Determination of N-Heterocyclic Carbene (NHC) Steric and Electronic Parameters using the [(NHC)Ir(CO)$_2$Cl] System

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Complexes of iridium bearing NHC (NHC = N-heterocyclic carbene) ligands were synthesized and fully characterized. The series [(NHC)Ir(cod)Cl] were obtained by simple cleavage of [Ir(cod)Cl]$_2$. The [(NHC)Ir(cod)Cl] complexes were reacted with excess carbon monoxide, leading to [(NHC)Ir(CO)$_2$Cl]. The infrared carbonyl stretching frequencies of these were recorded to quantify the electronic parameter of NHC ligands. X-ray diffraction study results allow for determination of NHC steric parameters within this series. These data allow for comparison with other ligand families.

Introduction

Since the first report on N-heterocyclic carbenes (NHCs) by Wanzlick[1] in 1962 and the following seminal research[2,3] describing metal−NHC complexes, NHCs have attained a special status in organometallic chemistry.[4] Subsequent to the isolation and crystallographic characterization of a stable free NHC by Arduengo et al.[5] in the 1990s, NHC−transition metal complexes have attracted significant attention as homogeneous catalysts. First reserved to a limited number of practitioners in the area, the field of TM−NHC catalysis has experienced rapid growth with remarkable achievements in ruthenium-based olefin metathesis,[6] hydrosilylation,[7] hydrogenation,[8] and isomerization reactions.[9] Palladium-catalyzed C−C[10] and C−N[11] coupling reactions have also benefited from the use of NHCs as supporting ligands. Structures of the most frequently encountered NHCs are shown in Figure 1.

Initially considered as simple tertiary phosphine mimics in organometallic chemistry,[12] there is increasing experimental evidence that NHC−metal catalysts surpass their phosphine-based counterparts in both activity and scope. Among the advantages associated with replacing a tertiary phosphine with a NHC are (1) the reduced need for excess ligand in a catalytic reaction due to the stronger NHC binding to the TM compared to PR_3 ligands, (2) improved air and moisture stability of TM−NHC complexes compared to metal−phosphine analogues, stemming from the tendency for the phosphine to frequently oxidize in air, and (3) the remarkable activity in catalysis, generally attributed to the unique combination of strong σ-donor, poor π-acceptor, and steric properties of NHCs. Interestingly, the properties of tertiary phosphine ligands were first characterized in terms of electronic effects, until Tolman[13] reported the importance of steric factors. Contrary to tertiary phosphines, studies on NHC ligands have focused principally on steric properties, because of the analogy with phosphines and/or the possible formation of dimeric species. A comprehensive study

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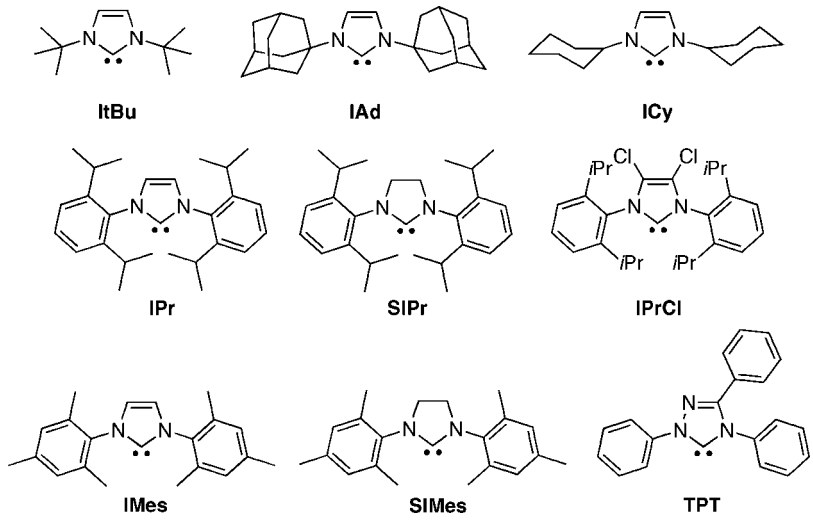

Figure 1. Unsaturated and saturated NHCs used in this work.

of the stereoelectronic parameters associated with NHCs[14] appears vital and is fundamental to understand the factors governing their reactivity, as well as necessary for the development of ever more active NHC-containing catalytic systems.

Our group has made use of the [(NHC)Ni(CO)$_3$] system (in an analogous manner to Tolman) to describe steric and electronic properties of the most widely employed NHC ligands.[15] According to Tolman,[13] electronic and steric effects are intimately related and difficult to separate. A practical and useful separation can be made through the steric parameter (θ) and the electronic parameter (ν). The θ parameter represents the ligand cone angle where space occupation about a static metal−phosphorus (or central ligand atom) bond is quantified. The measure of electronic effects ν can be obtained using the fundamental CO stretching frequency A_1 of [(L)Ni(CO)$_3$] since the ligand L does not influence ν by crowding the Ni(CO)$_3$ moiety, the square-planar structure being optimum in this regard. Notwithstanding the handling problem of the extremely toxic [Ni(CO)$_4$], this system did not allow for a complete comparison of commonly used NHCs. The use of the bulkiest NHCs, I^{t}Bu and IAd, in an exchange reaction with Ni(CO)$_4$ led to the formation of very unusual three-coordinate [(NHC)Ni(CO)$_2$] complexes.[16] We believe the reasons behind the stabilization of such coordinatively unsaturated organometallic species are steric in nature. In order to place all commonly encountered NHC ligands on the same stereoelectronic scale, we began a search for a more universal organometallic system enabling the synthesis of isostructural complexes with NHC ligands.

Results and Discussion

Among the different carbonyl-containing transition metal systems that could be employed as standards for the present study and with the aim to place every NHC on a unique scale, [(L)Rh(CO)$_2$Cl][17] and [(L)M(CO)$_5$], with M = Cr, Mo, or W,[18] were considered. In the end, the system found to be the most general is the [(L)Ir(CO)$_2$Cl] series.[19] Crabtree and co-workers reported on the use of this [(L)Ir(CO)$_2$Cl] system to compare the electronic donating property of two NHC ligands that were developed in the Yale laboratory.[20] Interestingly, Crabtree noted that by correlating the average infrared stretching frequency of the Ir system and the A_1 stretch from [(L)Ni(CO)$_3$], a linear correlation could be obtained for a series of phosphines where data was available for both systems. By extrapolation, it was possible to evaluate the Tolman electronic parameter (TEP, θ)[13,21] of these new NHCs, a process that normally required the well-established Ni−carbonyl system. As a consequence of these observations, the [(L)Ni(CO)$_3$] system was set aside and the Ir system considered. Crabtree followed his initial observation with a study in which the [(L)Ir(CO)$_2$Cl] system was used to explore the ligand-donating properties of other NHCs.[22] Glorius then reported on the use of this same Ir system to determine the donating ability of a series of bisoxazoline-derived NHCs that have been used effectively in the Suzuki−Miyaura reaction.[23] Herrmann has also used [(L)Ir(CO)$_2$Cl] in a study of Ir− and Rh−NHC complexes used as catalysts in borylation reactions.[24] In this report, Herrmann isolated two [(NHC)Ir(CO)$_2$Cl] complexes, one of which contained an ICy ligand. Unfortunately, to the best of our knowledge, the detailed

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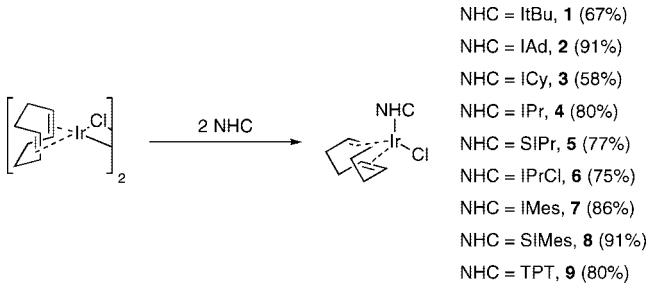
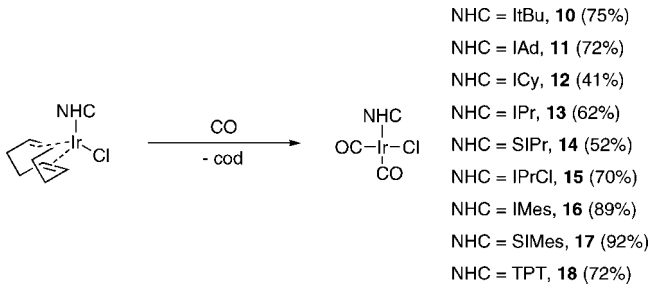
Scheme 1. Synthesis of [(NHC)Ir(cod)Cl] Complexes



Scheme 2. Synthesis of [(NHC)Ir(CO)$_2$Cl] Complexes



correlation between the TEP and the CO stretching frequency of [(NHC)Ir(CO)$_2$Cl] complexes has not been demonstrated so far for various NHCs.[25]

The overall synthetic strategy devised to isolate the complexes of interest involves a simple two-step approach shown in Schemes 1 and 2. The first step involves the coordination of the NHC to the iridium center by simple cleavage of [Ir(cod)Cl]$_2$ (cod = cyclooctadiene). The second step is the displacement of the cyclooctadiene ligand by carbon monoxide. Ligands and yields for each reaction are presented below.

Synthesis of [(NHC)Ir(cod)Cl] Complexes. The [(NHC)Ir-(cod)Cl] complexes were synthesized in moderate to excellent yields using the free carbene in slight excess and the dimer [Ir(cod)Cl]$_2$ (Scheme 1). To ensure the formation of [(ICy)Ir-(cod)Cl], **3**, a substoichiometric amount of free ICy was required. When this reaction was carried out using an excess of ICy, a byproduct was formed and identified as [(ICy)$_2$ Ir(cod)]$^+$Cl$^-$. We found it interesting that only ICy showed this unique reaction of binding two NHC onto the Ir−cod system with associated displacement of the chlorine to the outer sphere.

The ^{1}H NMR spectra of complexes **1–4**, **7**, and **9** with unsaturated NHC ligands show a single low-field resonance around 7 ppm corresponding to the imidazole protons, while the ^{1}H NMR spectra of complexes **5** and **8** with saturated NHC backbones have resonances at 4 ppm for these imidazole protons. ^{13}C NMR spectra of the unsaturated complexes have a characteristic resonance for the carbonic carbon around 180 ppm, while the carbenic carbon resonance for the saturated complex is found at lower field, around 210 ppm. Single-crystal X-ray diffraction experiments were carried out to unambiguously determine the atom connectivity, with the exception of complexes **6** and **9**, where all attempts to obtain suitable crystals failed.[26]

Synthesis of [(NHC)Ir(CO)$_2$Cl] Complexes. Dissolving the [(NHC)Ir(cod)Cl] complexes in dichloromethane and bubbling carbon monoxide through the solution results in the clean formation of the corresponding [(NHC)Ir(CO)$_2$Cl] in moderate to good isolated yield. While ligand exchange was straightforward for complexes **10** and **12–18**, the synthesis of [(IAd)Ir(CO)$_2$Cl] (**11**) required high pressures of CO. The high-pressure cell was fitted with an IR probe in order to obtain *in situ* reaction data. As shown in Figure 2, during the first 75 min of reaction, there is a general increase in all bands of the infrared spectra as [(IAd)Ir(cod)Cl] undergoes carbonylation. Two intermediates of the ligand replacement reactions were detected. The bands due to the first intermediate (**Int-1**, 2025 cm^{-1}) grow in initially, as well as bands due to a second intermediate (**Int-2**, 1956 cm^{-1}) and also bands due to the final product *cis*-[(IAd)Ir(CO)$_2$Cl] (*cis* refers to the position of CO ligands) (2063 and 2048 cm^{-1}). Spectra recorded after overnight reaction times showed the complete disappearance of **Int-1**; however a reaction time of over 6 days at 20 °C and 34 atm CO was required to completely convert **Int-2** into the final product.

The very slow nature of the carbonylation of **11** was surprising. The most common mechanism of ligand substitution of square-planer d^8 complexes involves associative displacement in which the incoming ligand typically approaches along the *z* axis. As shown in the crystal structure, the approach along that axis appears to be blocked by the pendant adamantyl groups to a greater extent than in the other complexes shown. The identity of the two intermediates present in this reaction remains unknown. The time course of the reaction (Figure 3) is consistent with a mechanism in which [(IAd)Ir(cod)Cl] (**11**) is converted into **Int-1** and in which **Int-1** is converted to a mixture of **Int-2** and product. The conversion of **Int-2** to product is much slower than initial formation of **Int-1**. Examination of the band near 1605 cm^{-1} due to free 1,5-cyclooctadiene shows that following the first day of reaction there is no further buildup of free cod. One mechanism consistent with these observations is shown in eqs 1–3.

$$[(\text{lAd})\text{lr}(\text{cod})\text{Cl}] + \text{CO} \rightarrow [(\text{lAd})\text{lr}(\text{cod})(\text{CO})]^+\text{Cl}^- \quad (1)$$

$$[(\text{lAd})\text{lr}(\text{cod})\text{CO}]^+\text{Cl}^- + \text{CO} \rightarrow \textit{cis}\text{-}[(\text{lAd})\text{lr}(\text{CO})_2\text{Cl}] + \textit{trans}\text{-}[(\text{lAd})\text{lr}(\text{CO})_2\text{Cl}] \quad (2)$$

$$\textit{trans}\text{-}[(\text{lAd})\text{lr}(\text{CO})_2\text{Cl}] \rightarrow \textit{cis}\text{-}[(\text{lAd})\text{lr}(\text{CO})_2\text{Cl}] \quad (3)$$

In this postulated mechanism, **Int-1** is formed in step 1 in a pressure-dependent equilibrium. It reacts further with CO in step 2 to produce both product and a second intermediate *trans*-[(IAd)Ir(CO)$_2$Cl] (which would have only one CO band from symmetry). Step 3 would correspond to slow *trans–cis* isomerization to produce cleanly the final product. While this appears consistent with our observations, it is speculative. The goal of this work was primarily synthesis of the desired *cis*-[(IAd)Ir(CO)$_2$Cl]. The difficulty encountered in this preparation is due to the steric strain in **11** that may also carry over to a different mechanism of replacement in this system than the usual smooth associative substitution typically seen in similar systems. Additional mechanistic work in this area may be called for to understand more fully the interesting slow conversion of **3** into [(ICy)Ir(CO)$_2$Cl], **12**.

The structures of [(NHC)Ir(CO)$_2$Cl] complexes **10**−**14**, **16**, and **17** were unambiguously determined by single-crystal X-ray diffraction studies. Unfortunately, for **15** and the triazolylidene-containing complex **18**, a suitable single crystal could not been obtained. Ball-and-stick representations are shown in Figure 4. Similarly to the cod-containing complexes, the ^{1}H NMR data for the complexes with unsaturated NHCs show resonances around 7 ppm for the imidazole protons and 4 ppm for the

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(26) For further details, see the Supporting Information.

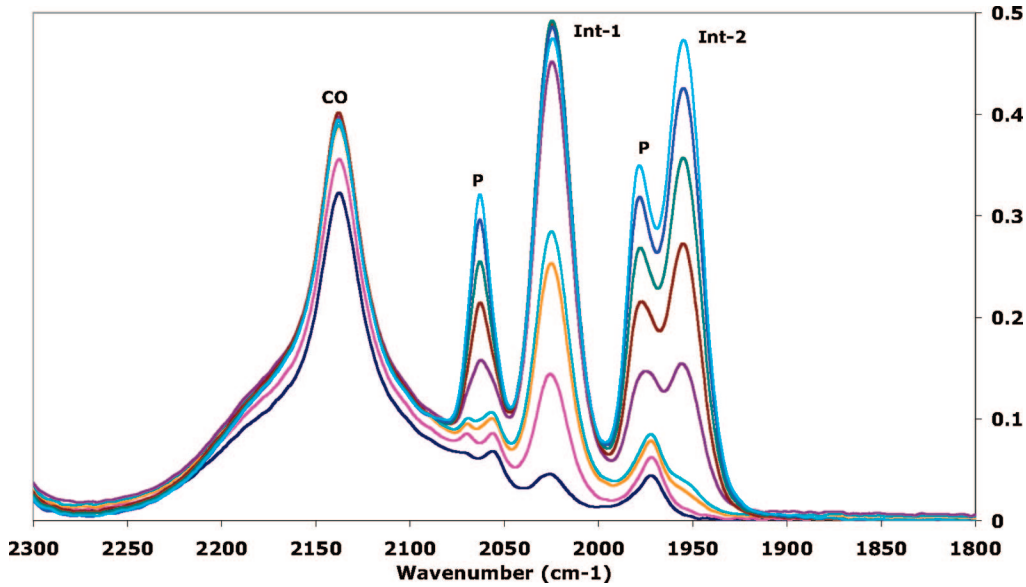

Figure 2. *In situ* monitoring of [(IAd)Ir(CO)$_2$Cl] (**11**) formation at 500 psi of CO during the first 75 min.

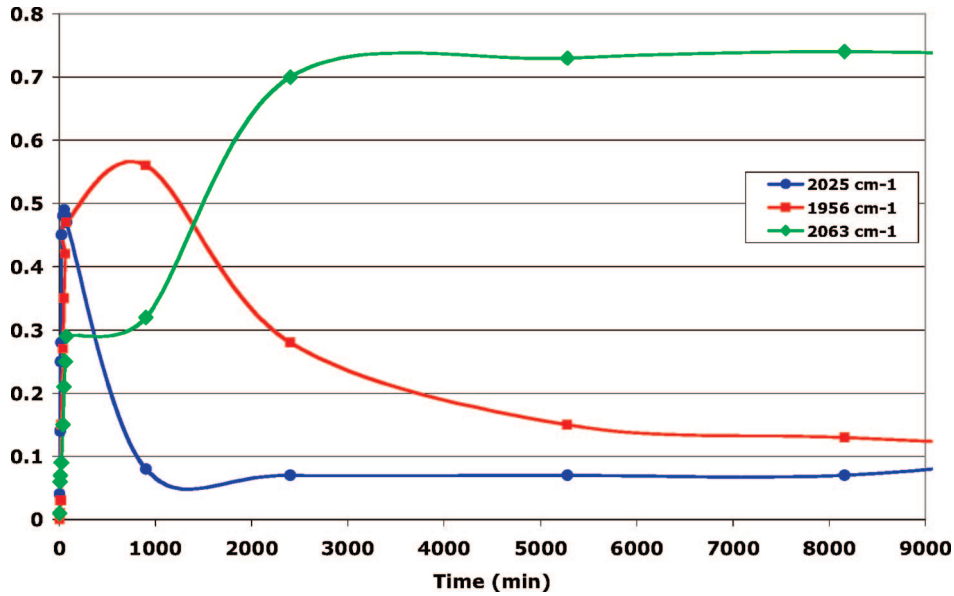

Figure 3. Time course of reaction of [(IAd)Ir(cod)Cl] with CO showing the formation and/or disappearance of intermediate species and product.

imidazole protons on complexes bearing saturated NHCs. Of note, for **15** bearing the NHC = IPrCl, this characteristic signal could not be employed, but the other signals allow for structure confirmation. The ^{13}C NMR shows another similar pattern with the carbene carbon resonance around 180 ppm for complexes **10**−**13**, **15**, and **16** as well as for the triazolylidene-containing **18**, while complexes **17** and **19** have lower field resonances (201.9 and 204.9 ppm, respectively). All complexes show the expected square-planar geometry around the metal center with bond angles between 86.5° and 96.1°. Selected bond lengths and angles are shown respectively in Tables 1 and 2. The Ir−NHC distances are in the range 2.07–2.12 Å and suggest *exclusive* σ-bond characteristics.[27]

Infrared Spectroscopy. In order to gain insight into the relative electronic donor ability of the NHCs, and to then be able to compare this class of ligands to commonly used tertiary phosphines, the carbonyl stretching frequencies of compounds **10**–**18** were recorded (Table 3). Tolman used the A_1 stretching frequency of the Ni−carbonyl system as the meter to quantify the donor properties of the tertiary phosphines. This has subsequently been called the Tolman electronic parameter (TEP).[13] We examined the correlation between the [(L)Ir(CO)$_2$Cl] and the TEP (Figure 5). The phosphine data used are literature values.[28] Upon examination of the data, we found it necessary to take the average values of the two carbonyl stretching frequencies as first presented by Crabtree.[20] The experimental values obtained for five NHC−containing systems support that the TEP/ν_{CO} [(L)Ir(CO)$_2$Cl] relationship for tertiary phosphines can be extended to NHC ligands. Moreover, these additional values allow to correct the linear regression equation initially described by Crabtree, since the present correlation

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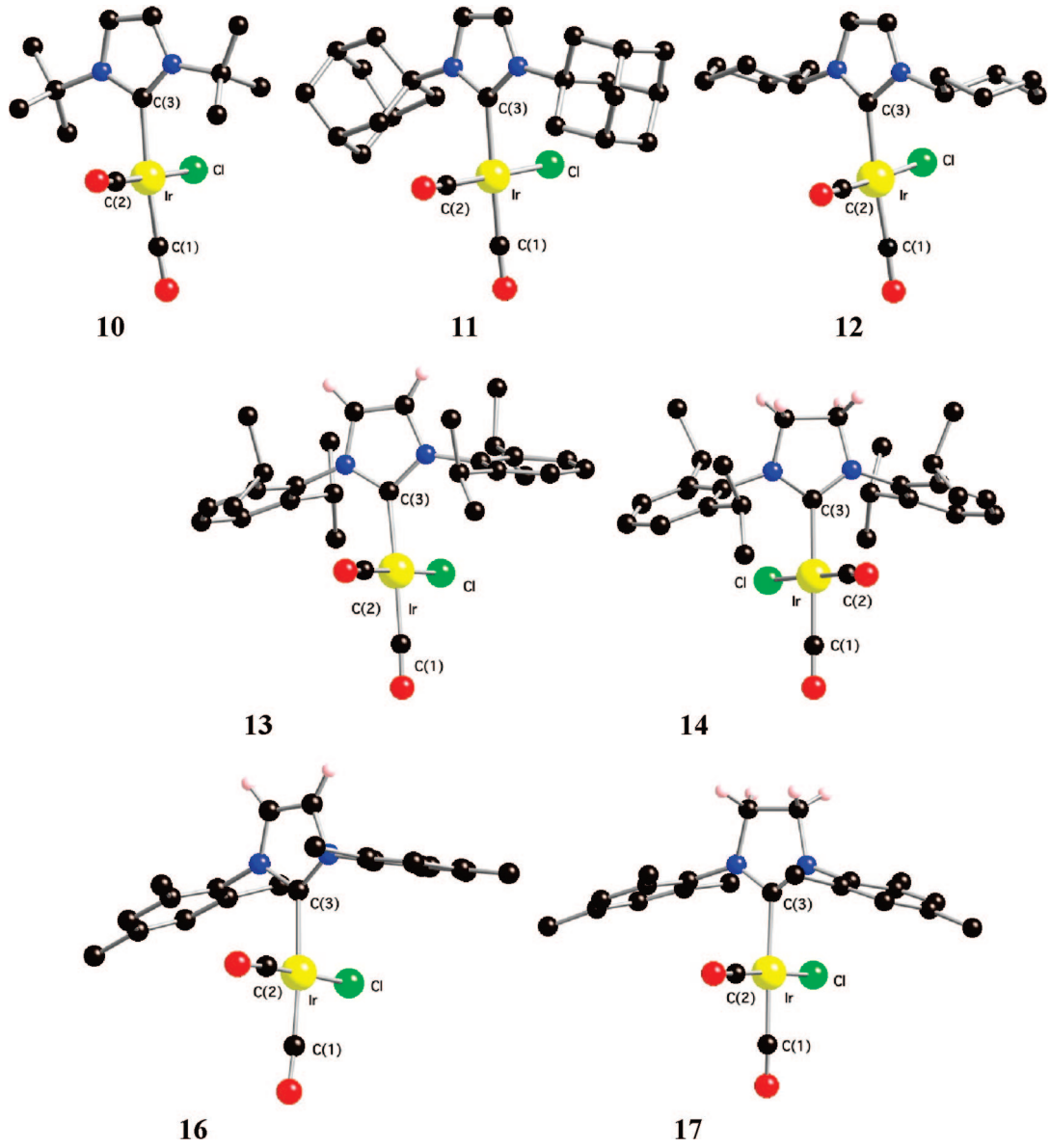

Figure 4. Ball-and-stick representation of [(NHC)Ir(CO)$_2$Cl] complexes. Most hydrogen atoms are omitted for clarity.

Table 1. Selected Bond Lengths (Å) for [(NHC)Ir(CO)$_2$Cl] Complexes

complex	Ir−C^{NHC}	Ir−Cl	Ir−C$^{cis\text{-}CO a}$	Ir−C$^{trans\text{-}CO a}$
[(ItBu)Ir(CO)$_2$Cl] 10	2.114(5)	2.435(3)	1.813(11)	1.873(6)
[(IAd)Ir(CO)$_2$Cl] 11	2.102(7)	2.377(3)	1.869(9)	1.958(10)
[(ICy)Ir(CO)$_2$Cl] 12	2.078(3)	2.3281(13)	1.611(6)	1.847(6)
[(IPr)Ir(CO)$_2$Cl] 13	2.079(2)	2.3426(8)	1.857(4)	1.886(3)
[(SIPr)Ir(CO)$_2$Cl] 14	2.071(4)	2.2933(17)	1.883(5)	1.959(4)
[(IMes)Ir(CO)$_2$Cl] 16	2.108(12)	2.331(4)	1.65(2)	1.86(2)
[(SIMes)Ir(CO)$_2$Cl] 17	2.121(14)	2.367(5)	1.72(2)	1.915(19)

[a] *cis* and *trans* are relative to the NHC.

coefficient was found to be appreciably higher ($R^2 = 0.971$). Thus, we used the new equation TEP (cm^{-1}) = 0.847[ν_{CO}(average)] + 336 cm^{-1} to calculate the TEP values for IAd, ItBu, IPrCl, and TPT (Table 3). We believe that, in using this equation, it is quite feasible to use these organometallic systems almost interchangeably when necessary.

By examining the carbonyl stretching frequencies of the NHC−Ir complexes in this study (Table 3 and Figure 5), we observe an important difference between NHCs and tertiary phosphines. With the exception of special NHCs such as IPrCl and TPT, the most strongly donating phosphine (PCy$_3$) is much weaker than the weakest of the NHCs (SIPr), and the gap is significant (ca. 4 cm^{-1}). Contrary to tertiary phosphine ligands, the difference between NHC electronic parameters is very small (Figure 5). As shown with IPrCl, bearing chlorine on the imidazole backbone, and the triazolylidene TPT (respectively TEP = 2055.1 and 2057.3 cm^{-1}), simple modifications on the imidazole ring allow for efficient tuning of the NHC electronic properties. As expected, alkyl-substituted NHCs are more donating than aryl congeners, and the most donating ligand is the adamantyl derivative. For the first time, the bulky ItBu and IAd have been directly compared to the rest of the NHCs, showing electronic properties very close to ICy. We also found that saturated NHCs are slightly less donating than the unsaturated analogues. However, between the two substituent pairs (mesityl and diisopropylphenyl) there is almost no difference; IMes and IPr are both slightly more donating than SIMes and SIPr. This confirms the results found in work performed with

(29) (a) Hillier, A. C.; Sommer, W. J.; Yong, B. S.; Peterson, J. L.; Cavallo, L.; Nolan, S. P. *Organometallics* **2003**, *22*, 4322–4326. (b) Fantasia, S.; Petersen, J. L.; Jacobsen, H.; Cavallo, L.; Nolan, S. P. *Organometallics* **2007**, *26*, 5880–5889.

Table 2. Selected Angles (deg) for [(NHC)Ir(CO)$_2$Cl] Complexes

complex	Cl−Ir−C^{NHC}	C^{NHC}−Ir−C^{cis}-CO[a]	C^{NHC}−Ir−C$^{trans\text{-}CO}$[a]
[(ItBu)Ir(CO)$_2$Cl] 10	88.2(4)	91.1(4)	175.0(9)
[(IAd)Ir(CO)$_2$Cl] 11	89.9(2)	89.9(3)	178.0(3)
[(ICy)Ir(CO)$_2$Cl] 12	86.97(2)	90.0(2)	177.1(2)
[(IPr)Ir(CO)$_2$Cl] 13	89.61(7)	91.71(11)	176.55(11)
[(SIPr)Ir(CO)$_2$Cl] 14	87.04(12)	95.0(17)	175.00(19)
[(IMes)Ir(CO)$_2$Cl] 16	88.8(3)	92.5(6)	174.8(6)
[(SIMes)Ir(CO)$_2$Cl] 17	87.6(5)	95.0(6)	178.2(8)

[a] *cis* and *trans* are relative to the NHC.

Table 3. A$_1$ Carbonyl Stretching Frequencies for Compounds [(L)Ir(CO)$_2$Cl] and [(L)Ni(CO)$_3$]

L	solvent	ν_{CO} (cm^{-1})	ν_{CO}^{av} (cm^{-1})	TEP (cm^{-1})
PPh_3	$CHCl_3$	2085, 2002	2043.5	2068.9
$PMePh_2$	$CHCl_3$	2085, 2003	2044	2067.0
PMe_2Ph	$CHCl_3$	2084, 1999	2041.5	2065.3
PEt_3	$CHCl_3$	2081, 1994	2037.5	2061.7
P(*p*-MeC$_6$H$_4$)$_3$	$CHCl_3$	2079, 1999	2039	2066.7
P(iPr)$_3$	CH_2Cl_2	2077, 1986	2031.5	2059.2
PCy_3	CH_2Cl_2	2072, 1984	2028.0	2056.4
TPT	CH_2Cl_2	2072.2, 1989.3	2030.8	2057.3[a]
IPrCl	CH_2Cl_2	2071.4, 1985.1	2028.3	2055.1[a]
SIPr	CH_2Cl_2	2068.0, 1981.8	2024.9	2052.2
SIMes	CH_2Cl_2	2068.0, 1981.2	2024.6	2051.5
IPr	CH_2Cl_2	2066.8, 1981.0	2023.9	2051.5
IMes	CH_2Cl_2	2066.4, 1979.8	2023.1	2050.7
ItBu	CH_2Cl_2	2064.6, 1980.0	2022.3	2050.1[a]
ICy	CH_2Cl_2	2064.8, 1981.2	2023.0	2049.6
IAd	CH_2Cl_2	2063.4, 1979.8	2021.6	2049.5[a]

[a] Values calculated by linear regression.

$Ni(CO)_4$ as well as similar trends in the relative bond disruption enthalpies of ruthenium complexes involving the aforementioned ligands.[29]

The NHCs bearing a phenyl group on the backbone developed by Crabtree appear as more strongly donating ligands (TEP = 2046 cm^{-1}).[22] The TEP of bioxazoline-derived NHCs[23] and of those recently reported by Plenio[24] are in the range of common alkyl- and aryl-substituted NHCs (2052 cm^{-1} > TEP > 2049 cm^{-1}). Nonetheless, the introduction of functional groups on aryl N-substituents appears to allow for variation of the electronic parameter ν, as sulfoxide and sulfone in *para* positions led to weaker TEP (2057–2054 cm^{-1}).[24]

The carbonyl stretching frequencies were also determined using DFT calculations (Table 4). Good agreement with experimental values is obtained. The weaker values (≈2000 cm^{-1}) correspond to the asymmetric CO stretching and the higher (≈2070 cm^{-1}) to the symmetric CO stretching. For NHCs with alkyl substituents, DFT values replicate perfectly the experimental increase in the wavenumber values. Comparing the saturated NHCs (SIPr and SIMes) with their unsaturated counterparts, the DFT values reproduce the experimental finding that both CO stretchings are about 1 or 2 cm^{-1} smaller in the unsaturated. We believe that in the saturated NHC-containing complexes there is a higher d → π* (NHC) back-donation, which consequently results in reduced d → π* (CO) back-donation.[29b]

This study is further evidence that the relative reactivity of catalysts with these ligands is due to factors other than electronic donation. For that reason, we quantified the steric factors characterizing them in measuring the amount of volume of a sphere centered on the metal, occupied by atoms of various NHC, % V_{Bur}. The volume of this sphere represents the space around the metal atom that must be shared by the different ligands upon coordination. We examined the DFT-optimized geometries of the free ligands and positioned them at various distances from the metal center (Table 5). The 2 and 2.28 Å values correspond respectively to typical NHC−Ni and PR_3−Ni distances in the nickel carbonyl system. The results support the previous findings obtained with the nickel carbonyl system.[15] The ItBu exhibits steric requirements similar to IAd and largely superior to the other NHCs, the amount occupied by the ligand inside the sphere being around 1.5 times more important. Interestingly, these values point out undoubtedly the bulkier effect of saturated NHCs (3% of V_{Bur} between SIPr and IPr); this could explain some differences observed in catalysis.[10d] The smaller size of ICy explains why, with this NHC, introduction of two or more NHCs on a metal center is commonly observed during TM complex formation.[30]

Conclusion

We have synthesized a series of NHC-containing iridium complexes and measured their carbonyl stretching frequencies in order to determine the exact order of electron-donating strength. We have shown that commonly used NHCs are much more strongly donating ligands than the strongest tertiary phosphine. Furthermore, there is surprisingly little difference between the NHCs themselves, showing the weak influence of N-substituents on electronic properties. At this point, we believe the differences of behavior between the complexes bearing these NHCs are more closely associated with their steric properties. On the other hand, IPrCl as well as the triazolylidene exhibits significantly lower donating ability, demonstrating that modifications on the imidazole ring allow for effective tuning of electronic properties. We have also established a single metal–ligand system ([(L)Ir(CO)$_2$Cl]) that can accurately compare the donating strength of all ligands tested and eliminate some drawbacks of other methods currently in use.

Experimental Section

General Considerations. All reactions were carried out using standard Schlenk techniques under an atmosphere of dry argon or in a MBraun glovebox containing dry argon with less than 1 ppm oxygen. Solvents were distilled from appropriate drying agents or were passed through an alumina column in an MBraun solvent purification system. Other anhydrous solvents were purchased from commercial sources and degassed prior to use by purging with dry argon and were kept over molecular sieves. Solvents for NMR spectroscopy were degassed with argon and dried over molecular sieves. NMR spectra were collected on a 400 MHz Varian Gemini spectrometer or 300 and 400 MHz Bruker Avance spectrometers. Infrared spectra were recorded on a PE 2000 FT-IR and a Tensor 27 Bruker FT-IR spectrometer. Elemental analyses were performed

(30) (a) For nickel, see: Herrmann, W. A.; Gerstberger, G.; Spiegler, M. *Organometallics* **1997**, *16*, 2209–2212. (b) For ruthenium, see: Weskamp, T.; Schattenmann, W. C.; Spiegler, M.; Herrmann, W. A. *Angew. Chem., Int. Ed.* **1998**, *37*, 2490–2493. (c) For rhodium, see: Douglas, S.; Lowe, J. P.; Mahon, M. F.; Warren, J. E.; Whittlesey, M. K. *J. Organomet. Chem.* **2005**, *690*, 5027–5035. (d) For palladium, see: Frey, G. D.; Schütz, J.; Herdtweck, E.; Herrmann, W. A. *Organometallics* **2005**, *24*, 4416–4426. (e) For iridium, see this work.

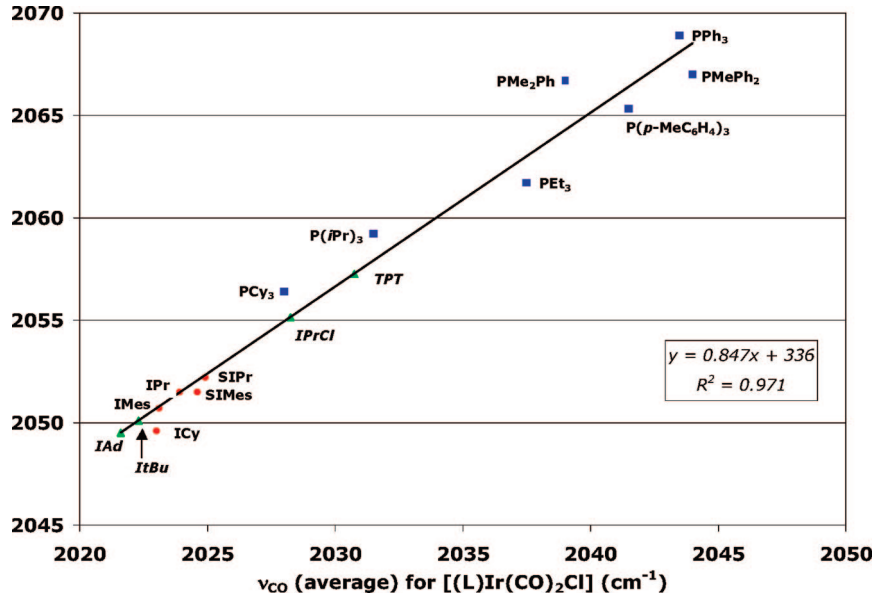

Figure 5. Correlation of the average ν_{CO} values for [(L)Ir(CO)$_2$Cl] complexes with the Tolman electronic parameters (TEP). (■) experimental values for phosphines; (●) experimental values for NHCs; (▲) values obtained by linear regression for NHCs.

Table 4. Experimental and DFT-Calculated Carbonyl Stretching of Several NHCs

complex	ν_{CO}(exp) (cm^{-1})	ν_{CO}(DFT) (cm^{-1})
[(ItBu)Ir(CO)$_2$Cl], **10**	2064.6, 1980.0	2085, 2012
[(IAd)Ir(CO)$_2$Cl], **11**	2063.4, 1979.8	2082, 2010
[(ICy)Ir(CO)$_2$Cl], **12**	2064.8, 1981.2	2083, 2015
[(IPr)Ir(CO)$_2$Cl], **13**	2066.8, 1981.0	2083, 2005
[(SIPr)Ir(CO)$_2$Cl], **14**	2068.0, 1981.8	2084, 2007
[(IMes)Ir(CO)$_2$Cl], **16**	2066.4, 1979.8	2084, 2007
[(SIMes)Ir(CO)$_2$Cl], **17**	2068.0, 1981.8	2085, 2008

Table 5. Calculated % V_{Bur} of the NHC at Various Ir−NHC Distances

complex	distance Ir−C^{NHC} (Å)	% V_{Bur} at various Ir−C^{NHC} distance (Å)		
		2.00	X-ray	2.28
[(ItBu)Ir(CO)$_2$Cl], **10**	2.114	33	31	28
[(IAd)Ir(CO)$_2$Cl], **11**	2.102	33	31	27
[(ICy)Ir(CO)$_2$Cl], **12**	2.078	23	23	19
[(IPr)Ir(CO)$_2$Cl], **13**	2.079	26	24	20
[(SIPr)Ir(CO)$_2$Cl], **14**	2.071	29	27	23
[(IMes)Ir(CO)$_2$Cl], **16**	2.108	26	24	20
[(SIMes)Ir(CO)$_2$Cl], **17**	2.121	27	24	21

by Quantitative Technologies Inc. and by Robertson Microlit Laboratories and at the Universidad Complutense de Madrid on a LECO CHNS 932 microanalyzer. [Ir(cod)Cl]$_2$ was purchased from Strem Chemicals and used as received. NHC ligands were synthesized following literature procedures.[31]

Synthesis of [(NHC)Ir(cod)Cl]. General Procedure. A benzene solution (10 mL) of NHC (1.79 mmol, 2.4 equiv) was added dropwise to a benzene solution (5 mL) of [Ir(cod)Cl]$_2$ (500 mg, 0.74 mmol). The reaction was stirred overnight, and the formation of a yellow precipitate was observed. The solid was collected, washed with pentane (2 × 5 mL), and dried under vacuum to provide the product as a yellow solid. The solid was dissolved in a minimum amount of ethyl acetate and purified by passing it through a short column of silica. X-ray quality crystals were obtained by slow evaporation of a saturated pentane solution.

(31) (a) Arduengo, A. J., III; Krafczyk, R.; Craig, H. A.; Goerlich, J. R.; Marshall, W. J.; Unverzagt, M. *Tetrahedron* **1999**, *55*, 14523–14534. (b) Nolan, S. P. U.S. Patent 653688, 2003. (c) Enders, D.; Breuer, K.; Kallfass, U. Balensiefer, T. *Synthesis* **2003**, 1292–1295. (d) Some NHCs such as IMes and IPr are commercially available from Strem.

[(ItBu)Ir(cod)Cl] (1). The general procedure yielded 515 mg (67%). ^{1}H NMR (CDCl$_3$, 400 MHz, δ): 7.15 (s, 2H, NCH=CHN), 4.48 (m, 2H, CH^{cod}), 2.71 (m, 2H, CH^{cod}), 2.17 (m, 4H, CH$_2^{cod}$), 1.95 (s, 18H, CH$_3$), 1.52 (m, 2H, CH$_2^{cod}$), 1.33 (m, 2H, CH$_2^{cod}$). ^{13}C NMR (CDCl$_3$, 100 MHz, δ): 179.9 (C, N-C-N), 119.7 (CH, NCH=CHN), 78.3 (CH, CH^{cod}), 59.7 (C, C(CH$_3$)$_3$), 51.5 (CH, CH^{cod}), 33.6 (CH$_3$, CH$_3$), 33.0 (CH$_2$, CH$_2^{cod}$), 29.3 (CH$_2$, CH$_2^{cod}$). Anal. Calcd for $C_{19}H_{32}N_2ClIr$ (MW 516.14): C, 44.21; H, 6.25; N, 5.43. Found: C, 44.17; H, 6.23; N, 5.47.

[(IAd)Ir(cod)Cl] (2). The general procedure yielded 912 mg (91%). ^{1}H NMR (CDCl$_3$, 400 MHz, δ): 7.18 (s, 2H, NCH=CHN), 4.49 (m, 2H, CH^{cod}), 2.77 (d, J = 12.0 Hz, 6H, CH$_2^{Ad}$), 2.53 (d, J = 11.6 Hz, 6H, CH$_2^{Ad}$), 2.27 (m, 6H, CH^{Ad}), 2.17 (m, 2H, CH^{cod}), 1.75 (s, 12H, CH$_2^{IAd}$), 1.52 (m, 4H, CH$_2^{cod}$), 1.35 (m, 4H, CH$_2^{cod}$). ^{13}C NMR (CDCl$_3$, 100 MHz, δ): 179.1 (C, N-C-N), 118.2 (CH, NCH=CHN), 76.9 (CH, CH^{cod}), 60.5, (C, C^{Ad}), 51.3 (CH, CH^{cod}), 45.6 (CH$_2$, CH$_2^{Ad}$), 36.3 (CH$_2$, CH$_2^{Ad}$), 33.2 (CH$_2$, CH$_2^{cod}$), 31.8 (CH$_2$, CH$_2^{Ad}$), 30.5 (CH, CH^{Ad}), 29.4 (CH$_2$, CH$_2^{cod}$), 22.9 (CH, CH^{Ad}). Anal. Calcd for $C_{31}H_{44}N_2ClIr$ (MW 672.36): C, 55.38; H, 6.60; N, 4.17. Found: C, 55.37; H, 6.70; N, 3.99.

[(ICy)Ir(cod)Cl] (3). The general procedure using 1.8 equiv of ICy yielded 490 mg (58%). ^{1}H NMR (CDCl$_3$, 400 MHz, δ): 6.82 (s, 2H, NCH=CHN), 5.12 (m, 2H, CH^{Cy}), 4.55 (m, 2H, CH^{cod}), 2.92 (m, 2H, CH^{cod}), 2.20 (m, 6H, CH$_2^{Cy}$), 1.99 (d, J = 12.0 Hz, 2H, CH$_2^{Cy}$), 1.92 (dd, J = 12.9 and 2.1 Hz, 2H, CH$_2^{Cy}$), 1.83 (dd, J = 13.3, 2.1 Hz, 2H, CH$_2^{Cy}$), 1.73 (m, 4H, CH$_2^{Cy}$), 1.60 (m, 4H, CH$_2^{cod}$), 1.48 (m, 4H, CH$_2^{cod}$), 1.20 (m, 4H, CH$_2^{Cy}$). ^{13}C NMR (CDCl$_3$, 100 MHz, δ): 178.1 (C, N-C-N), 117.1 (CH, NCH=CHN), 83.5 (CH, CH^{cod}), 60.1 (CH, CH^{Cy}), 51.0 (CH, CH^{cod}), 34.5 (CH$_2$, CH$_2^{Cy}$), 34.4 (CH$_2$, CH$_2^{Cy}$), 34.0 (CH$_2$, CH$_2^{cod}$), 29.9 (CH$_2$, CH$_2^{cod}$), 26.0 (CH$_2$, CH$_2^{Cy}$), 25.6 (CH$_2$, CH$_2^{Cy}$). Anal. Calcd for $C_{23}H_{36}N_2ClIr$ (MW 568.22): C, 48.62; H, 6.39; N, 4.93. Found: C, 48.52; H, 6.36; N, 4.82.

[(IPr)Ir(cod)Cl] (4). The general procedure yielded 865 mg (80%). ^{1}H NMR (CDCl$_3$, 400 MHz, δ): 7.45 (t, J = 7.7 Hz, 2H, CH^{Ar}), 7.33 (m, 4H, CH^{Ar}), 7.01 (s, 2H, NCH=CHN), 4.18 (m, 2H, CH^{cod}), 3.42 (m, 2H, CH(CH$_3$)$_2$), 2.88 (m, 2H, CH^{cod}), 2.68 (m, 2H, CH(CH$_3$)$_2$), 1.68 (m, 4H, CH$_2^{cod}$), 1.50 (m, 2H, CH$_2^{cod}$), 1.40 (m, 12H, CH(CH$_3$)$_2$), 1.30 (m, 2H, CH$_2^{cod}$), 1.08 (d, J = 6.6 Hz, 12H, CH(CH$_3$)$_2$). ^{13}C NMR (CDCl$_3$, 100 MHz, δ): 182.6 (s, N-C-N), 136.3 (C, C^{Ar}), 130.0 (C, C^{Ar}), 124.5 (CH, CH^{Ar}), 123.0 (CH, NCH=CHN), 83.0 (CH, CH^{cod}), 51.6 (CH, CH^{cod}), 33.7 (CH$_2$, CH$_2^{cod}$), 29.1 (CH$_2$, CH$_2^{cod}$), 28.9 (CH$_2$, CH$_2^{cod}$), 26.6 (CH,

CH(CH$_3$)$_2$), 22.6 (CH$_3$, CH(**C**H$_3$)$_2$), 23.4 (CH$_3$, CH(**C**H$_3$)$_2$). Anal. Calcd for $C_{35}H_{48}N_2ClIr$ (MW 724.44): C, 58.03; H, 6.68; N, 3.87. Found: C, 58.05; H, 6.66; N, 3.71.

[(SIPr)Ir(cod)Cl] (5). The general procedure yielded 830 mg (77%). ^{1}H NMR (CDCl$_3$, 400 MHz, δ): 7.38 (t, J = 7.7 Hz, 2H, C**H**^{Ar}), 7.30 (d, J = 7.5 Hz, 2H, C**H**^{Ar}), 7.20 (d, J = 7.5 Hz, 2H, C**H**^{Ar}), 4.15 (m, 2H, C**H**^{cod}), 3.95 (s, 4H, NC**H$_2$-CH$_2$**N), 3.84 (m, 2H, C**H**(CH$_3$)$_2$), 3.16 (m, 2H, C**H**(CH$_3$)$_2$), 2.92 (m, 2H, C**H**^{cod}), 1.59 (m, 4H, C**H$_2$**^{cod}), 1.20 (m, 4H, C**H$_2$**^{cod}), 1.45 (d, J = 6.8 Hz, 6H, CH(C**H**$_3$)$_2$), 1.38 (d, J = 6.8 Hz, 6H, CH(C**H**$_3$)$_2$), 1.24 (d, J = 6.8 Hz, 6H, C**H**(CH$_3$)$_2$), 1.18 (d, J = 6.8 Hz, 6H, C**H**(CH$_3$)$_2$). ^{13}C NMR (CDCl$_3$, 100 MHz, δ): 209.5 (C, N-**C**-N), 149.3 (C, **C**^{Ar}), 146.3 (C, **C**^{Ar}), 136.8 (C, **C**^{Ar}), 129.1 (CH, **C**H^{Ar}), 125.0 (CH, **C**H^{Ar}), 123.5 (CH, **C**H^{Ar}), 83.9 (CH, **C**H^{cod}), 54.3 (CH, **C**H^{cod}), 51.6 (CH$_2$, **C**H$_2$^{cod}), 33.5 (CH$_2$, NCH$_2$-**C**H$_2$N), 31.8 (CH, **C**H(CH$_3$)$_2$), 29.2 (CH$_2$, **C**H$_2$^{cod}), 28.9 (CH, **C**H(CH$_3$)$_2$), 28.6 (CH$_3$, CH(**C**H$_3$)$_2$), 27.1 (CH$_3$, CH(**C**H$_3$)$_2$), 24.3 (CH$_3$, CH(**C**H$_3$)$_2$), 23.3 (CH$_3$, CH(**C**H$_3$)$_2$), 22.9 (CH$_3$, CH(**C**H$_3$)$_2$). Anal. Calcd for $C_{35}H_{50}N_2ClIr$ (MW 726.45): C, 57.87; H, 6.94; N, 3.86. Found: C, 57.83; H, 6.98; N, 3.98.

[(IPrCl)Ir(cod)Cl] (6). The general procedure yielded 880 mg (75%). ^{1}H NMR (CDCl$_3$, 400 MHz, δ): 7.56 (t, J = 7.7 Hz, 2H, C**H**^{Ar}), 7.48–7.43 (m, 4H, C**H**^{Ar}), 4.33–4.28 (m, 2H, C**H**^{cod}), 3.65–3.56 (bs, 2H, C**H**(CH$_3$)$_2$), 2.98–2.95 (m, 2H, C**H**^{cod}), 2.38 (bs, 2H, C**H**(CH$_3$)$_2$), 1.66–1.61 (m, 2H, C**H$_2$**^{cod}), 1.42–1.32 (m, 14H, CH(C**H**$_3$)$_2$ and C**H$_2$**^{cod}), 1.25–1.19 (m, 12H, CH(C**H**$_3$)$_2$). ^{13}C NMR (CDCl$_3$, 100 MHz, δ): 187.6 (s, N-**C**-N), 132.8 (C, **C**^{Ar}), 130.6 (CH, **C**H^{Ar}), 128.5 (C, **C**^{Ar}), 119.7 (CH, N**C**Cl=**C**ClN), 83.8 (CH, **C**H^{cod}), 51.4 (CH, **C**H^{cod}), 35.3 (CH, **C**H(CH$_3$)$_2$), 33.4 (CH$_2$, **C**H$_2$^{cod}), 28.7 (CH$_2$, **C**H$_2$^{cod}),. Anal. Calcd for $C_{35}H_{46}Cl_3N_2Ir$ (MW 793.33): C, 52.99; H, 5.84; N, 3.53. Found: C, 53. 29; H, 5.81; N, 3.68.

[(IMes)Ir(cod)Cl] (7). The general procedure yielded 822 mg (86%). ^{1}H NMR (CDCl$_3$, 400 MHz, δ): 6.98 (d, J = 13.3 Hz, 2H, NC**H**=C**H**N), 6.94 (s, 4H, C**H**^{Mes}), 4.13 (m, 2H, C**H**^{cod}), 2.95 (m, 2H, C**H**^{cod}), 2.35 (s, 12H, C**H**$_3$), 2.15 (s, 6H, C**H**$_3$), 1.65 (m, 4H, C**H$_2$**^{cod}), 1.3 (m, 4H, C**H$_2$**^{cod}). ^{13}C NMR (CDCl$_3$, 100 MHz, δ): 180.9 (C, N-**C**-N), 138.8 (C, **C**^{Mes}), 137.5 (C, **C**^{Mes}), 136.2 (C, **C**^{Mes}), 134.6 (C, **C**^{Mes}), 129.7 (CH, **C**H^{Mes}), 128.3 (CH, **C**H^{Mes}), 123.5 (CH, N**C**H=**C**HN), 82.7 (CH, **C**H^{cod}), 51.7 (CH, **C**H^{cod}), 33.7 (CH$_2$, **C**H$_2$^{cod}), 29.2 (CH$_2$, **C**H$_2$^{cod}), 21.4 (CH$_3$, **C**H$_3$^{Mes}), 19.9 (CH$_3$, **C**H$_3$^{Mes}), 18.45 (CH$_3$, **C**H$_3$^{Mes}). Anal. Calcd for $C_{29}H_{36}N_2ClIr$ (MW 640.28): C, 54.40; H, 5.67; N, 4.38. Found: C, 54.50; H, 5.78; N, 4.24.

[(SIMes)Ir(cod)Cl] (8). The general procedure yielded 870 mg (91%). ^{1}H NMR (CDCl$_3$, 400 MHz, δ): 6.94 (d, J = 14.1 Hz, 4H, C**H**^{Ar}), 4.08 (d, J = 2.9 Hz, 2H, C**H**^{cod}), 3.88 (s, 4H, NC**H$_2$-CH$_2$**N), 3.06 (d, J = 1.7 Hz, 2H, C**H**^{cod}), 2.54 (s, 6H, C**H**$_3$^{Mes}), 2.33 (s, 6H, C**H**$_3$^{Mes}), 2.30 (s, 6H, C**H**$_3$^{Mes}), 1.60 (m, 4H, C**H$_2$**^{cod}), 1.25 (m, 4H, C**H$_2$**^{cod}). ^{13}C NMR (CDCl$_3$, 100 MHz, δ): 207.4 (s, N-**C**-N), 138.2 (C, **C**^{Ar}), 138.0 (C, **C**^{Ar}), 136.4 (C, **C**^{Ar}), 135.4 (C, **C**^{Ar}), 130.0 (CH, **C**H^{Ar}), 128.6 (CH, **C**H^{Ar}), 83.9 (CH$_2$, **C**H$_2$^{cod}), 52.0 (CH, **C**H^{cod}), 51.7 (CH$_2$, NCH$_2$-**C**H$_2$N), 33.6 (CH, **C**H^{cod}), 29.9 (CH, **C**H^{cod}), 21.3 (CH$_3$, **C**H$_3$^{Mes}), 20.1 (CH$_3$, **C**H$_3$^{Mes}), 18.7 (CH$_3$, **C**H$_3$^{Mes}). Anal. Calcd for $C_{29}H_{38}N_2ClIr$ (MW 642.30): C, 54.23; H, 5.96; N, 4.36. Found: C, 54.15; H, 5.95; N, 4.10.

[(TPT)Ir(cod)Cl] (9). The general procedure yielded 852 mg (91%). ^{1}H NMR (CD$_2$Cl$_2$, 300 MHz): δ 8.67–8.63 (m, 2H, C**H**^{Ph}), 7.73–7.70 (m, 2H, C**H**^{Ph}), 7.58–7.52 (m, 3H, C**H**^{Ph}), 7.51–7.41 (m, 6H, C**H**^{Ph}), 7.36–7.31 (m, 2H, C**H**^{Ph}), 4.53–4.48 (m, 2H, C**H**^{cod}), 2.63–2.58 (m, 1H, C**H**^{cod}), 2.46–2.42 (m, 1H, C**H**^{cod}), 2.07–1.95 (m, 1H, C**H$_2$**^{cod}), 1.81–1.33 (m, 6H, C**H$_2$**^{cod}), 1.28–1.18 (m, 1H, C**H$_2$**^{cod}). ^{13}C NMR (CD$_2$Cl$_2$, 75 MHz) δ 186.1 (C, N-**C**-N), 153.7 (C, **C**=N), 140.0 (C, **C**^{Ph}), 137.5 (C, **C**^{Ph}), 131.0 (CH, **C**H^{Ph}), 129.6 (CH, **C**H^{Ph}), 129.3 (CH, **C**H^{Ph}), 129.1 (CH, **C**H^{Ph}), 129.0 (CH, **C**H^{Ph}), 129.0 (CH, **C**H^{Ph}), 128.9 (CH, **C**H^{Ph}), 128.4 (CH, **C**H^{Ph}), 125.5 (C, **C**^{Ph}), 123.9 (CH, **C**H^{Ph}), 86.3 (CH, **C**H^{cod}), 84.5 (CH, **C**H^{cod}), 53.6 (CH, **C**H^{cod}), 52.7 (CH, **C**H^{cod}), 34.1 (CH$_2$, **C**H$_2$^{cod}), 32.3 (CH$_2$, **C**H$_2$^{cod}), 30.1 (CH$_2$, **C**H$_2$^{cod}), 28.8 (CH$_2$, **C**H$_2$^{cod}). Anal. Calcd for $C_{28}H_{27}N_3ClIr$ (MW 633.20): C, 53.11; H, 4.30; N, 6.64. Found: C, 53.22; H, 4.09; N, 6.65.

Synthesis of [(NHC)Ir(CO)$_2$Cl]. General Procedure. A dichloromethane solution (5 mL) of [(NHC)Ir(cod)Cl] (200 mg) was placed under 1 atm of CO. The reaction was stirred until a color change from bright yellow to very pale yellow was observed, ca. 10 min. The solvent was removed under reduced pressure. Hexane was added, and the collected precipitate was washed with pentane (2 × 5 mL) and dried under vacuum to give the corresponding product as a yellow solid. X-ray quality crystals were obtained by slow evaporation of a saturated pentane solution.

[(I^{t}Bu)Ir(CO)$_2$Cl] (10). The general procedure yielded 139 mg (75%). ^{1}H NMR (CDCl$_3$, 400 MHz, δ): 7.21 (s, 2H, NC**H**=C**H**N), 1.86 (s, 18H, C**H**$_3$). ^{13}C NMR (CDCl$_3$, 100 MHz, δ): 179.7 (C, N-**C**-N), 172.9 (C, **C**O), 168.7 (C, **C**O), 118.8 (CH, N**C**H=**C**HN), 83.1 (s, **C**-I^{t}Bu), 60.2 (C, **C**(CH$_3$)$_3$), 33.1 (CH$_3$, C(**C**H$_3$)$_3$), 30.6 (CH$_3$, C(**C**H$_3$)$_3$). Anal. Calcd for $C_{13}H_{20}N_2O_2ClIr$ (MW 463.98): C, 33.65; H, 4.34; N, 6.04. Found: C, 33.50; H, 4.22; N, 6.01. IR ν_{CO} (CH$_2$Cl$_2$, cm^{-1}): 2064.6, 1980.0.

[(IAd)Ir(CO)$_2$Cl] (11). A dichloromethane solution (5 mL) of **2** (100 mg, 0.149 mmol) was placed under 600 psi of CO. The reaction was stirred for 5 days and monitored *in situ* for the appearance of the product. The solvent was removed under reduced pressure. Hexane was added, and the collected precipitate was washed with pentane (2 × 5 mL) and dried under vacuum to give **11** as a yellow solid. Yield: 66 mg (72%). ^{1}H NMR (CDCl$_3$, 400 MHz, δ): 7.28 (s, 2H, NC**H**=C**H**N), 2.54 (m, 12H, C**H$_2$**^{Ad}), 2.27 (m, 4H, C**H**^{IAd}), 1.74 (m, 12H, C**H$_2$**^{Ad}). ^{13}C NMR (CDCl$_3$, 100 MHz, δ): 179.8 (C, N-**C**-N), 172.1 (C, **C**O), 168.8 (C, **C**O), 117.7 (CH, N**C**H=**C**HN), 61.0 (CH, **C**H^{IAd}), 45.2 (C, **C**^{Ad}), 36.1 (CH$_2$, **C**H$_2$^{Ad}), 30.4 (CH, **C**H^{Ad}). Anal. Calcd for $C_{25}H_{32}N_2O_2ClIr$ (MW 620.20): C, 48.41; H, 5.20; N, 4.52. Found: C, 48.47; H, 5.07; N, 4.39. IR ν_{CO} (CH$_2$Cl$_2$, cm^{-1}): 2063.4, 1979.8.

[(ICy)Ir(CO)$_2$Cl] (12). The general procedure yielded 77 mg (41%). ^{1}H NMR (CDCl$_3$, 400 MHz, δ): 6.99 (s, 2H, NC**H**=C**H**N), 4.82 (m, 2H, C**H**^{Cy}), 2.20 (d, J = 7.1 Hz, 2H, C**H$_2$**^{Cy}), 2.05 (m, 2H, C**H$_2$**^{Cy}), 1.87 (m, 4H, C**H$_2$**^{Cy}), 1.75 (d, J = 13.3 Hz, 2H, C**H$_2$**^{Cy}), 1.48 (m, 6H, C**H$_2$**^{Cy}), 1.20 (m, 4H, C**H$_2$**^{Cy}). ^{13}C NMR (CDCl$_3$, 100 MHz, δ): 181.9 (C, N-**C**-N), 171.2 (C, **C**O), 168.5 (C, **C**O), 118.1 (s, N**C**H=**C**HN), 60.8 (CH, **C**H^{Cy}), 34.2 (CH$_2$, **C**H$_2$^{Cy}), 33.8 (CH$_2$, **C**H$_2$^{Cy}), 25.8 (CH$_2$, **C**H$_2$^{Cy}), 25.7 (CH$_2$, **C**H$_2$^{Cy}), 25.5 (CH$_2$, **C**H$_2$^{Cy}), 25.4 (CH$_2$, **C**H$_2$^{Cy}). Anal. Calcd for $C_{17}H_{24}N_2O_2ClIr$ (MW 516.05): C, 39.57; H, 4.69; N, 5.43. Found: C, 39.84; H, 4.59; N, 5.29. IR ν_{CO} (CH$_2$Cl$_2$, cm^{-1}): 2064.8, 1981.2.

[(IPr)Ir(CO)$_2$Cl] (13). The general procedure yielded 115 mg (62%). ^{1}H NMR (CDCl$_3$, 400 MHz, δ): 7.49 (t, J = 7.8 Hz, 2H, C**H**^{Ar}), 7.31 (d, J = 7.9 Hz, 4H, C**H**^{Ar}), 7.17 (s, 2H, NC**H**=C**H**N), 2.87 (m, 4H, C**H**(CH$_3$)$_2$), 1.37 (d, J = 6.6 Hz, 12H, CH(C**H**$_3$)$_2$), 1.15 (d, J = 6.8 Hz, 12H, CH(C**H**$_3$)$_2$). ^{13}C NMR (CDCl$_3$, 100 MHz, δ): 180.1 (C, **C**O), 178.6 (C, N-**C**-N), 168.6 (C, **C**O), 146.2 (C, **C**^{Ar}), 134.8 (C, **C**^{Ar}), 130.7 (CH, **C**H^{Ar}), 124.9 (CH, **C**H^{Ar}), 124.3 (CH, N**C**H=**C**HN), 29.1 (CH, **C**H(CH$_3$)$_2$), 26.3 (CH$_3$, CH(**C**H$_3$)$_2$), 22.8 (CH$_3$, CH(**C**H$_3$)$_2$). Anal. Calcd for $C_{29}H_{36}N_2O_2ClIr$ (MW 672.28): C, 51.81; H, 5.40; N, 4.17. Found: C, 552.03; H, 5.17; N, 3.96. IR ν_{CO} (CH$_2$Cl$_2$, cm^{-1}): 2066.8, 1981.0.

[(SIPr)Ir(CO)$_2$Cl] (14). The general procedure yielded 97 mg (52%). ^{1}H NMR (CDCl$_3$, 400 MHz, δ): 7.39 (t, J = 7.9 Hz, 2H, C**H**^{Ar}), 7.25 (d, J = 6.2 Hz, 4H, C**H**^{Ar}), 4.07 (s, 4H, NC**H$_2$-CH$_2$**N), 3.35 (m, 4H, C**H**(CH$_3$)$_2$), 1.44 (d, J = 5.4 Hz, 12H, CH(C**H**$_3$)$_2$), 1.25 (d, J = 5.8 Hz, 12H, CH(C**H**$_3$)$_2$). ^{13}C NMR (CDCl$_3$, 100 MHz, δ): 204.9 (C, N-**C**-N), 180.3 (C, **C**O), 168.8 (C, **C**O), 147.2 (C, **C**^{Ar}), 135.0 (C, **C**H^{Ar}), 129.9 (CH, **C**H^{Ar}), 124.7 (CH, **C**H^{Ar}), 54.6 (CH$_2$, NCH$_2$-CH$_2$N), 29.1 (CH, **C**H(CH$_3$)$_2$), 27.1 (CH$_3$, CH(**C**H$_3$)$_2$), 23.7 (CH$_3$, CH(**C**H$_3$)$_2$). Anal. Calcd for $C_{29}H_{38}N_2O_2ClIr$ (MW

674.29): C, 51.66; H, 5.68; N, 4.15. Found: C, 51.90; H, 5.49; N, 3.98. IR ν_{CO} (CH_2Cl_2, cm^{-1}): 2068.0, 1981.8.

[(IPrCl)Ir(CO)$_2$Cl] (15). The general procedure yielded 135 mg (70%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ): 7.60 (t, J = 7.8 Hz, 2H, C**H**^{Ar}), 7.39 (d, J = 7.8 Hz, 4H, C**H**^{Ar}), 2.84 (sept, J = 6.7 Hz, 4H, C**H**$(CH_3)_2$), 1.42 (d, J = 6.7 Hz, 12H, CH(C**H**$_3)_2$), 1.23 (d, J = 6.7 Hz, 12H, CH(C**H**$_3)_2$). ^{13}C NMR ($CDCl_3$, 100 MHz, δ): 179.5 (C, **C**O), 178.5 (C, N-**C**-N), 168.5 (C, **C**O), 146.7 (C, **C**^{Ar}), 131.7 (C, **C**^{Ar}), 131.4 (CH, **C**H^{Ar}), 124.7 (CH, **C**H^{Ar}), 120.9 (C, N**C**Cl=**C**ClN), 29.0 (CH, **C**H$(CH_3)_2$), 25.2 (CH_3, CH(**C**H$_3)_2$), 24.0 (CH_3, CH(**C**H$_3)_2$). Anal. Calcd for $C_{29}H_{36}N_2O_2Cl_3Ir$ (MW 743.18): C, 46.87; H, 4.88; N, 3.77. Found: C, 47.01; H, 4.58; N, 3.88. IR ν_{CO} (CH_2Cl_2, cm^{-1}): 2071.4, 1985.1.

[(IMes)Ir(CO)$_2$Cl] (16). The general procedure yielded 164 mg (89%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ): 7.10 (m, 2H, NC**H**=C**H**N), 7.00 (s, 4H, C**H**^{Mes}), 2.35 (s, 6H, C**H**$_3^{Mes}$), 2.20 (s, 12H, C**H**$_3^{Mes}$). ^{13}C NMR ($CDCl_3$, 100 MHz, δ): 180.2 (C, **C**O), 176.2 (C, N-**C**-N), 168.6 (C, **C**O), 139.7 (C, **C**^{Mes}), 135.3 (C, **C**^{Mes}), 135.0 (C, **C**^{Mes}), 129.5 (CH, **C**H^{Mes}), 123.8 (CH, N**C**H=**C**HN), 21.4 (CH_3, **C**H$_3^{Mes}$), 18.71 (CH_3, **C**H$_3^{Mes}$). Anal. Calcd for $C_{23}H_{24}N_2O_2ClIr$ (MW 588.12): C, 46.97; H, 4.11; N, 4.76. Found: C, 46.82; H, 4.00; N, 4.88. IR ν_{CO} (CH_2Cl_2, cm^{-1}): 2066.4, 1979.8.

[(SIMes)Ir(CO)$_2$Cl] (17). The general procedure yielded 170 mg (92%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ): 6.95 (m, 4H, C**H**^{Mes}), 3.99 (m, 4H, NC**H**$_2$-C**H**$_2$N), 2.42 (s, 12H, C**H**$_3^{Mes}$), 2.31 (s, 6H, C**H**$_3^{Mes}$). ^{13}C NMR ($CDCl_3$, 100 MHz, δ): 201.9 (C, N-**C**-N), 180.5 (C, **C**O), 168.8 (C, **C**O), 138.9 (C, **C**^{Mes}), 136.1 (C, **C**^{Mes}), 134.8 (C, **C**^{Mes}), 129.8 (CH, **C**H^{Mes}), 52.0 (CH_2, N**C**H$_2$-**C**H$_2$N), 21.4 (CH_3, **C**H$_3^{Mes}$), 18.9 (CH_3, **C**H$_3^{Mes}$). Anal. Calcd for $C_{23}H_{26}N_2O_2ClIr$ (MW 590.13): C, 46.81; H, 4.44; N, 4.75. Found: C, 46.75; H, 4.35; N, 4.48. IR ν_{CO} (CH_2Cl_2, cm^{-1}): 2068.0, 1981.2.

[(TPT)Ir(CO)$_2$Cl] (18). The general procedure yielded 138 mg (72%). ^{1}H NMR (CD_2Cl_2, 300 MHz, δ): 8.29–8.24 (m, 2H, C**H**^{Ph}), 7.59–7.52 (m, 7H, C**H**^{Ph}), 7.48–7.46 (m, 1H, C**H**^{Ph}), 7.44–7.41 (m, 2H, C**H**^{Ph}), 7.37–7.34 (m, 3H, C**H**^{Ph}). ^{13}C NMR (CD_2Cl_2, 75 MHz, δ): 180.5 (C, **C**O), 178.8 (C, N-**C**-N), 167.8 (C, **C**O), 154.5 (CH, **C**H=N), 139.4 (C, **C**^{Ph}), 136.4 (C, **C**^{Ph}), 131.6 (CH, **C**H^{Ph}), 130.7 (CH, **C**H^{Ph}), 129.9 (CH, **C**H^{Ph}), 129.4 (CH, **C**H^{Ph}), 129.3 (CH, **C**H^{Ph}), 129.2 (CH, **C**H^{Ph}), 128.8 (CH, **C**H^{Ph}), 125.4 (C, **C**^{Ph}), 124.5 (CH, **C**H^{Ph}). Anal. Calcd for $C_{22}H_{17}N_3OClIr$ (583.06): C, 45.24; H, 3.11; N, 7.19. Found: C, 45.55; H, 2.96; N, 7.12. IR ν_{CO} (CH_2Cl_2, cm^{-1}): 2072.2, 1989.3.

Computational Details. The density functional calculations were performed on all the systems at the GGA level with the Gaussian03 set of programs.[32] The Perdew, Burke, and Ernzerhof functional was used for all the calculations.[33] The electronic configuration of the molecular systems was described by the split-valence basis set with polarization functions of Ahlrichs and co-workers (standard SVP basis set in Gaussian03), for main group atoms.[34] For Ir the small-core, quasi-relativistic Stuttgart/Dresden effective core potential (standard SDD basis set in Gaussian03) basis set, with an associated (8s7p6d)/[6s5p3d] valence basis set contracted according to a (311111/22111/411) scheme, was used.[35–37] Frequency calculations were performed on the optimized geometries.

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Supporting Information Available: Crystallographic informations files (CIF) of complexes **1**−**18**. This material is available free of charge via the Internet http://pubs.acs.org. The CIF files have also been deposited with the CCDC, No. CCDC-659466 to 659479. Copies of the data can be obtained free of charge on applications to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, fax: +44 1223 336 033;http://www.ccdc.cam.ac.uk; e-mail: deposit@ccdc.cam.ac.uk.

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