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Published on Web 08/07/2002

Abnormal Ligand Binding and Reversible Ring Hydrogenation in the Reaction of Imidazolium Salts with $IrH_5(PPh_3)_2$

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Received April 30, 2002

Abstract: We show that imidazolium salts do not always give normal or even aromatic carbenes on metalation, and the chemistry of these ligands can be much more complicated than previously thought. *N,N′*-disubstituted imidazolium salts of type $[(2\text{-py})(CH_2)_n(C_3H_3N_2)R]BF_4$ react with $IrH_5(PPh_3)_2$ to give N,C-chelated products ($n = 0$, 1; 2-py = 2-pyridyl; $C_3H_3N_2$ = imidazolium; R = mesityl, *n*-butyl, *i*-propyl, methyl). Depending on the circumstances, three types of kinetic products can be formed: in one, the imidazole metalation site is the normal C2 as expected; in another, the metalation occurs at the abnormal C4 site; and in the third, C4 metalation is accompanied by hydrogenation of the imidazolium ring. The bonding mode is confirmed by structural studies, and spectroscopic criteria can also distinguish the cases. Initial hydrogen transfer can take place from the metal to the carbene to give the imidazolium ring hydrogenation product, as shown by isotope labeling; this hydrogen transfer proves reversible on reflux when the abnormal aromatic carbene is obtained as final product. Care may therefore be needed in the future in verifying the structure(s) formed in cases where a catalyst is generated in situ from imidazolium salt and metal precursor.

Introduction

N-heterocyclic carbenes **1** show promise as ligands for the development of new or improved catalyst systems.[1] While the synthesis of the ligand precursors is fairly simple,[2] introduction of the metal is more challenging and, as shown here, can give unexpected products. Typical procedures are (i) proton abstraction with bases (e.g. BuLi) prior to metalation (free carbene route),[3] (ii) metalation with a basic metal precursor such as $Pd(OAc)_2$ and $[Ir(COD)(OEt)]_2$ (direct metalation),[4] (iii) metal exchange starting from silver carbenes (transmetalation),[5] and (iv) oxidative addition of carbon−halogen bonds to low-valent metal precursors.[6] Direct base-free CH-bond activation, by analogy with arene mercuration,[7] was long elusive and is still rare. Experiment and calculations by Cavell and co-workers indicate that an oxidative addition of imidazolium CH bonds is feasible,[6b,c] and Nolan et al.[6d] have also proposed an example. Recently we[8] and others[9] have shown that low-valent metal precursors are not essential for this CH-bond activation. In particular, the reaction between an imidazolium salt and metal hydride precursors with release of H_2 according to eq 1 is suitable for the synthesis of N-heterocyclic carbene complexes. Very recently, however, we briefly reported that the facile

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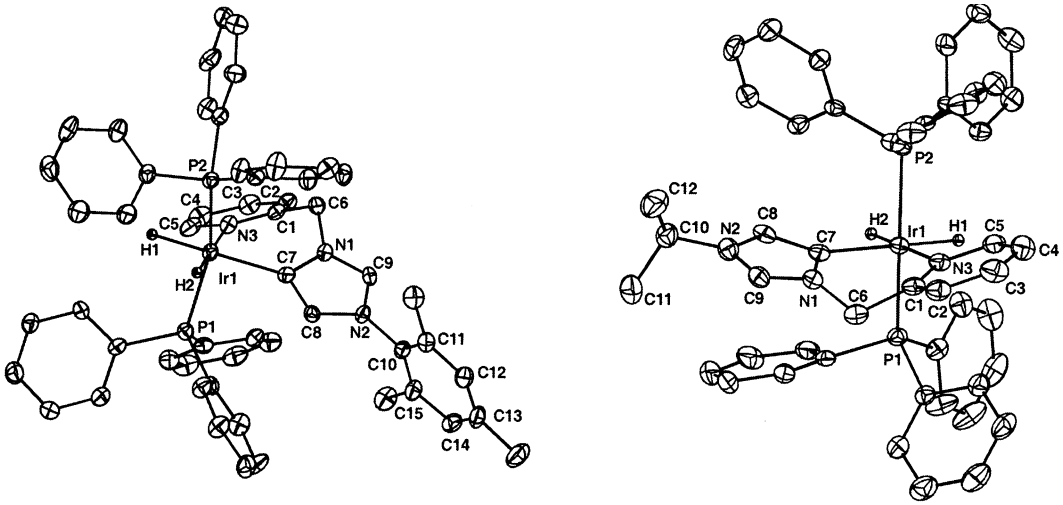
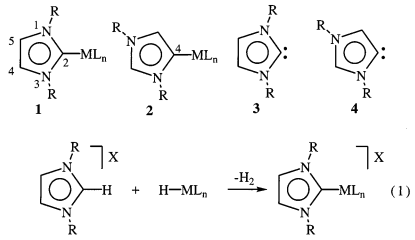


Figure 1. Molecular structure of the cations of **12a** (left) and **12b** (right), showing 50% probability thermal ellipsoids. Only the metal bound hydrogens (calculated positions) are shown.

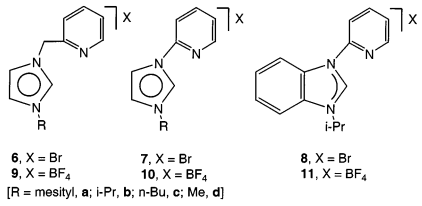
reaction between a pyridine substituted imidazolium salt and $IrH_5(PPh_3)_2$ (**5**) gives good yields of unprecedented carbenes of type **2** in which the N-heterocyclic ring is bound in a novel way via C4(C5).[10] This observation is surprising since not only is the free carbene **3** much more stable than **4** but theoretical density functional (DFT; B3PW91) calculations[11] predict that binding to the C4(C5)-position can be thermodynamically much less favored (23.3 kcal/mol) than C2-binding (e.g., for R = H, $ML_n = PtCl_3^-$). N−H···Cl hydrogen bonding, present in the $[(imidazole)PtCl_3]^-$ quantum model system, provides an additional stabilizing factor for the C2 bound form in this case, however.



In this paper we look at the factors that favor normal versus abnormal binding, such as variation of wingtip groups and ligand bite angles. We also look at the unexpected reversible hydrogen transfer from metal to ligand and suggest a mechanism based on labeling experiments. The transformations and intermediates reported here appear to be unprecedented but could occur quite generally in other systems where they could escape detection, especially in cases where catalysts are formed in situ by heating imidazolium precursors and metal salts.

Results

Synthesis of the Ligands. The new pyridine functionalized imidazolium bromide salts **6b**,**c**, **7d**, and **8** having different wingtip groups, R, have been synthesized according to known procedures.[2a] Anion exchange from Br^- to BF_4^- was accomplished with stoichiometric $AgBF_4$ or excess $NaBF_4$ to give the ligand fluoroborates, **9**−**11**. Successful anion exchange is indicated by a diagnostic high-field shift of the ^1H NMR signal of the C2−H proton from 10 to 11 ppm to about 9 ppm in $CDCl_3$ as a result of strong ion pairing of bromide with C2−H of the imidazolium cation.[12]



Nonclassical Carbene Formation in the Large Bite-Angle Case. The reaction of methylene linked salts **9a**−**c** with $IrH_5(PPh_3)_2$ in refluxing tetrahydrofuran (THF) for 2 h gives the iridium(III) complexes **12a**−**c** in virtually quantitative yields (eq 2). Air- or moisture-free conditions are unnecessary for this reaction. After recrystallization from THF/pentane, **12a**−**c** are obtained as colorless solids that are stable toward air and moisture. Carbene coordination via the C4-position was unequivocally confirmed by X-ray structure determinations of **12a**[13a] and **12b**,[13b] the latter result having been communicated previously.[10] The structures (Figure 1) show an octahedral iridium center with two trans phosphines. The positions of the

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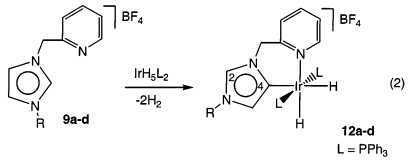
(13) (a) Crystal data for **12a**·$CHCl_3$: triclinic, space group $P\bar{1}$ (No. 2), a = 14.1010(6) Å, b = 14.2829(7) Å, c = 14.4166(5) Å, α = 79.144(3)°, β = 64.676(3)°, γ = 88.336(3)°, V = 2573.2(2) Å^3, Z = 2, T = 183.2 K; full matrix least squares refinement of F (622 parameters) was based on 5911 observed reflections ($I > 5.00\sigma(I)$) and converged to R = 0.038, R_w = 0.046 (GOF = 1.19). (b) Crystal data for **12b**: monoclinic, space group $P2_1/c$ (No. 14), a = 9.4493(2) Å, b = 20.6687(6) Å, c = 22.0865(6) Å, β = 90.160(2)°, V = 4313.6(2) Å^3, Z = 4, T = 183.2 K; full matrix least squares refinement of F (532 parameters) was based on 4789 observed reflections ($I > 3.00\sigma(I)$) and converged to R = 0.033, R_w = 0.035 (GOF.= 0.88). (c) Crystal data for **15**·$CHCl_3$: monoclinic, space group $P2_1/m$ (No. 11), a = 10.7855(4) Å, b = 22.7449(11) Å, c = 11.3115(4) Å, β = 101.571(3)°, V = 2718.5(2) Å^3, Z = 2, T = 183.2 K; full matrix least squares refinement of F (354 parameters) was based on 3416 observed reflections ($I > 3.00\sigma(I)$) and converged to R = 0.039, R_w = 0.041 (GOF.= 1.01). The anion and cation were on a plane of symmetry, and the $CHCl_3$ was disordered. (d) Crystal data for **16a**: monoclinic, space group $P2_1/c$ (No. 14), a = 11.6490(6) Å, b = 26.0118(11)) Å, c = 16.281(9) Å, β = 105.335(3)°, V = 4757.6(16) Å^3, Z = 4, T = 183.2 K; full matrix least squares refinement of F (577 parameters) was based on 3056 observed reflections ($I > 3.00\sigma(I)$) and converged to R = 0.033, R_w = 0.033 (GOF.= 0.75).

Table 1. Selected Bond Lengths and Angles for **12a** and **12b**

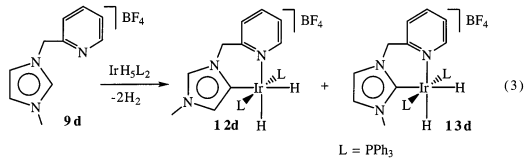
	12a	12b
	Bond Lengths (Å)	
Ir1−P1	2.297(2)	2.287(2)
Ir1−P2	2.284(2)	2.301(2)
Ir1−N3	2.197(6)	2.193(5)
Ir1−C7	2.092(6)	2.100(6)
N1−C6	1.478(9)	1.461(7)
N1−C7	1.400(8)	1.404(7)
N1−C9	1.331(8)	1.335(8)
N2−C8	1.392(8)	1.390(8)
N2−C9	1.315(9)	1.327(8)
N2−C10	1.447(9)	1.459(8)
C7−C8	1.373(9)	1.380(8)
	Bond Angles (deg)	
N3−Ir1−C7	88.9(2)	89.3(2)
P1−Ir1−P2	158.59(6)	163.86(6)
	Dihedral Angles (deg)	
N1−C9−N2−C10	178.3(6)	182.0(6)
C7−Ir1−N3−C1	22.3(6)	18.2(5)
N3−Ir1−C7−N1	22.6(5)	17.6(5)

benzylic substituent and the R group (R = mesityl, i-Pr) define the positions of the imidazole nitrogen atoms. In both cases the imidazole ring is undoubtedly attached via the C4-carbon (C7 in the crystallographic numbering), a previously unknown type of carbene binding. Both molecules are chiral owing to noncoplanarity of the imidazole with the pyridine. The NMR data (see below) show equivalent isopropyl methyl and methylene protons, so the molecule is fluxional on the NMR time scale at 298 K probably via a boat−boat six-membered ring-flip.



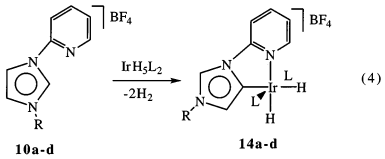
The pertinent NMR spectroscopic data of the complexes **12a**−**c** are similar and consistent with rigid abnormal carbene binding in solution. The ^{1}H NMR features of **12b** are representative: a low-field peak at 8.72 ppm is assigned to the acidic C2 proton; the proton at C5 is high field shifted to 5.17 ppm, and the CH_2 linker group appears as a singlet at 4.70 ppm, consistent with a nonrigid ligand conformation and an effective C_s symmetry in solution. The two inequivalent hydrides have high-field resonances at −10.83 ppm (probably trans to N) and −21.49 ppm (trans to C)[14] both split into doublets of triplets by mutual coupling ($^2J_{HH}$ = 4.9 Hz, typical for cis hydrides[15]) and coupling to apparently equivalent phosphorus nuclei ($^2J_{PH}$ = 19.6 and 18.6 Hz, respectively). The singlet at 21.4 ppm in the ^{31}P{^{1}H} NMR spectrum is consistent with magnetically equivalent phosphorus nuclei and hence with C_s symmetry. The ^{13}C{^{1}H} NMR spectrum confirms C4−carbene binding because the C4 resonance at 141.1 ppm is a triplet by coupling to phosphorus (J_{PC} = 7.1 Hz).

Two ^{1}H NMR spectroscopic characteristics appear to be diagnostic for abnormal C4 carbene binding: (i) a large shift difference between the two heterocyclic protons (>3 ppm for C2 and C5 in abnormal carbenes compared to <1 ppm for C4 and C5 in normal carbenes) and (ii) a difference in chemical shift of the metal bound carbon ($\delta \sim 140$ ppm in abnormal versus $\delta \sim 170$ ppm in normal cases, vide infra). Large wingtip groups such as i-Pr at N(1) lead to exclusive formation of the abnormal C4 isomer. For smaller R, we expected that the normal C2 carbene might be formed. Indeed, when R = Me, both isomers are formed: normal **13** and abnormal **12d**. Integration of the NMR spectra gives a **12d**/**13** ratio of ca. 55:45. The spectrum of **12d** was identified by analogy with **12a**−**c**, but a full assignment for C2 bound **13** was only achieved by 2D NMR spectroscopy. Characteristically, no proton was seen in the low-field region near 8.7 ppm; instead the imidazole protons show resonances at 7.44 and 6.31 ppm. In the ^{13}C{^{1}H} NMR spectrum, the metal bound carbon appears at 169.9 ppm (J_{PC} = 7.0 Hz). These observations are fully consistent with a C2 bound carbene **13** (eq 3). The ^{31}P{^{1}H} NMR spectrum has a single peak at 17.1 ppm. Due to the similar solubilities of **12d** and **13**, we have not yet been able to separate the two species. As isomeric mixtures, however, correct microanalytical data were obtained (see Experimental Section).



Once the normal or abnormal compounds have formed, they do not easily interconvert. Attempted interconversion by heating the mixture of **12d** and **13** in dimethyl sulfoxide (DMSO) solution at 100 °C failed. After several hours the initial ratio is unchanged, and even on prolonged heating (3 days) only decomposition products were observed. The same result was obtained when a sample was heated to 50 °C for 18 h in the presence of 5 equiv of CF_3COOH in DMSO.

Nonclassical Carbene Formation in the Small Bite-Angle Case. The ligand precursors **10b**−**d** also react with $IrH_5(PPh_3)_2$ (eq 4) like their methylene-linked analogues. Under identical reaction conditions the products are the abnormal carbene complexes **14b**−**d**. The reaction of the very bulky mesitylene substituted **10a** with $IrH_5(PPh_3)_2$ is substantially slower, and we did not see full conversion to **14a**. After recrystallization from $CHCl_3$/pentane or THF/pentane, **14b**−**d** were obtained as colorless, high-melting (>200 °C) solids. Notably, for R = Me, where a mixture was seen previously (**12d**/**13**), only the C4 carbene was now observed. The spectroscopic data ($CDCl_3$, 298 K) for **14** are very similar to that for **12** and indicate C4 carbene binding. For example, in the case of **14b** the two imidazole protons appear to be well-separated at 9.28 and 5.97 ppm, and in the ^{13}C{^{1}H} NMR C2 appears at 149.0 ppm (t, J_{PC} = 4.7 Hz).



Normal Carbene Formation in the Small-Bite-Angle Case. If abnormal binding is blocked, however, we find that normal carbene binding can occur, so this is not forbidden for the small-

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(15) Gründemann, S.; Limbach, H.-H.; Buntkowsky, G.; Sabo-Etienne, S.; Chaudret, B. *J. Phys. Chem. A* **1999**, *103*, 4752.

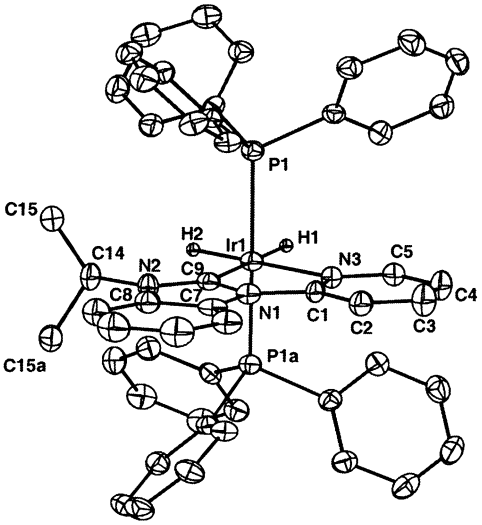
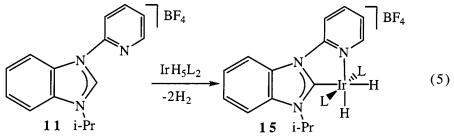


Figure 2. Molecular structure of the cation of **15**, showing 50% probability thermal ellipsoids. Only the metal bound hydrogens (calculated positions) are shown.

Table 2. Selected Bond Lengths and Angles for **15**

Bond Lengths (Å)	
Ir1−P1	2.312(2)
Ir1−P1a	2.312(2)
Ir1−N3	2.167(7)
Ir1−C9	2.027(9)
N1−C1	1.410(10)
N1−C7	1.413(11)
N1−C9	1.384(10)
N2−C8	1.401(11)
N2−C9	1.339(10)
N2−C14	1.475(11)
C7−C8	1.418(13)
Bond Angles (deg)	
N3−Ir1−C9	76.0(3)
P1−Ir1−P2	163.77(8)
Dihedral Angle (deg)	
N1−C9−N2−C14	180.0

bite-angle ligands. The reaction of $IrH_5(PPh_3)_2$ with the benzimidazolium salt **11** under the same conditions (refluxing THF, 2 h) gave the C2 carbene complex **15** (eq 5).



Recrystallization from $CHCl_3$/pentane yielded crystals suitable for single-crystal diffraction.[13c] The structure (Figure 2, Table 2) unambiguously proved normal carbene binding. The molecule is positioned on a crystallographic mirror plane, defined by the pyridine, the Ir−C9 bond to benzimidazole, and the IrH_2 moieties. The carbene Ir−C distance (2.027(9) Å) in **15** is significantly shorter than in the abnormal carbenes **12a** and **12b** (Ir1−C7 = 2.09 Å (**12a**) and 2.10 Å (**12b**), respectively). Similar but less pronounced trends are seen with the Ir−N bond lengths, which are slightly shorter than in C4 carbenes. The length of the C7−C8 bond (1.418 Å (**15**)) is consistent with a delocalized aromatic ring. The NMR spectroscopic data are consistent with the X-ray structure. In the $^{13}C\{^1H\}$ NMR spectrum, the metal bound carbon appears at δ 192.5 (t, J_{PC} = 6.3 Hz) closer to the value obtained for **13**.

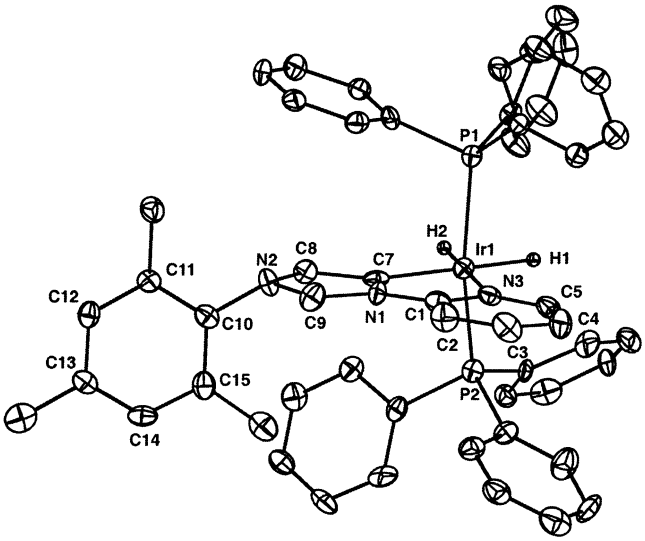
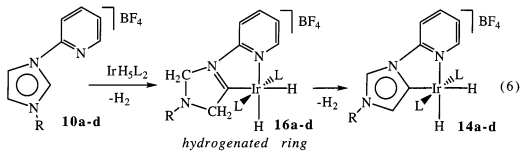


Figure 3. Molecular structure of the cation of **16a**, showing 50% probability thermal ellipsoids. Only the metal bound hydrogens (calculated positions) are shown.

Hydrogen Transfer to and from the Imidazole Ring. A very unexpected hydrogenated intermediate, **16**, was seen at early reaction times in the synthesis of **14**. This proved to result from hydrogen transfer from the metal to the imidazolium ring with formation of a hydrogenated abnormal carbene, **16**. This type of reaction seems to be quite unknown for any previous metal σ-aryl or heterocycle complexes, although hydrogenation of arenes via π-bonding is of course known.[16] When the reaction of **10** with $IrH_5(PPh_3)_2$ was quenched after 10−15 min by rapid cooling of the reaction mixture followed by addition of pentane, **16** was precipitated along with starting material and small quantities of the final product **14** (eq 6).



It was hard to isolate **16** because it usually rapidly converted to **14**, so we turned our attention to more slowly reacting imidazolium salts. Particularly attractive is the mesitylene-substituted ligand, **10a**, which allowed isolation and full characterization of the corresponding intermediate **16a**. Recrystallization from THF/pentane yielded crystals suitable for diffraction.[13d] Like **14,** the structure of **16a** (Figure 3) shows an octahedral iridium(III) center. Remarkably, the imidazolyl heterocycle is fully hydrogenated and best described as an imidazolidinium system. This is reflected, for example, in the bonding situation around N2 (N2 denotes crystallographic numbering). Bond lengths and angles clearly reveal sp^3 hybridization at N2, which requires saturation of the C8−N2−C9 fragment. Furthermore the C−N bonds around C9 have single

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Table 3. Selected Bond Lengths and Angles for **16a**

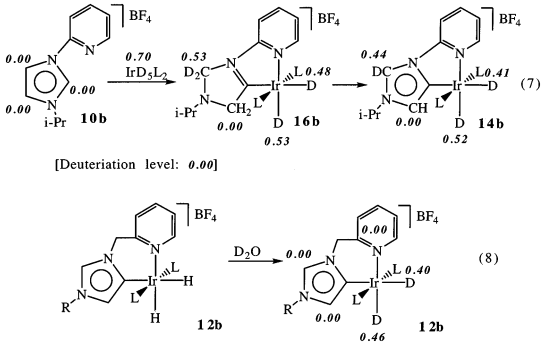
Bond Lengths (Å)	
Ir1−P1	2.293(2)
Ir1−P2	2.304(3)
Ir1−N3	2.132(7)
Ir1−C7	2.004(9)
N1−C1	1.413(11)
N1−C7	1.335(10)
N1−C9	1.494(11)
N2−C8	1.462(10)
N2−C9	1.428(11)
N2−C10	1.428(10)
C7−C8	1.484(12)
Bond Angles (deg)	
N3−Ir1−C7	77.8(3)
P1−Ir1−P2	158.97(8)
Dihedral Angles (deg)	
N1−C9−N2−C10	142.7(8)

bond character because they are significantly stretched, 1.43 and 1.49 Å, versus 1.33 Å in **12**. A remarkably short N1−C7 bond length indicates predominant double bond character, as does the Ir1−C7 distance (2.004 Å).

More definitively, the NMR data (298 K, $CDCl_3$) is also consistent with the hydrogenated structure. The methylene proton signals for C(2) and C(5) at 5.13 and 3.98 ppm are considerably highfield shifted relative to **14**. Each integrates for two protons and shows mutual coupling (triplets, $^4J_{HH}$ = 4.1 Hz) which is confirmed by decoupling of ^{31}P. Further evidence comes from the $^{13}C\{^1H\}$ NMR spectroscopy. The metal bound carbon appears at 247.7 ppm, a value typical for Fischer carbenes of the type $L_nMCR(NR_2)$.[17] In addition, C2 and C5 at 73.0 and 71.8 ppm, respectively, are shifted into the aliphatic region. Compounds **16b**−**d** are metastable and at 298 K slowly convert to the final product **14**. Hence attempts to crystallize them failed, and their characterization was limited to spectroscopic techniques. However, the spectroscopic properties of **16b**−**d** are very similar to those of the fully characterized example, **16a,** which suggests a similar structure for all four compounds. Independent support for C4 binding in **16b** comes from NOESY experiments: significant NOE's were detected between the methyl protons of the isopropyl group and both the C2 and C5 protons. In control experiments it was shown that recrystallized **16a** can also be converted to **14a** in vigorously refluxing THF. We find that the rate of this transformation is strongly dependent on the vigor of the reflux, probably resulting from the varying rate of removal of H_2 from the system. This has so far prevented the extraction of reliable kinetic data. No analogues of **16** have been observed for the reactions between the methylene linked ligand, **9**, and $IrH_5(PPh_3)_2$.

Attempts to reverse this dehydrogenation by hydrogenation of **14** failed. When H_2 was bubbled through a THF solution of **14b** at 298 K for 18 h, traces of $IrH_5(PPh_3)_2$ along with some unidentified decomposition products were formed, but no **16** was detected.

Mechanistic Aspects. The mechanism seems to be complex, and we can do no more than give initial indications here; a full study, now in progress, will be reported in future. $IrD_5(PPh_3)_2$ (d-**5**), obtained from D_2 and $[Ir(cod)(PPh_3)_2]PF_6$, had a deuteration level of 70%. Since the hydrides in **5** undergo exchange with water, we performed the reaction with **10b** under anhydrous conditions. Careful integration of the ^1H NMR spectra of the intermediate, **16b**, and final product, **14b**, gave the deuteration levels shown in eq 7. Deuterium appeared at C2, but the original deuterium level in the hydride positions was diluted by approximately 25%. No deuterium incorporation was ever seen into C5. Experiments for various reaction times, from a few minutes up to 2 h, always gave the same deuteration levels. Additionally, starting $IrD_5(PPh_3)_2$ with 44% deuterium content resulted in a qualitatively similar deuterium distribution (Ir−H, 33% each; C2, 33%). Reaction of **9b** with $IrD_5(PPh_3)_2$ gave no deuterium incorporation into the unreacted free ligand. A control experiment in which undeuterated **12b** was monitored in the presence of D_2O over a period of 2 h showed that no exchange takes place with aromatic hydrogens (eq 8).



Discussion

The formation of abnormal C4 carbenes, so far unique to this system, contrasts with theoretical calculations and also with previous studies on C−H bond activation in imidazolium systems which have so far always predicted or generated normal C2 carbenes.[1] Steric congestion favors abnormal carbene binding, while the sterically least demanding Me group promoted C2−H bond activation and formation of normal carbenes. Neither thermal nor acid-mediated interconversion of the C4 carbene into the C2 form or vice versa was ever observed. Due to the kinetic stability of the products, it has not been possible to determine the thermodynamic product distribution experimentally. The fact that carbene formation is irreversible, however, points to kinetic control of product formation.

The observed hydrogenation and dehydrogenation in the reaction of **10a**−**d** with $IrH_5(PPh_3)_2$ are unprecedented. It is not yet clear why the hydrogenated intermediate is only seen for the smaller bite-angle ligand, however. We can only speculate about the explanation, but it seems possible that the smaller bite angle could align the imidazole ring to favor H transfer.

The deuteriation study shows that we do not have a simple C−H activation with a choice between two possible C−H bonds. Branching presumably occurs between two independent pathways, one that gives normal metalation and the other that gives hydrogenation and then the abnormal aromatic carbene. At the request of a reviewer we provide a working mechanistic hypothesis (Figure 4) that fits the facts currently known, but we hope to obtain a better picture in future experimental work and theoretical work in collaboration with O. Eisenstein and E. Clot. In this proposal, the H/D exchange at C2 is accomplished by reversible CH oxidative addition to an $[IrD_3L_2]$ intermediate;

(17) Luecke, H.; Arndtsen, B. A.; Burger, P.; Bergman, R. G. *J. Am. Chem. Soc.* **1996**, *118*, 2517.

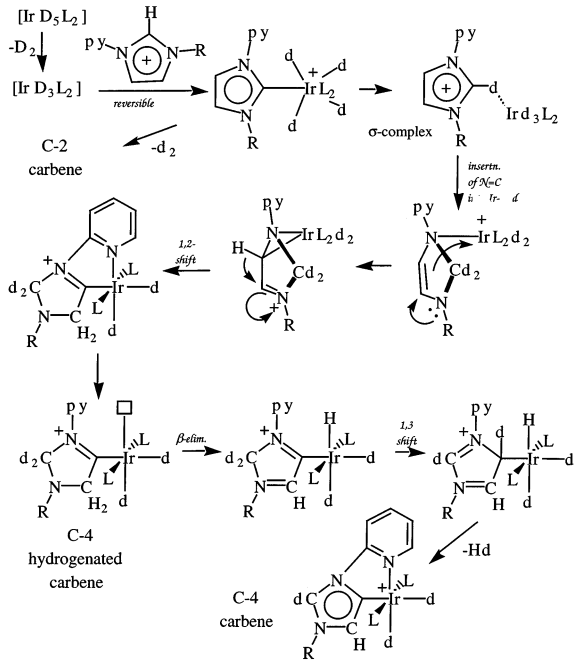


Figure 4. Current working hypothesis for the mechanism (d denotes lower deuteration level).

in this process the initial 70% deuteration level, represented as D, is diluted to the final lower level, *d*, by exchange of three D with one H. Subsequent insertion of the imidazolium N=C bond into an Ir−H bond leads to hydrogenation of the C2 position with the adjacent N3 bound to Ir. The metal can now bind to the C4 position, followed by a 1,2 hydride shift to give the hydrogenated product. The ring dehydrogenation is proposed to proceed by β-elimination, followed by a 1,3-H shift and loss of H_2. The feasibility of these steps is under active study.

Complications of the sort described here, abnormal C4 binding and ring hydrogenation, may be most likely in reactions with hydride complexes, but the generality of this chemistry has not yet been assessed. The use of benzimidazole prevents abnormal C4 binding as no doubt would use of other 4,5-substituted imidazoles. Large wingtip R groups commonly used in the area should favor abnormal binding. Other abnormal binding modes may be possible with heterocyclic ligands in general.

Conclusions

This work has established that imidazolium salts do not always give normal carbenes on metalation, implying that the chemistry of this ligand system can be more complicated than currently thought. Binding can occur at C2 or C4, and we give spectroscopic criteria for distinguishing the two cases. Hydrogen transfer from the metal to the imidazolium-derived carbene is possible in some cases to give a fully hydrogenated ring, but this proved reversible on reflux and the abnormal aromatic carbene was obtained as final product. Abnormal binding is blocked in benzimidazole. This work shows that a surprising variety of structures are available from imidazolium salts. Care must be taken to verify what structure has been formed in any given case, especially when a catalyst is generated in situ from imidazolium salt and metal precursor. Transformations between the various structures could allow reactions to occur during catalysis that could not occur if normal binding were alone possible, so these possibilities also need to be considered in future mechanistic work.

Experimental Section

General Methods. $IrH_5(PPh_3)_2$ (**5**),[18] *N*-mesityl-*N*′-(2-pyridylmethyl)imidazolium bromide (**6a**),[2a] *N*-methyl-*N*′-(2-pyridylmethyl)imidazolium bromide (**6d**),[5a] *N*-mesityl-*N*′-2-pyridylimidazolium bromide (**7a**),[8] *N*-butyl-*N*′-2-pyridylimidazolium bromide (**7c**),[1j] and *N*-isopropyl-*N*′-2-pyridylimidazolium bromide (**7b**)[8] were prepared according to literature methods; all other reagents are commercially available and were used as received. All NMR spectra were recorded at room temperature on Bruker spectrometers operating at 400 or 500 MHz (^{1}H NMR) and 100 or 125 MHz (^{13}C NMR), respectively, and referenced to $SiMe_4$ (δ in parts per million, *J* in hertz). Assignments are based on COSY and HMQC spectroscopies. Melting points are uncorrected. Elemental analyses were performed by Atlantic Microlab, Inc; residual solvent molecules have been identified by ^{1}H NMR spectroscopy.

***N*-Butyl-*N*′-(2-pyridylmethyl)imidazolium Bromide (6c).** A modification of the procedure of Tulloch et al. was used.[2a] 2-(Bromomethyl)pyridine hydrobromide (4 g, 16 mmol) was neutralized using a saturated aqueous solution of sodium carbonate. The liberated 2-(bromomethyl)pyridine was extracted into diethyl ether (3 × 30 mL) at 0 °C, dried with magnesium sulfate, and filtered. 1-Butylimidazole (1.95 g, 16 mmol) in methanol (100 mL) was added at 0 °C to the filtrate, the ether removed under reduced pressure, and the solution stirred at room temperature for 12 h. The methanol is evaporated under reduced pressure, and the formed oil was purified by repetitive precipitation from CH_2Cl_2/Et_2O mixtures. The resulting oily product was dried in vacuo. Yield: 4.52 g (95%).^{1}H NMR ($CHCl_3$, 298 K): δ 10.44 (s, 1H, NCHN), 8.49 (d, 1H, $^3J_{HH}$ = 5.0 Hz, H_{py}), 7.80 (d, 1H, $^3J_{HH}$ = 7.7 Hz, H_{py}), 7.74−7.69 (m, 1H, H_{py}), 7.67 (s, 1H, H_{im}), 7.42 (s, 1H, H_{im}), 7.28−7.24 (m, 1H, H_{py}), 5.77 (s, 2H, CH_2), 4.27 (t, 2H, $^3J_{HH}$ = 7.5 Hz, CH_2), 1.91−1.82 (m, 2H, CH_2), 1.39−1.29 (m, 2H, CH_2), 0.91 (t, 3H, $^3J_{HH}$ = 7.5 Hz, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 298 K): δ 152.32 (C_{py}), 149.52 (C_{py}), 137.80 (C_{py}), 136.98 (NCN), 124.08 (C_{py}), 123.99 (C_{py}), 122.80 (C_{im}), 121.56 (C_{im}), 53.61 (CH_2), 49.86 (CH_2), 31.92 (CH_2), 19.36 (CH_2), 13.33 (CH_3); Anal. Calcd for $C_{13}H_{18}BrN_3$ (296.21)·1.5H_2O: C, 48.31; H, 6.55; N, 13.00. Found: C, 47.85; H, 6.54; N, 12.96.

***N*-Isopropyl-*N*′-(2-pyridylmethyl)imidazolium Bromide (6b).** 2-(Bromomethyl)pyridine hydrobromide (1.01 g, 4 mmol) was neutralized using a saturated aqueous solution of sodium carbonate. The liberated 2-(bromomethyl)pyridine was extracted into diethyl ether (3 × 30 mL) at 0 °C, dried with magnesium sulfate, and filtered into a solution of 1-isopropylimidazole (0.44 g, 4 mmol) in 1,4-dioxane (30 mL). The ether was removed under reduced pressure and the solution refluxed for 12 h. The volatiles were removed in vacuo, and the formed oil was purified by repetitive precipitation from MeOH/Et_2O and finally recrystallized from CH_2Cl_2/Et_2O to give colorless crystals Yield: 0.68 g (60%).^{1}H NMR ($CHCl_3$, 298 K): δ 10.97 (s, 1H, NCHN), 8.56−8.52 (m, 1H, H_{py}), 7.93 (d, 1H, $^3J_{HH}$ = 7.8 Hz, H_{py}), 7.75 (dt, 1H, $^4J_{HH}$ = 1.7 Hz, $^3J_{HH}$ = 7.5 Hz, H_{py}), 7.65 (t, 1H, $^3J_{HH}$ = 1.5 Hz, H_{im}), 7.31−7.24 (m, 1H, H_{py}), 7.22 (t, 1H, $^3J_{HH}$ = 1.5 Hz, H_{im}), 5.81 (s, 2H, CH_2), 4.74 (septet, 1H, $^3J_{HH}$ = 6.7 Hz, CH), 1.63 (d, 6H, $^3J_{HH}$ = 6.7 Hz, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 298 K): δ 152.57 (C_{py}), 149.72 (C_{py}), 137.80 (C_{py}), 136.80 (NCN), 124.60 (C_{py}), 124.06 (C_{py}), 122.78 (C_{im}), 118.65 (C_{im}), 53.86 (CH_2), 53.43 (CH), 23.09 (2C, CH_3). Mp = 85−86 °C. Anal. Calcd for $C_{12}H_{16}BrN_3$ (282.18)·H_2O: C, 48.01; H, 6.04; N, 14.00. Found: C, 48.33; H, 5.81; N, 14.10.

***N*-Methyl-*N*′-2-pyridylimidazolium Bromide (7d).** A mixture of 2-bromopyridine (3.16 g, 20.0 mmol) and 1-methylimidazole (1.64 g, 20.0 mmol) was kept neat at 160 °C for 48 h. After cooling, the formed

(18) Crabtree, R. H.; Felkin, H.; Morris, G. E. *J. Organomet. Chem.* **1977**, *141*, 205.

oily mixture was purified by repetitive precipitation from $CHCl_3/Et_2O$ mixtures and the resulting brownish oil precipitated and dried in vacuo. Yield: 2.74 g (56%). An analytically pure sample (white needles) was obtained from CH_2Cl_2/Et_2O. ^1H NMR ($CHCl_3$, 298 K): δ 11.84 (s, 1H, NCHN), 8.54−8.48 (m, 2H, H_{py}), 8.29 (t, 1H, $^3J_{HH} = 1.8$ Hz, H_{im}), 8.06 (dt, 1H, $^4J_{HH} = 1.8$ Hz, $^3J_{HH} = 7.9$ Hz, H_{py}), 7.49−7.44 (m, 2H, H_{py}, H_{im}), 4.29 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 298 K): δ 148.97 (C_{py}), 145.82 (C_{py}), 140.74 (C_{py}), 136.54 (NCN), 125.22 (C_{py}), 123.21 (C_{im}), 118.75 (C_{im}), 115.00 (C_{py}), 37.17 (CH_3). Mp = 148−149 °C (dec). Anal. Calcd for $C_9H_{10}BrN_3$ (240.01)·H_2O: C, 41.88; H, 4.69; N, 16.28. Found: C, 41.45; H, 4.65; N, 15.96.

***N*-Isopropyl-*N*′-2-pyridylbenzimidazolium Bromide (8).** A mixture of 2-bromopyridine (986 mg, 6.2 mmol) and 1-isopropylbenzimidazole (1.0 g, 6.2 mmol) was kept neat at 185 °C for 20 h. After cooling, the formed oily mixture was purified by repetitive precipitation from CH_2Cl_2/Et_2O mixtures, and the resulting brownish oil was precipitated, washed with small amounts of acetone, and dried in vacuo. An analytically pure sample (colorless needles) was obtained from $CHCl_3$/pentane.Yield: 0.15 g (8%). ^1H NMR ($CHCl_3$, 298 K): δ 11.99 (s, 1H, NCHN), 9.02 (d, 1H, $^3J_{HH} = 8.3$ Hz, H_{py}), 8.78−8.71 (m, 1H, H_{ar}), 8.67−8.62 (m, 1H, H_{py}), 8.15 (dt, 1H, $^4J_{HH} = 1.8$ Hz, $^3J_{HH} = 7.8$ Hz, H_{py}), 8.87−7.80 (m, 1H, H_{ar}), 7.74−7.67 (m, 2H, H_{ar}), 7.53−7.47 (m, 1H, H_{py}), 5.37 (septet, 1H, $^3J_{HH} = 6.8$ Hz, CH), 1.99 (d, 6H, $^3J_{HH} = 6.8$ Hz, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 298 K): δ 148.60 (C_{py}), 148.00 (C_{py}), 140.65 (C_{py}), 140.29 (NCN), 130.68 (C_{ar}), 130.44 (C_{ar}), 128.0 (C_{ar}), 127.52 (C_{ar}), 124.73 (C_{py}), 118.00 (2C, C_{py}, C_{ar}), 113.27 (C_{ar}), 53.14 (CH), 22.08 (2C, CH_3). Mp = 219−221 °C (dec). Anal. Calcd for $C_{15}H_{16}BrN_3$ (318.21): C, 56.62; H, 5.07; N, 13.21. Found: C, 56.50; H, 5.12; N, 13.13.

Protocol for Anion Exchange of the Ligands 6−8 To Give 9−11. A 1:1 mixture of the halide ligand and $AgBF_4$ was stirred in CH_2Cl_2 or acetone in the dark for 12 h. The reaction mixture was filtered through Celite and the solvent of the filtrate removed in vacuo. The ligands were used without further purification.

(η^2-*C*,*N*)(*N*-Mesityl-*N*′-(2-pyridylmethyl)imidazole-4-ylidene)bis-(hydrido)bis(triphenylphosphine)iridium(III) Tetrafluoroborate (12a). A mixture of **9a** (50.5 mg, 0.14 mmol) and **5** (100 mg, 0.14 mmol) in THF (5 mL) was refluxed in air. After 45 min a clear solution was obtained. Refluxing was continued for 2 h more. After the reaction mixture had cooled to room temperature, the crude product was precipitated with 75 mL of pentane. Yield: 120 mg (79%). An analytically pure sample was obtained from THF/pentane. Crystals suitable for X-ray analysis were grown from $CHCl_3$/pentane.^1H NMR ($CDCl_3$, 298 K): δ 8.75 (s, 1H, NCHN), 8.11 (d, 1H, $^3J_{HH} = 5.6$ Hz, H_{py}), 7.37−7.15 (m, 32H, H_{py}, H_{ph}), 6.86 (s, 2H, H_{ar}), 6.02 (t, $^3J_{HH} = 6.0$ Hz, H_{py}), 5.12 (s, 1H, H_{im}), 4.93 (s, 2H, CH_2), 2.30 (s, 3H, CH_3), 1.88 (s, 6H, CH_3), −11.10 (dt, $^3J_{HH} = 4.8$ Hz, $^2J_{PH} = 20.7$ Hz, Ir−H), −21.23 (dt, $^3J_{HH} = 4.8$ Hz, $^2J_{PH} = 18.2$ Hz, Ir−H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 298 K): δ 161.48 (C_{py}), 152.91 (C_{py}), 140.53 (t, $J_{PC} = 6.1$ Hz, $C_{carbene}$), 139.41 (C_{ar}), 137.14 (C_{py}), 135.06 (t, $J_{PC} = 26.5$, C_{ph}), 134.85 (C_{ar}), 134.07 (NCN), 133.61 (t, $J_{PC} = 5.9$, C_{ph}), 132.09 (C_{ar}), 129.70 (C_{ph}), 129.10 (C_{ar}), 127.95 (t, $J_{PC} = 5.0$, C_{ph}), 127.61 (C_{im}), 126.35 (C_{py}), 124.17 (C_{py}), 55.43 (CH_2), 21.03 (CH_3), 17.27 (CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 298 K): δ 21.39. Mp = 255−257 °C (dec). Anal. Calcd for $C_{54}H_{51}BF_4IrN_3P_2$ (1082.97)·H_2O: C, 58.91; H, 4.85; N, 3.82. Found: C, 58.88; H, 4.78; N, 3.94.

(η^2-*C*,*N*)(*N*-Isopropyl-*N*′-(2-pyridylmethyl)imidazole-4-ylidene)-bis(hydrido)bis(triphenylphosphine)iridium(III) Tetrafluoroborate (12b). A mixture of **9b** (40 mg, 0.14 mmol) and **5** (100 mg, 0.14 mmol) in THF (5 mL) was refluxed in air. After 15 min a clear solution was obtained. Refluxing was continued for 2 h more. After the reaction mixture had cooled to room temperature, the product was precipitated by addition of 25 mL of pentane. The yellow solid was filtered off and dried in vacuo. Yield: 120 mg (85%). The complex can be recrystallized from THF/pentane. Crystals suitable for X-ray analysis can be obtained from CH_2Cl_2/Et_2O. ^1H NMR ($CDCl_3$, 298 K): δ 8.72 (s, 1H, NCHN), 8.23 (d, 1H, $^3J_{HH} = 5.5$ Hz, H_{py}), 7.37−7.14 (m, 32H, H_{py}, H_{ph}), 6.07 (t, $^3J_{HH} = 6.3$ Hz, H_{py}), 5.17 (s, 1H, H_{im}), 4.70 (s, 2H, CH_2), 4.25 (septet, 1H, $^3J_{HH} = 6.5$ Hz, CH), 1.19 (d, 6H, $^3J_{HH} = 6.5$ Hz, CH3), −10.83 (dt, $^2J_{PH} = 19.6$ Hz, $^3J_{HH} = 4.9$ Hz, Ir−H), −21.49 (dt, $^2J_{PH} = 18.6$ Hz, $^3J_{HH} = 4.9$ Hz, Ir−H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 298 K): δ 161.78 (C_{py}), 153.10 (C_{py}), 141.07 (t, $J_{PC} = 7.1$ Hz, $C_{carbene}$), 137.04 (C_{py}), 134.93 (t, $J_{PC} = 26.3$, C_{ph}), 133.55 (t, $J_{PC} = 6.0$, C_{ph}), 132.40 (NCN), 129.55 (C_{ph}), 127.84 (t, $J_{PC} = 5.8$, C_{ph}), 125.87 (C_{py}), 124.15 (C_{py}), 123.56 (C_{im}), 55.03 (CH_2), 50.47 (CH), 22.94 (CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 298 K): δ 21.36. Mp = 246−248 °C (dec). Anal. Calcd for $C_{48}H_{47}BF_4IrN_3P_2$ (1006.88)·THF: C, 57.88; H, 5.14; N, 3.89. Found: C, 57.84; H, 5.32; N, 3.74.

(η^2-*C*,*N*)(*N*-Butyl-*N*′-(2-pyridylmethyl)imidazole-4-ylidene)bis-(hydrido)bis(triphenylphosphine)iridium(III) Tetrafluoroborate (12c). A mixture of **9c** (54 mg, 0.18 mmol) and **5** (129 mg, 0.18 mmol) in THF (8 mL) was refluxed in air. After 20 min a clear solution was obtained. Refluxing was continued for 2 h more. After the reaction mixture had cooled to room temperature, it was layered with 10 mL of heptane. Over a period of 12 h crystals formed which were filtered off and dried in vacuo. Yield: 124 mg (68%). The complex can be recrystallized from THF/pentane. ^1H NMR ($CDCl_3$, 298 K): δ 8.71 (s, 1H, NCHN), 8.19 (d, 1H, $^3J_{HH} = 5.1$ Hz, H_{py}), 7.37−7.15 (m, 32H, H_{py}, H_{ph}), 6.07 (t, $^3J_{HH} = 5.9$ Hz, H_{py}), 5.03 (s, 1H, H_{im}), 4.72 (s, 2H, CH_2), 1.47 (m, 2H, CH_2), 1.17 (m, 2H, CH_2), 0.90 (t, 3H, $^3J_{HH} = 7.7$ Hz, CH_3), −10.89 (dt, $^2J_{PH} = 19.6$ Hz, $^3J_{HH} = 5.1$ Hz, Ir−H), −19.61 (dt, $^2J_{PH} = 18.4$ Hz, $^3J_{HH} = 5.1$ Hz, Ir−H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 298 K): δ 161.77 (C_{py}), 153.07 (C_{py}), 141.30 (t, $J_{PC} = 6.9$ Hz, $C_{carbene}$), 137.09 (C_{py}), 134.96 (t, $J_{PC} = 26.3$, C_{ph}), 133.79 (NCN), 133.61 (t, $J_{PC} = 6.0$, C_{ph}), 129.59 (C_{ph}), 127.86 (t, $J_{PC} = 4.7$, C_{ph}), 126.13 (C_{im}), 125.90 (C_{py}), 124.18 (C_{py}), 55.08 (CH_2), 47.89 (CH_2), 31.96 (CH_2), 19.36 (CH_2), 13.37 (CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 298 K): δ 21.39. Mp = 229 °C (dec). Anal. Calcd for $C_{49}H_{49}BF_4IrN_3P_2$ (1020.98)·THF: C, 58.24; H, 5.26; N, 3.84. Found: C, 58.23; H, 5.29 N, 3.90.

Isomeric Mixture of (η^2-*C*,*N*)(*N*-Methyl-*N*′-(2-pyridylmethyl)-imidazole-4-ylidene)bis(hydrido)bis(triphenylphosphine)-iridium(III) Tetrafluoroborate (12d) and (η^2-*C*,*N*)(*N*-Methyl-*N*′-(2-pyridylmethyl)imidazole-2-ylidene)bis(hydrido)bis(triphenyl-phosphine)iridium(III) Tetrafluoroborate (13). A mixture of **9d** (40 mg, 0.15 mmol) and **5** (110 mg, 0.15 mmol) in THF (12 mL) was refluxed in air for 2 h. After the reaction mixture had cooled to room temperature, the precipitation was completed by addition of 75 mL of pentane. The product was filtered to give a yellowish powder. Yield: 110 mg (75%). An analytically pure sample of the mixture (55% abnormal carbene and 45% normal carbene) can be obtained by recrystallization from $CHCl_3$/pentane.

(a) Spectroscopic Data for the Abnormal Carbene 12d. ^1H NMR ($CDCl_3$, 298 K): δ 8.66 (s, 1H, NCHN), 8.19 (d, 1H, $^3J_{HH} = 5.5$ Hz, H_{py}), 7.35−7.15 (m, 32H, H_{py}, H_{ph}), 6.10−6.04 (m, 1H, H_{py}), 4.88 (s, 1H, H_{im}), 4.69 (s, 2H, CH_2), 3.38 (s, 3H, CH_3), −10.89 (dt, $^3J_{HH} = 4.7$ Hz, $^2J_{PH} = 19.8$ Hz, Ir−H), −21.53 (dt, $^3J_{HH} = 4.7$ Hz, $^2J_{PH} = 18.5$ Hz, Ir−H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 298 K): δ 161.83 (C_{py}), 153.71 (C_{py}), 141.97 (t, $J_{PC} = 7.6$ Hz, $C_{carbene}$), 137.13 (C_{py}), 134.92 (t, $J_{PC} = 26.1$, C_{ph}), 134.27 (NCN), 133.62 (t, $J_{PC} = 5.8$, C_{ph}), 129.59 (C_{ph}), 127.84 (t, $J_{PC} = 5.0$, C_{ph}), 127.48 (C_{im}), 125.83 (C_{py}), 124.21 (C_{py}), 55.08 (CH_2), 34.56 (CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 298 K): δ 21.14.

(b) Spectroscopic Data for the Normal Carbene 13. ^1H NMR ($CDCl_3$, 298 K): δ 8.03 (d, 1H, $^3J_{HH} = 5.5$ Hz, H_{py}), 7.64 (d, 1H, $^3J_{HH} = 7.4$ Hz, H_{py}), 7.52 (t, 1H, $^3J_{HH} = 7.5$ Hz, H_{py}), 7.44 (d, 1H, $^3J_{HH} = 2.0$ Hz, H_{im}), 7.35−7.15 (m, 30H, H_{py}, H_{ph}), 6.31 (d, 1H, $^3J_{HH} = 2.0$ Hz, H_{im}), 6.16 (t, 1H, $^3J_{HH} = 7.4$ Hz, H_{py}), 4.83 (s, 2H, CH_2), 2.54 (s, 3H, CH_3), −11.04 (dt, $^3J_{HH} = 5.3$ Hz, $^2J_{PH} = 19.8$ Hz, Ir−H), −21.00 (dt, $^3J_{HH} = 5.5$ Hz, $^2J_{PH} = 17.1$ Hz, Ir−H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 298 K): δ 169.90 (t, $J_{PC} = 7.0$ Hz, $C_{carbene}$), 160.82 (C_{py}), 153.04 (C_{py}), 137.93 (C_{py}), 134.15 (t, $J_{PC} = 26.7$, C_{ph}), 133.28 (t, $J_{PC} = 5.8$, C_{ph}), 130.04 (C_{ph}), 128.16 (t, $J_{PC} = 5.0$, C_{ph}), 126.29 (C_{py}), 123.60 (C_{py}), 123.26 (C_{im}), 120.58 (C_{im}), 55.08 (CH_2), 37.20 (CH_3). $^{31}P\{^1H\}$ NMR

($CDCl_3$, 298 K): δ 17.14. Anal. Calcd for $C_{46}H_{43}BF_4IrN_3P_2$ (978.82)·2$CHCl_3$: C, 47.35; H, 3.73; N, 3.45. Found: C, 47.35; H, 3.69; N, 3.41.

(η^2-*C,N*)(*N*-Isopropyl-*N*′-(2-pyridyl)imidazole-4-ylidene)bis-(hydrido)bis(triphenylphosphine)iridium(III) Tetrafluoroborate (14b). A mixture of **10b** (32 mg, 0.12 mmol) and **5** (80 mg, 0.12 mmol) in THF (50 mL) was heated to reflux in air. After 10 min a clear yellow solution was obtained. After heating was continued for another 15 h, the reaction mixture was cooled to room temperature and concentrated to 10 mL of THF. The product was precipitated by addition of 50 mL of pentane. The product was filtered off and dried in vacuo to give a yellow solid. Yield: 70 mg (65%). The complex can be crystallized from $CHCl_3$/pentane. ^{1}H NMR ($CDCl_3$, 298 K): δ 9.28 (s, 1H, NCHN), 7.74 (d, 1H, $^3J_{HH}$ = 8.2 Hz, H_{py}), 7.67 (d, $^3J_{HH}$ = 5.5 Hz, H_{py}), 7.57 (t, $^3J_{HH}$ = 7.9 Hz H_{py}), 7.44−7.17 (m, 30 H, H_{ph}), 6.26 (t, $^3J_{HH}$ = 6.5 Hz, H_{py}), 5.97 (s, 1H, H_{im}), 4.44 (septet, $^3J_{HH}$ = 6.9 Hz, CH), 1.25 (d, $^3J_{HH}$ = 6.9 Hz, CH_3), −11.35 (dt, $^3J_{HH}$ = 5.5 Hz, $^2J_{PH}$ = 17.9 Hz, Ir−H), −19.73 (dt, $^3J_{HH}$ = 5.5 Hz, $^2J_{PH}$ = 16.8 Hz, Ir−H). ^{13}C{^{1}H} NMR ($CDCl_3$, 298 K): δ 155.28 (C_{py}), 149.0 (t, J_{PC} = 4.7 Hz), 151.3 (C_{py}), 138.4 (C_{py}), 133.5 (t, J_{PC} = 26.5, C_{ph}), 133.4 (t, J_{PC} = 6.6, C_{ph}), 131.1 (NCN), 129.7 (C_{ph}), 127.8 (t, J_{PC} = 4.4, C_{ph}), 122.9 (C_{py}), 122.6 (C_{im}), 112.8 (C_{py}), 51.6 (CH), 22.8 (CH_3). ^{31}P{^{1}H} NMR ($CDCl_3$, 298 K): δ 21.9. Mp = 250−252 °C (dec). Anal. Calcd for $C_{47}H_{45}BF_4IrN_3P_2$ (993.27)·$CHCl_3$: C, 51.83; H, 4.17; N, 3.78. Found: C, 52.27; H, 4.36; N, 3.82.

(η^2-*C,N*)(*N*-Butyl-*N*′-(2-pyridyl)imidazole-4-ylidene)bis(hydrido)-bis(triphenylphosphine)iridium(III) Tetrafluoroborate (14c). A mixture of **10c** (57 mg, 0.19 mmol) and **5** (143 mg, 0.19 mmol) in THF (11 mL) were refluxed in air. After 30 min of refluxing, a clear yellow solution was obtained. After another 30 min, precipitation started. Refluxing was then continued for another 2 h. After the reaction mixture was cooled to room temperature, 100 mL of pentane was added to complete precipitation. The product was filtered off as a yellow solid which was dried in vacuo. Yield: 155 mg (80%). The complex can be recrystallized from THF/pentane. ^{1}H NMR ($CDCl_3$, 298 K): δ 9.29 (s, 1H, NCHN), 7.71 (d, 1H, $^3J_{HH}$ = 5.5 Hz, H_{py}), 7.65 (d, $^3J_{HH}$ = 8.5 Hz, H_{py}), 7.53 (t, $^3J_{HH}$ = 8.3 Hz, H_{py}), 7.49−7.15 (m, 30 H, H_{ph}), 6.27 (t, $^3J_{HH}$ = 6.9 Hz, H_{py}), 5.92 (s, 1H, H_{im}), 3.91 (t, 1H, $^3J_{HH}$ = 6.9 Hz, CH_2), 1.56−1.46 (m, 2H, CH_2), 1.07−0.94 (m, 2H, CH_2), 0.82 (t, $^3J_{HH}$ = 7.6 Hz, CH_3), −11.44 (dt, $^3J_{HH}$ = 5.5 Hz, $^2J_{PH}$ = 18.2 Hz, Ir−H), −19.65 (dt, $^3J_{HH}$ = 5.5 Hz, $^2J_{PH}$ = 15.8 Hz, Ir−H). ^{13}C{^{1}H} NMR ($CDCl_3$, 298 K): δ 155.4 (C_{py}), 151.1 (C_{py}), 151.0 (t, J_{PC} = 6.9 Hz, $C_{carbene}$), 138.3 (C_{py}), 133.5 (t, J_{PC} = 26.5, C_{ph}), 133.4 (t, J_{PC} = 6.6, C_{ph}), 132.6 (NCN), 129.7 (C_{ph}), 127.9 (t, J_{PC} = 5.5, C_{ph}), 125.6 (C_{im}), 122.9 (C_{py}), 112.7 (C_{py}), 48.8 (CH_2), 32.1 (CH_2), 19.2 (CH_2), 13.5 (CH_3). ^{31}P{^{1}H} NMR ($CDCl_3$, 298 K): δ 22.2. Mp = 237−239 °C (dec). Anal. Calcd for $C_{48}H_{47}BF_4IrN_3P_2$ (1006.88)·$CHCl_3$: C, 52.26; H, 4.30; N, 3.73. Found: C, 52.91; H, 4.51; N, 3.70.

(η^2-*C,N*)(*N*-Methyl-*N*′-(2-pyridyl)imidazole-4-ylidene)bis(hydrido)bis(triphenylphosphine)iridium(III) Tetrafluoroborate (14d). A mixture of **10d** (34 mg, 0.14 mmol) and **5** (100 mg, 0.14 mmol) in THF (50 mL) was refluxed in air. The mixture is vigorously refluxed in air for 9 h. It never became clear. After the reaction mixture was cooled to room temperature, it was concentrated to 15 mL and 100 mL of pentane was added to complete precipitation. The product was filtered off as a yellow solid which was dried in vacuo. Yield: 80 mg (59%). The complex can be recrystallized from $CHCl_3$/pentane.^{1}H NMR ($CDCl_3$, 298 K): δ 9.27 (s, 1H, NCHN), 7.78 (d, 1H, $^3J_{HH}$ = 5.5 Hz, H_{py}), 7.60 (d, $^3J_{HH}$ = 8.2 Hz, H_{py}), 7.53 (t, $^3J_{HH}$ = 7.6 Hz, H_{py}), 7.48−7.17 (m, 30 H, H_{ph}), 6.31 (t, $^3J_{HH}$ = 6.9 Hz, H_{py}), 5.84 (s, 1H, H_{im}), 3.62 (s, 3H, CH_3), −11.42 (dt, $^3J_{HH}$ = 5.5 Hz, $^2J_{PH}$ = 17.9 Hz, Ir−H), −19.70 (dt, $^3J_{HH}$ = 5.5 Hz, $^2J_{PH}$ = 16.5 Hz, Ir-*H*).^{13}C{^{1}H} NMR ($CDCl_3$, 298 K): δ 155.4 (C_{py}), 151.5 (t, J_{PC} = 7.3 Hz, $C_{carbene}$), 151.1 (C_{py}), 138.3 (C_{py}), 133.5 (t, J_{PC} = 26.4, C_{ph}), 133.4 (t, J_{PC} = 5.7, C_{ph}), 133.3 (NCN), 129.7 (C_{ph}), 127.9 (t, J_{PC} = 4.6, C_{ph}), 126.9 (C_{im}), 122.9 (C_{py}), 112.6 (C_{py}), 35.4 (CH_3). ^{31}P{^{1}H} NMR ($CDCl_3$, 298 K): δ 22.0. Mp = 230−233 °C (dec). Anal. Calcd for $C_{45}H_{41}BF_4IrN_3P_2$ (964.80)·0.5$CHCl_3$: C, 54.20; H, 4.36; N, 3.99. Found: C, 53.96; H, 4.41; N, 4.35.

(η^2-*C,N*)(*N*-Isopropyl-*N*′-(2-pyridyl)benzimidazole-2-ylidene)bis-(hydrido)bis(triphenylphosphine)iridium(III) Tetrafluoroborate (15). A mixture of **11** (20 mg, 0.061 mmol) and **5** (44 mg, 0.061 mmol) in THF (25 mL) was refluxed in air overnight. It becomes clear after a few minutes. After the reaction mixture was cooled to room temperature, it is concentrated to 15 mL and 50 mL of pentane was added to complete precipitation. The product was filtered off as a yellow solid which was dried in vacuo. Yield: 51 mg (80%). Crystals suitable for X-ray analysis can be obtained from $CHCl_3$/pentane.^{1}H NMR ($CDCl_3$, 298 K): δ 8.17 (d, $^3J_{HH}$ = 8.5 Hz, H_{ar}), 7.98 (d, $^3J_{HH}$ = 8.5 Hz, H_{py}), 7.90 (t, 1H, $^3J_{HH}$ = 7.5 Hz, H_{py}), 7.73 (d, 1H, $^3J_{HH}$ = 5.7 Hz, H_{py}), 7.49−7.43 (m, 1H, H_{ar}), 7.26−7.22 (m, 2H, H_{ar}), 7.19−7.02 (m, 30 H, H_{ph}), 6.40 (t, $^3J_{HH}$ = 6.5 Hz, H_{py}), 4.96 (septet, 1H, $^3J_{HH}$ = 7.0 Hz, CH), 0.55 (d, 6H, $^3J_{HH}$ = 7.0 Hz, CH_3), −11.42 (dt, $^3J_{HH}$ = 5.5 Hz, $^2J_{PH}$ = 19.4 Hz, Ir−H), −19.12 (dt, $^3J_{HH}$ = 5.5 Hz, $^2J_{PH}$ = 15.9 Hz, Ir−H). ^{13}C{^{1}H} NMR ($CDCl_3$, 298 K): δ 192.5 (t, J_{PC} = 6.3 Hz, $C_{carbene}$), 154.2 (C_{py}), 153.0 (C_{py}), 141.0 (C_{py}), 133.0 (t, J_{PC} = 6.0, C_{ph}), 132.6 (t, J_{PC} = 27.2, C_{ph}), 132.6 (C_{ar}), 132.3 (C_{ar}), 130.4 (s, C_{ph}), 128.3 (t, J_{PC} = 5.0, C_{ph}), 125.2 (C_{ar}), 124.2 (C_{ar}), 122.0 (C_{py}), 113.6 (C_{py}), 113.5 (C_{ar}), 112.3 (C_{ar}), 56.3 (CH), 19.4 (CH_3). ^{31}P{^{1}H} NMR ($CDCl_3$, 298 K): δ 18.4. Mp = 263−265 °C (dec). Anal. Calcd for $C_{51}H_{47}BF_4IrN_3P_2$ (1042.91)·2$CHCl_3$: C, 49.67; H, 3.85; N, 3.28. Found: C, 49.57; H, 4.00; N, 3.32.

(η^2-*C,N*)(*N*-Mesityl-*N*′-(2-pyridyl)imidazolidine-4-ylidene)bis(hydrido)bis(triphenylphosphine)iridium(III) Tetrafluoroborate (16a). A mixture of **9a** (50 mg, 0.14 mmol) and **5** (100 mg, 0.14 mmol) in THF (50 mL) was heated to reflux in air. After 15 min a clear yellow solution was obtained. After heating was continued for another 2 min the reaction mixture was immersed in an ice bath until it was cooled to room temperature, when 60 mL of pentane was added to precipitate the product, which was then filtered off and dried in vacuo. Yield: 111 mg (74%). Crystals suitable for X-ray analysis can be obtained from THF/pentane.^{1}H NMR ($CDCl_3$, 298 K): δ 7.91 (t, 1H, $^3J_{HH}$ = 7.9 Hz, H_{py}), 7.62 (d, 1H, $^3J_{HH}$ = 8.2 Hz, H_{py}), 7.53 (d, $^3J_{HH}$ = 5.2 Hz, H_{py}), 7.44−7.27 (m, 30 H, H_{ph}), 6.71 (s, 2H, H_{ar}), 6.41 (t, $^3J_{HH}$ = 6.5 Hz, H_{py}), 5.13 (t, 2H, $^4J_{HH}$ = 4.1 Hz, NCH_2N), 3.98 (br s, 2H, H_{im}), 2.20 (s, 3H, CH_3), 1.61 (s, 6H, CH_3), −10.03 (dt, $^3J_{HH}$ = 5.0 Hz, $^2J_{PH}$ = 20.5 Hz, Ir−H), −18.56 (dt, $^3J_{HH}$ = 5.0 Hz, $^2J_{PH}$ = 16.15 Hz, Ir−H). ^{13}C{^{1}H} NMR ($CDCl_3$, 298 K): δ 247.7 (s, $C_{carbene}$), 154.1 (C_{py}), 152.4 (C_{py}), 140.4 (C_{py}), 138.1 (2C, C_{ar}), 137.1 (C_{ar}), 136.8 (C_{ar}), 133.0 (t, J_{PC} = 6.6, C_{ph}), 132.6 (t, J_{PC} = 28.75, C_{ph}), 130.6 (C_{ph}), 129.6 (2C, C_{ar}), 128.4 (t, J_{PC} = 5.5, C_{ph}), 123.3 (C_{py}), 115.5 (C_{py}), 73.0 (NCN), 71.8 (C_{im}), 20.8 (CH_3), 17.7 (2C, CH_3). ^{31}P{^{1}H} NMR ($CDCl_3$, 298 K): δ 19.5. Mp = 203−205 °C (dec). Anal. Calcd for $C_{54}H_{53}BF_4IrN_3P_2$ (1084.99): C, 59.44; H, 4.80; N, 3.92. Found: C, 59.14; H, 4.94; N, 3.98.

Characterization of (η^2-*C,N*)(*N*-Isopropyl-*N*′-(2-pyridyl)imidazolidine-4-ylidene)bis(hydrido)bis(triphenylphosphine)iridium(III) Tetrafluoroborate (16b). A mixture of **10b** (32 mg, 0.12 mmol) and **5** (80 mg, 0.12 mmol) in THF (10 mL) was heated to reflux in air. After 15 min a clear yellow solution was obtained. After heating was continued for another 2 min, the reaction mixture was immersed in an ice bath until it was cooled to room temperature, when 60 mL of pentane was added to precipitate the product, which was then filtered off and dried in vacuo. Yield: 100 mg (86%).^{1}H NMR ($CDCl_3$, 298 K): δ 7.84 (t, 1H, $^3J_{HH}$ = 7.9 Hz, H_{py}), 7.69 (d, 1H, $^3J_{HH}$ = 8.2 Hz, H_{py}), 7.62 (d, $^3J_{HH}$ = 5.5 Hz, H_{py}), 7.40−7.28 (m, 30 H, H_{ph}), 6.45 (t, $^3J_{HH}$ = 6.5 Hz, H_{py}), 4.64 (s, 2H, NCH_2N), 3.20 (s, 2H, H_{im}), 2.36 (septet, $^3J_{HH}$ = 6.2 Hz, CH), 0.78 (d, $^3J_{HH}$ = 6.2 Hz, CH_3), −9.94 (dt, $^3J_{HH}$ = 4.8 Hz, $^2J_{PH}$ = 20.6 Hz, Ir−H), −18.74 (dt, $^3J_{HH}$ = 4.8 Hz, $^2J_{PH}$ = 16.1 Hz, Ir−H). ^{13}C{^{1}H} NMR ($CDCl_3$, 298 K): δ 248.8 (t, J_{PC} = 4.0 Hz, $C_{carbene}$), 154.1 (C_{py}), 152.9 (C_{py}), 140.1 (C_{py}), 133.0 (t, J_{PC} = 6.1, C_{ph}), 132.6 (t, J_{PC} = 28.75, C_{ph}), 130.5 (C_{ph}), 128.4 (t, J_{PC}

= 5.5, C_{ph}), 122.8 (C_{py}), 115.3 (C_{py}), 72.7 (NCN), 69.8 (C_{im}), 52.1 (CH), 20.5 (CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 298 K): δ 19.3.

Characterization of (η^2-*C,N*)(*N*-Butyl-*N'*-(2-pyridyl)imidazolidine-4-ylidene)bis(hydrido)bis(triphenylphosphine)iridium(III) Tetrafluoroborate (16c). A mixture of **10c** (35 mg, 0.12 mmol) and **5** (80 mg, 0.12 mmol) in THF (10 mL) was heated to reflux in air. After 15 min a clear yellow solution was obtained. After heating was continued for another 2 min, the reaction mixture was immersed in an ice bath until it was cooled to room temperature, when 60 mL of pentane was added to precipitate the product, which was then filtered off and dried in vacuo. Yield: 66 mg (58%). ^1H NMR ($CDCl_3$, 298 K): δ 7.85 (t, 1H, $^3J_{HH}$ = 7.9 Hz, H_{py}), 7.73 (d, 1H, $^3J_{HH}$ = 8.3 Hz, H_{py}), 7.55 (d, 1H, $^3J_{HH}$ = 6.2 Hz, H_{py}), 7.40−7.15 (m, 30 H, H_{ph}), 6.41 (t, $^3J_{HH}$ = 6.2 Hz, H_{py}), 4.67 (s, 2H, H_{im}), 3.23 (s, 2H, H_{im}), 1.95 (t, 1H, $^3J_{HH}$ = 6.9 Hz, CH_2), 1.18−1.05 (m, 4H, CH_2), 0.82 (t, $^3J_{HH}$ = 7.6 Hz, CH_3), −9.98 (dt, $^3J_{HH}$ = 4.8 Hz, $^2J_{PH}$ = 20.6 Hz, Ir−H), −18.69 (dt, $^3J_{HH}$ = 4.8 Hz, $^2J_{PH}$ = 16.5 Hz, Ir−H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 298 K): δ 248.6 (br s, $C_{carbene}$), 154.1 (C_{py}), 153.0 (C_{py}), 140.1 (C_{py}), 133.0 (t, J_{PC} = 5.5, C_{ph}), 132.7 (t, J_{PC} = 28.75, C_{ph}), 130.5 (C_{ph}), 128.39 (t, J_{PC} = 5.5, C_{ph}), 122.9 (C_{py}), 115.6 (C_{py}), 75.9 (NCN), 73.0 (C_{im}), 54.6 (CH_2), 30.6 (CH_2), 19.9 (CH_2), 13.8 (CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 298 K): δ 19.1.

Characterization of (η^2-*C,N*)(*N*-Methyl-*N'*-(2-pyridyl)imidazolidine-4-ylidene)bis(hydrido)bis(triphenylphosphine)iridium(III) Tetrafluoroborate (16d). A mixture of **10d** (27 mg, 0.12 mmol) and **5** (80 mg, 0.12 mmol) in THF (10 mL) was heated to reflux in air. After 10 min of vigorous boiling, a clear yellow solution was obtained. After heating was continued for another 2 min, the reaction mixture was immersed in an ice bath until it cooled to room temperature, when a precipitate formed. After 60 mL of pentane was added to complete precipitation, the product was then filtered off and dried in vacuo. Yield: 93 mg (87%). ^1H NMR ($CDCl_3$, 298 K): δ 7.83 (t, 1H, $^3J_{HH}$ = 7.1 Hz, H_{py}), 7.72 (d, 1H, $^3J_{HH}$ = 8.2 Hz, H_{py}), 7.52 (d, $^3J_{HH}$ = 5.5 Hz, H_{py}), 7.41−7.27 (m, 30 H, H_{ph}), 6.39 (t, $^3J_{HH}$ = 6.6 Hz, H_{py}), 4.67 (s, 2H, NCH_2N), 3.22 (s, 2H, im-H), 1.78 (s, 3H, CH_3), −10.01 (dt, $^3J_{HH}$ = 4.9 Hz, $^2J_{PH}$ = 20.3 Hz, Ir−H), −18.66 (dt, $^3J_{HH}$ = 4.9 Hz, $^2J_{PH}$ = 15.9 Hz, Ir−H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 298 K): δ 248.8 (bs, $C_{carbene}$), 154.1 (C_{py}), 152.9 (C_{py}), 139.9 (C_{py}), 133.0 (t, J_{PC} = 6.2, C_{ph}), 132.6 (t, J_{PC} = 28.43, C_{ph}), 130.5 (C_{ph}), 128.4 (t, J_{PC} = 5.2, C_{ph}), 122.9 (C_{py}), 115.6 (C_{py}), 77.6 (NCN), 75.2 (C_{im}), 42.4 (CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 298 K): δ 19.0.

Acknowledgment. We gratefully acknowledge financial support from Deutsche Akademie der Naturforscher Leopoldina (Grant BMBF-LPD 9901/8-37; S.G.), the Swiss National Foundation (M.A.), Johnson Matthey, and the U.S. DOE and NSF (R.H.C., J.W.F.) and helpful suggestions from a reviewer.

Supporting Information Available: Detailed crystallographic data, atomic positional parameters, bond lengths and angles for**12a**, **12b**, **15**, and **16a** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA026735G