Rhodium and Iridium Complexes of Abnormal N-Heterocyclic Carbenes Derived from Imidazo[1,2-*a*]pyridine

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Rhodium and iridium complexes of a new type of abnormal N-heterocyclic carbenes (NHCs) derived from imidazo[1,2-*a*]pyridiniums have been prepared via silver transmetalation, where metalation can be directed to either the C-2 or the C-3 position of imidazo[1,2-*a*]pyridine ring provided that the other position is appropriately blocked. The donating abilities of these new NHC ligands have been assessed from the average CO stretching frequencies of their corresponding iridium dicarbonyl complexes. By varying the N-alkyl groups or fusing the pyridine moiety with an aromatic ring, electronic effects of abnormal NHCs of this type can be readily tuned to match the extremely donating imidazole-derived abnormal NHCs or the relatively less donating normal NHCs (imidazolin-2-ylidenes). Both VT NMR studies and CO stretching frequency values strongly support the π-accepting ability of an abnormal NHC derived from imidazo[1,2-*a*]quinoline.

Introduction

Ever since their isolation in the free state,[1] N-heterocyclic carbenes (NHCs) have attracted increasing attention as ligands in organometallic chemistry and catalysis, and they are rapidly challenging the ubiquitous trivalent phosphines.[2,3] In many cases NHC complexes show higher catalytic activities and thermal stability partially owing to the strong NHC−metal bonds and the high σ-donating ability of NHC ligands.[4,5] Despite the large number of NHC complexes reported using various synthetic methods,[6] the synthesis of NHCs with tunable electronic and steric properties remains a challenge. Consequently, acyclic carbenes[7] and six-[8] and seven-membered[9,10] NHCs have been reported on various platforms besides the more common five-membered imidazole- or benzimidazole-based NHC systems.

In 2002 Crabtree and co-workers discovered that metalation could take place at the C(4/5) position of imidazolium ions,[11] in addition to the more common normal C(2) positions. The resulting zwitterions can be treated as "abnormal" NHCs (Figure 1). It was subsequently shown that NHCs of this mode are more donating than the strongest donating neutral ligands such as P^tBu_3 and common normal NHCs.[12a] Several groups have reported chelating or monodentate NHCs of this binding mode since then (Figure 1).[13–18] The relative rarity of this binding mode of NHCs is possibly due to the synthetic challenges since the C(4/5)-*H* is less acidic than the C(2)-*H*. So far, abnormal NHCs are mostly in chelating systems if the active C(2) positions are left unblocked. Applications of these abnormal NHC complexes in catalysis are still rather limited, although Nolan has shown that a palladium abnormal NHC complex is more active in catalyzing Suzuki reactions than its normal analogue.[14]

Here we report the synthesis, characterization, solution dynamics, and electronic effects of a new type of abnormal NHC ligand based on imidazo[1,2-*a*]pyridine, where metalation can be directed to either the C(2) or C(3) position of this hetero-

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10.1021/om800109a CCC: $40.75
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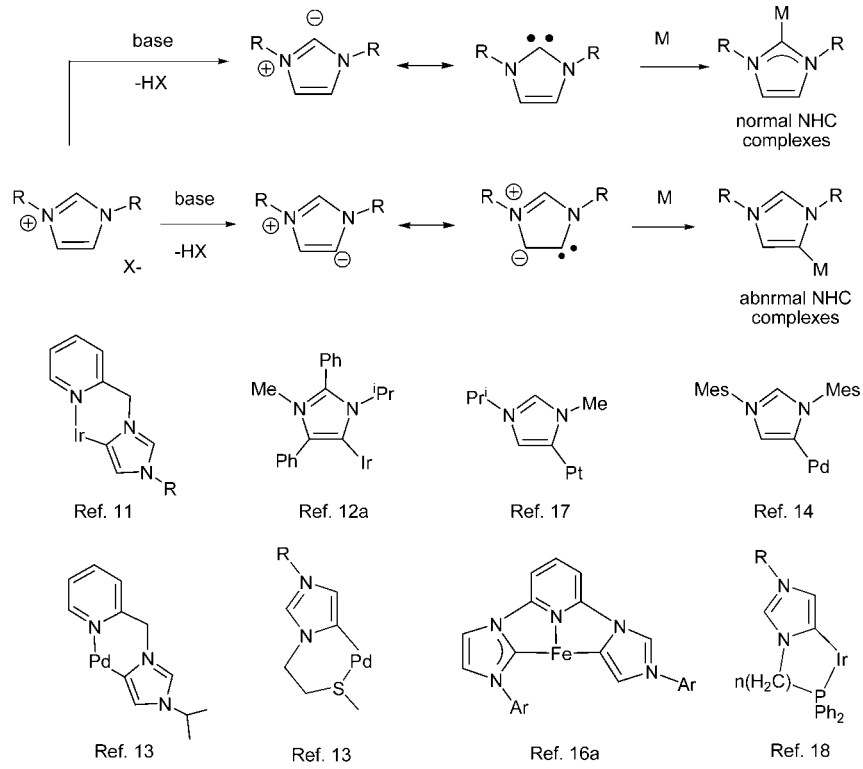


Figure 1. Abnormal NHC complexes.

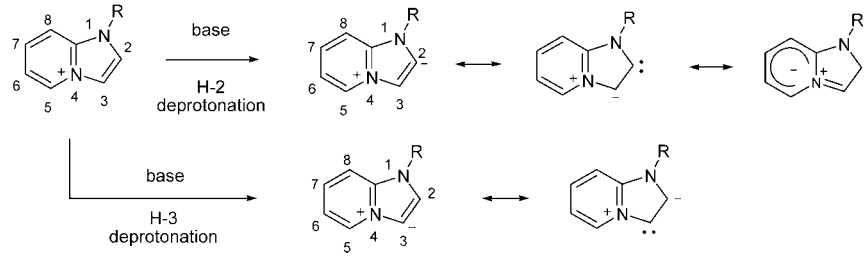
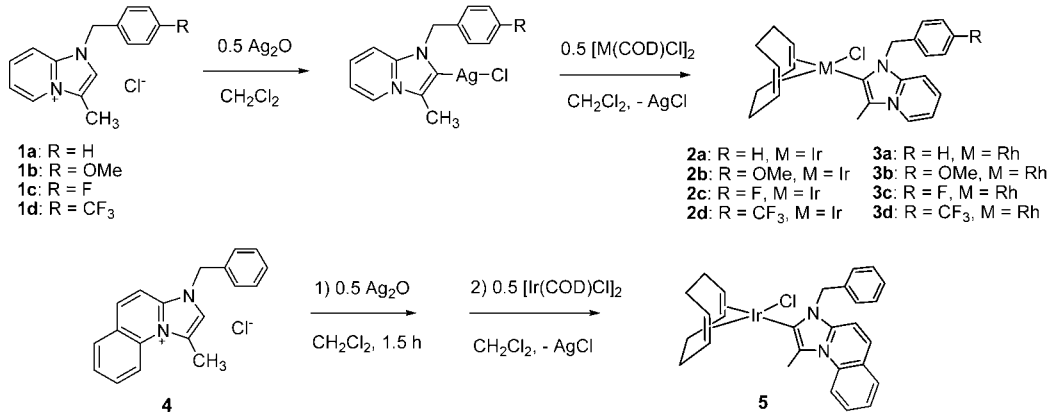


Figure 2. Deprotonation at the 2- vs 3-position.

Scheme 1. Synthesis of Ir and Rh Abnormal NHC Complexes via Silver Transmetalation

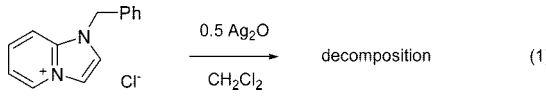


cyclic. Abnormal NHCs of this type have great tunability by varying the N-alkyl groups or by fusing the pyridine moiety with an aromatic ring.

Results and Discussion

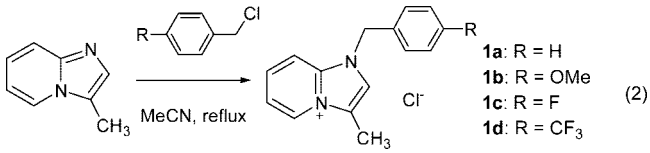
N-Alkylated Imidazo[1,2-*a*]pyridines. N-Alkylation of imidazo[1,2-*a*]pyridine takes place at the 1-position to give imidazo[1,2-*a*]pyridinium ions, structurally analogous to imidazolium ions, which are commonly used as NHC precursors. Deprotonation at the 2- or 3-position of an imidazo[1,2-*a*]pyridinium ion can be expected when treated with a base. However, H-2 should be more acidic since the resulting negative charge can be further delocalized to the pyridine ring (Figure 2), while that obtained from H-3 deprotonation is localized in the imidazole ring.

Synthesis of Metal Complexes. Imidazolium halides with blocked C-2 positions have been used as precursors to abnormal NHCs for the synthesis of transition metal complexes via the silver transmetalation.[12] Therefore, initial attempts were made by reacting 1-benzylimidazo[1,2-*a*]pyridinium chloride with Ag_2O, and metalation at the more acidic C-2 position was anticipated (eq 1). However, only unidentifiable species were obtained. We reasoned that blocking the 3-position with an alkyl group should enhance the regioselectivity of silver carbene formation and it might also offer steric protection against decomposition such as protonolysis.[12a]



(1)

Hence 3-methylimidazo[1,2-*a*]pyridine was synthesized according to literature reports.[19,20] Alkylation using *para*-substituted benzyl chlorides gives imidazo[1,2-*a*]pyridinium ions **1a**−**d** (eq 2). Indeed, stirring a mixture of Ag_2O (0.5 equiv) and **1a**−**d** in CH_2Cl_2 afforded the corresponding silver carbene chlorides, which were used as transmetalation reagents without isolation (Scheme 1).[12] Addition of 0.5 equiv of $[M(COD)Cl]_2$ (M = Ir or Rh) immediately afforded complexes **2a**−**d** and **3a**−**d** with isolated yields ranging from 79% to 91%. Analogously, compound **4** was also successfully applied as a carbene precursor leading to iridium abnormal NHC complex **5** (Scheme 1). It should be noted that no silver carbene complex could be obtained when 1-allyl-3-methylimidazo[1,2-*a*]pyridinium or 1-*n*-propyl-3-methylimidazo[1,2-*a*]pyridinium chloride was treated with Ag_2O. The higher acidity of the C(2)-*H* in **1a**−**d** might be accountable.



(2)

NMR Characterization. All these rhodium and iridium NHC complexes were fully characterized by NMR spectroscopy, and complexes **3a** and **3d** were further analyzed by X-ray crystallography. In the ^1H NMR spectra, all the methylene protons show AB patterns in $CDCl_3$, indicative of C_1 symmetry for all these molecules. No line broadening of the CH_2 signals was observed when the NMR sample was heated to 60 °C in $CDCl_3$, which suggests that the rotation along $Ir-C_{carbene}$ carries a quite high barrier.[12a] However, when measured in CD_2Cl_2, the appearance of the methylene proton signals of **3a**−**d** was quite different, and they are generally closer in chemical shifts. For example, the CH_2 protons in **3c** are accidentally equivalent in CD_2Cl_2 (δ 6.18, s), while an AB pattern (δ 6.40 and 5.92, $^2J_{HH}$ = 15.9 Hz) was observed in $CDCl_3$. In the ^{13}C NMR spectra, the $C_{carbene}$ atoms resonate within a narrow range of δ 167 to 170, which are slightly more deshielded than those abnormal NHCs derived from imidazolium ions.[12a]

X-ray Crystallography. Single crystals of **3a** and **3d** suitable for X-ray crystallographic analysis were obtained by layering their CH_2Cl_2 solutions with pentane. Crystallographic analysis confirmed the C-2 [labeled as C(9) in Figures 3 and 4] binding mode in both **3a** (Figure 3) and **3d** (Figure 4). The coordination sphere is square planar for both complexes, and the selected bond lengths, bond angles, and torsion angles are shown in Table 1. As expected for NHCs, the $Rh-C_{carbene}$ distance is 2.039(2) Å for **3a** and 2.021(5) Å for **3d** and is consistent with a Rh−C single bond. The most remarkable difference between these two structures probably lies in their torsion angles [N(1)−C(9)−Rh(1)−Cl(1)]. The NHC ring in complex **3d** (−81.3° torsion angle) is nearly perpendicular to the coordination plane, while in complex **3a** there is significant deviation from this orientation (−70.6° torsion angle).

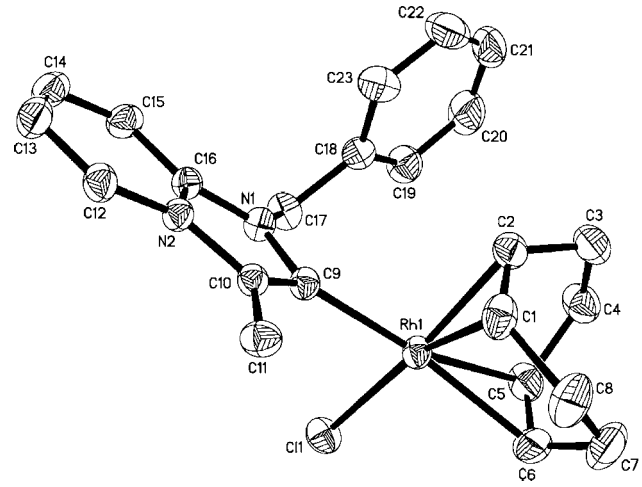


Figure 3. ORTEP diagram of **3a**, showing 50% probability ellipsoids.

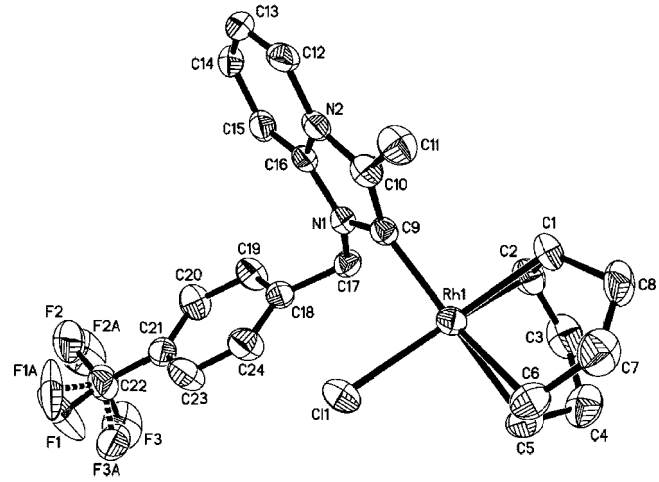


Figure 4. ORTEP diagram of **3d**, showing 50% probability ellipsoids.

Table 1. Selected Bond Lengths and Angles of Complexes 3a and 3d

	3a	3d
Bond Lengths (Å)		
Rh(1)−C(9)	2.039(2)	2.021(5)
Rh(1)−C(1)	2.097(2)	2.101(5)
Rh(1)−C(2)	2.110(2)	2.103(6)
Rh(1)−C(5)	2.194(2)	2.222(6)
Rh(1)−C(6)	2.218(2)	2.189(6)
C(9)−N(1)	1.412(2)	1.422(7)
C(9)−C(10)	1.380(2)	1.368(8)
N(2)−C(16)	1.368(2)	1.383(7)
Bond Angles (deg)		
C(9)−Rh(I)−Cl(1)	89.83(5)	89.72(14)
N(1)−C(9)−C(10)	104.6(2)	104.3(4)
Torsion Angle (deg)		
N(1)−C(9)−Rh(1)−Cl(1)	−70.6	−81.3

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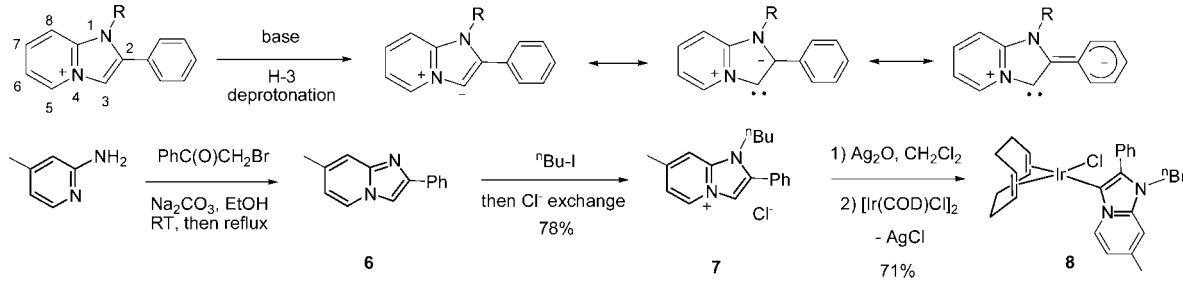
Scheme 2. Metalation at the 3-Position of an Imidazo[1,2-*a*]pyridinium



Metalation at the Complementary Position. Although H-3 is less acidic than H-2 in imidazo[1,2-*a*]pyridiniums, we reason that blocking the 2- position by a withdrawing group such as a phenyl group should favor the deprotonation of H-3, and the resulting negative charge can be stabilized (Scheme 2). Carbene precursor **7** was then synthesized by the N-alkylation of **6** followed by halide exchange using a chloride exchange resin. Indeed, silver transmetalation to iridium was successful, and complex **8** was isolated in 71% yield. Fluxionality in the NMR time scale was observed for **8**. In the NMR spectrum (CD_2Cl_2) at −20 °C, all the methylene protons in the ^{n}Bu group are sharp and diastereotopic, while they are all broad at 25 °C and coalescence of the NCH_2 signals was observed. This clearly shows that the barrier of the Ir−$C_{carbene}$ bond rotation is lower. In the ^{13}C NMR spectrum of **8**, the carbene C atom resonates at δ 151.9, and it is more shielded than those in **2a**−**d**. It is worth mentioning that no analogous silver carbene could be obtained when 1-*n*-butyl-2-methylimidazo[1,2-*a*]pyridinium chloride was treated with Ag_2O. The acidity of H-3 might play an important role here, although steric differences might also be accountable.

Synthesis of Iridium Biscarbonyl Complexes. The electronic effects of these new ligands were analyzed for all the iridium complexes. Iridium carbonyl complexes of the generic structure Ir(NHC)$(CO)_2$Cl were synthesized by bubbling CO (1 atm, 15 min) through solutions of **2a**−**d**, **5**, and **8**, resulting in the substitution of the COD ligand. The *cis* geometry proposed in Figure 5 is supported by IR spectroscopy, which shows two CO stretching (symmetric and asymmetric) vibrations of similar intensity. Inequivalent CO carbon atoms have also been observed by ^{13}C NMR spectroscopy.

Crystal Structure of 9d. Single crystals of **9d** suitable for X-ray analysis were obtained by layering its CH_2Cl_2 solution with pentane. As shown in Figure 6, the two CO ligands are in a *cis* arrangement. The NHC plane is nearly perpendicular to the iridium coordination plane. The Ir−$C_{carbene}$ distance is 2.075(4) Å and is comparable to those in Ir-NHC complexes.[12a,c,22] The Ir(1)−C(18) distance [1.899(4) Å] is significantly longer than the Ir(1)−C(17) distance [1.841(6) Å], undoubtedly due to the high *trans* influence of the NHC ligand.

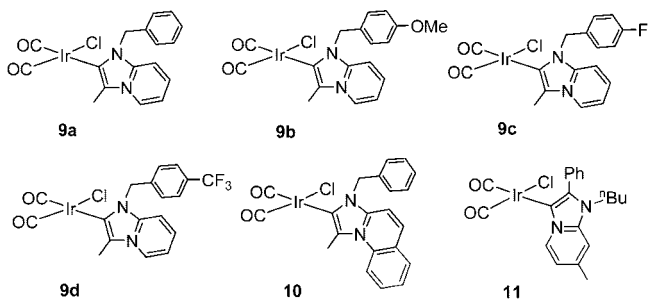


Figure 5. Iridium abnormal NHC carbonyl complexes.

Solution Dynamics. The methylene protons of complexes **9a**−**d** and **11** all showed broad singlet signals in the ^{1}H NMR spectra at room temperature ($CDCl_3$), indicating that the rotation along the Ir−$C_{carbene}$ bond is within the NMR time scale. Decoalescence of the CH_2 peaks was observed for **9a**−**d** and **11** at temperatures below −10 °C. VT NMR (−50 to −20 °C) and line shape analysis of the CH_2 signals of **9a** afforded enthalpy of activation $\Delta H^{\ddagger}$ =14.4 kcal/mol for the rotation along the Ir−$C_{carbene}$ bond.

The appearance of methylene protons signals for **10** is, however, significantly different from that of **9a**−**d** or **11**. Although they are broad ($W_{1/2}$ = 12.4 Hz) at room temperature, these signals are not coalesced and an AB pattern was observed (δ 6.27 and 5.82, $^2J_{HH}$ = 15.4 Hz), indicating a higher barrier of rotation along the Ir−$C_{carbene}$ here. Indeed, VT NMR (−10 to 25 °C) line shape analysis of those CH_2 signals of **10** afforded $\Delta H^{\ddagger}$ = 17.9 kcal/mol for the rotation along the Ir−$C_{carbene}$ bond. Here the barrier of rotation along Ir−$C_{carbene}$ is clearly higher

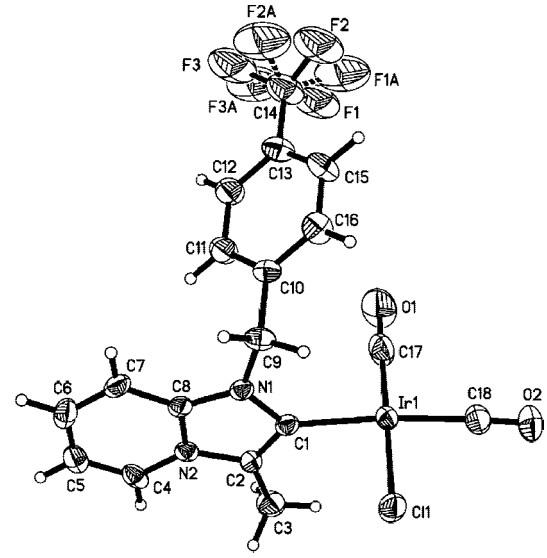


Figure 6. ORTEP diagram of **9d**, showing 50% probability ellipsoids. Selected lengths (Å) and angles (deg): Ir(1)−C(1) 2.075(4), Ir(1)−C(18) 1.899(4), Ir(1)−C(17) 1.841(6), Ir(1)−Cl(1) 2.075(4), C(1)−C(2) 1.364(5), C(1)−N(1) 1.413(5), C(17)−Ir(1)−C(18) 90.3(2), C(1)−Ir(1)−Cl(1) 88.53(11), N(1)−C(1)−Ir(1)−Cl(1) (torsion angle) 91.72.

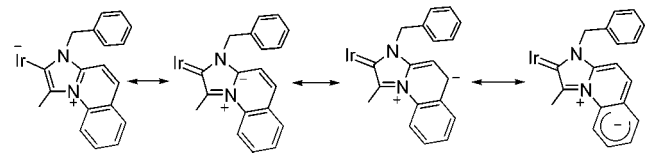
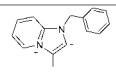
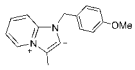
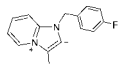
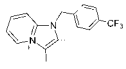
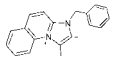


Figure 7. Back-donation to an abnormal NHC derived from imidazo[1,2-*a*]quinoline.

Table 2. Carbonyl Stretching Frequencies of Compounds *cis*-Ir(L)(CO)$_2$Cl

Ir(L)(CO)$_2$Cl	ν(CO) (cm^{-1})	ν_{av}(CO) (cm^{-1})	Ref.
	2041, 1957	1999	this work
	2049, 1967	2008	this work
	2054, 1986	2020	this work
	2050, 1984	2017	this work
	2050, 1981	2015	this work
	2046, 1965	2006	this work
	2045, 1961	2003	12a
	2059, 1974	2017	12c
	2062, 1978	2020	24
	2072, 1989	2031	24
	2058, 1973	2016	9
PCy$_3$	2072, 1984	2028	12c

than that in **9a**. It follows that the steric differences between the NHC ligands in **10** and **9a** are rather small; therefore, the differences of the barrier of rotation along the Ir−C$_{carbene}$ bond is very likely electronic in origin. The significantly higher barrier of bond rotation in **10** is ascribed to a higher bond order of the Ir−C$_{carbene}$ bond here. With the presence of an extra fused ring, this imidazo[1,2-*a*]quinoline-derived NHC ligand should be a better π-acceptor and consequently less electron-donating (Figure 7). Hence the Ir−C bond in **10** has more double-bond character as a result of the back-donation and carries a higher barrier of rotation. Further evidence to support the less electron-donating nature of the NHC ligand in **10** has been obtained from IR analysis of an iridium biscarbonyl complex (see the next paragraph). As a comparison with normal NHC complexes of transition metals, there have been debates on the significance of π-back-bonding effects in these complexes.[21a] Herrmann[4a] reported that π-back-bonding in NHC-transition metal complexes was negligible, and this conclusion was supported by theoretical studies.[21b] This idea of negligible back-donation is, however, challenged by some recent reports.[21a,c,d] Heinicke also reported that annulation of normal NHCs could efficiently increase the π-back-bonding interactions as a result of extended NHC π-systems,[21e,f] a scenario directly analogous to ours in abnormal NHC complexes.

Electronic Effects. The infrared carbonyl stretching frequencies of the rhodium and iridium complexes *cis*-M(CO)$_2$(L)Cl are well documented as a good measure of the donor ability of the L ligand: the more basic the ligand, the lower the observed ν(CO) values. In Table 2 the carbonyl frequencies of Ir(CO)$_2$(NHC)Cl are listed and compared with those of analogous complexes. The average CO stretching frequency [ν_{av}(CO) = 1999 cm^{-1}] of **9a** is the lowest among all the iridium complexes in this work and is lower than those in all related complexes in the literature. The fact that ν_{av}(CO) of **10** (2015 cm^{-1}) is significantly higher than that of **9a** (1999 cm^{-1}) indicates that the NHC in **10** is less electron-donating, consistent with the aforementioned VT NMR data, and the imidazo[1,2-*a*]quinoline-derived NHC in **10** can be best described as a stronger π-acceptor. Furthermore, the NHC ligand becomes less donating when a OMe, F, or CF$_3$ group is introduced to the *para* position of the benzyl group. The difference between the ν_{av}(CO) of **9a** and that of **9b** or **9d** is surprisingly large considering that the metal center and the *para*-substituted aromatic groups are isolated by a methylene group. As a contrast, changing the N-alkyl/aryl group of imidazole-based normal NHC ligands, however, has very limited influence on the electronic effects.[24] A plot of the average CO frequency of **9a**−**d** against the inductive substituent constant[23] (σ_I) of the *para* substituent is shown in Figure 8. The good correlation here ($R^2 = 0.99$) indicates that electron density on the iridium is inductively and sensitively tuned by the *para* substituent.

Table 2 shows the wide tunability of these new abnormal NHCs. They can be tuned to meet the donating level of abnormal NHCs derived from imidazolium ions (considering the resolution of 4 cm^{-1} in IR spectroscopy) or the relatively less electron-donating normal NHCs (imidazolin-2-ylidenes).

Conclusions

Rhodium and iridium complexes of a new type of abnormal NHCs derived from imidazo[1,2-*a*]pyridinium ions have been prepared via silver transmetalation and fully characterized by NMR and IR spectroscopy and X-ray crystallography. Metalation can take place at the C-2 or the C-3 positions provided that the other position is appropriately blocked. The electron-donating abilities of these new NHC ligands have been analyzed from the ν_{av}(CO) values of their corresponding iridium dicarbonyl complexes, which show a wide range of tunability. Both VT NMR studies and CO stretching frequency values support the π-accepting ability of an NHC ligand derived from imidazo[1,2-*a*]quinoline. The wide range of tunability of these abnormal NHCs is a desirable characteristic in many catalytic applications, and further studies on the catalytic properties of these carbene complexes are currently in progress.

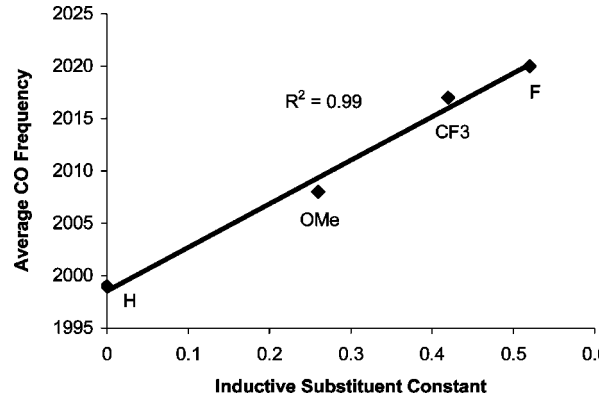


Figure 8. Correlation between the average CO frequency and the inductive effect of the *para* substituent in complexes **9a**−**d**.

Experimental Section

General Considerations. All manipulations were performed using standard Schlenk techniques. All solvents and chemicals were used as received without any further purification unless otherwise mentioned. NMR spectra were obtained on a Bruker DPX 300, AMX400, or 500 spectrometer. Spectra were recorded at room temperature unless otherwise specified. The sample temperature in VT NMR analysis was calibrated by 4% methanol in methanol-d_4. The chemical shift is given as dimensionless δ values and is frequency referenced relative to TMS for ^{1}H and ^{13}C NMR spectroscopy. Elemental analyses were performed in the Division of Chemistry and Biological Chemistry, Nanyang Technological University. HRMS spectra were obtained in EI or ESI mode on a Finnigan MAT95XP GC/HRMS system (Thermo Electron Corp.). X-ray crystallographic analyses were performed on a Bruker X8 APEX diffractometer. IR spectra were recorded on a Shimadzu IRPESTIGE-21 FTIR spectrometer from 4000 to 600 cm^{-1} with 4 cm^{-1} resolution.

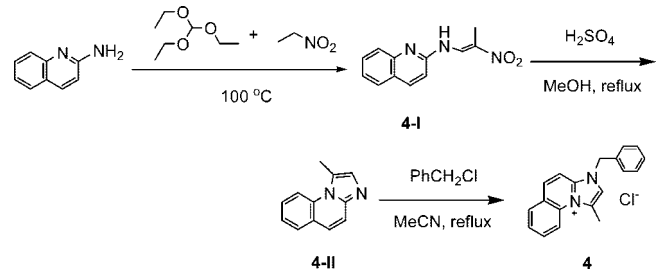
General Method for the Synthesis of 1a−d. 3-Methylimidazo[1,2-*a*]pyridine[19,20] and *para*-substituted benzyl chloride (1.5 equiv) were dissolved in CH_3CN, and the mixture was stirred under reflux for 12 h. The solvent was then removed under vacuum. The white solids obtained were washed with diethyl ether and used for complex formation without further purification.

Compound 1a. Yield: 86%. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.86 (d, J = 6.8 Hz, 1H), 8.43 (d, J = 9.1 Hz, 1H), 8.33 (s, 1H), 8.06 (t, J = 7.4 Hz, 1H), 7.60 (t, J = 6.8 Hz, 1H), 7.45–7.47 (m, 2H), 7.33–7.36 (m, 3H), 5.80 (s, 2H, CH_2), 2.59 (s, 3H, CH_3). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 138.9, 135.6, 133.7, 129.4, 128.9, 128.4, 128.2, 124.1, 122.9, 117.4, 111.6, 50.0, 9.1. HRMS (ESI$^+$): 223.1266, calcd for [$C_{15}H_{15}N_2^+$] 223.1235.

Compound 1b. Yield: 91%. ^{1}H NMR (300 MHz, DMSO-d_6): δ 8.83 (d, J = 6.8 Hz, 1H), 8.44 (d, J = 9.2 Hz, 1H), 8.26 (s, 1H), 8.07 (t, J = 8.5 Hz, 1H), 7.60 (t, J = 7.0 Hz, 1H), 7.44 (d, J = 8.7 Hz, 1H), 6.95 (d, J = 8.7 Hz, 1H), 5.68 (s, 2H, CH_2), 3.74 (s, 3H, OCH_3), 2.58 (s, 3H, CH_3). ^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6): δ 159.9, 138.8, 133.6, 130.2, 128.1, 127.4, 124.0, 122.7, 117.3, 114.7, 111.6, 55.7, 49.6, 9.0. HRMS (ESI$^+$): 253.1349, calcd for [$C_{16}H_{17}N_2O^+$] 253.1341.

Compound 1c. Yield: 87%. ^{1}H NMR (300 MHz, DMSO-d_6): δ 8.82 (d, J = 6.8 Hz, 1H), 8.42 (d, J = 9.2 Hz, 1H), 8.26 (s, 1H), 8.05 (t, J = 8.2 Hz, 1H), 7.52–7.61 (m, 3H), 7.22 (t, J = 8.8 Hz, 2H), 5.75 (s, J = 0.7 Hz, 2H, CH_2), 2.57 (s, 3H, CH_3). ^{19}F{^{1}H} NMR (282 MHz, DMSO-d_6): δ −113.4 (s). ^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6): δ 162.6 (d, J_{F-C} = 243.5 Hz), 138.9, 133.8, 131.7 (d, J_{F-C} = 3.1 Hz), 130.9 (d, J_{F-C} = 8.4 Hz), 128.1, 124.1, 122.7, 117.4, 116.2 (d, J_{F-C} = 21.5 Hz), 111.5, 49.3, 9.0. HRMS (ESI$^+$): 241.1114, calcd for [$C_{15}H_{14}N_2F^+$] 241.1141.

Compound 1d. Yield: 93%. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.87 (d, J = 6.5 Hz, 1H), 8.41 (d, J = 9.2 Hz, 1H), 8.32 (s, 1H), 8.08 (t, J = 7.1 Hz, 1H), 7.77 (d, J = 8.2 Hz, 2H), 7.61–7.70 (m, 3H), 5.92 (s, 2H, CH_2), 2.60 (s, 3H, CH$_3$). ^{19}F{^{1}H} NMR (282 MHz, DMSO-d_6): δ −61.1 (s). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 140.2, 139.2, 133.9, 129.4 (q, J_{F-C} = 31.7 Hz), 129.1, 128.2, 126.2 (q, J_{F-C} = 3.7 Hz), 124.5 (q, J_{F-C} = 270.6 Hz, CF_3), 124.3, 122.9, 117.5, 111.5, 49.4, 9.1. HRMS (ESI$^+$): 291.1058, calcd for [$C_{16}H_{14}N_2F_3^+$] 291.1109.



Synthesis of Compound 4-I. A mixture of 3-aminoquinoline (1.44 g, 10.0 mmol), triethyl orthoformate (1.48 g, 10.0 mmol), and nitroethane (0.71 g, 10.0 mmol) was stirred at 100 °C for 16 h.[19,20] All the volatiles were then removed under reduced pressure. **4-I** was obtained as a yellow solid after silica gel chromatography using hexanes/ethyl acetate as an eluent. Yield: 31% (0.71 mg). ^{1}H NMR (400 Hz, $CDCl_3$): δ 10.84 (d, J = 11.0 Hz, 1H), 8.50 (d, J = 12.3 Hz, 1H), 8.11 (d, J = 8.6 Hz, 1H), 7.89 (d, J = 8.4 Hz, 1H), 7.75 (d, J = 8.0 Hz, 1H), 7.69 (t, J = 7.8 Hz, 1H), 7.45 (t, J = 7.5 Hz, 1H), 7.01 (d, J = 8.7 Hz, 1H), 2.26 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 149.1, 147.0, 139.2, 133.6, 130.6, 127.7, 127.6, 126.0, 125.3, 122.9, 112.9, 16.5.

Compound 4. Compound **4-I** (400 mg, 1.75 mmol) was dissolved in a 40% sulfuric acid solution of methanol (10 mL), and the solution was stirred under reflux for 6 h. The solution was diluted with ice–water, neutralized by sodium carbonate, and extracted by dichloromethane. The organic layer was dried by sodium sulfate, and the solvent was removed under vacuum, followed by silica gel chromatography using hexanes/ethyl acetate as an eluent to give compound **4-II**. Yield: 40% (127 mg). ^{1}H NMR (400 Hz, $CDCl_3$): δ 8.28 (d, J = 8.6 Hz, 1H), 7.68 (d, J = 8.4 Hz, 1H), 7.13–7.50 (m, 5H), 2.82 (s, 3H). Compound **4** was synthesized from the alkylation of **4-II** with benzyl chloride in MeCN under reflux. Yield: 90%. ^{1}H NMR (400 Hz, DMSO-d_6): 8.73 (d, J = 8.7 Hz, 1H), 8.50 (d, J = 9.6 Hz, 1H), 8.34 (d, J = 9.6 Hz, 1H), 8.28 (br s, 2H), 7.99 (t, J = 7.5 Hz, 1H), 7.84 (t, J = 7.5 Hz, 1H), 7.30–7.47 (m, 5H), 5.85 (s, 2H, CH_2), 3.05 (s, 3H, CH_3). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 139.4, 135.3, 135.2, 133.7, 132.1, 130.7, 129.4, 129.0, 128.3, 128.2, 127.8, 124.9, 123.3, 118.1, 109.7, 50.3, 14.9. HRMS (ESI$^+$): 273.1359, calcd for [$C_{19}H_{17}N_2^+$] 273.1386.

Compound 6. A mixture of 4-methylpyridin-2-amine (1.08 g, 10 mmol), 2-bromoacetophenone (1.99 g, 10 mmol), and sodium bicarbonate (2.1 g, 15 mmol) in ethanol (25 mL) was stirred for 3 h under reflux. After removal of ethanol under vacuum, dichloromethane was added to the residue and any insoluble was removed by filtration, followed by silica gel chromatography. Yield: 91% (1.89 g). ^{1}H NMR (400 Hz, $CDCl_3$): δ 7.96 (t, J = 7.2 Hz, 3H), 7.77 (s, 1H), 7.44 (t, J = 7.4 Hz, 2H), 7.39 (s, 1H), 7.31 (t, J = 7.4 Hz, 1H), 6.59 (d, J = 6.9 Hz, 1H), 3.40 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 146.2, 145.5, 135.6, 134.0, 128.7, 127.8, 125.9, 124.8, 115.9, 115.0, 107.5, 21.4. HRMS (EI): 208.1039, calcd for [$C_{14}H_{12}N_2$] 208.1000.

Compound 7. Compound **6** (800 mg, 3.85 mmol) and 1-iodobutane (1.06 g, 5.78 mmol) were dissolved in acetonitrile (15 mL), and the mixture was stirred under reflux for 12 h. After removal of all volatiles, the residue was washed with diethyl ether to give the iodide salt as a yellow solid in 96% yield. Iodide to chloride exchange was performed by stirring a mixture of the iodide salt (200 mg, 0.51 mmol) and DOWEX 21K chloride exchange resin (2 g) in methanol for 10 h. A residue was obtained after the removal of methanol, to which was added CH_2Cl_2 (20 mL). A clear solution was obtained after filtration. Product **7** was obtained as a

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white solid after the removal of CH_2Cl_2. Yield: 148 mg (97%). ^{1}H NMR (400 Hz, $CDCl_3$): δ 9.54 (d, J = 6.4 Hz, 1H), 8.87 (s, 1H), 7.91 (s, 1H), 7.48–7.55 (m, 5H), 7.19 (d, J = 6.2 Hz, 1H), 4.39 (t, J = 7.5 Hz, 2H, N−CH_2), 2.63 (s, 3H, Me), 1.61–1.68 (m, 2H, CH_2), 1.17–1.23 (m, 2H, CH_2), 0.76 (t, J = 7.3 Hz, 3H, CH_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 146.9, 139.5, 137.1, 131.0, 129.9, 129.8, 129.4, 125.1, 119.9, 113.5, 109.7, 45.2, 31.4, 22.3, 19.6, 13.5. HRMS (ESI$^+$): 265.1732, calcd for [$C_{18}H_{21}N_2$] 265.1705.

General Procedure for Synthesis of Rhodium and Iridium Complexes 2, 3, 5, and 8. Imidazo[1,2-*a*]pyridinium chloride was dissolved in dry dichloromethane. Several drops of methanol could be added if the solubility is poor. Silver oxide (0.5 equiv) was added, and the mixture was stirred at room temperature in the dark for 0.5–1 h. The mixture was then filtered to give a clear solution, to which was added 0.5 equiv of [M(COD)Cl]$_2$ (M = Ir or Rh); the mixture was stirred for 1 h. The suspension was filtered through Celite to remove AgCl, and the solvent was removed under reduced pressure. The residue was filtered through a short column of Al_2O_3 using dichloromethane to give analytically pure products after the removal of dichloromethane.

Complex 2a. Yield: 83%. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.94 (d, J = 6.7 Hz, 1H), 7.27–7.36 (m, 5H), 7.16–7.19 (m, 2H), 7.05 (t, J = 6.7 Hz, 1H), 6.06 (d, J = 15.8 Hz, 1H, CH_2), 6.01 (d, J = 15.8 Hz, 1H, CH_2), 4.36 (m, 2H, COD), 3.07 (m, 1H, COD), 2.71 (s, 3H, CH_3), 2.68–2.71 (m, 1H, COD), 2.10–2.29 (m, 3H, COD), 1.83–1.87 (m, 1H, COD), 1.59–1.65 (m, 3H, COD), 1.38–1.41 (m, 1H, COD). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 168.6 (Ir-*C*), 140.3, 136.6, 128.6, 127.7, 127.3, 125.0, 122.2, 122.1, 114.6, 109.0, 82.0 (*C*H of COD), 80.9 (*C*H of COD), 53.6 (Ph-*C*H$_2$), 52.9(*C*H of COD), 50.8 (*C*H of COD), 33.7 (*C*H$_2$ of COD), 33.3(*C*H$_2$ of COD), 29.9 (*C*H$_2$ of COD), 29.5(*C*H$_2$ of COD), 11.0 (*C*H$_3$). Anal. Calcd for $C_{23}H_{26}ClIrN_2$ (558.1): C, 49.49; H, 4.70; N, 5.02. Found: C, 49.81; H, 4.52; N, 5.09.

Complex 2b. Yield: 87%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.88 (d, J = 6.6 Hz, 1H), 7.28–7.30 (m, 2H), 7.13–7.22 (m, 2H), 7.04 (t, J = 6.4 Hz, 1H), 6.86 (d, J = 8.6 Hz, 2H), 6.16 (d, J = 15.6 Hz, 1H, CH_2), 5.85 (d, J = 15.6 Hz, 1H, CH_2), 4.50 (m, 2H, COD), 3.78 (s, 3H, OCH_3), 3.07–3.11 (m, 1H, COD), 2.72 (br, 4H, CH_3 and 1H of COD), 2.17–2.33 (m, 3H, COD), 1.90–1.92 (m, 1H, COD), 1.51–1.69 (m, 3H, COD), 1.42–1.43 (m, 1H, COD). ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.1 (Ir-*C*), 159.2, 140.2, 128.6, 128.4, 124.6, 122.2, 121.7, 114.5, 114.2, 109.2, 82.5 (*C*H of COD), 81.4 (*C*H of COD), 77.2, 55.3 (*C*H of COD), 53.4, 53.1, 50.8 (*C*H of COD), 34.0 (*C*H$_2$ of COD), 33.4 (*C*H$_2$ of COD), 30.0 (*C*H$_2$ of COD), 29.4 (*C*H$_2$ of COD), 11.3 (*C*H$_3$). Anal. Calcd for $C_{24}H_{28}ClIrN_2O$ (588.2): C, 49.01; H, 4.80; N, 4.76. Found: C, 49.21; H, 4.70; N, 4.65.

Complex 2c. Yield: 79%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, J = 6.7 Hz, 1H), 7.32–7.35 (m, 2H), 7.20–7.22 (m, 1H), 7.12–7.14 (m, 1H), 7.07 (t, J = 6.8 Hz, 1H), 7.01 (d, J = 8.6 Hz, 2H), 6.14 (d, J = 15.8 Hz, 1H, CH_2), 5.92 (d, J = 15.8 Hz, 1H, CH_2), 4.50 (t, J = 2.8 Hz, 2H, COD), 3.07 (t, J = 7.1 Hz, 1H, COD), 2.72 (s, 3H, CH_3), 2.68 (td, J = 7.2, 3.0 Hz, 1H, COD), 2.10–2.34 (m, 3H, COD), 1.81–1.90 (m, 1H, COD), 1.58–1.71 (m, 3H, COD), 1.39–1.45 (m, 1H, COD). ^{19}F{^{1}H} NMR (282 MHz, $CDCl_3$): δ −114.2 (s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.1 (C−Ir), 162.3 (d, J_{F-C} = 245.2 Hz, *C*-F), 140.2, 132.1 (d, J_{F-C} = 3.2 Hz), 129.1 (d, J_{F-C} = 8.1 Hz), 124.9, 122.4, 121.9, 115.7 (d, J_{F-C} = 21.4 Hz), 114.7, 108.9, 82.8 (*C*H of COD), 81.8 (*C*H of COD), 53.2 (*C*H of COD), 50.0 (*C*H$_2$), 50.8 (*C*H of COD), 33.9 (*C*H$_2$ of COD), 33.4 (*C*H$_2$ of COD), 30.0 (*C*H$_2$ of COD), 29.4 (*C*H$_2$ of COD), 11.3 (*C*H$_3$). Anal. Calcd for $C_{23}H_{25}ClFIrN_2$ (576.1): C, 47.95; H, 4.37; N, 4.86. Found: C, 47.59; H, 4.21; N, 4.70.

Complex 2d. Yield: 82%. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.97 (d, J = 6.7 Hz, 1H), 7.60 (d, J = 8.2 Hz, 2H), 7.49 (d, J = 8.1 Hz, 2H), 7.25–7.31 (m, 1H), 7.10–7.16 (m, 2H), 6.11 (s, 2H, accidentally equivalent CH_2), 4.36 (m, 2H, COD), 3.07 (m, 1H, COD), 2.72 (s, 3H, CH_3), 2.59–2.65 (m, 1H, COD), 2.11–2.30 (m, 3H, COD), 1.82–1.90 (m, 1H, COD), 1.59–1.69 (m, 3H, COD), 1.39–1.41 (m, 1H, COD). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.94 (d, J = 6.6 Hz, 1H), 7.59 (d, J = 8.0 Hz, 2H), 7.49 (d, J = 8.1 Hz, 2H), 7.25–7.31 (m, 1H), 7.08–7.14 (m, 2H), 6.30 (d, J = 16.3 Hz, 1H, diastereotopic CH_2), 5.98 (d, J = 16.3 Hz, 1H, diastereotopic CH_2), 4.50 (m, 2H, COD), 3.09 (m, 1H, COD), 2.74 (s, 3H, CH_3), 2.58–2.64 (m, 1H, COD), 2.00–2.40 (m, 3H, COD), 1.82–1.90 (m, 1H, COD), 1.59–1.69 (m, 3H, COD), 1.30–1.50 (m, 1H, COD). ^{19}F{^{1}H} NMR (282 MHz, CD_2Cl_2): δ −62.9 (s). ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2): δ 168.6 (Ir-*C*), 140.7, 140.3, 129.7 (q, J_{F-C} = 32.2 Hz), 127.7, 125.5 (q, J_{F-C} = 3.8 Hz), 125.4, 124.2 (q, J_{F-C} = 270.4 Hz, *C*F$_3$), 122.5, 122.2, 114.8, 108.7, 82.4 (*C*H of COD), 81.3 (*C*H of COD), 53.0 (*C*H of COD), 52.9 (*C*H$_2$), 50.8 (*C*H of COD), 33.8 (*C*H$_2$ of COD), 33.3(*C*H$_2$ of COD), 29.9(*C*H$_2$ of COD), 29.4(*C*H$_2$ of COD), 10.0 (*C*H$_3$). Anal. Calcd for $C_{24}H_{25}ClF_3IrN_2$ (626.1) C, 46.04; H, 4.02; N, 4.47. Found: C, 46.16; H, 3.92; N, 4.61.

Complex 3a. Yield: 87%. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.91 (d, J = 6.7 Hz, 1H), 7.31–7.40 (m, 5H), 7.15–7.21 (m, 2H), 7.05 (t, J = 6.5 Hz, 1H), 6.30 (d, J = 16.0 Hz, 1H, CH_2), 6.10 (d, J = 15.9 Hz, 1H, CH_2), 4.84 (br, 2H, COD), 3.41 (br, 1H, COD), 3.03 (br, 1H, COD), 2.78 (s, 3H, CH_3), 2.20–2.49 (m, 3H, COD), 1.83–1.93 (m, 4H, COD), 1.72 (br, 1H, COD). ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2): δ 169.3 (d, J_{Rh-C} = 46.0 Hz, Rh-*C*), 140.4, 136.8, 128.7, 127.7, 127.2, 124.8, 121.8, 121.6 (d, J_{Rh-C} = 2.5 Hz), 114.3, 108.7, 96.9 (d, J_{Rh-C} = 6.7 Hz, *C*H of COD), 96.2 (d, J_{Rh-C} = 6.6 Hz, *C*H of COD), 68.8 (d, J_{Rh-C} = 14.7 Hz, *C*H of COD), 67.0 (d, J_{Rh-C} = 14.7 Hz, *C*H of COD), 54.0 (Ph-*C*H$_2$), 32.9 (d, J_{Rh-C} = 14.3 Hz, *C*H$_2$ of COD), 28.9(s, *C*H$_2$ of COD), 11.3 (*C*H$_3$). Anal. Calcd for $C_{23}H_{26}ClN_2Rh$ (468.8): C, 58.92; H, 5.59; N, 5.98. Found: C, 58.76; H, 5.60; N, 5.89.

Complex 3b. Yield: 87%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.85 (d, J = 6.6 Hz, 1H), 7.26–7.30 (m, 2H), 7.13–7.22 (m, 2H), 7.01 (td, J = 6.5, 2.3 Hz, 1H), 6.86 (d, J = 8.7 Hz, 2H), 6.41 (d, J = 15.7 Hz, 1H, diastereotopic CH_2), 5.93 (d, J = 15.7 Hz, 1H, diastereotopic CH_2), 4.96 (m, 2H, COD), 3.79 (s, 3H, OCH_3), 3.41–3.46 (m, 1H, COD), 3.07–3.12 (m, 1H, COD), 2.78 (s, 3H, CH_3), 2.26–2.55 (m, 3H, COD), 2.01–2.06 (m, 1H, COD), 1.85–1.92 (m, 4H, COD). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 168.9 (d, J_{Rh-C} = 45.8 Hz, Rh-*C*), 158.2, 139.2, 127.6, 127.5, 123.5, 120.6 (d, J_{Rh-C} = 2.3 Hz), 120.5, 113.2, 113.1, 107.9, 96.3 (d, J_{Rh-C} = 6.8 Hz, *C*H of COD), 95.6 (d, J_{Rh-C} = 6.8 Hz, *C*H of COD), 67.9 (d, J_{Rh-C} = 15.0 Hz, *C*H of COD), 65.9 (d, J_{Rh-C} = 14.8 Hz, *C*H of COD), 55.3, 54.3 (*C*H$_2$), 32.0 (d, J_{Rh-C} = 17.9 Hz, *C*H$_2$ of COD), 28.9(d, J_{Rh-C} = 13.3 Hz, *C*H$_2$ of COD), 10.6 (*C*H$_3$). Anal. Calcd for $C_{24}H_{28}ClN_2ORh$ (498.9): C, 57.78; H, 5.66; N, 5.62. Found: C, 57.35; H, 5.71; N, 5.55.

Complex 3c. Yield: 91%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (d, J = 6.7 Hz, 1H), 7.32–7.36 (m, 2H), 7.17–7.21 (m, 1H), 7.10–7.12 (m, 1H), 7.01–7.06 (m, 3H), 6.40 (d, J = 15.9 Hz, 1H, CH_2), 5.92 (d, J = 15.9 Hz, 1H, CH_2), 4.96 (br, 2H, COD), 3.40–3.43 (m, 1H, COD), 3.02–3.05 (m, 1H, COD), 2.79 (s, 3H, CH_3), 2.39–2.51 (m, 2H, COD), 2.24–2.27 (m, 1H, COD), 1.85–2.01 (m, 4H, COD), 1.75–1.76 (m, 1H, COD). ^{19}F{^{1}H} NMR (282 MHz, $CDCl_3$): δ −114.3 (s). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 169.9 (d, J_{Rh-C} = 45.9 Hz, Rh-*C*), 162.3 (d, J_{F-C} = 245.0 Hz, *C*-F), 140.2, 132.3 (d, J_{F-C} = 3.1 Hz), 128.9 (d, J_{F-C} = 8.0 Hz), 124.7, 121.8 (d, J_{Rh-C} = 2.2 Hz), 121.6, 115.8 (d, J_{F-C} = 21.4 Hz), 114.4, 108.7, 97.5 (d, J_{Rh-C} = 6.9 Hz, *C*H of COD), 96.7 (d, J_{Rh-C} = 6.9 Hz, *C*H of COD), 69.0 (d, J_{Rh-C} = 15.0 Hz, *C*H of COD), 67.0 (d, J_{Rh-C} = 14.9 Hz, *C*H of COD), 53.6 (*C*H$_2$), 33.0 (d, J_{Rh-C} = 13.9 Hz, *C*H$_2$ of COD), 28.9(d, J_{Rh-C} = 11.6 Hz, *C*H$_2$ of COD), 11.7 (*C*H$_3$). Anal. Calcd for $C_{23}H_{25}ClFN_2Rh$ (486.8): C, 56.75; H, 5.18; N, 5.75. Found: C, 56.49; H, 5.24; N, 5.65.

Complex 3d. Yield: 88%. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.97 (d, J = 6.6 Hz, 1H), 7.65 (d, J = 8.2 Hz, 2H), 7.54 (d, J = 8.1 Hz,

2H), 7.27–7.31 (m, 1H), 7.11–7.18 (m, 2H), 6.39 (d, $J = 16.3$ Hz, 1H, CH_2), 6.25 (d, $J = 16.3$ Hz, 1H, CH_2), 4.88 (br, 2H, COD), 3.43–3.46 (m, 1H, COD), 2.99–3.03 (m, 1H, COD), 2.74 (s, 3H, CH_3), 2.38–2.58 (m, 2H, COD), 2.21–2.28 (m, 1H, COD), 1.86–2.03 (m, 4H, COD), 1.74–1.76 (m, 1H, COD). ^{19}F NMR (282 MHz, CD_2Cl_2): δ −62.8. $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2): δ 169.4 (d, $J_{Rh-C} = 45.8$ Hz, *C*-Rh), 141.1, 140.3, 129.7 (q, $J_{C-F} = 32.0$ Hz), 127.7, 125.5 (q, $J_{C-F} = 3.6$ Hz), 125.4, 124.8 (q, $J_{C-F} = 272.0$ Hz, *C*F$_3$), 122.0, 121.9 (d, $J_{Rh-C} = 2.3$ Hz), 114.6, 108.5, 97.2 (d, $J_{Rh-C} = 6.7$ Hz, *C*H of COD), 96.5 (d, $J_{Rh-C} = 6.7$ Hz, *C*H of COD), 69.0 (d, $J_{Rh-C} = 14.9$ Hz, *C*H of COD), 67.1 (d, $J_{Rh-C} = 14.9$ Hz, *C*H of COD), 53.4 (*C*H$_2$), 32.9 (d, $J_{Rh-C} = 14.1$ Hz, *C*H$_2$ of COD), 28.8(s, *C*H$_2$ of COD), 11.3 (*C*H$_3$). Anal. Calcd for $C_{24}H_{25}ClF_3N_2Rh$ (536.8): C, 53.70; H, 4.69; N, 5.22. Found: C, 53.61; H, 4.47; N, 5.39.

Complex 5. Yield: 85%. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 8.67 (d, $J = 8.8$ Hz, 1H), 7.87 (dd, $J = 7.9$, 1.3 Hz, 1H), 7.75 (td, $J = 8.8$, 1.6 Hz, 1H), 7.52–7.60 (m, 2H), 7.28–7.36 (m, 5H), 7.16 (d, $J = 9.4$ Hz, 1H), 6.12 (s, 2H, CH_2), 4.36 (br, 2H, COD), 3.32 (s, 3H, CH_3), 3.09 (td, $J = 6.9$, 2.5 Hz, 1H, COD), 2.57 (td, $J = 7.2$, 3.1 Hz, 1H, COD), 2.06–2.35 (m, 3H, COD), 1.81–1.93 (m, 1H, COD), 1.58–1.68 (m, 3H, COD), 1.34–1.37 (m, 1H, COD). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 168.8 (Ir-*C*), 140.0, 136.9, 133.2, 130.2, 129.7, 129.1, 128.1, 127.6, 127.4, 126.9, 126.3, 125.0, 117.9, 108.8, 81.9 (*C*H of COD), 81.0 (*C*H of COD), 54.0 (*C*H$_2$), 53.4 (*C*H of COD), 51.3 (*C*H of COD), 34.2 (*C*H$_2$ of COD), 33.8(*C*H$_2$ of COD), 30.3 (*C*H$_2$ of COD), 30.3 (*C*H$_2$ of COD), 18.2 (*C*H$_3$). Anal. Calcd for $C_{27}H_{28}ClIrN_2$ (608.2) C, 53.32; H, 4.64; N, 4.61. Found: C, 53.43; H, 4.71; N, 4.65.

Complex 8. Yield: 71%. ^{1}H NMR (300 MHz, CD_2Cl_2, 253 K): δ 9.23 (d, $J = 6.9$ Hz, 1H), 7.88 (d, $J = 6.8$ Hz, 2H), 7.45–7.53 (m, 3H), 7.18 (s, 1H), 6.94 (d, $J = 6.9$ Hz, 1H), 4.31–4.34 (m, 1H, diastereotopic N-CH_2), 4.23 (m, 1H, diastereotopic N-CH_2), 4.12 (m, 2H, COD), 2.82 (m, 1H, COD), 2.52 (s, CH_3), 2.31–2.34 (m, 1H, COD), 1.90–2.13 (m, 3H, COD), 1.72–1.77 (m, 2H, CH_2), 1.44–1.50 (m, 4H, COD), 1.27–1.30 (m, 2H, CH_2), 1.24–1.27 (m, 1H, COD), 0.86 (t, $J = 7.3$ Hz, 3H, CH$_2$CH_3). ^{13}C NMR (75 MHz, CD_2Cl_2, 298 K): δ 151.9 (Ir-*C*), 141.7, 141.0, 136.5, 132.9, 131.4, 130.8, 127.9, 116.1, 107.7, 79.7, 44.3, 31.5, 29.9, 21.5, 19.8, 13.2. Anal. Calcd $C_{26}H_{32}ClIrN_2$ (600.2): C, 52.03; H, 5.37; N, 4.67. Found: C, 51.90; H, 5.42; N, 4.55.

General Method for the Synthesis of Bicarbonyl Complexes 9, 10, and 11. An iridium COD complex (**2**, **5**, or **8**) was dissolved in dry dichloromethane to give a solution, through which was bubbled CO for 15 min. The solvent was removed under vacuum, followed by addition of diethyl ether to afford the biscarbonyl complexes.

Complex 9a. Yield: 95%. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 8.07 (d, $J = 6.8$ Hz, 1H), 7.32–7.48 (m, 7H), 7.22 (t, $J = 6.8$ Hz, 1H), 5.87 (br, 2H, CH_2), 2.66 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): δ 183.4, 169.6, 160.1, 140.3, 135.7, 128.8, 128.1, 127.7, 127.2, 126.4, 123.6, 115.3, 109.9, 53.3, 11.2. FTIR (Nujol): ν_{CO} 2041, 1957 cm^{-1}. Anal. Calcd for $C_{17}H_{14}ClIrN_2O_2$ (506.0): C, 40.35; H, 2.97; N, 5.54; C, 40.19; H, 3.17; N, 5.51. Found: C, 40.31; H, 3.04; N, 5.40.

Complex 9b. Yield: 96%. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 8.05 (d, $J = 6.8$ Hz, 1H), 7.42–7.47 (m, 2H), 7.37–7.39 (m, 2H), 7.20–7.21 (m, 1H), 6.85 (d, $J = 6.7$ Hz, 2H), 5.80 (br, 2H, CH_2), 3.76 (s, 3H, OCH_3), 2.66 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): δ 183.4, 169.6, 160.1, 159.6, 139.5, 130.7, 128.7, 127.7, 127.6, 123.5, 115.3, 114.0, 109.9, 55.2, 52.7, 11.2. FTIR (Nujol): ν_{CO} 2049, 1967 cm^{-1}. Anal. Calcd for $C_{18}H_{16}ClIrN_2O_3$ (536.0): C, 40.33; H, 3.01; N, 5.23. Found: C, 40.26; H, 3.29; N, 5.47.

Complex 9c. Yield: 97%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, $J = 6.7$ Hz, 1H), 7.44–7.46 (m, 1H), 7.34–7.39 (m, 3H), 7.20–7.24 (m, 1H), 7.02 (t, $J = 7.5$ Hz, 2H), 5.74 (br, 2H, CH_2), 2.70 (s, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 182.7, 169.3, 162.5 (d, $J_{F-C} = 246$ Hz, C−F), 160.6, 140.1, 131.2 (d, $J_{F-C} = 3.0$ Hz), 129.1 (d, $J_{F-C} = 8.1$ Hz), 127.5, 126.5, 123.4, 115.9 (d, $J_{F-C} = 21.6$ Hz), 115.4, 109.9, 52.7, 11.5. FTIR (Nujol): ν_{CO} 2054, 1986 cm^{-1}. Anal. Calcd for $C_{17}H_{13}ClFIrN_2O_2$ (524.0): C, 38.97; H, 2.50; N, 5.35. Found C, 39.02; H, 2.66; N, 5.21.

Complex 9d. Yield: 93%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.07 (d, $J = 6.8$ Hz, 1H), 7.59 (d, $J = 8.0$ Hz, 2H), 7.42–7.48 (m, 2H), 7.28–7.31 (m, 3H), 5.97 (br, 2H, CH_2), 2.70 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 183.4, 169.2, 160.8, 140.2, 139.2, 130.5 (q, $J_{F-C} = 32.4$ Hz), 127.8, 127.5, 126.7, 125.9 (q, $J_{F-C} = 3.8$ Hz), 123.8 (q, $J_{F-C} = 270$ Hz), 123.5, 115.6, 109.7, 52.9, 11.5. FTIR (Nujol): ν_{CO} 2050, 1984 cm^{-1}. Anal. Calcd for $C_{18}H_{13}ClF_3IrN_2O_2$ (574.0): C, 37.67; H, 2.28; N, 4.88. Found C, 37.39; H, 2.45; N, 4.96.

Complex 10. Yield: 94%. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 8.73 (d, $J = 8.8$ Hz, 1H), 7.98 (d, $J = 7.9$ Hz, 1H), 7.86 (t, $J = 8.8$ Hz, 1H), 7.78 (d, $J = 8.9$ Hz, 1H), 7.69 (t, $J = 8.0$ Hz, 1H), 7.34–7.37 (m, 6H), 6.27 (d, $J = 15.4$ Hz, 1H, diastereotopic CH_2), 5.82 (d, $J = 15.4$ Hz, 1H, diastereotopic CH_2), 3.27 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): δ 183.2, 169.5, 158.9, 139.3, 135.6, 133.2, 130.6, 130.5, 130.0, 129.6, 128.8, 128.1, 127.0, 126.5, 124.6, 117.4, 108.5, 53.5, 18.1. FTIR (Nujol): ν_{CO} 2050, 1981 cm^{-1}. Anal. Calcd for $C_{21}H_{16}ClIrN_2O_2$ (556.0): C, 45.36; H, 2.90; N, 5.04. Found: C, 45.45; H, 3.11; N, 4.94.

Complex 11. Yield: 93%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.20 (d, $J = 7.0$ Hz, 1H), 7.64–7.66 (m, 2H), 7.48–7.50 (m, 3H), 7.20 (s, 1H), 6.93 (d, $J = 7.0$ Hz, 1H), 4.10 (t, $J = 7.7$ Hz, 2H, N−CH_2), 2.54 (s, 3H, Ph-CH_3), 1.64 (quintet, $J = 7.1$ Hz, 2H, CH_2), 1.23 (sextet, $J = 7.2$ H, CH_2), 0.82 (t, $J = 7.3$ Hz, 3H, CH$_2$-CH_3). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 182.8, 168.8, 145.4, 143.2, 141.6, 140.9, 133.0, 131.3, 130.0, 129.2, 128.4, 116.7, 107.7, 44.4, 31.5, 21.9, 19.8, 13.4. FTIR (Nujol): ν_{CO} 2046, 1965 cm^{-1}. Anal. Calcd for $C_{20}H_{20}ClIrN_2O_2$ (548.1): C, 43.83; H, 3.68; N, 5.11. Found: C, 43.54; H, 3.80; N, 4.89.

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Supporting Information Available: VT NMR data of complexes **9a** and **10** and X-ray crystallographic data (PDF and CIF) of **3a**, **3d**, and **9d**. This material is available free of charge via the Internet at http://pubs.acs.org.

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