ORGANOMETALLICS
Article

Organometallics **2010,** *29,* 3019–3026 3019
DOI: 10.1021/om100302g

Iridium Complexes of CCC-Pincer N-Heterocyclic Carbene Ligands: Synthesis and Catalytic C−H Functionalization

Anthony R. Chianese,* Allen Mo, Nicole L. Lampland, Raymond L. Swartz, and Paul T. Bremer

Department of Chemistry, Colgate University, 13 Oak Drive, Hamilton, New York 13346

Received April 14, 2010

A series of four meta-phenylene-bridged bis-benzimidazolium chlorides were synthesized as precursors to rigid, monoanionic, CCC-pincer N-heterocyclic carbene ligands. For ligands with mesityl, 3,5-xylyl, or 3,5-di-*tert*-butylphenyl side groups, reaction with $[Ir(1,5\text{-cyclooctadiene})Cl]_2$ in acetonitrile with either excess triethylamine or stoichiometric cesium fluoride as base gave neutral, iridium(III) pincer complexes of the formula Ir(CCC)HCl(MeCN), which were purified by chromatography on silica gel. Metalation failed under these conditions for a 2,6-diisopropylphenyl-substituted derivative. In combination with NaO^{t}Bu, these complexes form active catalysts for the acceptorless dehydrogenation of cyclooctane and for arene C−H borylation in neat arene solvent.

Introduction

The selective functionalization of weakly reactive C−H bonds is a central challenge in organometallic chemistry. The development of methods for transition-metal-catalyzed C−H bond functionalization has expanded dramatically in the past decade, with the most practical and predictable transformations beginning to find routine use in organic synthesis.[1] The pincer[2] ligand motif has proved especially useful for the stabilization of low-valent metal fragments capable of C−H activation and subsequent functionalization, especially in the case of monoanionic PCP-pincer ligands,[3] iridium complexes of which have provided exceptionally active catalysts for the dehydrogenation of alkanes, either with or without an added hydrogen acceptor.[4]

N-Heterocyclic carbenes (NHCs) are now routinely employed as supporting ligands for catalysis,[5] and a diverse array of pincer ligands bearing the NHC motif have been synthesized, including those based on neutral CNC,[6] CNN,[7] PCP,[8] SCS,[9] and CSC;[10] anionic CNC;[11] and dianionic OCO[12] motifs. Because of the utility of the anionic $P-C_{aryl}-P$ framework, especially with regard to iridium-catalyzed alkane dehydrogenation, analogous monoanionic ligands with a $C_{NHC}-C_{aryl}-C_{NHC}$ framework are an attractive target.

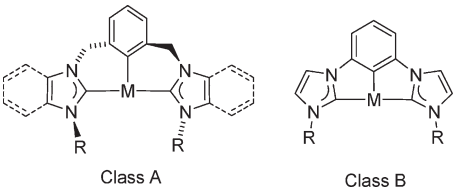

Figure 1. Known CCC-pincer ligands.

Aside from ligands derived from unexpected alkyne chlorometalation[13] and side-group C−H activation,[14] most reported CCC-pincer ligands fall into two classes (Figure 1).

In class **A**,[6a,f,h,15] the central aryl fragment is connected to two imidazole- or benzimidazole-based NHC fragments through CH_2 linkers. The ligand forms two six-membered,

*To whom correspondence should be addressed. E-mail: achianese@colgate.edu.

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Published on Web 06/16/2010

boat-shaped chelate rings, and metal complexes are chiral with varying barriers to enantiomerization.[6f,h] Even though class **A** has been known since 2001,[6a] pincer complexes bearing this structure have only been isolated for palladium[6a,f,15a] and the rare-earth metals scandium, lutetium, and samarium.[15b] Metalation to palladium has required heating to 125 °C or above[6a,f] or the installation of the central M−C_{aryl} bond via C−Br oxidative addition to palladium(0).[6f,15a] Under a wide variety of reaction conditions for metalation to rhodium and iridium, Braunstein and co-workers observed only the formation of nonpincer mono- and dinuclear complexes.[15c−e]

In class **B**, no CH_2 linker is present, so two five-membered chelate rings form and a rigid, flat backbone is expected. Hollis and co-workers initially reported the synthesis of class **B** ligand precursors (R = ^{n}Bu, Me, CH_2SiMe_3)[16] and later described their metalation (R = ^{n}Bu) to zirconium,[17] transmetalation from zirconium to rhodium[17,18] and iridium,[18] and catalytic applications in hydroamination[18,19] and hydrosilylation.[20] Braunstein and co-workers have more recently described the metalation of class **B** ligand precursors (R = ^{n}Bu, ^{i}Pr) to iridium directly from the imidazolium salt precursors, by refluxing with $[Ir(cod)Cl]_2$,[21] NEt_3, and KI in acetonitrile.[15c] The same group has recently reported a thorough examination of the metalation of the butyl-substituted precursor to iridium, including the characterization of intermediates and unproductive side reactions, and has prepared a modified ligand with methyl substituents on the central aryl group, designed to prevent cyclometalation at undesired positions on the backbone.[22] By employing stoichiometric Cs_2CO_3 as base instead of excess NEt_3, octahedral complexes of the formula Ir(CCC)HI(MeCN) were isolated in good yield. Complexes of this formula are closely related to five-coordinate Ir(PCP)HCl complexes that have previously been shown to form highly active alkane dehydrogenation catalysts upon HCl elimination promoted by NaO^{t}Bu[4i−k] and might be expected to exhibit similar reactivity, although Braunstein reported a lack of catalytic activity for the transfer dehydrogenation of cyclooctane with *tert*-butylethylene using this method.[22]

To this point, all of the imidazolium precursors to class **B** ligands reported in the literature have been synthesized by the N-alkylation of 1,3-bis(1-imidazolyl)benzene or 1,3-bis(1-imidazolyl)-4,6-dimethylbenzene.[16,22] By this approach, only primary or secondary alkyl side groups may be installed. We anticipated that bulky, aromatic side groups might offer steric protection of reactive iridium(I) intermediates, especially from forming bi- or multinuclear aggregates.[4o,23]

Herein, we report the synthesis of a series of rigid-backbone, monoanionic CCC-pincer ligands with bulky, aromatic side groups, along with their metalation to form complexes of the formula Ir(CCC)HCl(MeCN). Initial experiments indicate that these complexes are precursors to active catalysts for cyclooctane dehydrogenation, as well as arene C−H borylation.

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(21) Abbreviations: cod = 1,5-cyclooctadiene, DPEPHOS = bis-(2-diphenylphosphinophenyl)ether; dba = dibenzylideneacetone.

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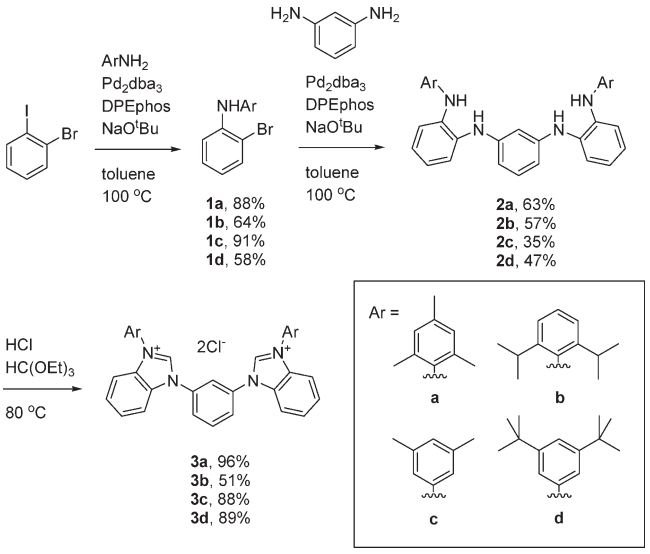
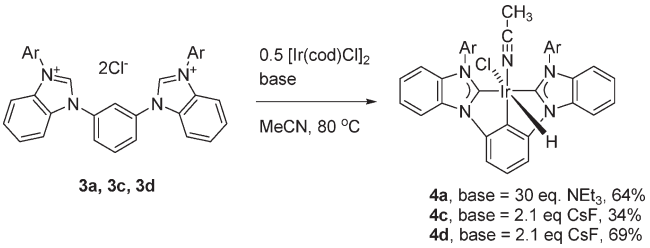
Scheme 1. Synthesis of Benzimidazolium Salts 3a−d[21]



Scheme 2. Synthesis of Iridium Complexes 4a, 4c, and 4d



Results and Discussion

Ligand Synthesis and Metalation. Benzimidazolium salts **3a−d** were synthesized as shown in Scheme 1. Selective Buchwald−Hartwig[24] monoamination of iodobromobenzene gave the ortho-bromoanilines **1a−d**. Palladium-catalyzed coupling with 1,3-diaminobenzene then gave the tetraamines **2a−d**, and cyclization[25] in triethylorthoformate with a slight excess of concentrated hydrochloric acid gave the dicationic ligand precursors **3a−d**.[26]

Initially, the mesityl-substituted precursor **3a** was combined with 0.5 equiv of $[Ir(cod)Cl]_2$ and 3 equiv of triethylamine in acetonitrile, and the mixture was stirred at 80 °C and monitored by ^{1}H NMR spectroscopy. The formation of several complexes was observed, including one with a singlet hydride resonance at −23.16 ppm. After some experimentation, we found that this hydride-containing complex was the major product after 24 h if a solution of 30 equiv of triethylamine was added slowly to a dilute, heated solution of **3a** and $[Ir(cod)Cl]_2$ over the course of an hour. Following this method, we were able to isolate the hydride complex after column chromatography on silica gel in 64% yield. By NMR spectroscopy and X-ray crystallography (vide infra), the complex was identified as **4a**, which contains the fully metalated pincer ligand, in addition to chloride, hydride, and acetonitrile ligands (Scheme 2). Complex **4a** is stable to air and moisture, as solutions in untreated CD_2Cl_2 remain unchanged for days.

Attempts to metalate the ligand precursors **3b−d** following this protocol were unsuccessful. Using ligand precursors **3c** and **3d**, the desired hydride complexes were formed as part of a mixture after a few hours, but continued heating led to decomposition to several unidentified products. After experimentation with a variety of bases and iridium sources, we were pleased to discover that cesium fluoride is an effective base for the metalation of **3c** and **3d**, provided that only a slight excess of base is employed. After heating a mixture of **3d**, $[Ir(cod)Cl]_2$, and CsF overnight in acetonitrile at 80 °C, the hydride complex **4d** was the only species observed in solution and was isolated in 69% yield following chromatography. Using benzimidazolium salt **3c**, complex **4c** forms as part of the mixture and slowly decomposes over the course of a day. By carefully monitoring the reaction and stopping after a few hours when **4c** comprised about half the ligand-containing species, complex **4c** was isolated in 34% yield following chromatography. Thus far, we have not been able to prepare analogous complexes of ligand precursor **3b**. Under the conditions in Scheme 2, using either NEt_3 or CsF as base, we observed consumption of the benzimidazolium precursor and formation of a complex mixture of products by ^{1}H NMR spectroscopy. Although a small amount of a product with a hydride signal analogous to that of **4a**, **4c**, and **4d** was observed, we were not able to isolate this species.

Solution and Solid-State Structural Characterization of 4a, 4c, and 4d. By ^{1}H and ^{13}C NMR spectroscopy, complexes **4a**, **4c**, and **4d** appear to have averaged C_s symmetry in solution, as indicated by the chemical equivalence of the two benzimidazol-2-ylidene fragments and the nonequivalence of the ortho- and meta-substituents on the mesityl (**4a**), 3,5-xylyl (**4c**), and 3,5-di-*tert*-butylphenyl (**4d**) side groups. Complete assignment of the ^{1}H NMR spectra was facilitated by phase-sensitive NOESY, which revealed a correlation between the iridium-bound hydride and an ortho-methyl group (**4a**) or an ortho-hydrogen (**4d**) on the aromatic N-substituent. Additionally, NOESY reveals a correlation between the acetonitrile CH_3 group and the para-methyl group (**4a**) or the para-hydrogen (**4c** and **4d**) on the aromatic N-substituent. Taken together, these data indicate that the solution geometry is as shown in Scheme 2, with the acetonitrile ligand trans to C_{aryl}, and the chloride and hydride ligands mutually trans. In the ^{1}H NMR spectra of **4a** and **4d**, no resonances are broadened at room temperature, indicating that potential rotation about the side-group N−C bonds is slow on the NMR time scale. By contrast, in the ^{1}H NMR spectrum of **4c**, the resonances for the ortho-hydrogens and meta-methyl groups of the 3,5-xylyl substituents are slightly broadened, indicating slow-but-observable rotation about the N−C bond. Exchange between the two ortho-hydrogens and meta-methyl groups was confirmed by NOESY/EXSY. The iridium-bound hydrides appeared at approximately −23.2 ppm, the carbene carbons appeared between 184.4 and 186.6 ppm, and the iridium-bound aryl carbons appeared between 143.9 and 145.2 ppm.

The structures of **4a**, **4c**, and **4d** were confirmed by X-ray crystallography. ORTEP diagrams are presented in Figures 2, 3, and 4, respectively. The solution geometries suggested by NMR spectroscopy are confirmed in the solid state: the

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(26) See Supporting Information for details of ligand synthesis and characterization.

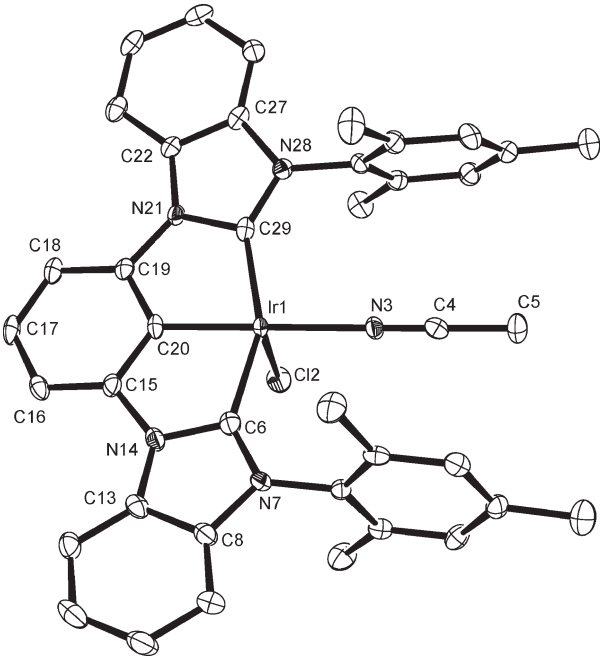


Figure 2. ORTEP diagram of **4a**, showing 50% probability ellipsoids. Hydrogen atoms are omitted for clarity.

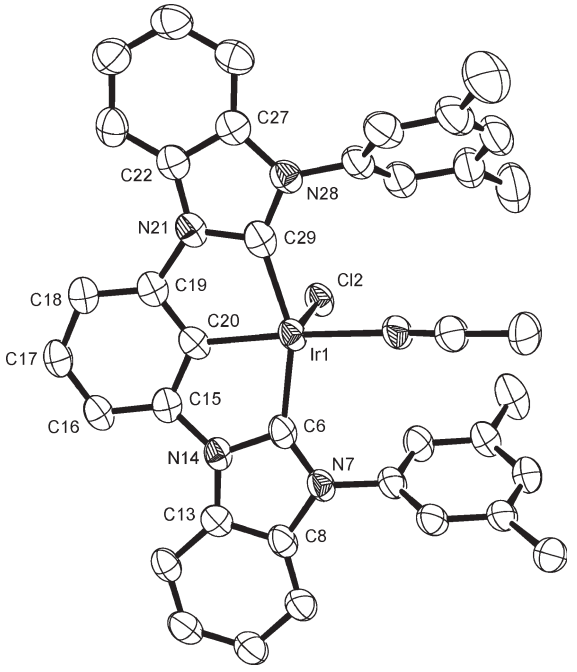


Figure 3. ORTEP diagram of **4c**, showing 50% probability ellipsoids. Hydrogen atoms are omitted for clarity. One of two independent molecules in the asymmetric unit is shown.

acetonitrile ligands are trans to the C_{aryl} donor atom, and the hydride and chloride ligands are mutually trans. Complexes **4a** and **4c** have approximate C_s symmetry, while **4d** lies on a crystallographic mirror plane. As would be expected, the ligand "backbone", consisting of the central aromatic ring and the two benzimidazole rings, is nearly flat in each complex, while the aromatic N-substituents are out-of-plane to varying extents.

Selected bond lengths and angles are given in Table 1. All three complexes possess a pseudo-octahedral geometry,

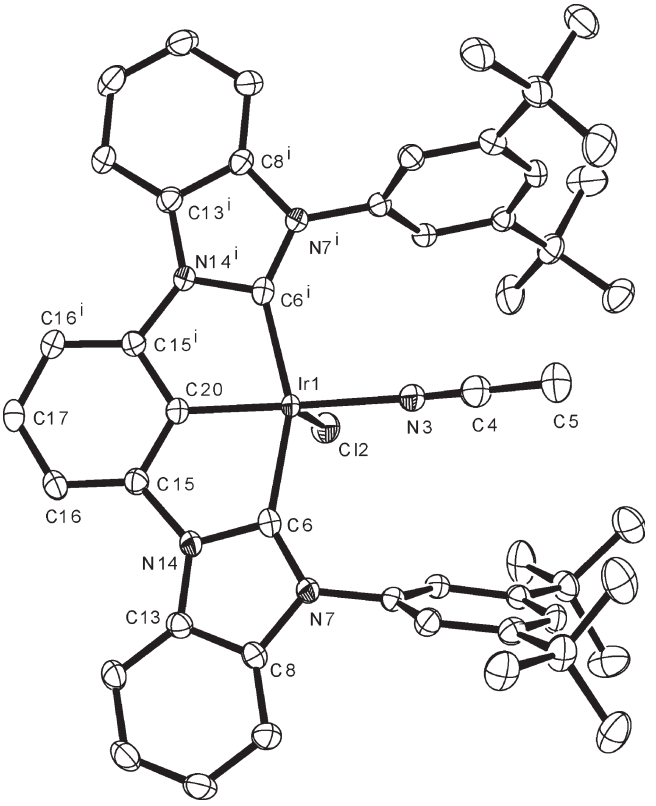


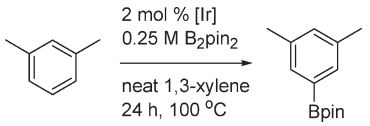
Figure 4. ORTEP diagram of **4d**, showing 50% probability ellipsoids. Hydrogen atoms are omitted for clarity. Atoms C(17), C(20), Ir(1), Cl(2), N(3), C(4), and C(5) lie on a crystallographic mirror plane.

Table 1. Selected Bond Lengths and Angles for 4a, 4c, and 4d

	4a	4c	4d
Bond Lengths (Å)			
Ir(1)—C(20)	1.958(3)	1.971(4)	1.944(5)
Ir(1)—C(6)	2.008(4)	2.019(4)	2.041(4)
Ir(1)—C(29)	2.014(4)	2.033(5)	
Ir(1)—Cl(2)	2.5036(10)	2.5066(10)	2.5129(13)
Ir(1)—N(3)	2.105(3)	2.123(3)	2.104(4)
C(6)—N(7)	1.362(5)	1.351(5)	1.350(5)
C(6)—N(14)	1.388(5)	1.383(5)	1.384(4)
C(29)—N(28)	1.363(5)	1.368(5)	
C(29)—N(21)	1.386(4)	1.377(5)	
Bond Angles (deg)			
C(6)—Ir(1)—C(20)	78.17(16)	78.37(16)	78.33(10)
C(29)—Ir(1)—C(20)	78.38(15)	77.94(16)	
C(6)—Ir(1)—N(3)	101.79(14)	99.80(14)	101.37(10)
C(29)—Ir(1)—N(3)	101.69(13)	103.56(15)	
Cl(2)—Ir(1)—C(6)	93.69(12)	93.65(11)	93.48(10)
Cl(2)—Ir(1)—C(20)	90.55(11)	98.56(11)	98.47(16)
Cl(2)—Ir(1)—C(29)	91.66(10)	90.77(11)	
Cl(2)—Ir(1)—N(3)	89.05(9)	89.04(10)	88.30(13)
N(7)—C(6)—N(14)	105.1(3)	105.3(3)	105.5(3)
N(28)—C(29)—N(21)	105.3(3)	105.6(4)	

distorted by the rigid chelate geometry of the CCC-pincer ligands. Metric parameters are in close agreement with a related structure recently reported by Braunstein and coworkers.[22] The iridium−$C_{carbene}$ distances, ranging from 2.008 to 2.041 Å, are well within the range of previously studied iridium complexes of benzimidazole-derived NHCs. The iridium−C_{aryl} distances, ranging from 1.944 to 1.971 Å,

Table 2. Comparison of Iridium Precatalysts for the Borylation of *m*-Xylene



precatalyst	additive	conversion[a] [%]
4a	none	41
4a	4% NaO^{t}Bu	57
4a	4% NaO^{t}Bu	42[b]
4c	4% NaO^{t}Bu	29
4d	4% NaO^{t}Bu	22

[a] Conversion determined by ^{1}H NMR spectroscopy of the crude reaction mixture. Conversions are based on boron atom in B_2pin_2. [b] Reaction run with 0.05 M B_2pin_2.

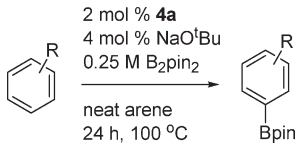
are among the shorter distances known for iridium bound to an aryl group: a Cambridge Structural Database[27] search returns 628 structures, with an average Ir−C distance of 2.021 ± 0.043 Å (median ± SD). Additionally, 57 crystal structures have been reported for iridium complexes of monoanionic P−C_{aryl}−P pincer complexes, using either methylene-bridged bis(phosphine) or oxygen-bridged bis(phosphinite) ligands. For this set, the Ir−C_{aryl} distances range from 1.986 to 2.124 Å, with a median distance of 2.048 ± 0.033 Å. The uncommonly short Ir−C_{aryl} distances for CCC-pincer complexes apparently result from the constrained nature of the chelate rings.

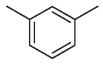
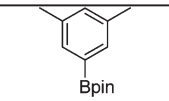
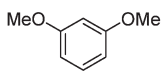
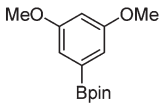
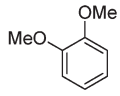
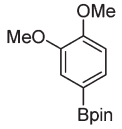
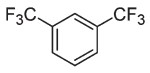
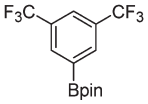
Catalytic Borylation of Arenes. The iridium-catalyzed borylation of arene C−H bonds has been developed into one of the most practically useful methods for C−H functionalization.[1f] Selectivity for more sterically accessible aromatic hydrogens is predictable and complementary to classical methods for the formation of arylboron compounds, which derive from directing effects in electrophilic aromatic halogenation. Iridium complexes of mono- and bidentate NHCs have previously been shown to effect the borylation of arenes with bis-pinacolatodiboron (B_2pin_2) and pinacolborane (HBpin), under either thermal[28] or microwave[29] conditions.

We have found that complexes **4a**, **4c**, and **4d** catalyze the borylation of *m*-xylene when a limiting amount of B_2pin_2 is employed in neat arene solvent (Table 2). The addition of a catalytic amount sodium *tert*-butoxide gave a moderately higher yield of borylated product, although the origin of this effect is currently uncertain. Employing more dilute conditions (0.05 M vs 0.25 M) showed no benefit.

As **4a**/NaO^{t}Bu was the most efficient catalyst system, its activity for the borylation of a small group of substrates was examined (Table 3). For *m*-xylene, 1,3-dimethoxybenzene, and 1,2-dimethoxybenzene, approximately 50% yield of borylated product was formed, consistent with complete transfer of one boron atom per molecule of B_2pin_2, which is likely due to the sluggish reaction of the intermediate HBpin under our conditions. The electron-deficient substrate 1,3-bis(trifluoromethyl)-benzene was transformed more efficiently, giving 94% yield by

Table 3. Borylation of a Range of Arenes with Mesityl-Substituted 4a



Reactant	Product	Conversion (Yield)[a] [%]
		57 (44)
		51 (32)[b]
		53 (50)
		94 (74)[c]

[a] Conversion determined by ^{1}H NMR spectroscopy of the crude reaction mixture. Isolated yield in parentheses. Yields are based on boron atom in B_2pin_2. [b] Approximately 6% yield of the isomeric product of borylation at the 4-position was observed in the crude ^{1}H NMR spectrum. [c] Sodium *tert*-butoxide was not added.

NMR even without the addition of NaO^{t}Bu. In most cases, we observed products from borylation at the least sterically hindered arene C−H bond, but approximately 6% yield of the product of borylation at the more-hindered 4-position, ortho to one methoxy group, was observed in the borylation of 1,3-dimethoxybenzene. Initial attempts at borylation using limiting quantities of arene in solvents such as tetrahydrofuran, dioxane, and cyclohexane[30] were unsuccessful.

Catalytic Dehydrogenation of Cyclooctane. The catalytic dehydrogenation of alkanes has the potential to enable the production of value-added alkenes, especially 1-alkenes, from relatively abundant saturated petroleum feedstocks. Although a variety of homogeneous transition-metal systems have been studied,[31] the highest catalytic activities have been achieved with iridium catalysts bound to monoanionic,

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(29) Rentzsch, C. F.; Tosh, E.; Herrmann, W. A.; Kuhn, F. E. *Green Chem.* **2009**, *11*, 1610–1617.

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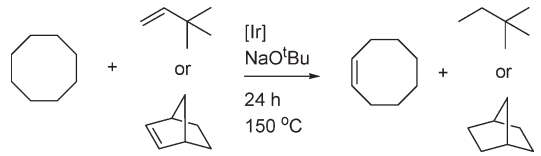
(31) (a) Crabtree, R. H.; Mihelcic, J. M.; Quirk, J. M. *J. Am. Chem. Soc.* **1979**, *101*, 7738–7740. (b) Baudry, D.; Ephritikhine, M.; Felkin, H.; Holmes-Smith, R. *J. Chem. Soc., Chem. Commun.* **1983**, 788–789. (c) Burk, M. J.; Crabtree, R. H.; Parnell, C. P.; Uriarte, R. J. *Organometallics* **1984**, *3*, 816–817. (d) Felkin, H.; Fillebeen-Khan, T.; Holmes-Smith, R.; Yingrui, L. *Tetrahedron Lett.* **1985**, *26*, 1999–2000. (e) Burk, M. J.; Crabtree, R. H. *J. Am. Chem. Soc.* **1987**, *109*, 8025–8032. (f) Maguire, J. A.; Boese, W. T.; Goldman, A. S. *J. Am. Chem. Soc.* **1989**, *111*, 7088–7093. (g) Maguire, J. A.; Goldman, A. S. *J. Am. Chem. Soc.* **1991**, *113*, 6706–6708. (h) Maguire, J. A.; Petrillo, A.; Goldman, A. S. *J. Am. Chem. Soc.* **1992**, *114*, 9492–9498. (i) Belli, J.; Jensen, C. M. *Organometallics* **1996**, *15*, 1532–1534. (j) Wang, K.; Goldman, M. E.; Emge, T. J.; Goldman, A. S. *J. Organomet. Chem.* **1996**, *518*, 55–68.

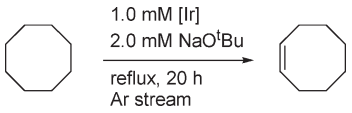
Table 4. Transfer Dehydrogenation of Cyclooctane[a]



[Ir]	acceptor[b]	TON of cyclooctene
4a	NBE	10[c]
4c	NBE	0
4d	NBE	0[d]
4a	TBE	1[c]
4d	TBE	2[d]

[a] Reactions performed with 4 μmol of [Ir], 8 μmol of NaO^{t}Bu, and 200 μmol of acceptor in 1 mL of cyclooctane. [b] Abbreviations: NBE = norbornene; TBE = *tert*-butylethylene. [c] Average of four experiments. [d] Average of two experiments.

Table 5. Acceptorless Dehydrogenation of Cyclooctane



[Ir]	TON[a]
4a	68
4c	0
4d	26

[a] Average of 2 runs, 4 mL reaction volume.

PCP-pincer bis(phosphine)[4a−h,l,m,o] or bis(phosphinite)[4i−k,n] ligands. A useful test substrate is cyclooctane, whose positive standard enthalpy of dehydrogenation is unusually low, at 24 kcal·mol^{-1}.[32] We have examined the potential activity of **4a**, **4c**, and **4d** for the dehydrogenation of cyclooctane, both with and without an added hydrogen acceptor. Results for transfer dehydrogenation are shown in Table 4, and results for acceptorless dehydrogenation are shown in Table 5.

For the transfer dehydrogenation of cyclooctane using norbornene (NBE) as hydrogen acceptor, we found that **4a** was a weakly effective precatalyst when initiated with NaO^{t}Bu, giving 10 turnovers in a 24 h period. Complexes **4c** and **4d** gave no cyclooctene under these conditions. The common hydrogen acceptor *tert*-butylethylene (TBE), which has given turnover numbers in the thousands for several Ir-PCP systems,[4j,m,n] was completely ineffective under our conditions, which is consistent with Braunstein's recent report.[22]

For acceptorless dehydrogenation of cyclooctane under reflux conditions (bp = 151 °C), where H_2 was continually removed from the system by passing argon over the reflux condenser, we observed encouraging reactivity for complexes **4a** and **4d**, activated in situ by the addition of catalytic NaO^{t}Bu (Table 5). For **4a**, 68 turnovers were observed, while 26 turnovers were observed for **4d**. For comparison, Ir-PCP systems have given up to 190 turnovers for this transformation[4c,e] and up to 3050 turnovers for the acceptorless dehydrogenation of cyclodecane (bp = 201 °C).[4c,e,l,o] Complex **4c** was completely inactive under these conditions, which may result from reduced stability of iridium(I) intermediates under the catalytic conditions when less bulky side groups are employed.

(32) Afeefy, H. Y.; Liebman, J. F.; Stein, S. E. Neutral Thermochemical Data. In *NIST Chemistry WebBook, NIST Standard Reference Database Number 69*; Linstrom, P. J.; Mallard, W. G., Eds.; National Institute of Standards and Technology: Gaithersburg, MD, http://webbook.nist.gov (retrieved April 9, 2010).

Conclusions

In summary, we have presented the synthesis of a series of rigid-backbone, CCC-pincer bis(carbene) ligands with aromatic side groups of varying steric bulk. Pincer-iridium complexes were formed under mild conditions and were shown to be active catalysts for the C−H borylation of arenes with B_2pin_2, as well as the dehydrogenation of cyclooctane. Further studies, including catalyst optimization, dehydrogenation of less "active" alkanes, and attempts to isolate and characterize catalyst resting states, are in progress.

Experimental Section

General Methods. $[Ir(cod)Cl]_2$ was prepared as previously described.[33] All other materials were commercially available and were used as received, unless otherwise noted. Solvents were generally purified by sparging with argon and passing through columns of activated alumina, using an MBraun solvent purification system. Acetonitrile (AcroSeal Extra Dry) was handled under argon and used as received. Flash chromatography using solvent gradients was performed using a Combiflash RF system. NMR spectra were recorded at room temperature on a Bruker spectrometer operating at 400 MHz (^{1}H NMR) and 100 MHz (^{13}C NMR) and referenced to the residual solvent resonance (δ in parts per million, and J in Hz). Elemental analyses were performed by Robertson Microlit, Madison, NJ. Detailed NMR assignments for complexes **4a**, **4c**, and **4d**, along with detailed procedures for ligand synthesis and characterization, are given in the Supporting Information.

Iridium Complex 4a. Benzimidazolium salt **3a** (0.791 mmol, 490 mg) and $[Ir(cod)Cl]_2$ (0.395 mmol, 263 mg) were added to a flame-dried Schlenk flask. Acetonitrile (120 mL) was added, and the reaction mixture was heated to 75 °C. A solution of triethylamine (23.7 mmol, 3.3 mL) in acetonitrile (125 mL) was added dropwise over an hour. The reaction was stirred at 75 °C for 10 h. The solvent was evaporated, and the residue was purified by flash chromatography, using a gradient of 0 to 30% ethyl acetate in dichloromethane. Yield: 414 mg, 64%. ^{1}H NMR (CD_2Cl_2): δ 8.20 (d, 2H, $^3J_{HH}$ = 8.1 Hz); 7.71 (d, 2H, $^3J_{HH}$ = 7.9 Hz); 7.47 (t, 2H, $^3J_{HH}$ = 8.1 Hz); 7.35 (t, 1H, $^3J_{HH}$ = 7.9 Hz); 7.31 (t, 2H, $^3J_{HH}$ = 8.1 Hz); 7.08 (s, 2H); 7.04 (s, 2H); 6.98 (d, 2H, $^3J_{HH}$ = 8.1 Hz); 2.38 (s, 6H); 2.25 (s, 6H); 1.99 (s, 6H); 1.47 (s, 3H); −23.16 (s, 1H). ^{13}C NMR (CD_2Cl_2): δ 186.6 (Ir−$C_{carbene}$), 147.0, 145.2 (Ir−C_{aryl}), 139.0, 138.8, 137.6, 136.0, 133.6, 132.9, 129.4, 128.8, 123.7, 123.0, 121.5, 116.0, 111.4, 110.8, 108.3, 21.3, 18.4, 18.1, 2.9. Anal. Calcd for $C_{40}H_{37}ClIrN_5$: C, 58.92; H, 4.57; N, 8.59. Found: C, 58.68; H, 4.31; N, 8.35.

Iridium Complex 4c. Benzimidazolium salt **3c** (0.169 mmol, 100 mg), $[Ir(cod)Cl]_2$ (0.085 mmol, 57 mg), and CsF (0.371 mmol, 56 mg) were added to a flame-dried Schlenk flask. Acetonitrile (100 mL) was added, and the reaction mixture was stirred at 80 °C for four hours. The solvent was evaporated, and the residue was purified by flash chromatography, using a gradient of 0 to 30% ethyl acetate in 99:1 dichloromethane/acetonitrile. Yield: 45 mg, 34%. ^{1}H NMR (CD_2Cl_2): δ 8.20 (d, 2H, $^3J_{HH}$ = 8.1 Hz); 7.99 (br s, 2H); 7.73 (d, 2H, $^3J_{HH}$ = 7.9 Hz); 7.48 (m, 2H); 7.13−7.37 (m, 5H); 7.28 (br s, 2H); 7.16 (s, 2H); 2.50 (s, 6H); 2.45 (s, 6H); 1.49 (s, 3H); −23.26 (s, 1H). ^{13}C NMR: δ 184.4 (Ir−$C_{carbene}$), 146.5, 143.9 (Ir−C_{aryl}), 139.2, 138.4, 137.6, 136.7, 132.3, 130.1, 128.3, 124.7, 123.5, 122.5, 121.0, 116.6, 111.2, 110.8, 108.1, 21.1, 21.0, 2.3. Anal. Calcd for $C_{38}H_{33}ClIrN_5$: C, 57.97; H, 4.22; N, 8.89. Found: C, 57.84; H, 4.46; N, 8.68.

(33) Lin, Y.; Nomiya, K.; Finke, R. G. *Inorg. Chem.* **1993**, *32*, 6040–6045.

Table 6. Crystal Data and Structure Refinement for 4a, 4c, and 4d

	4a	4c	4d
color, shape	yellow, rod	yellow, block	yellow, block
empirical formula	$C_{42}H_{40}N_5Cl_5Ir$	$C_{38}H_{33}N_5Cl_1Ir$	$C_{51}H_{58}N_5Cl_3Ir$
fw	984.30	786.38	1039.63
radiation	Mo Kα, 0.71073	Cu Kα, 1.5418	Mo Kα, 0.71073
temperature (K)	110	110	110
cryst syst	monoclinic	triclinic	orthorhombic
space group	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	*Pnma* (No. 62)
unit cell dimens			
a (Å)	12.8180(3)	14.1102(4)	18.6843(2)
b (Å)	7.93105(16)	14.3525(5)	26.8186(3)
c (Å)	39.8998(11)	21.3146(7)	9.11513(12)
α (deg)	90.0	77.637(3)	90.0
β (deg)	94.406(2)	78.668(2)	90.0
γ (deg)	90.0	76.019(3)	90.0
V (Å^3)	4044.23(17)	4043.6(2)	4567.46(17)
Z	4	4	4
D_{calc} (g cm^{-3})	1.616	1.292	1.512
μ(Mo Kα) (mm^{-1})	3.663	7.269	3.139
cryst size (mm)	0.14 × 0.11 × 0.02	0.16 × 0.08 × 0.04	0.19 × 0.13 × 0.13
θ range for data coll. (deg)	3.34 < θ < 29.23	4.08 < θ < 67.31	3.73 < θ < 29.44
total, unique no. of refl.	32 928, 9671	72 312, 14336	26 510, 5735
R_{int}	0.0434	0.0379	0.0299
no. of params, restraints	478, 0	957, 276	311, 48
R, wR_2 for all data	0.0625, 0.0642	0.0386, 0.0798	0.0435, 0.0878
R, wR_2 for $I > 2\sigma$	0.0378, 0.0616	0.0273, 0.0776	0.0328, 0.0855
GOF	1.033	0.9488	0.9618
resid density (e Å^{-3})	−4.56, 2.51	−0.58, 1.15	−1.85, 3.66

Iridium Complex 4d. Benzimidazolium salt **3d** (0.217 mmol, 167 mg), $[Ir(cod)Cl]_2$ (0.109 mmol, 73 mg), and CsF (0.456 mmol, 69 mg) were added to a flame-dried Schlenk flask. Acetonitrile (100 mL) was added, and the reaction mixture was stirred at 80 °C for 24 h. The solvent was evaporated, and the residue was purified by flash chromatography, using a gradient of 0 to 70% ethyl acetate in 98:2 dichloromethane/acetonitrile. Yield: 142 mg, 69%. ^{1}H NMR (CD_2Cl_2): δ 8.20 (d, 2H, $^3J_{HH}$ = 8.1 Hz); 8.04 (t, 2H, $^4J_{HH}$ = 1.6 Hz); 7.74 (d, 2H, $^3J_{HH}$ = 8.0 Hz); 7.58 (t, 2H, $^4J_{HH}$ = 1.6 Hz); 7.48 (t, 2H, $^3J_{HH}$ = 8.1 Hz); 7.45 (t, 2H, $^4J_{HH}$ = 1.6 Hz); 7.36 (t, 1H, $^3J_{HH}$ = 8.0 Hz); 7.32 (t, 2H, $^3J_{HH}$ = 8.1 Hz); 7.19 (d, 2H, $^3J_{HH}$ = 8.1 Hz); 1.44 (s, 18H); 1.40 (s, 18H); 1.28 (s, 3H); −23.23 (s, 1H). ^{13}C NMR: δ 185.1 (Ir−$C_{carbene}$), 153.1, 151.8, 146.9, 144.4 (Ir−C_{aryl}), 137.8, 137.8, 132.6, 126.0, 123.8, 122.9, 122.8, 121.2, 121.2, 116.1, 111.5, 111.1, 108.4, 35.5, 35.3, 31.9, 31.7, 2.9. Anal. Calcd for $C_{50}H_{57}ClIrN_5$: C, 62.84; H, 6.01; N, 7.33. Found: C, 62.10; H, 5.86; N, 6.79. Though a satisfactory analysis was not obtained after multiple attempts, **4d** appeared to be pure by ^{1}H and ^{13}C NMR spectroscopy (see images in the Supporting Information). We cannot rule out the possibilty of inorganic impurities, though this seems unlikely given the chromatographic purification procedure employed.

X-ray Crystallography, General Methods. Structure determinations were performed on an Oxford Diffraction Gemini-R diffractometer, using Mo Kα radiation. Single crystals were mounted on Hampton Research Cryoloops using Paratone-N oil. Unit cell determination, data collection and reduction, and analytical absorption correction were performed using the CrysAlisPro software package.[34] Direct methods structure solution was accomplished using SIR92,[35] and full-matrix least-squares refinement was carried out using CRYSTALS.[36] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions. Hydrogen positions were initially refined using distance and angle restraints and were fixed in place for the final refinement cycles. Disordered fragments were modeled using a refined group occupancy parameter; their relative geometries were restrained using the SAME command, and relative displacement parameters were restrained using the SIMU command. Details of data collection and refinement are given in Table 6.

X-ray Structure Determination of 4a. Diffraction-quality crystals were obtained by slow evaporation of a solution in dichloromethane and hexanes. Two molecules of dichloromethane were present in the asymmetric unit. The iridium-bound hydride was not located in the difference map.

X-ray Structure Determination of 4c. Diffraction-quality crystals were obtained by slow evaporation of a solution in dichloromethane and hexanes. Two independent molecules of **4c** were present in the asymmetric unit. The molecule shown in Figure 3 shows no disorder, while both the 3,5-xylyl groups of the second molecule were disordered over two positions. Highly disordered solvent was also present; correction for this residual density was performed using the option SQUEEZE in the program package PLATON.[37] A total of 196 electrons per unit cell were removed, from a total potential solvent-accessible void of 964.2 Å^3. The iridium-bound hydride was not located in the difference map.

X-ray Structure Determination of 4d. Diffraction-quality crystals were obtained by slow evaporation of a solution in dichloromethane and hexanes. Complex **4d** and one molecule of dichloromethane lie on a crystallographic mirror plane. One *tert*-butyl group in the asymmetric unit was disordered over two positions; only the major component is shown in Figure 4. The iridium-bound hydride was not located in the difference map.

Arene C−H Borylation Experiments (Tables 2,3). In an argon-filled glovebox, a vial was charged with an iridium complex (5 μmol), sodium *tert*-butoxide (0.96 mg, 10 μmol), and bis-(pinacolato)diboron (64 mg, 0.25 mmol). The appropriate arene (1 mL) was added, the vial was capped, and the mixture was stirred at 100 °C for 24 h. A small aliquot was removed for analysis by ^{1}H NMR. For experiments where the product was isolated, the reaction mixture was transferred directly to a silica gel column, and products were purified by gradient flash chromatography, generally using solutions of ethyl acetate in

(34) *Xcalibur CCD* system and *CrysAlisPro* software system, version 1.171.32; Oxford Diffraction Ltd., 2007.

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hexanes. For the volatile product of borylation of 1,3-bis-(trifluoromethyl)benzene, a solution of pentane and ether was employed as eluent. All products were pure by ^{1}H NMR and were identified by comparison with previously reported data.[38]

Cyclooctane Transfer-Dehydrogenation Experiments. In an argon-filled glovebox, a 4 mL medium-pressure screw-cap tube was charged with a stir-bar, an iridium complex (4 μmol), sodium *tert*-butoxide (0.77 mg, 8 μmol), 1.0 mL of cyclooctane, and 0.200 mmol of either norbornene or *tert*-butylethylene. The tube was capped, removed from the glovebox, and heated to 150 °C in an oil bath for 24 h. The mixture was cooled to room temperature, and a 25 μL aliquot was transferred to 975 μL of a standard solution of 1,3,5-trimethoxybenzene in $CDCl_3$. Cyclooctene and unconsumed hydrogen acceptor were quantified by integrating the ^{1}H NMR signals against the standard.

Acceptorless Cyclooctane Dehydrogenation Experiments. An oven-dried 25 mL round-bottom flask was charged with a stir-bar, an iridium complex (4 μmol), sodium *tert*-butoxide (0.77 mg, 8 μmol), and 4.0 mL of cyclooctane. A condenser was attached, and the solution was vigorously refluxed under argon in an oil bath heated to 175 °C, while the atmosphere above the condenser was purged with a steady stream of argon. After 20 h, the mixture was cooled, and a 100 μL aliquot was transferred to 700 μL of a standard solution of 1,3,5-trimethoxybenzene in $CDCl_3$. Cyclooctene was quantified by integrating the ^{1}H NMR signals against the standard.

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Acknowledgment. We are grateful to the ACS Petroleum Research Fund (46754-GB3) and the National Science Foundation Major Research Instrumentation program (CHE-0819686) for generous support of this work.

Supporting Information Available: Details of the synthesis and characterization of new compounds, including images of ^{1}H and ^{13}C NMR spectra. CIF files giving X-ray diffraction data, atomic coordinates, thermal parameters, and complete bond distances and angles. This material is available free of charge via the Internet at http://pubs/acs/org.