other related nonchlorinated bisimidazolylidene and bisphosphine ligands, we recorded the carbonyl stretching frequencies of compounds **5** and **6** and compared them to other related complexes, as shown in Table 1. The data shown for compounds **7**,[10] **9**,[22] and **10**[23,24] were obtained from the literature, while compound **8** was obtained and characterized in the present work (see Experimental Section).

From the data shown in Table 1, we can see that the introduction of the chlorine substituents in the azole rings has important effects on the electron-donating nature of the ligand. Significant shifts to higher frequencies are observed when we compare the IR spectra of the nonchlorinated carbonyl complexes **7** and **8** with the chlorinated compounds **5** and **6**, thus implying a significant reduction of the electron-donating character of the bidentate ligand in the latter ones. This shift is equally important for both Rh and Ir complexes (ca. 18 cm^{-1}). Comparison to other related bisphosphine complexes[22−24] (entries 5 and 6) shows that the *σ*-donating character of the bis(dichloroimidazolylidene) ligand is similar to that shown by bis(dicyclohexylphosphino)ethane and more *σ*-donating than bis(diphenylphosphino)ethane. This result is important because we believe that the preparation of NHC ligands with electronic

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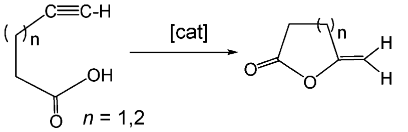
Table 2. Cyclization of 4-Pentynoic Acid and 5-Hexynoic Acid[a]



catalyst	M, 2L	substrate	time (h)	yield (%)
3	Rh, COD	4-pentynoic acid	96	>99
5	Rh, CO		17	>99
4	Ir, COD		144	>99
6	Ir, CO		24	85
3	Rh, COD	5-hexynoic acid	168	8
5	Rh, CO		168	8
4	Ir, COD		168	7
6	Ir, CO		168	15

[a] Reactions performed in acetone-d_6. $T = 50$ °C. 0.5% mol of catalyst. Yields determined by ^{1}H NMR spectroscopy.

properties similar to that shown by phosphines may provide interesting catalytic applications, since we can now use the special steric properties conferred by NHCs (fan shape vs cone angle) without significantly modifying the electronic properties provided by phosphines. The ν(CO) stretching frequencies of **5** and **6** are also higher than those observed for recently described carbonyl bisimidazolylidene-linked cyclophanes of Rh and Ir.[25]

Catalytic Properties. According to the results presented above, we thought that it would be interesting to test the catalytic properties of compounds **3**−**6**, since their electronic properties are substantially different from their analogue NHC nonchlorinated complexes. In recent studies, we pointed out that the catalytic properties of bis-NHC complexes of Rh and Ir are markedly influenced by the length of the linker between the two imidazolylidene rings.[7,10,19] For long biscarbene linkers we observed that the resulting complexes are particularly inert toward oxidation. This is probably the main reason that these complexes are highly inefficient for those catalytic reactions requiring an oxidative addition in any of the steps of the catalytic cycle. Compounds **3**−**6** have a trimethylene group linking the two NHC rings, thus favoring the orientation of the azole rings perpendicular to the coordination plane of the molecule, and hence sterically hindering the *z* axis. The catalytic experiments performed with the carbonyl complexes **7** and **8**, and their cyclooctadiene derivatives trimethylenebis((*N*-methyl)imidazol-2-ylidene)(cyclooctadiene)rhodium(I) hexafluorophosphate and trimethylenebis((*N*-methyl)imidazol-2-ylidene)(cyclooctadiene)-iridium(I) hexafluorophosphate, did not show any catalytic activity in reactions such as hydrosilylation of terminal alkynes and cyclization of acetylenic carboxylic acids, both reactions requiring an oxidative addition step in their catalytic cycles. With this in mind, we decided to test the activity of compounds **3**−**6** in the same reactions, aiming to confirm if the reaction performances were really due to the steric influence of the biscarbene ligand or if its electronic modification would have any effect on the catalytic activity.

(i) Cyclization of 4-Pentynoic Acid and 5-Hexynoic Acid. The reactions were performed in an NMR tube containing 0.6 mL of acetone-d_6, with a catalyst loading of 0.5 mol %. From the data shown in Table 2, we can observe 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.[7,26] From our results, we can conclude that our carbonyl catalysts **5** and **6** showed higher activity than the related cyclooctadienyl compounds **3** and **4**. The rhodium catalysts **3** and **5** show higher activity than the related iridium analogues **4** and **6**. Despite the relatively low efficiency of catalysts **3**−**6**, we consider these results interesting because the activity is clearly enhanced compared to our previously described carbonyl complexes **7** and **8** and their cyclooctadiene derivatives trimethylenebis((*N*-methyl)imidazol-2-ylidene)(cyclooctadiene)rhodium(I) hexafluorophosphate and trimethylenebis((*N*-methyl)-imidazol-2-ylidene)(cyclooctadiene)iridium(I) hexafluorophosphate, thus implying that less electron-donating bis-NHC ligands enhance the catalytic performance of the system for similar topological catalyst compounds.

(ii) Hydrosilylation of 1-Alkynes. Table 3 shows the catalytic results for the hydrosilylation of phenylacetylene and 1-hexyne with $HSiMe_2Ph$ and $HSi(OEt)_3$. The reactions were performed with catalyst loadings of 0.1, 1, and 5 mol %. As seen from the data shown, the rhodium catalysts **3** and **5** are significantly more active than the iridium analogues, **4** and **6**. For the reactions performed with phenylacetylene and $HSi(OEt)_3$ the process was highly selective in the production of the dehydrogenative silylation products (Scheme 3), as observed by the appeareance of the signals due to styrene in the ^{1}HNMR spectra (entries 7, 8, 11, 12, and 16). Although the reaction yields are low, it is important to point out that there is only one report in the literature where this reaction occurs selectively, without the formation of other undesired alkenylsilane products,[27] although there are other examples in which the formation of the dehydrogenative-silylated products is enhanced by using basic metal hydrides as reducing agents.[28] The products resulting from the dehydrogenative silylation are difficult to detect if reactions are followed by ^{1}HNMR spectroscopy, since the products are very easy to miss. The formation of styrene as hydrogen-trapping agent is the clearest indication that this process is occurring. In 1993 Crabtree and co-workers made a detailed study on the process and showed that many classical hydrosilylating catalysts also afforded the products resulting from the dehydrogenative silylation.[29]

The reactions implying the use of $HSiMe_2Ph$ and 1-hexyne showed a clear preference for the hydrosilylated products. Hydrosilylation of phenylacetylene is more favorable than 1-hexyne, and $HSiMe_2Ph$ behaves as a better hydrosilylating agent. The catalytic results shown for complexes **3** and **5** are comparable to our previous results for other rhodium bisimidazolylidene complexes.[6,17] Most of the recent efforts in the study of catalytic hydrosilylation concern the design of new and efficient catalysts, which enable the selective preparation of (*Z*)- and (*E*)-alkenylsilanes.[30,31] For the reactions performed at 60 °C (entries 1−6), our complexes do not seem to show a clear preference for any of the possible hydrosilylated products,

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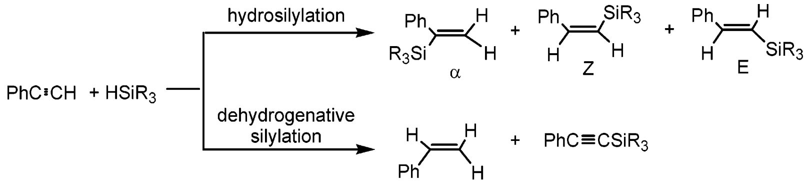
Table 3. Hydrosilylation of Terminal Alkynes[a]

entry	catalyst	RC≡CH	HSiR$_3$	*T* (°C)	% mol cat.	time (h)	*E*/*Z*/α/styrene	yield (%)
1	**3**	PhC≡CH	HSiMe$_2$Ph	60	0.1	24	19/69/10/**2**	>99
2	**4**					28	34/50/15/**1**	45
3	**5**					27	24/64/10/**2**	93
4	**6**					24	50/38/12/**0**	5
5	**3**	*n*BuC≡CH	HSiMe$_2$Ph			72	66/20/14/**0**	50
6	**5**					24	53/0/47/**0**	80
7	**3**	PhC≡CH	HSi(OEt)$_3$			30	0/0/0/**100**	20
8	**5**					24	0/0/0/**100**	25
9	**3**	PhC≡CH	HSiMe$_2$Ph	25	1	150	0/98/2/**0**	>99
10	**5**					24	14/40/6/**40**	58
11	**3**	PhC≡CH	HSi(OEt)$_3$			150	0/0/0/**100**	85
12	**5**					30	0/0/0/**100**	25
13	**3**	*n*BuC≡CH	HSiMe$_2$Ph			150	0/100/0/**0**	41
14	**5**					44	32/42/26/**0**	31
15	**5**	PhC≡CH	HSiMe$_2$Ph	25	5	30	10/26/6/**58**	72
16	**5**		HSi(OEt)$_3$			30	0/0/0/**100**	20

[a] 0.077 mol of alkyne, 0.085 mol of silane. Reactions performed in CDCl$_3$. Yields determined by ^{1}H NMR spectroscopy.

Scheme 3



although the *Z* isomer seems to be preferred in the initial steps of the reaction. For long reaction times, the initial preference for the *Z* isomer is decreased, probably due to a parallel process implying a *E*/*Z* isomerization process, as we have previously reported.[6,17] It has been reported that cationic Rh complexes catalyze the hydrosilylation of alkynes to preferentially give the β-*E*-vinylsilanes, while neutral Rh complexes showed a higher preference to yield the β-*Z* ones.[30,32] Our cationic compounds do not seem to follow this tendency, so the cationic nature of the catalyst should not be considered as a major contributing parameter to control the stereochemistry of the process.

It is important to point out that with this work we did not pursue finding highly effective catalysts for these two well-known reactions, but establishing the influence of the introduction of electron-accepting substituents on the catalytic performances of bis-NHC complexes. In this regard, we have observed that compounds **3**−**6** display a much higher activity than that shown for the nonchlorinated analogues, as we mentioned for the above-described catalytic process.

Conclusions

With this work we have provided evidence of the electronic modification of a chelate bis-NHC ligand by the introduction of two chlorine substituents in the 4 and 5 positions of the imidazolylidene rings. The IR analysis of the carbonyl complexes provides good evidence of the reduction of the σ-donor capability of the new ligand, compared to the nonchlorinated analogue. As seen from the data reported in the literature and summarized in Table 1, the electron-donating capability of the ligand would be close to that shown by bidentate phosphines. This effect has important implications on the catalytic properties of the compounds obtained, these being significantly enhanced when compared to the related nonchlorinated complexes, in reactions such as hydrosilylation of terminal acetylenes and cyclization of acetylenic carboxylic acids. In the absence of significant steric differences between chlorinated and nonchlorinated NHC ligands, we believe that one probable explanation for this enhanced catalytic behavior may lie in the coordination capabilities of the COD ligand. In the nonchlorinated-NHC complexes **7** and **8**, COD must be tightly bound to the metal, mainly due to the high basicity of the bis-NHC ligand, which would afford a high π-basic character to the metal. In complexes **5** and **6**, the lower basicity of the chlorinated-bis-NHC ligand may favor the substitution of the COD ligand, thus providing the required vacant coordination to start the catalytic cycle.

Experimental Section

General Procedures. NMR spectra were recorded on Varian Mercury 300 and Inova 500 MHz spectrometers, with acetone-d_6, CDCl$_3$, and DMSO-d_6 as solvents. 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 using nitrogen as drying and nebulizing gas. The complex trimethylenebis(*N*-*n*-butylimidazol-2-ylidene)(cyclooctadiene)iridium hexafluorophosphate was obtained according to literature procedures;[21] all other reagents are commercially available and were used as received.

Trimethylenebis(4,5-dichloroimidazole). A mixture of 4,5-dichloroimidazole (1.37 g, 10 mmol), KOH (841.6 mg, 15 mmol), 1,3-dibromopropane (507.54 μL, 5 mmol), and TBAB (0.03 mmol/1 mol imidazole, 96.72 mg, 0.3 mmol) was heated in a high-pressure Shlenck at 140 °C overnight without solvent. Then, the product was extracted in CH$_2$Cl$_2$/water. The crude solid was precipitated in CH$_2$Cl$_2$/hexanes. Yield: 90%. Anal. Calcd for C$_9$N$_4$H$_8$Cl$_4$: C, 34.4; H, 2.5; N, 17.8. Found: C, 34.5; H, 3.0; N, 17.8. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.32 (2H, s, NC*H*N), 3.90 (4H, t, $J = 6.99$ Hz, NC*H*$_2$CH$_2$C*H*$_2$N) and 2.24 (2H, q, $J = 6.60$ Hz, NCH$_2$C*H*$_2$-CH$_2$N). ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$): δ 134.34 (N*C*HN), 127.21, 113.35 (Cl-*C*), 43.21 (N*C*H$_2$CH$_2$*C*H$_2$N), 30.55 (NCH$_2$*C*H$_2$-CH$_2$N). Electrospray MS: *m*/*z* 348.9 [M + Cl]$^-$.

Trimethylenebis((*N*-methyl)-4,5-dichloroimidazolium)diiodide, 1. A mixture of trimethylenebis(4,5-dichloroimidazole) (300

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(32) Takeuchi, R.; Nitta, S.; Watanabe, D. *J. Chem. Soc., Chem. Commun.* **1994**, 1777. Takeuchi, R.; Nitta, S.; Watanabe, D. *J. Org. Chem.* **1995**, *60*, 3045. Mori, A.; Takahisa, E.; Kajiro, H.; Hirabayashi, K.; Nishihara, Y.; Hiyama, T. *Chem. Lett.* **1998**, 443.

mg, 0.95 mmol) and iodomethane (200 μL, 3.21 mmol) was refluxed in CH_3CN (10 mL) overnight. The product was filtered and washed in CH_2Cl_2. Yield: 79%. Anal. Calcd for $C_{11}Cl_4N_4H_{14}I_2$: C, 22.1; H, 2.3; N, 9.4. Found: C, 22.3; H, 2.3; N, 9.3. ^{1}H NMR (300 MHz, DMSO-d_6): δ 9.50 (2H, s, NC*H*N), 4.38 (4H, t, J = 7.20 Hz, NCH_2CH_2CH_2N), 3.85 (6H, s, CH_3) and 2.36 (2H, q, J = 6.90 Hz, NCH_2CH_2CH_2N). ^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6): δ 137.22 (N*C*HN), 120.31, 119.02 (Cl-*C*), 45.78 (N*C*H_2CH_2*C*H_2N), 35.92 (NCH_2*C*H_2CH_2N), and 28.00 (N*C*H_3). Electrospray MS: m/z 329.1 $[M - CH_3]^+$, 379.1 $[M + Cl]^+$, 471.0 $[M + I]^+$.

Methylenebis(4,5-dichloroimidazole). A mixture of 4,5-dichloroimidazole (1.37 g, 10 mmol), KOH (841.6 mg, 15 mmol), CH_2I_2 (403 μL, 5 mmol), and TBAB (0.03 mmol/1 mol imidazole, 96.72 mg, 0.3 mmol) was heated in a high-pressure Shlenck at 110 °C overnight without solvent. Then, the product was extracted in CH_2Cl_2. Yield: 70%. Anal. Calcd for $C_7N_4H_4Cl_4$: C, 29.4; H, 1.4; N, 19.6. Found: C, 29.3; H, 1.5; N, 19.6. ^{1}H NMR (300 MHz, DMSO-d_6): δ 8.17 (2H, s, NC*H*N) and 6.37 (2H, s, NCH_2N). ^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6): δ 137.96 (N*C*HN), 126.31, 112.91 (Cl-*C*), and 54.46 (N*C*H_2N). Electrospray MS: m/z 320.9 $[M + Cl]^-$.

Methylene[(4,5-dichloroimidazole)((*N*-methyl)-4,5-dichloroimidazolium)] Iodide, 2. A mixture of methylenebis(4,5-dichloroimidazole) (300 mg, 1.05 mmol) and iodomethane (200 μL, 3.21 mmol) was refluxed in CH_3CN (10 mL) overnight. The volatile components were removed under vacuum, and the product was crystallized and washed with CH_2Cl_2 to give **2** as a pale orange solid. Yield: 42%. Anal. Calcd for $C_8Cl_4N_4H_7I$: C, 22.4; H, 1.6; N, 13.0. Found: C, 22.5; H, 1.7; N, 13.1. ^{1}H NMR (500 MHz, DMSO-d_6): δ 9.77 (1H, s, NC*H*N), 8.23 (1H, s, NC*H*N), 6.64 (2H, s, NCH_2N), 3.90 (3H, s, CH_3). ^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6): δ 138.39, 138.35 (N*C*HN), 126.48, 121.23, 118.76, 113.71 (Cl-*C*), 55.90 (N*C*H_2N), 36.35 (*C*H_3). Electrospray MS: m/z 301.0 $[M^+]$.

Trimethylenebis((*N*-methyl)-4,5-dichloroimidazol-2-ylidene)-(cyclooctadiene)rhodium(I) Hexafluorophosphate, 3. A mixture of $[RhCl(cod)]_2$ (100 mg, 0.20 mmol), **1** (200 mg, 0.40 mmol), and NEt_3 (113 μL, 0.81 mmol) was heated at 60 °C in CH_3CN for 3 h. The volatile components were removed under vacuum, and the crude solid was purified by column chromatography. Elution with CH_2Cl_2/acetone (9:1) adding KPF_6 afforded **3** as yellow solid, which was then slowly recystallized from acetone/hexanes. Yield: 25%. Anal. Calcd for $C_{19}N_4H_{24}Cl_4RhPF_6$: C, 32.7; H, 3.5; N, 8.0. Found: C, 32.7; H, 3.3; N, 7.8. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.05 (2H, dd, J = 14.74 and 11.49 Hz, NC*H*HCH$_2$C*H*HN), 4.58 (4H, m, C*H* $_{COD}$), 4.51 (2H, dd, J = 15.24 and 6.00 Hz, NCH*H*CH$_2$CH*H*N), 3.96 (6H, s, CH_3), 2.59 (5H, m; 1H, NCH$_2$C*H*HCH$_2$N, 4H, CH_2 $_{COD}$), 2.29 (4H, m, CH_2 $_{COD}$), 1.66 (1H, m, NCH$_2$CH*H*CH$_2$N). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 182.81 (d, Rh-*C*, $^1J_{Rh-C}$ = 54.10 Hz), 117.49, 117.20 (Cl-*C*), 92.78 (d, $^1J_{Rh-C}$ = 7.77 Hz, *C*H $_{COD}$), 91.43 (d, $^1J_{Rh-C}$ = 7.39 Hz, *C*H $_{COD}$), 51.35 (N*C*H$_2$CH$_2$*C*H$_2$N), 37.58 (NCH$_2$*C*H$_2$CH$_2$N), 30.89 (*C*H$_3$), 30.77, 30.60 (*C*H$_2$ $_{COD}$). Electrospray MS: m/z 553.2 $[M^+]$.

Trimethylenebis((*N*-methyl)-4,5-dichloroimidazol-2-ylidene)-(cyclooctadiene)iridium(I) Hexafluorophosphate, 4. A mixture of $[IrCl(cod)]_2$ (100 mg, 0.15 mmol), **1** (150 mg, 0.25 mmol), and NEt_3 (105 μL, 0.75 mmol) was heated at 60 °C in CH_3CN for 3 h. The volatile components were removed under vacuum, and the crude solid was purified by column chromatography. Elution with CH_2Cl_2/acetone (6:4) adding KPF_6 afforded **4** as an orange solid. The product was precipitated with acetone/hexanes (Yield: 44%). Anal. Calcd for $C_{19}N_4H_{24}Cl_4IrPF_6$: C, 28.7; H, 3.1; N, 7.1. Found: C, 28.3; H, 3.0; N, 6.8. ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.81 (2H, dd, J = 15.24 and 10.99 Hz, NC*H*HCH$_2$C*H*HN), 4.51 (2H, dd, J = 15.24 and 6.49 Hz, NCH*H*CH$_2$CH*H*N), 4.19 (4H, m, C*H*$_{COD}$), 3.87 (6H, s, CH_3), 2.65 (1H, m, NCH$_2$C*H*HCH$_2$N), 2.43 (4H, CH_2 $_{COD}$), 2.15 (2H, m, C*H*$_2$ $_{COD}$), 2.06 (2H, m, C*H*$_2$ $_{COD}$), 1.73 (1H, m, NCH$_2$CH*H*CH$_2$N). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 178.06 (Ir-*C*), 117.53, 117.03 (Cl-*C*), 80.46, 79.12 (*C*H $_{COD}$), 50.62 (N*C*H$_2$CH$_2$*C*H$_2$N), 36.80 (NCH$_2$*C*H$_2$CH$_2$N), 31.45 (*C*H$_3$), and 31.21 (*C*H$_2$ $_{COD}$). Electrospray MS: m/z 640.7 $[M]^+$.

Synthesis of Carbonyl Derivatives. General Procedure. CO gas (1 atm, 10 mL/min) was passed through a solution of **3**, **4**, or trimethylenebis(*N*-*n*-butylimidazol-2-ylidene)(cyclooctadiene)iridium hexafluorophosphate (100 mg) in dichloromethane (15 mL) for 30 min at 0 °C. The solution was concentrated (ca. 5 mL) under reduced pressure, and hexanes were added to obtain dicarbonyl compounds **5**, **6**, and **8** in yields of 55−75%. Analytically pure samples were obtained by slow recrystallization of dichloromethane/hexanes mixtures.

Trimethylenebis((*N*-methyl)-4,5-dichloroimidazol-2-ylidene)-dicarbonylrhodium Hexafluorophosphate, 5. Yield: 54%. Anal. Calcd for $C_{13}N_4H_{12}Cl_4RhO_2PF_6$: C, 24.2; H, 1.9; N, 8.7. Found: C, 24.0; H, 2.0; N, 8.5. ^{1}H NMR (300 MHz, acetone-d_6): δ 4.89 (2H, dd, J = 15.30 and 10.80 Hz, NC*H*HCH$_2$C*H*HN), 4.63 (2H, dd, J = 15.30 and 5.49, NCH*H*CH$_2$CH*H*N), 4.00 (6H, s, C*H*$_3$), 3.13 (1H, m, NCH$_2$C*H*HCH$_2$N) and 2.52 (1H, m, NCH$_2$CH*H*CH$_2$N). ^{13}C{^{1}H} NMR (125 MHz, acetone-d_6): δ 186.75 (d, $^1J_{Rh-C}$ = 57.06 Hz, Rh-*C*O), 172.90 (d, $^1J_{Rh-C}$ = 46.25 Hz, Rh-*C*), 118.67, 118.08 (Cl-*C*), 51.67 (N*C*H$_2$CH$_2$*C*H$_2$N), 49.15 (NCH$_2$*C*H$_2$CH$_2$N), 37.40 (*C*H$_3$). IR (CH_2Cl_2): $\nu_{C=O}$ 2029, 2088 cm^{-1}. Electrospray MS: m/z 501.1 $[M^+]$, 445.2 $[M^+ - 2CO]$.

Trimethylenebis((*N*-methyl)-4,5-dichloroimidazol-2-ylidene)-dicarbonyliridium Hexafluorophosphate, 6. Yield: 64%. Anal. Calcd for $C_{13}N_4H_{12}Cl_4IrO_2PF_6$: C, 21.2; H, 1.6; N, 7.6. Found: C, 21.0; H, 1.8; N, 7.5. ^{1}H NMR (300 MHz, acetone-d_6): δ 4.62 (2H, m, NC*H*HCH$_2$C*H*HN), 4.51 (2H, dd, J = 14.85 and 6.60 Hz, NCH*H*CH$_2$CH*H*N), 3.84 (6H, s, C*H*$_3$), 2.43 (1H, m, NCH$_2$C*H*HCH$_2$N), 1.84 (1H, m, NCH$_2$CH*H*CH$_2$N). ^{13}C{^{1}H} NMR (75 MHz, acetone-d_6): δ 180.51 (Ir-*C*O), 168.48 (Ir-*C*), 118.86, 118.27 (Cl-*C*), 54.21 (N*C*H$_2$CH$_2$*C*H$_2$N), 51.57 (NCH$_2$*C*H$_2$CH$_2$N), and 37.31 (*C*H$_3$). IR (CH_2Cl_2): $\nu_{C=O}$ 2011, 2078 cm^{-1}. Electrospray MS: m/z 588.7 $[M]^+$.

Trimethylenebis(*N*-*n*-butylimidazol-2-ylidene)dicarbonyliridium Hexafluorophosphate, 8. Yield: 77%. Anal. Calcd for $C_{19}N_4H_{28}Cl_4IrO_2PF_6$: C, 33.5; H, 4.1; N, 8.2. Found: C, 33.6; H, 4.2; N, 8.3. ^{1}H NMR (300 MHz, acetone-d_6): δ 7.44 (2H, s, CH$_{imid}$), 7.46 (2H, s, CH$_{imid}$), 4.82 (2H, m, NC*H*HCH$_2$C*H*HN), 4.53 (4H, m, NC*H*$_2$CH$_2$CH$_2$CH$_3$), 4.18 (2H, m, NCH*H*CH$_2$CH*H*N), 2.52 (1H, m, NCH$_2$CH*H*CH$_2$N), 2.06 (1H, m, NCH$_2$CH*H*CH$_2$N), 1.86 (4H, m, NCH$_2$C*H*$_2$CH$_2$CH$_3$), 1.45 (4H, m, NCH$_2$CH$_2$C*H*$_2$CH$_3$), 0.98 (6H, t, J = 7.2 Hz, NCH$_2$CH$_2$CH$_2$C*H*$_3$). ^{13}C{^{1}H} NMR (75 MHz, acetone-d_6): δ 182.27 (Ir-*C*), 167.58 (Ir-*C*O), 124.36, 122.39 (N*C*H=*C*HN), 52.88 (N*C*H$_2$CH$_2$*C*H$_2$N), 51.31 (N*C*H$_2$CH$_2$CH$_2$CH$_3$), 32.60 (NCH$_2$*C*H$_2$CH$_2$CH$_3$), 31.87 (NCH$_2$*C*H$_2$CH$_2$N), 19.69 (2 x NCH$_2$CH$_2$*C*H$_2$CH$_3$), and 13.23 (NCH$_2$CH$_2$CH$_2$*C*H$_3$). IR (CH_2Cl_2): $\nu_{C=O}$ 1990, 2062 cm^{-1}. Electrospray MS: m/z 537 $[M]^+$.

X-ray Diffraction Studies. Crystals suitable for study were obtained by slow diffusion of hexanes into concentrated dichloromethane solution of the complexes. Single crystals of **3**, **5**, and **6** were mounted on a glass fiber in a random orientation. Crystal data are summarized in Table 4. Data collection was performed at room temperature on a Siemens Smart CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 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 structures were solved by direct methods with the aid of successive difference Fourier maps and were refined using the SHELXTL 6.1 software package.[33] 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

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[33] Sheldrick, G. M. *SHELXTL, version 6.1*; Bruker AXS, Inc.: Madison, WI, 2000.

Table 4. Crystallographic Data

	3·CH_2Cl_2	**6**
empirical formula	$C_{20}H_{26}Cl_6F_6N_4PRh$	$C_{13}H_{12}Cl_4F_6IrN_4O_2P$
fw	783.03	735.24
T (K)	273(2)	273(2)
wavelength (Å)	0.71073	0.71073
cryst syst	monoclinic	monoclinic
space group	*P*2(1)/*c*	*P*2(1)/*m*
a (Å)	9.8933(9)	8.0898(5)
b (Å)	22.248(2)	15.8913(10)
c (Å)	13.1699(12)	8.9124(5)
α (deg)	90.00	90.00
β (deg)	95.590(2)	104.8820(10)
γ (deg)	90.00	90.00
V $(Å)^3$	2885.0(5)	1107.32(12)
Z	4	2
density (calcd) (Mg/m^3)	1.803	2.205
absorp coeff (mm^{-1})	1.262	6.652
no. of reflns collected	22 550	8929
goodness-of-fit on F^2	1.029	1.117
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0659	R1 = 0.0389
	wR2 = 0.1766	wR2 = 0.1059

refinement are given in Table 4. The diffraction frames were integrated using the SAINT package and corrected for absorption with SADABS.

Hydrosilylation of 1-Alkynes and Olefins with Silanes. General Procedure. A mixture of *n*BuC≡CH or PhC≡CH (0.077 mmol), silane [$HSi(OEt)_3$ or $HSiMe_2Ph$, 0.085 mmol], and a catalytic amount of **3**, **4**, **5**, or **6** (catalyst loadings of 0.1, 1, and 5 mol %) was dissolved in $CDCl_3$ (2 mL). The mixture was kept at room temperature or 60 °C by immersion in a hot oil bath. The progress of the reaction was monitored by ^1H NMR spectroscopy, according to the data of the products obtained from the literature.[29]

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**, **4**, **5**, or **6** (0,5 mol %) were dissolved in acetone-d_6 (0.6 mL). The mixture was kept at 50 °C by immersion in a temperature-controlled oil bath. The progress of the reaction was monitored by ^1H NMR spectroscopy, according to the data of the products from the literature.[26]

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Supporting Information Available: Crystallographic data of compounds **3**, **5**, and **6** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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