Abnormal C5-Bound N-Heterocyclic Carbenes: Extremely Strong Electron Donor Ligands and Their Iridium(I) and Iridium(III) Complexes

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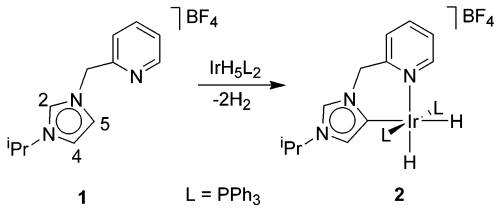
Imidazolium salts are found to bind abnormally via C5 to iridium(I) and iridium(III) to give air-stable monodentate N-heterocyclic carbene complexes. Abnormal ligand binding was verified by X-ray diffraction in both Ir(I) and Ir(III) complexes. In the case of Ir(I), it is necessary to block the C2 and C4 positions to form a stable sterically protected C5-bound complex. Infrared spectroscopy on carbonyl derivatives indicates that abnormally bound N-heterocyclic carbenes are much stronger electron donors than their ubiquitous C2-bound counterparts. The Tolman electronic parameter for 1-isopropyl-2,4-diphenyl-3-methylimidazolin-5-ylidene is 2039 cm^{-1}, compared to ca. 2050 cm^{-1} for typical NHCs.

Introduction

N-Heterocyclic carbenes (NHCs) first emerged as ligands for transition metals in 1968 with the pioneering work of Öfele[1] and Wanzlick.[2] The isolation of the first stable free carbene by Arduengo[3] in 1991 spurred a significant amount of work on NHCs as spectator ligands for homogeneous catalysis, led in large measure by Herrmann.[4−6] The NHCs are considered to behave similarly to tertiary phosphines in many ways, but bind to metal centers more strongly and are stronger electron donors than even trialkylphosphines. Thermochemical studies,[7,8] as well as infrared spectroscopy of metal−carbonyl complexes,[9−11] confirm these facts. New NHC ligands and NHC-supported catalytic transformations, including reactions where the phosphine analogues are less effective or ineffective, continue to be developed at a rapid pace.[12−24]

We have recently focused on the development and use of chelating NHC ligands for homogeneous catalysis, including bidentate CC-chelating[15] and tridentate CNC-pincer[18] ligands. When attempting to prepare an iridium complex of the potentially CN-chelating ligand **1**, we found that the imidazole ring binds via C5 rather than the usual C2 (eq 1).[25] The formation of the abnormal



(1)

NHC complex **2** is favored by the lower steric strain at the metal center.[26] We have also found that the nature of the counterion has a pronounced effect on the kinetic selectivity for C2 versus C5 binding.[27] This abnormal

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(1) Öfele, K. *J. Organomet. Chem.* **1968**, *12*, P42−P43.
(2) Wanzlick, H. W.; Schonherr, H. J. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 141−142.
(3) Arduengo, A. J.; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1991**, *113*, 361−363.
(4) Herrmann, W. A.; Elison, M.; Fischer, J.; Kocher, C.; Artus, G. R. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2371−2374.
(5) Herrmann, W. A.; Kocher, C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2163−2187.
(6) Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1290−1309.
(7) Huang, J. K.; Schanz, H. J.; Stevens, E. D.; Nolan, S. P. *Organometallics* **1999**, *18*, 2370−2375.
(8) Dorta, R.; Stevens, E. D.; Hoff, C. D.; Nolan, S. P. *J. Am. Chem. Soc.* **2003**, *125*, 10490−10491.
(9) Kocher, C.; Herrmann, W. A. *J. Organomet. Chem.* **1997**, *532*, 261−265.
(10) Huang, J. K.; Stevens, E. D.; Nolan, S. P. *Organometallics* **2000**, *19*, 1194−1197.
(11) Chianese, A. R.; Li, X. W.; Janzen, M. C.; Faller, J. W.; Crabtree, R. H. *Organometallics* **2003**, *22*, 1663−1667.
(12) Huang, J. K.; Stevens, E. D.; Nolan, S. P.; Petersen, J. L. *J. Am. Chem. Soc.* **1999**, *121*, 2674−2678.
(13) Clyne, D. S.; Jin, J.; Genest, E.; Gallucci, J. C.; RajanBabu, T. V. *Org. Lett.* **2000**, *2*, 1125−1128.
(14) Powell, M. T.; Hou, D. R.; Perry, M. C.; Cui, X. H.; Burgess, K. *J. Am. Chem. Soc.* **2001**, *123*, 8878−8879.
(15) Albrecht, M.; Miecznikowski, J. R.; Samuel, A.; Faller, J. W.; Crabtree, R. H. *Organometallics* **2002**, *21*, 3596−3604.
(16) Marko, I. E.; Sterin, S.; Buisine, O.; Mignani, R.; Branlard, P.; Tinant, B.; Declercq, J. P. *Science* **2002**, *298*, 204−206.
(17) Muehlhofer, M.; Strassner, T.; Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1745−1747.
(18) Loch, J. A.; Albrecht, M.; Peris, E.; Mata, J.; Faller, J. W.; Crabtree, R. H. *Organometallics* **2002**, *21*, 700−706.
(19) Bolm, C.; Focken, T.; Raabe, G. *Tetrahedron: Asymmetry* **2003**, *14*, 1733−1746.
(20) Ma, Y. D.; Song, C.; Jiang, W.; Wu, Q. S.; Wang, Y.; Liu, X. Y.; Andrus, M. B. *Org. Lett.* **2003**, *5*, 3317−3319.
(21) Poyatos, M.; Mas-Marza, E.; Mata, J. A.; Sanau, M.; Peris, E. *Eur. J. Inorg. Chem.* **2003**, 1215−1221.
(22) Pytkowicz, J.; Roland, S.; Mangeney, P.; Meyer, G.; Jutand, A. *J. Organomet. Chem.* **2003**, *678*, 166−179.
(23) Richel, A.; Delfosse, S.; Cremasco, C.; Delaude, L.; Demonceau, A.; Noels, A. F. *Tetrahedron Lett.* **2003**, *44*, 6011−6015.
(24) Viciu, M. S.; Zinn, F. K.; Stevens, E. D.; Nolan, S. P. *Organometallics* **2003**, *22*, 3175−3177.
(25) Gründemann, S.; Kovacevic, A.; Albrecht, M.; Faller, J. W.; Crabtree, R. H. *Chem. Commun.* **2001**, 2274−2275.
(26) Gründemann, S.; Kovacevic, A.; Albrecht, M.; Faller, J. W.; Crabtree, R. H. *J. Am. Chem. Soc.* **2002**, *124*, 10473−10481.

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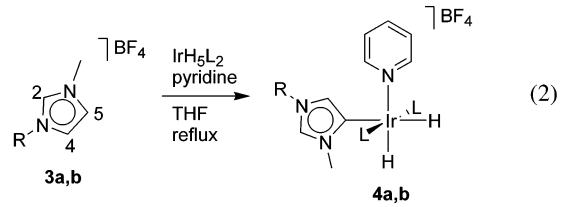
binding mode has also been seen by Meyer in the recent synthesis of a copper(I) complex of a tripodal tris-NHC ligand[28] and by Danopoulos in an iron(II) complex of a CNC-pincer ligand.[29] A pyrazole-based NHC, 1,2-dimethylpyrazolin-3-ylidene, known to form a stable complex with the $Cr(CO)_5$ fragment,[30] is electronically similar, with the carbene carbon flanked by N−R and C−H.

We were curious to explore the generality of abnormal NHC binding, as C5-bound NHCs could potentially offer a useful variant in electronic and steric properties compared to the usual C2 form. The presence of an easily functionalized nitrogen atom distal to the metal center also offers new possibilities for the design of multidentate or polymer-bound NHC ligands. In this work, we report the syntheses of Ir(III) and Ir(I) complexes of monodentate abnormal NHCs. An infrared spectroscopic study demonstrates that the C5-bound NHC is significantly more electron-donating than C2-bound analogues.

Results and Discussion

Synthesis and Characterization of Iridium(III) Complexes. Given the known syntheses of C5-bound compounds of type **2**, we first sought to prepare analogues where the abnormal NHC was monodentate, to determine if chelation is necessary for stability. When the simple imidazolium salts **3a**,**b** were refluxed with pyridine and $IrH_5(PPh_3)_2$ in tetrahydrofuran, C5-bound carbene complexes **4a**,**b** were formed in good yield, with the least sterically hindered of the three imidazole carbons selectively bound to iridium (eq 2). With 1,3-



(2)

a: R = Isopropyl, L = PPh_3
b: R = ^{n}Butyl, L = PPh_3

dimethylimidazolium tetrafluoroborate as ligand precursor, a mixture of two compounds was observed by NMR spectroscopy. Along with the expected abnormal complex, we also observed a smaller amount of a compound that we assign as $[Ir(pyridine)_2H_2(PPh_3)_2]^+$,[31] based on a control reaction between $[IrH_2(acetone)_2(PPh_3)_2][BF_4]$ and pyridine. Attempted recrystallization failed to remove this impurity.

Complexes **4a**,**b** have NMR spectra quite similar to those previously observed for CN-chelated abnormal carbenes.[26] Most notably, the imidazolium ^{13}C resonances at 151.1 ppm are characteristic of C5 ligand binding. The ^1H NMR spectrum is also informative, as the C4-bound proton proximal to iridium is significantly shielded, appearing at ca. 6.2 ppm. The isopropyl methyl resonances of **4a** are isochronous, indicating either that rotation about the M−C bond is rapid or that the imidazole ring rests in an environment that is symmetrical with respect to reflection through the imidazole plane. The same symmetry applies to the *n*-butyl methylene resonances of **4b**.

Compounds **4a**,**b** are noticeably less stable than the C,N-chelated abnormal carbene complexes previously prepared by us.[26] While complexes of type **2** are air-stable at room temperature in $CDCl_3$ solution for days, **4a** and **4b** decompose slowly under these conditions.

Structure Determination of 4a. X-ray quality crystals of **4a** were grown by layering a chloroform solution with pentane. The structure, shown in Figure 1, confirms the binding of imidazole through C5 (labeled as {C7}, the crystallographic numbering of Figure 1). Selected bond lengths and angles are shown in Table 1. The coordination is octahedral at the iridium(III) center. The geometry is the same as previously reported C,N-chelated complexes **2**,[26] with trans phosphines,

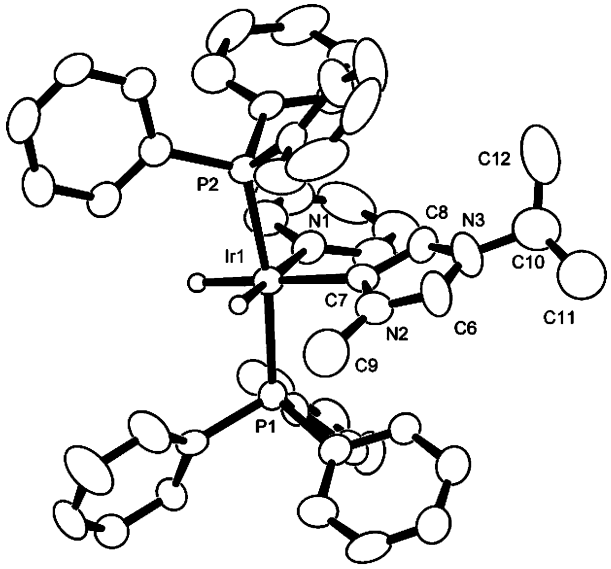


Figure 1. ORTEP diagram of **4a**, showing 50% probability ellipsoids.

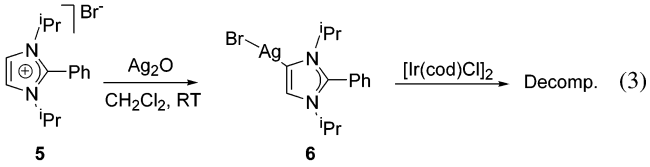
Table 1. Selected Bond Lengths and Angles for 4a

Bond Lengths (Å)	
Ir(1)−P(1)	2.300(2)
Ir(1)−P(2)	2.303(2)
Ir(1)−N(1)	2.169(7)
Ir(1)−C(7)	2.129(9)
C(7)−C(8)	1.345(12)
C(8)−N(3)	1.391(13)
N(3)−C(6)	1.342(13)
C(6)−N(2)	1.327(11)
N(2)−C(7)	1.419(11)
Bond Angles (deg)	
P(1)−Ir(1)−P(2)	170.88(9)
P(1)−Ir(1)−N(1)	91.8(2)
P(2)−Ir(1)−N(1)	93.0(2)
P(1)−Ir(1)−C(7)	97.5(2)
P(2)−Ir(1)−C(7)	89.6(2)
N(1)−Ir(1)−C(7)	97.4(3)
C(7)−C(8)−N(3)	109.9(9)
C(8)−N(3)−C(6)	109.6(9)
N(3)−C(6)−N(2)	104.9(10)
C(6)−N(2)−C(7)	113.5(9)
N(2)−C(7)−C(8)	102.1(8)

(27) Kovacevic, A.; Gründemann, S.; Miecznikowski, J. R.; Clot, E.; Eisenstein, O.; Crabtree, T. H. *Chem. Commun.* **2002**, 2580−2581.
(28) Hu, X.; Castro-Rodriguez, I.; Meyer, K. *Organometallics* **2003**, *22*, 3016−3018.
(29) Danopoulos, A. A.; Tsoureas, N.; Wright, J. A.; Light, M. E. *Organometallics* **2004**, *23*, 166−168.
(30) Tafipolsky, M.; Scherer, W.; Öfele, K.; Artus, G.; Pedersen, B.; Herrmann, W. A.; McGrady, G. S. *J. Am. Chem. Soc.* **2002**, *124*, 5865−5880.
(31) Howarth, O. W.; McAteer, C. H.; Moore, P.; Morris, G. E. *J. Chem. Soc., Dalton Trans.* **1981**, 1481−1485.

cis hydrides, and the pyridine cis to the NHC. The imidazole ring lies orthogonal to the Ir−P bonds, which is consistent with our observation of equivalent isopropyl methyl resonances by NMR spectroscopy.

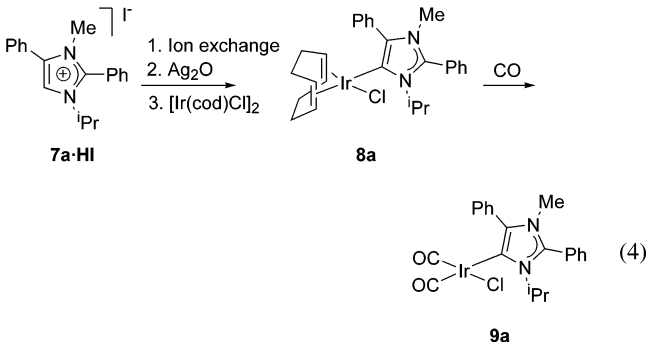
Synthesis and Characterization of Iridium(I) Complexes. Standard methods for preparing transition metal NHC complexes would be expected to give normal binding through C2 because of the higher acidity of this position. Blocking C2 with a substituent such as Me or Ph might be expected to encourage C5 binding by preventing C2 binding. This strategy of blocking the precursor imidazolium salt by substitution at C2 is of uncertain generality however. McLachan et al. have evidence for cleavage of a C−C bond at C2 by Pd(0) in a 2-phenyl imidazolium salt,[32] and we have initial data on cleavage of a C−C bond at C2 by Rh(I) in a 2-methyl imidazolium salt.[33] Conversely, we previously found that unblocked imidazolium salts having a proton at both C2 and C5 can nevertheless give abnormal C5 binding with $IrH_5(PPh_3)_2$.[26] Until further work reveals general patterns, we must anticipate a variety of possible outcomes in such reactions. To force deprotonation at C4,5, we initially chose to block C2 with a phenyl group. Commercial 2-phenylimidazole is readily N,N′-dialkylated with isopropyl bromide to give 1,3-diisopropyl-2-phenylimidazolium bromide **5** (eq 3). We attempted



5 **6** (3)

to prepare an iridium(I) complex of this ligand precursor using the mild transmetalation from silver developed for palladium by Lin[34] and extended by us[11] to rhodium and iridium. Reaction of the imidazolium precursor with silver oxide in dichloromethane at room temperature gives the C4-metalated NHC **6**, observable by the desymmetrization of the isopropyl resonances in the NMR spectrum. The mono-NHC complex shown is only one possible structure for **6**, as silver-NHC complexes are known to exchange ligands in solution, with solid state structures ranging from XAg(NHC) to $[Ag(NHC)_2][AgX_2]$ to polymers with silver−silver contacts.[34−36] Compound **6** decomposes rather quickly, so we chose to add $[Ir(cod)Cl]_2$ directly to a freshly prepared dichloromethane solution of the silver-carbene complex. No stable iridium complex could be isolated under these conditions, and the imidazolium salt was observed, presumably as a product of protonolysis. This is not unreasonable, as the imidazole C4 position is more basic than the C2 position.

In the hope that introduction of steric bulk to the imidazole C4 position would protect the iridium(I) complex from decomposition through protonolysis, the 2,4-blocked imidazolium salt **7a**·HI (eq 4) was prepared



7a·HI **8a** **9a** (4)

from 2,4-diphenylimidazole[37] by successive N-alkylation with isopropyl bromide followed by methyl iodide (see Experimental Section). The sterically controlled regiochemistry of alkylation shown was confirmed by X-ray diffraction analysis of the derived iridium compound **8a** (see below).

We attempted to prepare an abnormal iridium-NHC complex from **7a**·HI by transmetalation from the silver complex. Stirring **7a**·HI with silver oxide for 1.5 h in dichloromethane at room temperature gave a rather unstable silver complex, observed by NMR spectroscopy, which decomposed too quickly to be isolated. Direct addition of $[Ir(cod)Cl]_2$ to a freshly prepared solution of the silver-**7a** complex yielded upon workup a mixture of two compounds, each with a similar NMR resonance pattern. We propose that these are the chloride complex **8a** and the analogous iodide complex. It is likely that the iodide complex is observed here because the unstable silver-**7a** complex slowly decomposes during the reaction with $[Ir(cod)Cl]_2$, releasing iodide ions into solution, which can then replace chloride on the iridium center.

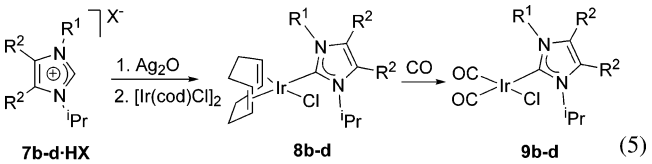
We wanted to obtain the pure chloride complex **8a** to facilitate electronic comparisons with other known iridium compounds. This was accomplished by first exchanging the iodide ion of **7a**·HI for chloride, using two methods that worked equally well. Method A involved stirring **7a**·HI for 16 h with DOWEX 21K Cl^- anion exchange beads. Method B involved ion exchange to acetate using silver acetate, followed by addition of HCl and removal of the acetic acid byproduct. The clear oil obtained by either method reacted with Ag_2O, followed by $[Ir(cod)Cl_2]$, to give pure **8a** in about 45% yield following flash chromatography. This reaction can be performed in air or under argon, with no change in yield. Compound **8a** is a yellow solid, air-stable both in the solid state and in solution. The diastereotopic isopropyl methyl resonances observed in the ^1H NMR spectrum indicate hindered rotation about the iridium−carbon bond. At room temperature, four aromatic carbons give broad resonances in the ^{13}C NMR spectrum, which become sharp at −50 °C. This is ascribed to hindered rotation of the phenyl group proximal to iridium. The structure of **8a** was confirmed unequivocally by X-ray crystallography (see below).

By passing CO over a dichloromethane solution of **8a** for 10 min, cyclooctadiene is completely replaced to give **9a**, which displays slow rotation about the iridium−

(32) McLachlan, F.; Mathews, C. J.; Smith, P. J.; Welton, T. *Organometallics* **2003**, *22*, 5350−5357.
(33) Chianese, A. R.; Zeglis, B. M.; Crabtree, R. H. Unpublished work, 2004.
(34) Wang, H. M. J.; Lin, I. J. B. *Organometallics* **1998**, *17*, 972−975.
(35) Tulloch, A. A. D.; Danopoulos, A. A.; Winston, S.; Kleinhenz, S.; Eastham, G. *J. Chem. Soc., Dalton Trans.* **2000**, 4499−4506.
(36) Lee, K. M.; Wang, H. M. J.; Lin, I. J. B. *J. Chem. Soc., Dalton Trans.* **2002**, 2852−2856.
(37) Li, B.; Chiu, C. K. F.; Hank, R. F.; Murry, J.; Roth, J.; Tobiassen, H. *Org. Process Res. Dev.* **2002**, *6*, 682−683.

carbon bond at room temperature, as indicated by broad isopropyl methyl resonances in the ^{1}H NMR spectrum. Compound **9a** provides a way to measure the electron donor strength of the abnormal carbene ligand **7a**, using the CO stretching frequencies observed by infrared spectroscopy. To compare the donor strength of the abnormal carbene with that of standard NHCs, a series of analogous normal carbene-iridium complexes was prepared.

Imidazolium salts **7b**·HI and **7c**,**d**·HBr (eq 5) were



(5)

b: R^1 = Me, R^2 = Ph, X = I
c: R^1 = ^{i}Pr, R^2 = Ph, X = Br
d: R^1 = Ph, R^2 = H, X = Br

prepared using standard N-alkylation methods, from commercial 4,5-diphenylimidazole (**7b**·HI, **7c**·HBr) or 1-phenylimidazole (**7d**·HBr) (see Experimental Section). Ligands **7b** and **7c** model the electronic properties of **7a**, with two phenyl C-substituents and two alkyl N-substituents. Ligand **7d** models the steric properties of **7a**, with a phenyl group and an isopropyl group facing the iridium center. Iridium compounds **8b**−**d** were prepared by the one-pot transmetalation from silver described above for **8a**, except that the ion exchange step was not necessary. Carbonyl derivatives **9b**−**d** were prepared in the same manner as **9a**.

To provide the closest possible comparison of the C2- and C5-bound NHCs, we have prepared the ligand precursor 1,2,3,4-tetramethylimidazolium iodide **7e**·HI, for comparison with the known ligand 1,3,4,5-tetramethylimidazolin-2-ylidene.[38] Following ion exchange of iodide for chloride as described above, one-pot transmetalation using silver oxide was attempted, as described for **8a**. This gave only decomposition products. We also attempted metalation using potassium *tert*-butoxide as an *in situ* base, as described previously.[39] Again, no stable complex was isolated under our conditions. This may be due to the decreased steric protection around the carbene **7e** as compared to **7a**, or it may indicate that methyl is not a suitable blocking group for imidazole C2 under our conditions.

Structure Determination of 8a. X-ray quality crystals of **8a** were grown by layering a dichloromethane solution with pentane. The X-ray analysis confirms abnormal ligand binding through C5 (labeled as {C1} in Figure 2). Selected bond lengths and angles are given in Table 2. The square planar geometry at the iridium(I) center, with the NHC plane orthogonal to the coordination plane, is similar to that observed in analogous normally bound Ir-NHC complexes.[11,40] The Ir−C bond length of 2.05(2) Å is in the range of previously observed Ir(I)-NHC complexes as well.[11,40]

Infrared Spectroscopy. Compounds **9a**−**d** were studied by FT-IR spectroscopy. Each spectrum showed two CO stretching bands of similar intensity, indicative of cis geometry. The CO stretching frequencies are given in Table 3. Previously, we[11] compared the average ν(CO) of compounds Ir(CO)$_2$ClL, where L = NHC or a tertiary phosphine,[41,42] with the Tolman electronic parameter

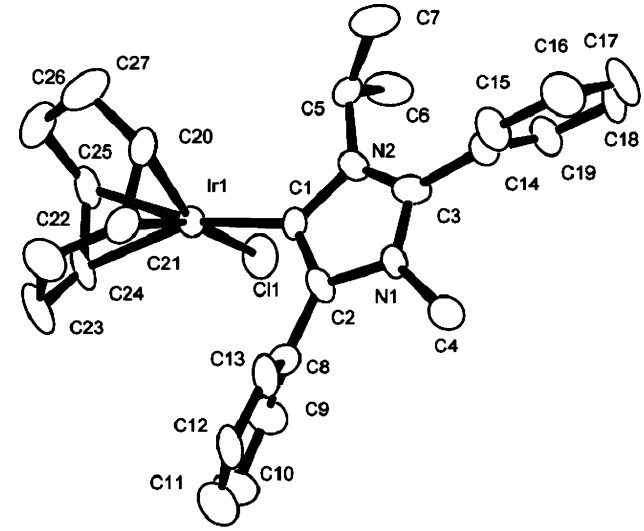


Figure 2. ORTEP diagram of **8a**, showing 50% probability ellipsoids.

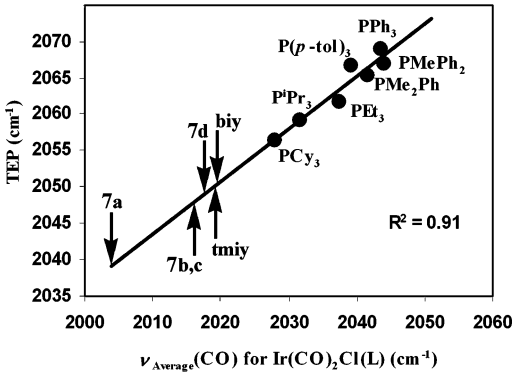


Figure 3. Correlation of the average ν(CO) values for compounds Ir(CO)$_2$Cl(L) with the Tolman electronic parameters (TEP). Extrapolated positions of the NHC ligands studied are indicated by arrows (tmiy = 1,3-di(4-tolylmethyl)imidazolin-2-ylidene, biy = 1,3-dibutylimidazolin-2-ylidene).

Table 2. Selected Bond Lengths and Angles for 8a

Bond Lengths (Å)	
Ir(1)−C(1)	2.05(2)
Ir(1)−Cl(1)	2.392(3)
Ir(1)−C(20)	2.065(10)
Ir(1)−C(21)	2.15(1)
Ir(1)−C(24)	2.168(10)
Ir(1)−C(25)	2.174(12)
C(1)−N(2)	1.418(13)
N(2)−C(3)	1.342(12)
C(3)−N(1)	1.338(11)
N(1)−C(2)	1.426(11)
C(2)−C(1)	1.42(2)
Bond Angles (deg)	
C(1)−N(2)−C(3)	111.0(9)
N(2)−C(3)−N(1)	109.3(8)
C(3)−N(1)−C(2)	108.4(7)
N(1)−C(2)−C(1)	107.4(8)
C(2)−C(1)−N(2)	103.9(11)

(38) McGuinness, D. S.; Cavell, K. J.; Skelton, B. W.; White, A. H. *Organometallics* **1999**, *18*, 1596−1605.
(39) Seo, H.; Kim, B. Y.; Lee, J. H.; Park, H.; Son, S. U.; Chung, Y. K. *Organometallics* **2003**, *22*, 4783−4791.
(40) Lee, H. M.; Jiang, T.; Stevens, E. D.; Nolan, S. P. *Organometallics* **2001**, *20*, 1255−1258.
(41) Morris, D. E.; Tinker, H. B. U.S. Patent 3948962, 1976.

Table 3. Carbonyl Stretching Frequencies for $Ir(CO)_2Cl(L)$

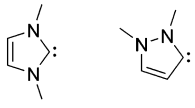
L	solvent	ν(CO) (cm^{-1})	ν_{av}(CO) (cm^{-1})	TEP (cm^{-1})
7a	CH_2Cl_2	2045, 1961	2003	2039[a]
7b	CH_2Cl_2	2059, 1974	2017	2048[a]
7c	CH_2Cl_2	2061, 1972	2017	2048[a]
7d	CH_2Cl_2	2061, 1976	2019	2050[a]
tmiy	CH_2Cl_2	2063, 1976	2020	2050[a]
biy	CH_2Cl_2	2062, 1978	2020	2051[a]
PCy_3	CH_2Cl_2	2072, 1984	2028	2056.4
P^iPr_3	CH_2Cl_2	2077, 1986	2032	2059.2
PEt_3	$CHCl_3$	2081, 1994	2038	2061.7
$P(p\text{-tolyl})_3$	$CHCl_3$	2079, 1999	2039	2066.7
PMe_2Ph	$CHCl_3$	2084, 1999	2042	2065.3
PPh_3	$CHCl_3$	2085, 2002	2044	2068.9
$PMePh_2$	$CHCl_3$	2085, 2003	2044	2067

[a] Values are calculated using linear regression, excluding L = $P(OBu)_3$ and $P(OPh)_3$.

(TEP)[43] of the same ligands.[44] A good linear fit was found, which allows for an estimate of the electron donor power of ligands bound to the $Ir(CO)_2Cl$ fragment in terms of the TEP. Figure 2 shows this comparison, with new compounds **9a**−**d** added. Two previously described[11] NHC ligands tmiy (1,3-di(4-tolylmethyl)imidazolin-2-ylidene) and biy (1,3-dibutylimidazolin-2-ylidene), as well as ligands **7b**−**d**, the normally bound models for **7a**, all fall within a very narrow range on the graph, at slightly higher donor power than PCy_3, one of the most donating phosphine ligands known.

In sharp contrast, ligand **7a** falls far to the left, indicating that it is significantly more donating than any normal carbene yet studied. Extrapolating from the known data for metal-phosphine complexes using the equation[11] $TEP = 0.722 \times \nu_{average}(CO) + 593\ cm^{-1}$ gives an estimated TEP of 2039 cm^{-1}, which is extremely low for a neutral ligand. This can be compared with values of 2048−2051 cm^{-1} for normal carbenes and 2056 cm^{-1} for PCy_3.

Scherer and co-workers[30] have calculated several parameters for the free and chromium-bound NHCs **10** and **11**. The predicted charge on the carbene carbon of



10 **11**

11 is +0.27 for the free carbene and +0.24 when bound to $Cr(CO)_5$. In contrast, the normal carbene carbon of **10** is more positive, with $q = +0.66$ for the free carbene and +0.65 bound to $Cr(CO)_5$. The abnormal carbene **11**, flanked by C-H and N-Me, likely has more electron density at carbon due to the lower inductive electron-withdrawing effect of the flanking carbon atom. This may account for the greater donating ability of carbene **11** as well as of our abnormal carbene **7a**. Although more studies are clearly warranted, our analysis indicates that N-heterocyclic carbenes, previously the most electron-donating neutral ligands known, are substantially exceeded in donor power by their C5-bound analogues. It is noteworthy that other recent modifications of the NHC, bis(diisopropylamino)carbene,[45] a perimidine-based ligand,[46] and a tetrahydropyrimidine-based ligand[47] also appear to be more electron-donating than normal NHCs.

Conclusion

By analogy with the C,N-chelating abnormal iridium(III)-NHC compounds previously prepared, we have synthesized iridium(III) complexes of monodentate NHCs bound through C5. We have also prepared an iridium(I) complex of an abnormal NHC. We find that steric bulk, specifically substitution of the carbon atom next to the metal-bound carbon, is necessary to prepare a stable complex in this case. IR ν(CO) measurements demonstrate that the abnormal C5-bound NHC is a substantially stronger electron donor than normal C2-bound carbenes. We are currently exploring the possible applications of this new category of ligand to homogeneous catalysis.

Experimental Section

General Methods. Disubstituted imidazolium tetrafluoroborate salts[48,49] $IrH_5(PPh_3)_2$,[50] $[IrH_2(acetone)_2(PPh_3)_2][BF_4]$,[51] $[Ir(cod)Cl]_2$,[52] and 2,4-diphenylimidazole[37] were prepared as previously described. All other materials are available from commercial sources and were used as received. All solvents were reagent grade. Iodide salts were stored in the dark. Reactions were generally performed using untreated solvents, without exclusion of air. For attempted metalation using potassium *tert*-butoxide as base, dried and degassed tetrahydrofuran was used and standard Schlenk techniques were followed. Isolated yields are given for all products. NMR spectra were recorded 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). NMR spectra were obtained at room temperature unless otherwise noted. Assignments are based on COSY and HMQC experiments. Infrared spectra were recorded on a Midac FT-IR spectrometer, using NaCl plates. Elemental analyses were performed by Atlantic Microlabs, Inc.; residual solvent was confirmed by ^{1}H NMR.

Dihydrido(pyridine)(1-isopropyl-3-methylimidazolin-4-ylidene)bis(triphenylphosphine)iridium(III) Tetrafluoroborate (4a). 1-Isopropyl-3-methylimidazolium bromide (29 mg, 0.14 mmol) was combined with $AgBF_4$ (27 mg, 0.14 mmol) in dichloromethane, and the mixture was stirred at room temperature in the dark for 12 h. The reaction mixture was then filtered through Celite, and the solvent was removed in vacuo. $IrH_5(PPh_3)_2$ (100 mg, 0.14 mmol), pyridine (12 μL, 0.14 mmol), and tetrahydrofuran (20 mL) were added, and the mixture was refluxed in air. After 10−15 min a clear solution was obtained. Refluxing was continued for 1 h. After cooling to room temperature, the solution was concentrated to 5 mL

(42) Chen, W. Z.; Esteruelas, M. A.; Martín, M.; Oliván, M.; Oro, L. A. *J. Organomet. Chem.* **1997**, *534*, 95−103.
(43) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313−348.
(44) Strohmeier, W.; Müller, F. J. *Chem. Ber.* **1967**, *100*, 2812−2821.
(45) Denk, K.; Sirsch, P.; Herrmann, W. A. *J. Organomet. Chem.* **2002**, *649*, 219−224.
(46) Bazinet, P.; Yap, G. P. A.; Richeson, D. S. *J. Am. Chem. Soc.* **2003**, *125*, 13314−13315.
(47) Mayr, M.; Wurst, K.; Ongania, K.-H.; Buchmeiser, M. R. *Chem. Eur. J.* **2004**, *10*, 1256−1266.
(48) Leadbeater, N. E.; Torenius, H. M. *J. Org. Chem.* **2002**, *67*, 3145−3148.
(49) Holbrey, J. D.; Seddon, K. R. *J. Chem. Soc., Dalton Trans.* **1999**, 2133−2139.
(50) Crabtree, R. H.; Felkin, H.; Morris, G. E. *J. Organomet. Chem.* **1977**, *141*, 205−215.
(51) Crabtree, R. H.; Mellea, M. F.; Mihelcic, J. M.; Quirk, J. M. *J. Am. Chem. Soc.* **1982**, *104*, 107−113.
(52) Lin, Y.; Nomiya, K.; Finke, R. G. *Inorg. Chem.* **1993**, *32*, 6040−6045.

under reduced pressure, and the product was precipitated by addition of 50 mL of pentane. The off-white solid was filtered off and dried in vacuo. Yield: 85 mg (60%). The complex can be recrystallized from chloroform/pentane or dichloromethane/pentane. ^{1}H NMR ($CDCl_3$, 298 K): δ 8.13 (d, 2H, $^3J_{H-H}$ = 5.7 Hz H_{py}), 7.92 (s, 1H, NCHN), 7.34−7.15 (m, 31H, H_{py}, H_{Ph}), 6.46 (t, 2H, $^3J_{H-H}$ = 6.8 Hz, H_{py}), 6.23 (s, 1H, H_{imid}), 4.35 (sept, 1H, $^3J_{H-H}$ = 6.6 Hz, CH_{iPr}), 2.71 (s, 3H, CH_{3-Me}), 1.26 (d, 6H, $^3J_{H-H}$ = 6.6 Hz, CH_{3-iPr}), −11.5 (dt, 1H, $^2J_{P-H}$ = 19.4 Hz, $^3J_{H-H}$ = 4.8 Hz, Ir-H), −22.1 (dt, 1H, $^2J_{P-H}$ = 17.2 Hz, $^3J_{H-H}$ = 4.7 Hz, Ir-H). ^{13}C{^{1}H} NMR (CD_2Cl_2, 298 K): δ 157.8 (C_{py}), 150.1 (t, J_{P-C} = 7.2 Hz, $C_{carbene}$), 135.5 (C_{py}), 134.64 (t, J_{P-C} = 25.9, C_{Ph}), 134.3 (t, J_{P-C} = 5.8, C_{Ph}), 131.7 (NCN), 130.3 (C_{Ph}), 128.4 (t, J_{P-C} = 4.9, C_{Ph}), 125.3 (C_{py}), 123.7 (C_{imid}), 51.4 (CH_{iPr}), 38.1 (CH_{3-Me}), 23.5 (CH_{3-iPr}). ^{31}P{^{1}H} NMR ($CDCl_3$, 298 K): δ 21.5. Anal. Calcd for $C_{48}H_{49}BF_4IrN_3P_2 \cdot CH_2Cl_2$ (1093.85): C, 53.80; H, 4.70; N, 3.84. Found: C, 53.54; H, 4.78; N, 4.18.

Dihydrido(pyridine)(1-butyl-3-methylimidazolin-4-ylidene)bis(triphenylphosphine)iridium(III) Tetrafluoroborate (4b). 1-Butyl-3-methylimidazolium bromide (31 mg, 0.14 mmol) was combined with $AgBF_4$ (27 mg, 0.14 mmol) in dichloromethane, and the mixture was stirred at room temperature in the dark for 12 h. The reaction mixture was then filtered through Celite, and the solvent was removed in vacuo. $IrH_5(PPh_3)_2$ (100 mg, 0.14 mmol), pyridine (12 μL, 0.14 mmol), and tetrahydrofuran (20 mL) were added, and the mixture was refluxed in air. After 10−15 min a clear solution was obtained. Refluxing was continued for 1 h. After cooling to room temperature, the solution was concentrated to 5 mL under reduced pressure, and the product was precipitated by addition of 50 mL of pentane. The off-white solid was filtered off and dried in vacuo. Yield: 90 mg (63%). The complex can be recrystallized from chloroform/pentane or dichloromethane/pentane. ^{1}H NMR ($CDCl_3$, 298 K): δ 8.14 (d, 2H, $^3J_{H-H}$ = 5.4 Hz, H_{py}), 7.88 (s, 1H, NCHN), 7.37−7.14 (m, 31H, H_{py}, H_{Ph}), 6.45 (t, 2H, $^3J_{H-H}$ = 7.3 Hz, H_{py}), 6.16 (s, 1H, H_{imid}), 3.89 (t, 2H, $^3J_{H-H}$ = 7.4 Hz, CH_2), 2.70 (s, 3H, CH_{3-Me}), 1.45 (m, 2H, CH_2), 1.12 (m, 2H, CH_2), 0.88 (t, 3H, $^3J_{H-H}$ = 7.0 Hz, CH_{3-nBu}), −11.5 (dt, 1H, $^2J_{P-H}$ = 19.6 Hz, $^3J_{H-H}$ = 4.8 Hz, Ir-H), −22.1 (dt, 1H, $^2J_{P-H}$ = 17.4 Hz, $^3J_{H-H}$ = 4.8 Hz, Ir-H). ^{13}C{^{1}H} NMR (CD_2Cl_2, 298 K): δ 157.7 (C_{py}), 150.1 (t, J_{P-C} = 7.1 Hz, $C_{carbene}$), 135.4 (C_{py}), 134.6 (t, J_{P-C} = 26.6, C_{Ph}), 134.2 (t, J_{P-C} = 5.9, C_{Ph}), 133.2 (NCN), 130.2 (C_{Ph}), 128.4 (t, J_{P-C} = 4.7, C_{Ph}), 126.1 (C_{imid}), 125.8 (C_{py}), 48.4 (CH_2), 38.0 (CH_{3-Me}), 33.1 (CH_2), 20.0 (CH_2), 13.9 (CH_{3-nBu}). ^{31}P{^{1}H} NMR ($CDCl_3$, 298 K): δ 21.4. Anal. Calcd for $C_{49}H_{51}BF_4IrN_3P_2 \cdot CH_2Cl_2$ (1107.87): C, 54.21; H, 4.82; N, 3.79. Found: C, 54.09; H, 4.87; N, 3.80.

1,3-Diisopropyl-2-phenylimidazolium Bromide (5). 2-Phenylimidazole (2.30 g, 15.9 mmol) was stirred with crushed KOH (24 g, 0.43 mol) in 250 mL of acetone for 1 h. 2-Bromopropane (37.3 g, 0.303 mol) was added, and the mixture was refluxed for 3 days. After cooling, the supernatant was collected, and the solid residue was extracted with 200 mL of acetone in 50 mL portions. These fractions were combined, and volatiles were removed under reduced pressure at 40 °C, to give approximately 50 mL of involatile material. To this mixture was added 250 mL of diethyl ether. The solution was filtered to remove any remaining insoluble material and then extracted with 100 mL of 2 M aqueous HCl in 3 portions. The acidic extract was basified to pH 12 by adding KOH, which caused an oil to separate from solution. The mixture was extracted with 200 mL of diethyl ether in 3 portions. These fractions were combined and washed three times with 50 mL of a 1:1 solution of 2 M aqueous KOH and dimethyl sulfoxide, then twice with 50 mL of water. The ether layer was dried over magnesium sulfate, filtered, and evaporated to give 1-isopropyl-2-phenylimidazole as an oil. Yield: 2.255 g, 76%. ^{1}H NMR ($CDCl_3$, 298 K): δ 7.53 (m, 2H, CH_{Ph}), 7.44 (m, 3H, CH_{Ph}), 7.15 (d, $^3J_{H-H}$ = 1.5 Hz, 1H, CH_{imid}), 7.10 (d, $^3J_{H-H}$ = 1.5 Hz, 1H, CH_{imid}), 4.57 (sept, $^3J_{H-H}$ = 6.7 Hz, 1H, CH^iPr), 1.42 (d, $^3J_{H-H}$ = 6.7 Hz, 6H, CH_3). ^{13}C NMR ($CDCl_3$, 298 K): δ 146.9, 131.0, 128.9, 128.6, 128.5, 128.4, 115.9 (C_{arom}), 47.7 (CH_{iPr}), 23.8 (CH_3).

The above product (2.255 g, 12.1 mmol) was refluxed in 25 mL of toluene with 2-bromopropane (14.9 g, 121 mmol) for 4 days. The white precipitate was collected and washed with 60 mL of diethyl ether in 3 portions and dried in air. Yield: 2.063 g, 74%. ^{1}H NMR ($CDCl_3$, 298 K): δ 8.08 (s, 2H, CH_{imid}), 7.77−7.54 (m, 5H, CH_{Ph}), 4.29 (sept, $^3J_{H-H}$ = 6.7 Hz, 1H, CH^iPr), 1.56 (d, $^3J_{H-H}$ = 6.7 Hz, 6H, CH_3). ^{13}C NMR ($CDCl_3$, 298 K): δ 142.0, 132.6, 130.0, 129.7, 120.7, 119.8 (C_{arom}), 51.4 (CH_{iPr}), 22.8 (CH_3). Anal. Calcd for $C_{15}H_{21}N_2Br$ (309.25): C, 58.26; H, 6.85; N, 9.06. Found: C, 58.26; H, 6.78; N, 9.04.

1-Isopropyl-2,4-diphenylimidazole. 2,4-Diphenylimidazole (5.428 g, 24.6 mmol) and powdered potassium hydroxide (7.3 g, 130 mmol) were stirred in 175 mL of acetone for 20 min. 2-Bromopropane (9.3 mL, 98 mmol) was added, and the mixture was refluxed while stirring vigorously for 16 h. The liquid phase was decanted, and residual solid was extracted with 100 mL of acetone in 2 portions. The liquid portions were combined and concentrated to 30 mL under reduced pressure. Water (100 mL) was added to give a pale orange precipitate. This crude material was washed with 100 mL of water, dried in air 1 h, and recrystallized from a hot 1:1 mixture of hexanes/ether at −20 °C. Yield: 5.069 g, 79%. ^{1}H NMR ($CDCl_3$, 298 K): δ 7.86 (m, 2H, CH_{arom}), 7.60 (m, 2H, CH_{arom}), 7.45 (m, 3H, CH_{arom}), 7.40 (s, 1H, CH_{imid}), 7.38 (m, 2H, CH_{arom}), 7.24 (m, 1H, CH_{arom}), 4.56 (sept, $^3J_{H-H}$ = 6.7 Hz, 1H, CH_{iPr}), 1.49 (d, $^3J_{H-H}$ = 6.7 Hz, 6H, CH_3). ^{13}C NMR ($CDCl_3$, 298 K): δ 147.5, 141.2, 134.3, 131.0, 129.2, 128.9, 128.6, 128.5, 126.6, 124.8, 111.9 (C_{arom}), 48.0 (CH_{iPr}), 23.9 (CH_3). Anal. Calcd for $C_{18}H_{18}N_2$ (262.36): C, 82.41; H, 6.92; N, 10.68. Found: C, 82.18; H, 6.91; N, 10.55.

1-Isopropyl-3-methyl-2,4-diphenylimidazolium Iodide (7a·HI). 1-Isopropyl-2,4-diphenylimidazole (4.284 g, 16.3 mmol) and iodomethane (3.1 mL, 50 mmol) were refluxed in toluene (50 mL) for 16 h. The white precipitate was collected and washed with ether (3 × 30 mL) to give analytically pure **7a**·HI. Yield: 6.393 g, 97%. ^{1}H NMR ($CDCl_3$, 298 K): δ 8.04 (m, 2H, CH_{arom}), 7.78 (m, 2H, CH_{arom}), 7.67 (m, 3H, CH_{arom}), 7.48 (m, 3H, CH_{arom}), 7.46 (s, 1H, CH_{imid}), 4.39 (sept, $^3J_{H-H}$ = 6.6 Hz, 1H, CH_{iPr}), 3.59 (s, 3H, NCH_3), 1.57 (d, $^3J_{H-H}$ = 6.6 Hz, 6H, CH_{3-iPr}). ^{13}C NMR ($CDCl_3$, 298 K): δ 144.1, 136.3, 132.7, 131.4, 130.6, 130.5, 129.9, 129.2, 125.5, 121.7, 115.6 (C_{arom}), 51.8 (CH_{iPr}), 34.8 (NCH_3), 23.5 (CH_{3-iPr}). Anal. Calcd for $C_{19}H_{21}N_2I$ (404.29): C, 56.45; H, 5.24; N, 6.93. Found: C, 56.34; H, 5.28; N, 7.16.

1-Isopropyl-4,5-diphenylimidazole. 4,5-Diphenylimidazole (2.596 g, 11.8 mmol) and powdered potassium hydroxide (3.5 g, 62 mmol) were stirred in 100 mL of acetone for 20 min. 2-Bromopropane (4.3 mL, 45 mmol) was added, and the mixture was refluxed while stirring vigorously for 16 h. The liquid phase was decanted, and residual solid was extracted with 100 mL of acetone in 2 portions. The liquid portions were combined and concentrated to 30 mL under reduced pressure. The residue was dissolved in 150 mL of 2 M HCl and washed with ether (3 × 50 mL). Solid potassium hydroxide was added to pH 12, and the mixture was extracted with diethyl ether (3 × 50 mL). These portions were combined and dried over $MgSO_4$, and the solvent was removed to give a solid. Yield: 2.870 g, 93%. ^{1}H NMR ($CDCl_3$, 298 K): δ 7.73 (s, 1H, CH_{imid}), 7.46 (m, 5H, CH_{arom}), 7.35 (m, 2H, CH_{arom}), 7.19 (m, 2H, CH_{arom}), 7.12 (m, 1H, CH_{arom}), 4.14 (sept, $^3J_{H-H}$ = 6.7 Hz, 1H, CH_{iPr}), 1.43 (d, $^3J_{H-H}$ = 6.7 Hz, 6H, CH_3). ^{13}C NMR ($CDCl_3$, 298 K): δ 137.8, 134.8, 133.4, 131.3, 131.2, 129.2, 128.8, 128.2, 128.1, 126.6, 126.2 (C_{arom}), 47.0 (CH_{iPr}), 24.0 (CH_3). Anal. Calcd for $C_{18}H_{18}N_2$ (262.36): C, 82.41; H, 6.92; N, 10.68. Found: C, 82.51; H, 7.02; N, 10.70.

1-Isopropyl-3-methyl-4,5-diphenylimidazolium Iodide (7b·HI). 1-Isopropyl-4,5-diphenylimidazole (500 mg, 1.90 mmol) and iodomethane (0.5 mL, 8.1 mmol) were refluxed in toluene (10 mL) for 16 h. The white precipitate was collected and

washed with ether (3 × 15 mL) to give analytically pure **7b**·HI. Yield: 707 mg, 92%. ^{1}H NMR ($CDCl_3$, 298 K): δ 10.50 (s, 1H, CH_{imid}), 7.46−7.34 (m, 6H, CH_{arom}), 7.28 (m, 4H, CH_{arom}), 4.43 (sept, $^3J_{H-H}$ = 6.5 Hz, 1H, CH_{iPr}), 4.01 (s, 3H, NCH_3), 1.66 (d, $^3J_{H-H}$ = 6.5 Hz, 6H, CH_{3-iPr}). ^{13}C NMR ($CDCl_3$, 298 K): δ 136.4, 132.7, 131.2, 130.8, 130.6, 130.5, 130.3, 129.3, 129.2, 125.2, 124.7 (C_{arom}), 51.5 (CH_{iPr}), 35.5 (NCH_3), 23.7 (CH_{3-iPr}). Anal. Calcd for $C_{19}H_{21}N_2I$ (404.29): C, 56.45; H, 5.24; N, 6.93. Found: C, 56.28; H, 5.29; N, 7.00.

1,3-Diisopropyl-4,5-diphenylimidazolium bromide (7c·HBr). 1-Isopropyl-4,5-diphenylimidazole (500 mg, 1.90 mmol) and 2-bromopropane (0.9 mL, 9.5 mmol) were refluxed in toluene (10 mL) for 48 h. The precipitate was dissolved in 100 mL of 5% KOH solution. The solution was filtered to remove the white precipitate (starting material) and washed with ether (3 × 50 mL). The solution was then extracted with dichloromethane (3 × 50 mL). These fractions were combined and dried over $MgSO_4$. The solution was reduced to 2 mL, and ether was slowly added to precipitate **7c**·HBr. Yield: 27%, 200 mg. ^{1}H NMR ($CDCl_3$, 298 K): δ 11.12 (s, 1H, CH_{imid}), 7.42 (m, 6H, CH_{arom}), 7.23 (m, 4H, CH_{arom}), 4.48 (sept, $^3J_{H-H}$ = 6.9 Hz, 2H, CH_{iPr}), 1.78 (d, $^3J_{H-H}$ = 6.9 Hz, 12H, CH_3). ^{13}C NMR ($CDCl_3$, 298 K): δ 135.1, 131.3, 130.7, 130.5, 129.4, 126.3 (C_{arom}), 52.3 (CH_{iPr}), 23.7 (CH_3). Anal. Calcd for $C_{21}H_{25}N_2Br$ (385.35): C, 65.46; H, 6.54; N, 7.27. Found: C, 65.37; H, 6.61; N, 7.19.

3-Isopropyl-1-phenylimidazolium Bromide (7d·HBr). 1-Phenylimidazole (374 mg, 2.59 mmol) and 2-bromopropane (0.74 mL, 7.8 mmol) were refluxed in toluene (30 mL) for 72 h to give an oily precipitate. Toluene was decanted off, and the oil was dissolved in a 5% KOH solution (20 mL). This solution was washed with diethyl ether (3 × 30 mL) and extracted with dichloromethane (3 × 50 mL). The dichloromethane fractions were combined and dried over $MgSO_4$. The solvent was removed to give an oil which retained fractional amounts of solvent, but was otherwise pure. Yield: 151 mg, 22%. ^{1}H NMR ($CDCl_3$, 298 K): δ 11.15 (t, $^4J_{H-H}$ = 1.6 Hz, 1H, CH_{imid}), 7.85 (m, 2H, CH_{arom}), 7.75 (t, $^{3,4}J_{H-H}$ = 1.6 Hz, 1H, CH_{imid}), 7.67 (t, $^{3,4}J_{H-H}$ = 1.6 Hz, 1H, CH_{imid}), 7.57 (m, 2H, CH_{arom}), 7.51 (m, 1H, CH_{arom}), 5.34 (sept, $^3J_{H-H}$ = 6.7 Hz, 1H, CH_{iPr}), 1.70 (d, $^3J_{H-H}$ = 6.7 Hz, 6H, CH_3). ^{13}C NMR (acetone-d_6, 298 K): δ 136.2, 136.1, 130.9, 130.4, 122.7, 122.3, 121.7 (C_{arom}), 54.4 (CH_{iPr}), 23.0 (CH_3).

1,2,3,4-Tetramethylimidazolium iodide (7e·HI). Commercial 2,4-dimethylimidazole (425 mg, 4.42 mmol), methyl iodide (6.28 g, 44.2 mmol), and sodium bicarbonate (750 mg, 8.84 mmol) were refluxed in 20 mL of acetonitrile for 72 h. After 24 and 48 h, 6.28 g of methyl iodide was added to the reaction mixture. The mixture was cooled, and 50 mL of diethyl ether was added to precipitate a solid. The supernatant was decanted off, and the solid was extracted with 100 mL of dichloromethane in 3 portions. The solution was concentrated to 10 mL under reduced pressure, and ether was added to precipiate **7e**·HI, which was dried in vacuo. Yield: 935 mg, 84%. ^{1}H NMR ($CDCl_3$, 298 K): δ 7.16 (q, $^4J_{H-H}$ = 1.0 Hz, 1H, CH_{imid}), 3.89 (s, 3H, NCH_3), 3.76 (s, 3H, NCH_3), 2.83 (s, 3H, CCH_3), 2.32 (d, $^4J_{H-H}$ = 1.0 Hz, 3H, CCH_3). ^{13}C NMR ($CDCl_3$, 298 K): δ 143.9, 130.0, 119.5 (C_{arom}), 36.3, 33.4 (NCH_3), 12.4, 10.1 (CCH_3). Anal. Calcd for $C_7H_{13}N_2I$ (252.1): C, 33.35; H, 5.20; N, 11.11. Found: C, 33.31; H, 5.21; N, 11.18.

Anion Exchange Method A. Compound **7a**·HI (461 mg, 1.14 mmol) was stirred with DOWEX 21K Cl^- anion exchange beads (5 g) in 20 mL of methanol for 16 h. The solvent was then decanted, and the beads were washed with methanol (2 × 10 mL). The fractions were combined, and methanol was removed under reduced pressure. The residue was extracted with acetone and filtered, and acetone was evaporated under reduced pressure to give a clear oil.

Method B. Compound **7a**·HI (461 mg, 1.14 mmol) was dissolved in 15 mL of 1:1 acetone/H_2O. Silver acetate (190 mg, 1.14 mmol) was added, and an off-white precipitate slowly formed. The mixture was stirred for 30 min and filtered through a fine frit. To this solution was added 1.14 mL of a 1 M HCl solution (1.14 mmol). The solution was filtered and heated at 50 °C under vacuum for 1 h to remove solvents and acetic acid, leaving a clear oil.

[1-Isopropyl-3-methyl-2,4-diphenylimidazolin-5-ylidene]-[(1,2,5,6-η)-1,5-cyclooctadiene]chloroiridium (8a). The oil directly obtained from either anion exchange procedure (1.14 mmol assuming quantitative recovery) was stirred with silver oxide (263 mg, 1.14 mmol) in 15 mL of dichloromethane in the dark for 1.5 h. The solution was filtered, and $[Ir(cod)Cl]_2$ (382 mg, 0.57 mmol) was added. The mixture was stirred for 1 h and filtered through Celite. Volatiles were removed, and the residue was purified by flash chromatography on silica gel using 1:1 ethyl acetate/hexanes as eluent. X-ray quality crystals were grown by layering a dichloromethane solution with pentane. Method A yield: 300 mg, 43%. Method B yield: 335 mg, 48%. ^{1}H NMR ($CDCl_3$, 298 K): δ 7.94 (m, 2H, CH_{arom}), 7.61 (m, 3H, CH_{arom}), 7.50−7.35 (m, 5H, CH_{arom}), 5.83 (sept, $^3J_{H-H}$ = 7.3 Hz, 1H, CH_{iPr}), 4.53 (m, 1H, CH_{cod}), 4.24 (m, 1H, CH_{cod}), 3.30 (s, 3H, NCH_3), 2.95 (m, 1H, CH_{cod}), 2.29 (m, 1H, CH_{cod}), 1.94−2.20 (m, 3H, CH_{2-cod}), 1.56−1.43 (m, 3H, CH_{2-cod}), 1.507 (d, $^3J_{H-H}$ = 7.3 Hz, 3H, CH_{3-iPr}), 1.39 (d, $^3J_{H-H}$ = 7.3 Hz, 3H, CH_{3-iPr}), 1.34 (m, 1H, CH_{2-cod}), 1.07 (m, 1H, CH_{2-cod}). ^{13}C NMR (acetone-d_6, 223 K): δ 162.0, 144.0, 134.4, 133.0, 132.9, 132.8, 132.7, 131.8, 130.6, 130.5, 128.9, 128.5, 127.8 (C_{arom}), 79.8, 77.5, 58.5, 52.6, (CH_{cod}), 51.2 (CH_{iPr}), 36.3, 34.6, 33.0, 31.8, 30.1 (CH_{2-cod}, NCH_3), 23.9, 23.8 (CH_{3-iPr}). Anal. Calcd for $IrClC_{27}H_{32}N_2$ (612.24): C, 52.97; H, 5.27; N, 4.58. Found: C, 53.00; H, 5.21; N, 4.64.

[1-Isopropyl-3-methyl-4,5-diphenylimidazolin-2-ylidene]-[(1,2,5,6-η)-1,5-cyclooctadiene]chloroiridium (8b). Compound **7b**·HI (173 mg, 0.43 mmol) was stirred with silver oxide (74 mg, 0.32 mmol) in 15 mL of dichloromethane in the dark for 1.5 h. The solution was filtered, and $[Ir(cod)Cl]_2$ (144 mg, 0.21 mmol) was added. The mixture was stirred for 1 h and filtered through Celite. Volatiles were removed, and the residue was purified by flash chromatography on silica gel using dichloromethane as eluent. Yield: 253 mg, 98%. ^{1}H NMR ($CDCl_3$, 298 K): δ 7.18−7.38 (m, 8H, CH_{arom}), 7.13 (m, 2H, CH_{arom}), 5.83 (sept, $^3J_{H-H}$ = 6.9 Hz, 1H, CH_{iPr}), 4.65 (m, 1H, CH_{cod}), 4.57 (m, 1H, CH_{cod}), 3.92 (s, 3H, NCH_3), 3.16 (m, 2H, CH_{cod}), 2.26 (m, 4H, CH_{2-cod}), 1.57−1.85 (m, 4H, CH_{2-cod}), 1.45 (d, $^3J_{H-H}$ = 6.9 Hz, 3H, CH_{3-iPr}), 1.34 (d, $^3J_{H-H}$ = 6.9 Hz, 3H, CH_{3-iPr}). ^{13}C NMR ($CDCl_3$, 298 K): δ 179.0 ($C_{carbene}$), 133.2, 132.5, 130.4, 130.2, 130.0, 129.0, 128.5, 128.4, 128.3, 128.0 (C_{arom}), 83.9, 83.1 (CH_{cod}), 55.0 (CH_{iPr}), 51.8, 51.5 (CH_{cod}), 36.2, 33.8, 33.4, 29.9, 29.4 (CH_{2-cod}, NCH_3), 23.4, 23.3 (CH_{3-iPr}). Anal. Calcd for $IrClC_{27}H_{32}N_2$ (612.24): C, 52.97; H, 5.27; N, 4.58. Found: C, 53.23; H, 5.36; N, 4.61.

[1,3-Diisopropyl-4,5-diphenylimidazolin-2-ylidene]-[(1,2,5,6-η)-1,5-cyclooctadiene]chloroiridium (8c). This compound was prepared analogously to **8b**, using **7c**·HBr as ligand precursor. Yield: 73%. ^{1}H NMR ($CDCl_3$, 298 K): δ 7.14−7.23 (m, 10H, CH_{arom}), 5.95 (sept, $^3J_{H-H}$ = 7.3 Hz, 2H, CH_{iPr}), 4.56 (m, 2H, CH_{cod}), 3.19 (m, 2H, CH_{cod}), 2.21 (m, 4H, CH_{2-cod}), 1.67 (m, 4H, CH_{2-cod}), 1.38 (sept, $^3J_{H-H}$ = 7.3 Hz, 6H, CH_{3-iPr}),1.29 (sept, $^3J_{H-H}$ = 7.3 Hz, 6H, CH_{3-iPr}).^{13}C NMR ($CDCl_3$, 298 K): δ 177.8 ($C_{carbene}$), 132.4, 132.2, 129.8, 128.7, 127.7 (C_{arom}), 82.7 (CH_{cod}), 54.9 (CH_{iPr}), 51.3 (CH_{cod}), 33.6, 29.6 (CH_{2-cod}), 23.4, 23.1 (CH_{3-iPr}). Anal. Calcd. for $IrClC_{29}H_{36}N_2$ (640.29): C, 54.40; H, 5.67; N, 4.78. Found: C, 54.47; H, 5.70; N, 4.37.

[3-Isopropyl-1-phenylimidazolin-2-ylidene][(1,2,5,6-η)-1,5-cyclooctadiene]chloroiridium (8d). This compound was prepared analogously to **8b**, using **7d**·HBr as ligand precursor. Yield: 75%. ^{1}H NMR ($CDCl_3$, 298 K): δ 7.93 (m, 2H, CH_{arom}), 7.40 (m, 2H, CH_{arom}), 7.34 (m, 1H, CH_{arom}), 7.08 (d, $^3J_{H-H}$ = 2.1 Hz, 1H, CH_{imid}), 6.96 (d, $^3J_{H-H}$ = 2.1 Hz, 1H, CH_{imid}), 5.69 (sept, $^3J_{H-H}$ = 6.7 Hz, 1H, CH_{iPr}), 4.63 (m, 1H, CH_{cod}), 4.36 (m, 1H, CH_{cod}), 2.83 (m, 1H, CH_{cod}), 2.14 (m, 1H, CH_{cod}), 2.05

Table 4. Crystallographic Data for 4a and 8a

	4a	8a
color, shape	yellow, prism	yellow, block
empirical formula	$C_{103}H_{112}B_2C_{l6}F_8Ir_2N_6P_4$	$C_{27}H_{32}ClIrN_2$
fw	2328.72	612.24
radiation, λ (Å)	Mo Kα (monochr), 0.71069	Mo Kα (monochr), 0.71069
T (°C)	−90	−100
cryst syst	monoclinic	orthorhombic
space group	$P2/c$ (No. 13)	$Pca2_1$ (No. 29)
unit cell dimens		
a (Å)	23.7717(10)	15.4595(2)
b (Å)	11.2208(6)	8.91820(10)
c (Å)	19.5813(9)	35.7820(5)
α (deg)		
β (deg)	104.554(3)	
γ (deg)		
V (Å^3)	5055.5(4)	4833.30(9)
Z	2	8
D_{calc} (g cm^{-3})	1.530	1.648
μ(Mo Kα) (cm^{-1})	29.23	55.52
cryst size (mm)	0.05 × 0.07 × 0.10	0.07 × 0.07 × 0.10
total, unique no. of reflns	20 640, 9799	23 046, 12 650
R_{int}	0.063	0.049
no. of params, restraints	567, 0	558, 0
R,[a] R_w[b]	0.040, 0.045	0.036, 0.045
GOF	1.05	1.24
min., max. resid density (e Å^{-3})	−0.70, 0.71	−1.91, 1.25

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$, for all $I > 3.00\sigma(I)$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$.

(m, 2H, CH_{2-cod}), 1.87 (m, 1H, CH_{2-cod}), 1.50 (m, 3H, CH_{2-cod}), 1.48 (d, $^3J_{H-H}$ = 6.7 Hz, 3H, CH_{3-iPr}), 1.45 (d, $^3J_{H-H}$ = 6.7 Hz, 3H, CH_{3-iPr}), 1.24 (m, 1H, CH_{2-cod}), 1.07 (m, 1H, CH_{2-cod}). ^{13}C NMR ($CDCl_3$, 298 K): δ 178.9 ($C_{carbene}$), 140.3, 128.6, 127.7, 125.2, 121.7, 116.9 (C_{arom}), 84.0, 82.8 (CH_{cod}), 53.2 (CH_{iPr}), 51.8, 51.7 (CH_{cod}), 34.4, 32.2, 29.7, 29.0 (CH_{2-cod}), 23.7, 23.6 (CH_{3-iPr}). Anal. Calcd for $IrClC_{20}H_{26}N_2$ (522.12): C, 46.01; H, 5.02; N, 5.37. Found: C, 45.82; H, 4.93; N, 5.26.

[1-Isopropyl-3-methyl-2,4-diphenylimidazolin-5-ylidene]-dicarbonylchloroiridium (9a). Compound **8a** (35 mg, 0.057 mmol) was dissolved in 5 mL of dichloromethane, and carbon monoxide gas was passed through the solution for 10 min. Solvent was removed under reduced pressure, and the residual oil was washed with a small amount of pentane and dried in vacuo for 30 min to give **9a** as a pale yellow solid. Yield: 29 mg, 91%. ^{1}H NMR ($CDCl_3$, 298 K): δ 7.61−7.72 (m, 5H, C_{arom}), 7.41−7.51 (m, 5H, CH_{arom}), 5.17 (sept, $^3J_{H-H}$ = 7.0 Hz, 1H, CH_{iPr}), 3.29 (s, 3H, NCH_3), 1.53 (br d, $^3J_{H-H}$ = 7.0 Hz, 6H, CH_{3-iPr}). ^{13}C NMR ($CDCl_3$, 298 K): δ 182.6, 169.7 (CO), 153.2, 143.5, 138.7, 131.9, 131.5, 130.7, 130.6, 129.7, 128.8, 128.4, 125.8 (C_{arom}), 56.0 (CH_{iPr}), 33.5 (NCH_3), 23.6 (CH_{3-iPr}). Anal. Calcd for $IrClOC_{21}H_{20}N_2$ (560.08): C, 45.03; H, 3.60; N, 5.00. Found: C, 45.24; H, 3.69; N, 4.90. FT-IR (CH_2Cl_2): ν(CO) 2045, 1961 cm^{-1}, similar intensities.

[1-Isopropyl-3-methyl-4,5-diphenylimidazolin-2-ylidene]-dicarbonylchloroiridium (9b). Compound **9b** was prepared analogously to **9a**, from **8b**. Yield: 93%. ^{1}H NMR ($CDCl_3$, 298 K): δ 7.29−7.40 (m, 6H, CH_{arom}), 7.25 (m, 2H, CH_{arom}), 7.18 (m, 2H, CH_{arom}), 5.03, (sept, $^3J_{H-H}$ = 7.0 Hz, 1H, CH_{iPr}), 3.85 (s, 3H, NCH_3), 1.56 (d, $^3J_{H-H}$ = 7.0 Hz, 3H, CH_{3-iPr}), 1.52 (d, $^3J_{H-H}$ = 7.0 Hz, 3H, CH_{3-iPr}). ^{13}C NMR ($CDCl_3$, 298 K): δ 181.1, 171.9, 168.6 (CO, $C_{carbene}$), 133.4, 131.9, 131.8, 130.5, 129.5, 129.1, 128.9, 128.7, 128.6, 127.6 (C_{arom}), 53.8 (CH_{iPr}), 37.8 (NCH_3). 24.4, 23.2 (CH_{3-iPr}). Anal. Calcd for $IrClOC_{21}H_{20}N_2$ (560.08): C, 45.03; H, 3.60; N, 5.00. Found: C, 45.31; H, 3.68; N, 5.02. FT-IR (CH_2Cl_2): ν(CO) 2059, 1974 cm^{-1}, similar intensities.

[1,3-Diisopropyl-4,5-diphenylimidazolin-2-ylidene]dicarbonylchloroiridium (9c). Compound **9c** was prepared analogously to **9a**, from **8c**. Yield: 90%. ^{1}H NMR ($CDCl_3$, 298 K): δ 7.25−7.33 (m, 6H, CH_{arom}), 7.19−7.24 (m, 4H, CH_{arom}), 5.34 (sept, $^3J_{H-H}$ = 6.8 Hz, 2H, CH_{iPr}), 1.49 (d, $^3J_{H-H}$ = 6.8 Hz, 6H, CH_{3-iPr}), 1.44 (d, $^3J_{H-H}$ = 6.8 Hz, 6H, CH_{3-iPr}). ^{13}C NMR ($CDCl_3$, 298 K): δ 180.9, 170.3, 168.7 (CO, $C_{carbene}$), 133.0, 131.9, 129.3, 129.0, 128.8, 128.2 (C_{arom}), 55.3 (CH_{iPr}), 23.8, 22.9 (CH_{3-iPr}). Anal. Calcd for $IrClO_2C_{23}H_{24}N_2$ (588.13): C, 46.97; H, 4.11; N, 4.76. Found: C, 46.70; H, 4.19; N, 4.60. FT-IR (CH_2Cl_2): ν(CO) 2061, 1972 cm^{-1}, similar intensities.

[3-Isopropyl-1-phenylimidazolin-2-ylidene]dicarbonylchloroiridium (9d). Compound **9d** was prepared analogously to **9a**, from **8d**. Yield: 94%. ^{1}H NMR ($CDCl_3$, 298 K): δ 7.69 (m, 2H, CH_{arom}), 7.50 (m, 3H, CH_{arom}), 7.25 (d, $^3J_{H-H}$ = 2.0 Hz, 1H, CH_{imid}), 7.20 (d, $^3J_{H-H}$ = 2.0 Hz, 1H, CH_{imid}), 5.52 (sept, $^3J_{H-H}$ = 7.0 Hz, 1H, CH_{iPr}), 1.55 (br, 6H, CH_3). ^{13}C NMR ($CDCl_3$, 298 K): δ 181.1, 172.5, 167.8 (CO, $C_{carbene}$), 139.5, 129.3, 129.1, 126.2, 123.0, 117.8 (C_{arom}), 53.7 (CH_{iPr}), 23.0 (br, CH_3). Anal. Calcd for $IrClO_2C_{14}H_{14}N_2$: (469.95): C, 35.78; H, 3.00; N, 5.96. Found: C, 35.84; H, 3.01; N, 5.83. FT-IR (CH_2Cl_2): ν(CO) 2061, 1976 cm^{-1}, similar intensities.

Structure Determination and Refinement of 4a. Crystals of **4a** suitable for study were obtained by layering a chloroform solution with pentane. Data were collected on a Nonius KappaCCD (Mo Kα radiation) and corrected for absorption (SORTAV).[53,54] The structure was solved by direct methods and refined on F for all reflections. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included at calculated positions. Relevant crystal and data parameters are presented in Table 4. The isopropyl group was disordered; only one rotamer is shown in Figure 1 for clarity. Correction for residual density of disordered solvent (pentane) used the option SQUEEZE in the program package PLATON.[55−57]

Structure Determination and Refinement of 8a. Crystals of **8a** suitable for study were obtained by layering a dichloromethane solution with pentane. Data were collected on a Nonius KappaCCD (Mo Kα radiation) and corrected for absorption (SORTAV).[53,54] The structure was solved by direct methods and refined on F for all reflections. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included at calculated positions. Relevant crystal and data parameters are presented in Table 4.

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Supporting Information Available: Details of the X-ray crystal structure determination of **4a** and **8a**, including atomic positions, bond distances, and bond angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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(53) Blessing, R. H. *Acta Crystallogr.* **1995**, *A51*, 33−38.
(54) Blessing, R. H. *J. Appl. Crystallogr.* **1997**, *30*, 421−426.
(55) Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, C34.
(56) Vandersluis, P.; Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, 194−201.
(57) Spek, A. L. *J. Appl. Crystallogr.* **2003**, *36*, 7−13.