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Iridium Complexes of Bulky CCC-Pincer N-Heterocyclic Carbene Ligands: Steric Control of Coordination Number and Catalytic Alkene Isomerization

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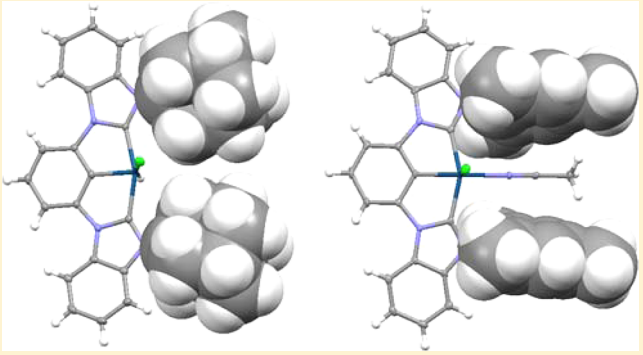
Supporting Information

ABSTRACT: Three new iridium complexes of *meta*-phenylene-bridged bis-N-heterocyclic carbene CCC-pincer ligands were synthesized and characterized. For a pincer ligand with 2,6-diisopropylphenyl N-substituents, a six-coordinate iridium(III) complex of the formula Ir(CCC)HCl(MeCN) was formed. In contrast, ligands with *t*-butyl or adamantyl N-substituents gave five-coordinate iridium(III) complexes of the formula Ir(CCC)HCl. These iridium complexes, along with two previously described iridium complexes, were tested for activity in the catalytic transfer-dehydrogenation of *n*-octane at 150 °C. The new complexes were inactive for this reaction, while two previously reported catalysts were modestly active: a mesityl-substituted derivative gave 12 turnovers, and a 3,5-di-*t*-butylphenyl-substituted variant gave 10 turnovers. In contrast, these complexes were shown to be highly active catalysts for the isomerization of terminal alkenes, under conditions much milder than those required for transfer-dehydrogenation.



INTRODUCTION

The selective activation and functionalization of C−H bonds is one of the broadest and most important challenges facing organometallic chemistry.[1] One of the simplest C−H bond transformations is the metal-catalyzed dehydrogenation of a saturated hydrocarbon or alkyl group to give a new C═C double bond.[2] Although this reaction has been known for more than 30 years,[3] only one highly active homogeneous catalyst motif has been discovered, based on the coordination of a monoanionic PCP-pincer[4] ligand to iridium, as originally demonstrated by Kaska and Jensen.[5] Steric and electronic modifications of the PCP-pincer ligand, including changing the phosphorus substituents,[6] employing an anthracenyl backbone,[7] introducing electron-withdrawing or -donating backbone substituents,[8] replacing the CH_2 linkers with oxygen atoms,[8a,c,9] replacing the aryl backbone with a ferrocenyl or ruthenocenyl unit,[10] or installing electron-withdrawing trifluoromethyl substituents on phosphorus,[11] have resulted in the discovery of iridium catalysts giving turnover numbers in the thousands for dehydrogenation involving net hydrogen transfer to a sacrificial acceptor alkene,[6b,8a,9,10] or for acceptorless dehydrogenation with direct removal of H_2.[6,8b] Notably, PCP−ruthenium complexes containing trifluoromethyl substituents on phosphorus were recently reported to be active catalysts for alkane dehydrogenation, giving turnover numbers approaching 200.[12]

Despite the success in designing highly active PCP−Ir catalysts for alkane dehydrogenation, achieving useful selectivity still remains a challenge. A long-standing goal has been the synthesis of terminal alkenes by selective dehydrogenation of linear alkanes. Although catalysts with high *initial* selectivity for 1-alkenes have been reported, competing isomerization of the initially produced terminal alkene into a mixture of internal isomers has been observed in each case.[6,8b,c]

In this context, we and others have recently begun examining the iridium chemistry of monoanionic CCC-pincer ligands, where the phosphorus-donor fragments are replaced with N-heterocyclic carbenes (NHCs, Figure 1). Iridium complexes of CCC-pincer ligands are expected to retain the strong binding and donor power of the PCP ligands, while producing a steric environment around the metal center that is both distinct from the PCP ligands and highly modular. Hollis and co-workers reported the first synthesis of iridium complexes of CCC-pincer ligands, via transmetalation from zirconium.[13] Braunstein and co-workers reported the direct metalation of the same bis-imidazolium precursor to iridium: depending on the conditions, either a hydridoiodide complex or a diiodide complex could be synthesized in good yield.[14] Complexes of this nature were not found to be active catalysts for alkane dehydrogenation,[14] possibly because the limited steric bulk of the ligands allowed

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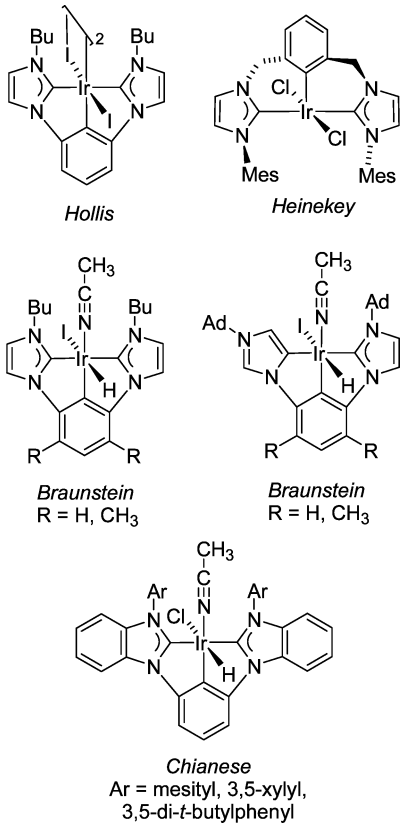


Figure 1. Previously reported iridium complexes of CCC-pincer ligands.

facile bimolecular decomposition of potential catalytic intermediates.[6b,15] Braunstein and co-workers have recently reported the synthesis of imidazolium precursors to CCC-pincer ligands incorporating bulkier adamantyl side groups;[16] metalation gave iridium complexes where one NHC fragment was bound abnormally.[17] This mixed normal/abnormal iridium–pincer complex was weakly active for alkane transfer-dehydrogenation, giving up to 3.6 turnovers. Heinekey and co-workers have described iridium complexes of more flexible CCC-pincer ligands, where the N-substituents are mesityl groups and the imidazole and central aryl rings are linked by methylene groups.[18] A tetrahydride derivative showed catalytic hydrogen exchange between H_2 and deuterated arene solvents, but no activation of alkanes was observed.

We recently reported the synthesis of a series of iridium complexes of CCC-pincer ligands.[19] Like the pincer ligand originally employed by Hollis[13] and Braunstein,[14] ours featured a direct linkage of the NHC fragment to the central aryl ring, giving the pincer ligand a rigid, flat backbone. Instead of imidazole rings, we have incorporated benzimidazole rings, where synthesis via successive aryl aminations[20] facilitates the installation of a wide variety of bulky N-substituents. Additionally, C(4) metalation of the imidazole ring to give abnormal NHC complexes[21] is blocked. Initially, we reported the syntheses of the complexes shown in Figure 1. One extremely bulky ligand, with 2,6-diisopropylphenyl N-substituents, failed to metalate under our original conditions. The iridium complexes were active catalysts for arene C–H borylation,[1f] and two derivatives were moderately active catalysts for alkane dehydrogenation.

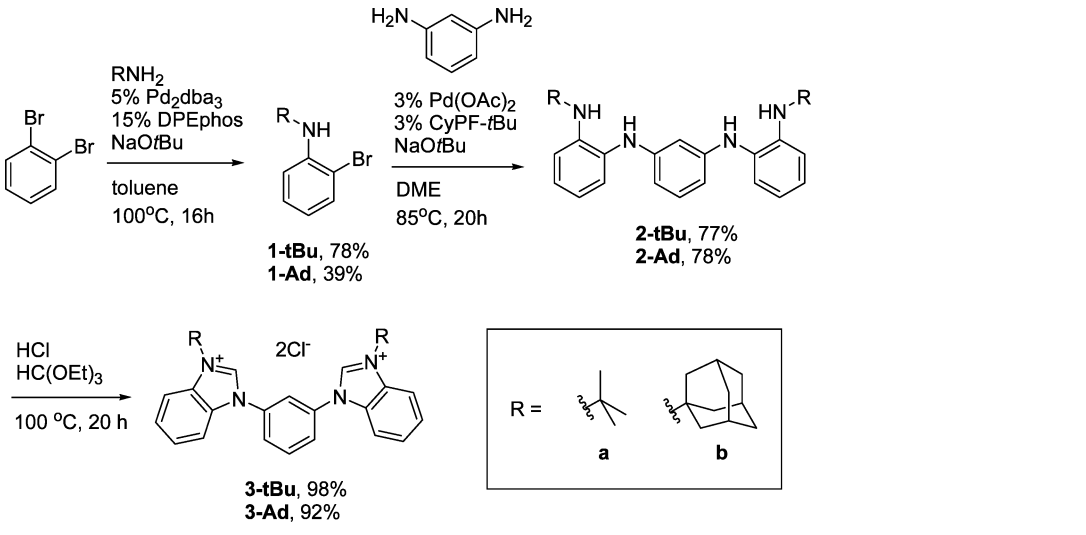
Here, we report the synthesis of new benzimidazolium precursors to CCC-pincer ligands, with the bulky aliphatic N-substituents, *t*-butyl and adamantyl. Metalation to iridium gives 5-coordinate hydridochloride complexes, common in PCP–iridium chemistry, but in striking contrast to the 6-coordinate acetonitrile-solvated complexes described in Braunstein's[14] and our[19] prior work. We also find that our previously reported 2,6-diisopropylphenyl pincer ligand metalates cleanly under more forcing conditions than previously employed.

We examined the iridium–pincer complexes for catalytic activity in the transfer-dehydrogenation of *n*-octane and found them to be only weakly active. In the course of testing a range of sacrificial hydrogen acceptors, we found that 1-hexene was isomerized rapidly to internal isomers. Upon further study, we demonstrated that these complexes are highly active catalysts for the isomerization of terminal alkenes to internal isomers, under significantly milder conditions than those typically required for alkane dehydrogenation.

RESULTS AND DISCUSSION

Synthesis of Ligands with Bulky Aliphatic Side Groups. We previously described a method to synthesize

Scheme 1. Synthesis of Bis-benzimidazolium Precursors to CCC-Pincer Ligands



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bis-benzimidazolium precursors to CCC-pincer ligands in three steps via successive Buchwald–Hartwig aminations on 1,2-bromoiodobenzene, followed by cyclization with triethyl orthoformate.[19] This method allows the installation of a range of aromatic N-substituents, including highly bulky mesityl and 2,6-diisopropylphenyl groups. Because bulky aliphatic substituents are expected to create a very different steric environment around the iridium center compared to aromatic substituents, we sought to synthesize CCC-pincer ligands with *t*-butyl and adamantyl side groups.

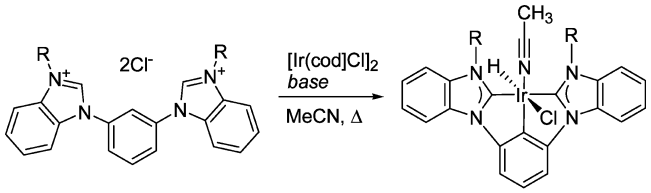
We successfully prepared bis-benzimidazolium chlorides **3-tBu** and **3-Ad** in good overall yields after several modifications of our original[19] synthetic procedure (Scheme 1). It was necessary to start with 1,2-dibromobenzene, as only trace amounts of **1-Ad** were formed in reactions between 1,2-bromoiodobenzene and 1-adamantylamine under similar conditions. For the second step, classical ligands for Buchwald–Hartwig cross-coupling, including DPEPHOS[22] and BINAP, were ineffective, but the recently developed CyPF-*t*Bu ligand[23] allowed the synthesis of tetraamines **2-tBu** and **2-Ad** in good yields with low catalyst loading. Cyclization with triethyl orthoformate required heating overnight with an excess of hydrochloric acid.

Synthesis of Iridium Complexes. Though NHCs are now widely employed as supporting ligands for transition-metal catalysis,[24] and numerous methods for the synthesis of metal–NHC complexes have been developed,[25] the metalation of multidentate NHCs remains challenging, especially when a chelating ligand contains more than one NHC unit. Often, the formation of multinuclear complexes competes with chelation; a primary reason for this difficulty appears to be the kinetic stability of the M–C_{NHC} bonds under mild conditions, which prevents the thermodynamic chelate effect from operating, except at very high temperatures.[26] For the C_{NHC}–C_{aryl}–C_{NHC} pincer ligands discussed here, metalation of the central aryl unit via C–H activation poses an additional challenge. Direct metalation of the imidazolium salts, using a weak base in combination with a low-valent metal precursor, has been successfully applied for the synthesis of group 9 complexes of a variety of chelating poly-NHC ligands,[26] including CCC-pincers. This method has proved useful for the metalation of our ligands as well, although the optimal conditions, especially the identity and amount of base, are highly dependent on the steric bulk of the ligand, so that the synthesis of each iridium complex often requires a moderate amount of experimentation to successfully complete.

We previously reported[19] the synthesis of iridium complex **4-Mes**, by treatment of the mesityl-substituted benzimidazolium salt **3-Mes** with $[Ir(cod)Cl]_2$ and an excess of triethylamine in acetonitrile at 80 °C (Scheme 2). The synthesis of complex **4-dtbp** proceeded optimally using a stoichiometric amount of cesium fluoride as base. When **3-dipp** was treated with excess triethylamine at 150 °C for 16 h in a sealed vessel, iridium complex **4-dipp** was the major product, isolated following chromatography in 36% yield. Complex **4-dipp** was characterized by NMR, elemental analysis, and X-ray crystallography. The crystal structure (Figure 2) confirms the geometry shown in Scheme 2. Analogous to **4-Mes** and **4-dtbp**, **4-dipp** is nearly octahedral, with an acetonitrile ligand trans to the aryl fragment of the CCC-pincer ligand.

When benzimidazolium salts **3-tBu** and **3-Ad** were subjected to similar reaction conditions, the only products isolated were the 5-coordinate hydridochloride complexes **4-tBu** and **4-Ad**

Scheme 2. Metalation of Aromatic-Substituted CCC-Pincer Ligands[a]



3-Mes, R = mesityl, *base* = NEt_3 — **4-Mes**, 64%[a]
3-dtbp, R = 3,5-di-*tert*-butylphenyl, *base* = CsF — **4-dtbp**, 69%[a]
3-dipp, R = 2,6-diisopropylphenyl, *base* = NEt_3 — **4-dipp**, 36%

[a]Previously reported in ref 19.

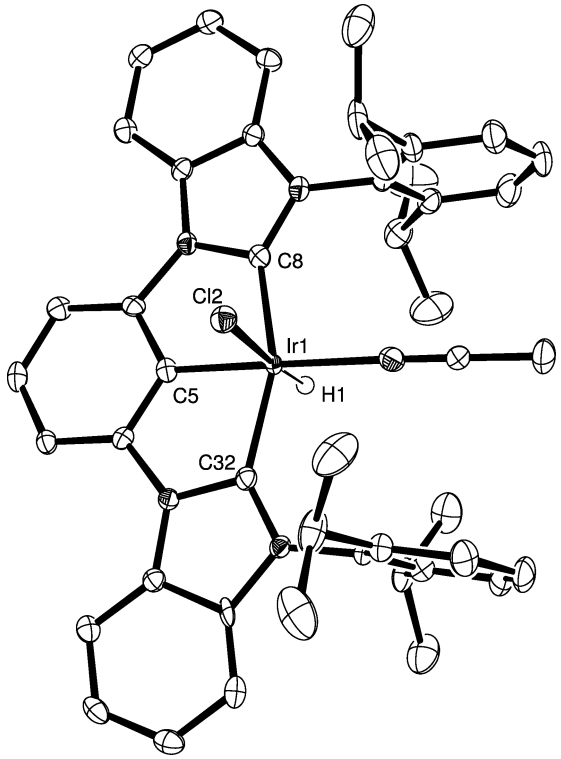
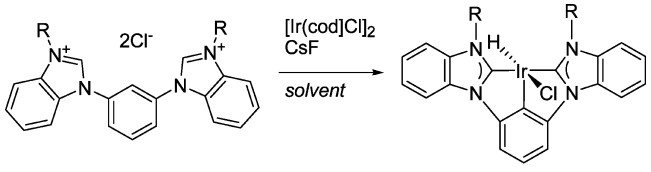


Figure 2. Crystal structure of **4-dipp**, showing 50% probability ellipsoids. Hydrogen atoms, except for the iridium-bound hydride, are omitted for clarity. Selected metric data (bond lengths in Å and angles in deg): Ir(1)–C(8), 2.007(3); Ir(1)–C(32), 2.015(3); Ir(1)–C(5), 1.951(3); Ir(1)–Cl(2), 2.4930(9); Ir(1)–H(1), 1.597; C(8)–Ir(1)–C(5), 78.87(14); C(32)–Ir(1)–C(5), 78.79(14); C(8)–Ir(1)–C(32), 157.60(13).

(Scheme 3). Better yields were obtained when using CsF as base than with triethylamine. The utility of CsF is worthy of note: although triethylamine is commonly employed for the

Scheme 3. Metalation of Aliphatic-Substituted CCC-Pincer Ligands



3-tBu, R = *t*-butyl, *solvent* = toluene — **4-tBu**, 42%
3-Ad, R = 1-adamantyl, *solvent* = acetonitrile — **4-Ad**, 59%

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metalation of chelating NHCs,[26] we are not aware of any examples of the use of CsF for NHC metalation, other than our previous study.[19] For the *t*-butyl-substituted complex **4-tBu**, metalation in toluene proved to be most effective, though acetonitrile was a more effective solvent for the synthesis of **4-Ad**. In contrast to **4-dipp** and previously described CCC-pincer–iridium complexes,[14,19] **4-tBu** and **4-Ad** lack a solvent-derived acetonitrile ligand in the coordination sphere, as verified by NMR spectroscopy and X-ray crystallography.

Both **4-tBu** and **4-Ad** were structurally characterized using X-ray crystallography. ORTEP diagrams are shown in Figures 3

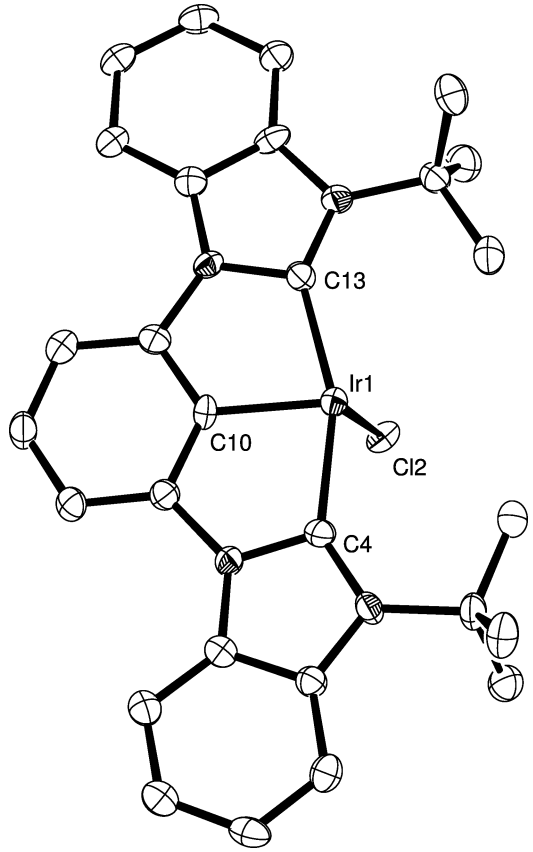

Figure 3. Crystal structure of **4-tBu**, showing 50% probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected metric data (bond lengths in Å and angles in deg): Ir(1)–C(13), 2.032(5); Ir(1)–C(4), 2.026(5); Ir(1)–C(10), 1.926(5); Ir(1)–Cl(2), 2.3961(15); C(13)–Ir(1)–C(10), 79.9(2); C(4)–Ir(1)–C(10), 80.1(2); C(4)–Ir(1)–C(13), 159.9(2).

and 4, respectively. In each complex, the chloride ligand is *cis* to the aryl fragment of the pincer ligand. The hydride ligand was located, and its position was freely refined for **4-Ad**, providing evidence for the square-pyramidal geometry shown in Scheme 3. The ^{1}H NMR chemical shifts (in ppm) for the hydride ligands are −22.2 for **4-tBu** and −22.0 for **4-Ad**, which correspond closely to the values of −23.2 for **4-Mes**, −23.2 for **4-dtbp**, and −22.7 for **4-dipp**. Additionally, the hydride is unlikely to lie preferentially trans to the aryl fragment, as the site is sterically crowded in both complexes, and the trans influence is expected to be greater for the aryl fragment than for the chloride ligand. Although the evidence is not unambiguous, we propose that the sites trans to the aryl fragments in **4-tBu** and **4-Ad** are vacant. The shortest distances from side-group hydrogen atoms to iridium are 2.73 Å for **4-tBu** and 2.71 Å for

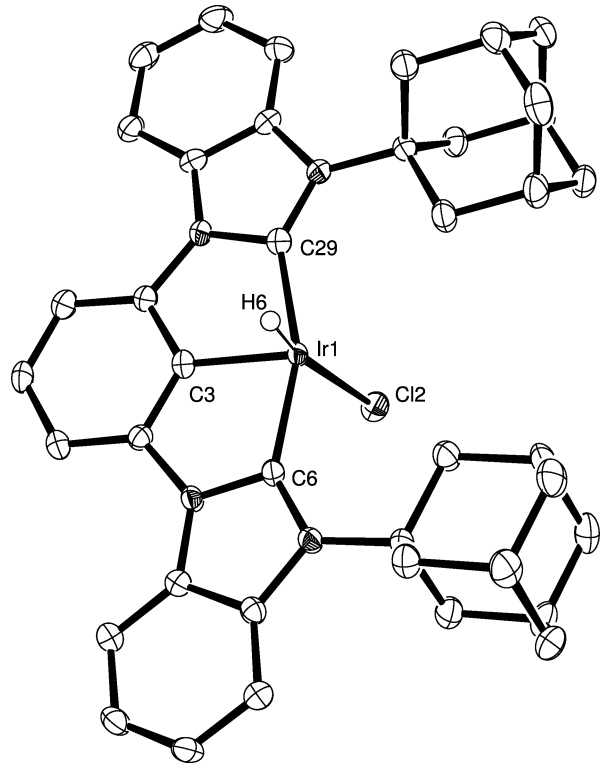

Figure 4. Crystal structure of **4-Ad**, showing 50% probability ellipsoids. Hydrogen atoms, except for the iridium-bound hydride, are omitted for clarity. Selected metric data (bond lengths in Å and angles in deg): Ir(1)–C(29), 2.029(3); Ir(1)–C(6), 2.024(3); Ir(1)–C(3), 1.915(3); Ir(1)–Cl(2), 2.4631(7); Ir(1)–H(6), 1.398; C(29)–Ir(1)–C(3), 80.07(12); C(6)–Ir(1)–C(3), 79.96(12); C(6)–Ir(1)–C(29), 159.98(11).

4-Ad, which is slightly less than the sum of the van der Waals radii of 3.1 Å.

Complexes **4** are closely related, differing only by the presence or absence of an acetonitrile ligand trans to the aryl fragment of the pincer ligand. As the electronic impact of substituting aliphatic N-substituents for aromatic ones on NHCs is known to be minimal,[27] this striking difference is likely steric in origin. Partial space-filling representations of complexes **4-Ad** and **4-Mes**,[19] shown in Figure 5, illustrate the difference in steric accessibility of the site trans to the aryl fragment. Because the rigid pincer backbone forces the N-substituent to point directly into the CCC plane, the fourth site in that plane is much more crowded in complexes with roughly spherical aliphatic groups than in complexes with flatter aromatic groups.

Transfer-Dehydrogenation. Although PCP–Ir catalysts have given high turnover numbers for the transfer-dehydrogenation of linear alkanes, selectivity for terminal alkenes has been limited by competing catalysis of alkene isomerization.[6,8b,c] We examined iridium complexes **4** for potential activity in the transfer-dehydrogenation of *n*-octane, in the presence of norbornene as a hydrogen acceptor. Sodium *tert*-butoxide, which promotes dehydrochlorination and reduction from iridium(III) to iridium(I), was necessary for catalysis. The results of this study are shown in Table 1.

The mesityl-substituted complex **4-Mes** and the di-*tert*-butylphenyl-substituted complex **4-dtbp** showed modest activity for the transfer-dehydrogenation of *n*-octane. In the analogous reaction with cyclooctane and norbornene, **4-Mes**

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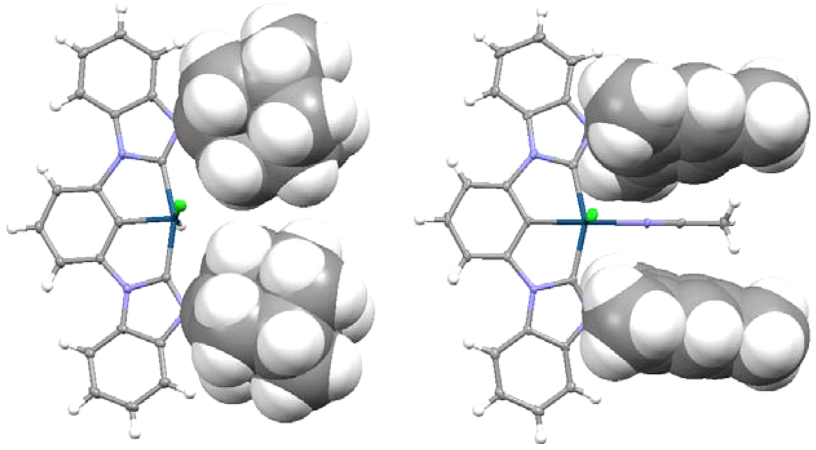
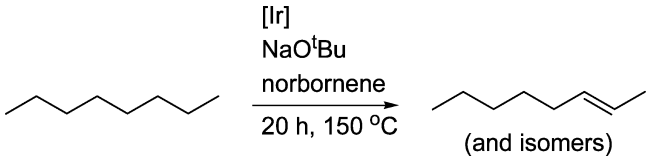


Figure 5. Crystal structures of **4-Ad** (left) and **4-Mes** (right), showing the N-substituents in a space-filling representation.

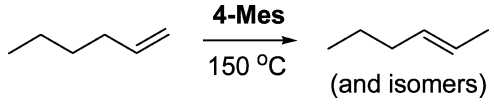
Table 1. Transfer-Dehydrogenation of *n*-Octane at 150 °C[a]



[Ir]	TON
4-tBu	0
4-Ad	0
4-Mes	12
4-dtbp	10
4-dipp	0

[a]Reactions performed in duplicate, with 200 mM norbornene, 1.0 mM [Ir], and 10 mM NaO^{t}Bu in 4 mL of *n*-octane. Only internal isomers of octene were observed.

Table 2. Isomerization of 1-Hexene by 4-Mes in *n*-Octane at 150 °C[a]



additive	time (min)	total TON	T/C/I[b]
2 mM NaO^{t}Bu	15	420	67:29:4
2 mM NaO^{t}Bu	60	730	65:26:8
none	60	280	58:38:4

[a]Reactions performed in duplicate, with 1.0 mM **4-Mes** and 1.0 M 1-hexene in 4 mL of *n*-octane. [b]T/C/I is the ratio of *trans*-2-hexene to *cis*-2-hexene to 3-hexenes.

was previously[19] shown to give 10 turnovers of cyclooctene, while **4-dtbp** was inactive. All of the newly reported iridium complexes (**4-tBu**, **4-Ad**, and **4-dipp**) show no activity for transfer-dehydrogenation of *n*-octane under the conditions reported. No catalysis was observed on replacing norbornene with *tert*-butylethylene, another commonly employed hydrogen acceptor.

None of our CCC−Ir complexes show activity for transfer-dehydrogenation that is comparable to previously studied PCP−Ir complexes, which give TONs in the thousands under ideal conditions.[6b,8a,9,10] However, the impact of steric bulk is noteworthy, especially as a seemingly subtle change from mesityl substituents (**4-Mes**) to 2,6-diisopropylphenyl substituents (**4-dipp**) eradicates any observable dehydrogenation of *n*-octane.

Because both of the commonly employed hydrogen acceptors, norbornene and *tert*-butylethylene, are significantly bulkier than *n*-octane, we considered the possibility that the steric bulk of the acceptor was inhibiting turnover. To examine this possibility, we attempted the transfer-dehydrogenation of *n*-octane using 1-hexene as hydrogen acceptor. Goldman and co-workers found that PCP−Ir complexes gave up to 111 turnovers of octene isomers for this substrate pair, along with some isomerization of the 1-hexene acceptor and the initial product, 1-octene.[6b] When using 1-hexene as the potential acceptor with complex **4-Mes**, we observed no transfer-dehydrogenation. Instead, 1-hexene was rapidly isomerized to internal isomers (Table 2). The conversion of 1-hexene to internal isomers is much more rapid than the hydrogen-transfer reactions shown in Table 1. Notably, the conversion of 1-hexene into a mixture of 2-hexene isomers is much faster than the following conversion to 3-hexene isomers, as only very small amounts of the 3-isomers were observed. It is also noteworthy that the isomerization proceeds with or without added sodium *tert*-butoxide, although the base causes a clear rate enhancement.

Isomerization of 1-Octene under Mild Conditions. The isomerization of alkenes is catalyzed by a wide variety of transition-metal catalysts, including Ti,[28] Fe,[29] Co,[30] Ni,[30a,31] Ru,[32] Rh,[29a,30a,33] Pd,[29a,30a] Ir,[34] and Pt.[30a] Recent noteworthy examples include Veige's NCN-pincer−chromium complexes for selective isomerization of 1-alkenes to 2-alkenes,[35] Strukul's platinum catalysts for the (*E*)-selective isomerization of allylbenzenes,[36] and Grotjahn's bifunctional ruthenium catalysts, capable of moving the alkene double bond selectively over one position[37] or over very many,[38] depending on the conditions. Very recently, Brookhart, Goldman, Krogh-Jespersen, and co-workers reported a detailed study of the mechanism of alkene isomerization catalyzed by PCP-pincer complexes of iridium, which are also highly active catalysts for alkane dehydrogenation.[39] They concluded that their catalysts facilitate alkene isomerization via π-allyl intermediates.

Transfer-dehydrogenation of alkanes has only been shown to occur at appreciable rates at temperatures of 150 °C or higher. In contrast, our CCC-pincer iridium complexes efficiently catalyze the isomerization of 1-octene into internal isomers at much lower temperatures. Although samples of precatalysts **4** purified by chromatography alone appeared to be pure by NMR spectroscopy, they were found to be much more active

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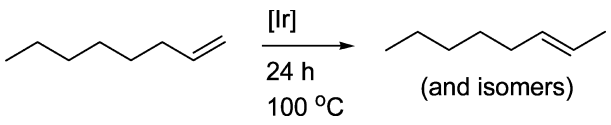
for alkene isomerization without added base than samples of the same precatalysts that were purified further by recrystallization. This indicates that a small quantity of an unidentified impurity, present after chromatographic purification, is a highly active isomerization catalyst. For all of the experiments described in Table 3, as well as Tables 1 and 2 above, the iridium precatalysts were recrystallized twice following chromatographic purification.

Table 3. Isomerization of 1-Octene in Toluene at 100 °C[a]



[Ir]	additive	TON (T/C/I)[b]
4-tBu	25 mM NaO^{t}Bu	487 (47:15:38)
4-tBu	none	15 (n.d.)
4-Ad	25 mM NaO^{t}Bu	488 (46:13:41)
4-Ad	none	16 (n.d.)
4-Mes	25 mM NaO^{t}Bu	484 (75:22:3)
4-Mes	none	24 (n.d.)

[a]Reactions performed with 2.5 mM [Ir] and 1.25 M 1-octene in 2.0 mL of toluene. [b]T/C/I is the ratio of *trans*-2-octene to *cis*-2-octene to the remaining internal isomers (3-octenes and 4-octenes). Not determined in experiments with no NaO^{t}Bu additive.

In the absence of added base, all three iridium complexes screened were minimally active for the isomerization of 1-octene at 100 °C. Because the activity decreases on repeated recrystallization, it is possible that even the activity observed after two recrystallizations is due to an unidentified residual impurity. The addition of 10 equiv of sodium *tert*-butoxide relative to the precatalyst resulted in substantial activity in all cases, which was not diminished on repeated recrystallization of the iridium precatalysts. In 24 h, the level of 1-octene was reduced to 2−3% of the reaction mixture. Precatalyst **4-Mes** primarily gave a mixture of *cis*- and *trans*-2-octene, while a substantial fraction of 3- and 4-octene isomers was produced by **4-tBu** and **4-Ad**. On the basis of available thermodynamic data,[40] we have estimated that a fully equilibrated mixture of linear octene isomers at 100 °C would contain 1% 1-octene, with a T/C/I ratio of 36:9:54, implying that reactions catalyzed by **4-tBu** and **4-Ad** have nearly reached equilibrium after 24 h.

Although all three catalysts gave nearly complete consumption of 1-octene after 24 h at 100 °C, the substantial production of 3- and 4-octene isomers by **4-tBu** and **4-Ad** implies that they are more active for alkene isomerization than **4-Mes**. To probe this distinction, the isomerization of 1-octene was monitored over time. In a reaction employing 0.2% **4-Mes** at 100 °C (Figure 6), the consumption of 1-octene required several hours. During the first 4 h of the reaction, the ratio of *trans*-2-octene to *cis*-2-octene remained nearly constant at about 4:1, while the buildup of 3- and 4-octene isomers was minimal even after 24 h. In a reaction employing 0.2% **4-Ad** at 60 °C (Figure 7), 1-octene was fully converted to a mixture of *cis*- and *trans*-2-octene in approximately 30 min, which further evolved to give an increasing fraction of 3- and 4-octene isomers over the 24 h course of the experiment. These experiments demonstrate that **4-Ad** is a substantially more active precatalyst for 1-octene isomerization than **4-Mes**.

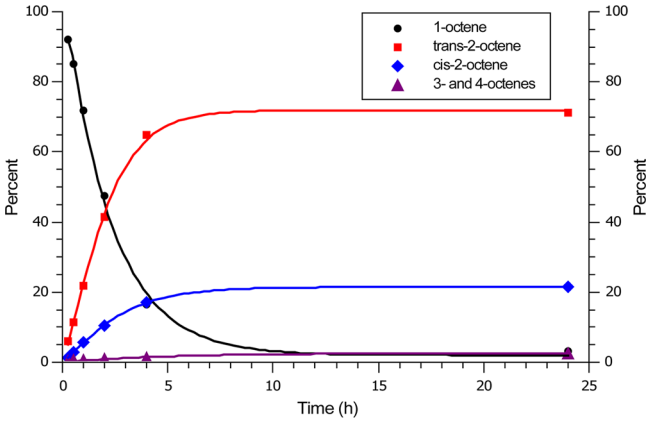


Figure 6. Isomerization of 1-octene catalyzed by **4-Mes** at 100 °C. The reaction was performed with 2.5 mM **4-Mes**, 25 mM NaO^{t}Bu, and 1.25 M 1-octene in 2.0 mL of toluene. Curves are plotted only as a guide to the eye.

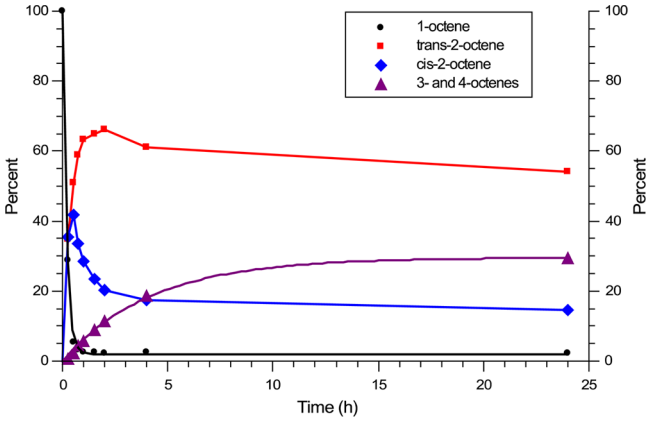


Figure 7. Isomerization of 1-octene catalyzed by **4-Ad** at 60 °C. The reaction was performed with 2.5 mM **4-Ad**, 25 mM NaO^{t}Bu, and 1.25 M 1-octene in 2.0 mL of toluene. Curves are plotted only as a guide to the eye.

SUMMARY

Three new CCC-pincer iridium complexes were synthesized and characterized. These complexes, as well as two previously described complexes, were tested as precatalysts for the transfer-dehydrogenation of *n*-octane. Although substantial activity for transfer-dehydrogenation was not observed, iridium complexes of the formula (CCC)IrHCl(MeCN) or (CCC)-IrHCl appear to be generally active catalysts for the isomerization of terminal alkenes to internal isomers with activation by sodium *tert*-butoxide. As these catalysts operate efficiently at 100 °C, while temperatures of 150 °C or higher have uniformly been required to achieve high activity in alkane dehydrogenation, it is unlikely that iridium complexes of this nature will facilitate the selective dehydrogenation of linear alkanes to produce linear α-olefins. Detailed studies on the catalysis of alkene isomerization by these complexes are in progress, focusing on substrate scope, kinetic selectivity, and mechanism.

EXPERIMENTAL SECTION

General Methods. $[Ir(cod)Cl]_2$ was prepared as previously described.[41] 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

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activated alumina, using an MBraun Solvent Purification System. 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 **4-tBu**, **4-Ad**, and **4-dipp**, along with procedures for ligand synthesis and characterization, are given in the Supporting Information.

Iridium Complex 4-tBu. Benzimidazolium salt **3-tBu** (0.646 mmol, 320 mg), $[Ir(cod)Cl]_2$ (0.323 mmol, 215 mg), CsF (1.94 mmol, 294 mg), and toluene (80 mL) were added to an oven-dried, medium-walled pressure vessel in the glovebox. The mixture was heated at 120 °C for 19 h, and then allowed to cool to room temperature. The solvent was evaporated, and the residue was purified by chromatography on activated alumina, first washing with dichloromethane, then eluting the yellow product with 30% ethyl acetate in dichloromethane. After removing the solvent under vacuum, the complex was analytically pure. Yield: 178 mg, 42%. Recrystallization for catalytic trials was performed at room temperature in an argon-filled glovebox by layering a solution in dichloromethane with pentane. ^{1}H NMR (CD_2Cl_2): δ 8.16 (d, 2H, $^3J_{HH}$ = 7.8 Hz), 7.90 (d, 2H, $^3J_{HH}$ = 8.0 Hz), 7.50 (d, 2H, $^3J_{HH}$ = 7.9 Hz), 7.48 (t, 2H, $^3J_{HH}$ = 7.5 Hz), 7.43 (t, 2H, $^3J_{HH}$ = 7.6 Hz), 7.26 (t, 1H, $^3J_{HH}$ = 7.9 Hz), 2.12 (s, 18H), −22.16 (s, 1H). ^{13}C NMR (CD_2Cl_2): δ 194.9, 145.1, 135.1, 134.3, 123.5, 122.3, 121.4, 115.0, 111.4, 108.3, 60.3, 30.2. The Ir−C_{aryl} carbon, expected at ∼124 ppm by analogy to compound **4-Ad**, was not observed and is likely isochronous with the H−C_{aryl} signal at 123.5 ppm. Anal. Calcd. for $C_{28}H_{30}ClIrN_4$: C, 51.72; H, 4.65; N, 8.62. Found: C, 51.49; H, 4.79; N, 8.50.

Iridium Complex 4-Ad. Benzimidazolium salt **3-Ad** (0.614 mmol, 400 mg), $[Ir(cod)Cl]_2$ (0.307 mmol, 205 mg), CsF (1.843 mmol, 280 mg), and acetonitrile (90 mL) were added to an oven-dried, medium-walled pressure vessel in the glovebox. The flask was brought outside of the glovebox, and the reaction mixture was stirred at 110 °C for 22 h behind a blast shield. After cooling to room temperature, the solvent was evaporated. The residue was purified by flash chromatography using a gradient of 0−25% ethyl acetate in dichloromethane. Yield: 292 mg, 59%. Recrystallization was performed at room temperature in an argon-filled glovebox by layering a solution in dichloromethane with pentane. Repeated attempts at analysis gave a low value for carbon; this appears to be due to retention of approximately 10% by mass of CH_2Cl_2 even upon prolonged storage under vacuum, which is observed by ^{1}H NMR. ^{1}H NMR (CD_2Cl_2): δ 8.11 (d, 2H, $^3J_{HH}$ = 8.0 Hz), 7.97 (d, 2H, $^3J_{HH}$ = 8.1 Hz), 7.46 (d, 2H, $^3J_{HH}$ = 8.0 Hz), 7.41 (t, 2H, $^3J_{HH}$ = 7.7 Hz), 7.36 (t, 2H, $^3J_{HH}$ = 7.7 Hz), 7.21 (t, 1H, $^3J_{HH}$ = 7.9 Hz), 2.97 (d, 6H, $^2J_{HH}$ = 11.5 Hz), 2.72 (d, 6H, $^2J_{HH}$ = 11.5 Hz), 2.34 (s, 12H), 1.96 (d, 6H, $^2J_{HH}$ = 12.3 Hz), 1.88 (d, 6H, $^2J_{HH}$ = 12.3 Hz), −22.01 (s, 1H,). ^{13}C NMR (CD_2Cl_2): δ 194.7, 145.2, 134.8, 134.3, 124.9, 123.3, 122.0, 121.3, 115.4, 111.5, 108.3, 61.6, 42.5, 36.6, 30.7. Anal. Calcd. for $C_{40}H_{42}ClIrN_4$: C, 59.57; H, 5.25; N, 6.95. Found: C, 58.69; H, 5.28; N, 6.62.

Iridium Complex 4-dipp. Benzimidazolium salt **3-dipp**[19] (0.568 mmol, 400 mg), $[Ir(cod)Cl]_2$ (0.284 mmol, 191 mg), acetonitrile (92 mL), and triethylamine (17.0 mmol, 2.38 mL) were added to an oven-dried medium-walled pressure vessel in an argon-filled glovebox. The flask was brought outside of the glovebox, and the reaction mixture was stirred at 150 °C for 16 h behind a blast shield. After cooling to room temperature, the solvent was evaporated, and the residue was purified by flash chromatography, using a gradient of 0−35% ethyl acetate in dichloromethane. After removing the solvent under vacuum, the complex was analytically pure. Yield: 186 mg, 36%. Recrystallization for catalytic trials was performed at room temperature in an argon-filled glovebox by layering a solution in dichloromethane with pentane. ^{1}H NMR (CD_2Cl_2): δ 8.21 (d, 2H, $^3J_{HH}$ = 8.0 Hz), 7.74 (d, 2H, $^3J_{HH}$ = 8.0 Hz), 7.47 (m, 4H), 7.40 (dd, 2H, $^3J_{HH}$ = 7.9 Hz, $^4J_{HH}$ = 1.5 Hz), 7.36 (t, 1H, $^3J_{HH}$ = 8.0 Hz), 7.31 (m, 4H), 6.96 (d, 2H, $^3J_{HH}$ = 8.0 Hz), 3.18 (sept, 2H, $^3J_{HH}$ = 6.9 Hz), 2.44 (sept, 2H, $^3J_{HH}$ = 6.9 Hz), 1.34 (s, 3H), 1.27 (d, 6H, $^3J_{HH}$ = 6.9 Hz), 1.07 (d, 6H, $^3J_{HH}$ = 6.9 Hz), 0.97 (d, 6H, $^3J_{HH}$ = 6.9 Hz), 0.88 (d, 7H, $^3J_{HH}$ = 6.9 Hz), −22.76 (s, 1H). ^{13}C NMR (CD_2Cl_2): δ 186.9, 149.3, 148.4, 146.8, 146.3, 137.9, 133.1, 132.7, 130.2, 124.2, 124.0, 123.7, 122.7, 121.5, 111.7, 111.3, 108.5, 28.57, 28.59, 25.6, 24.7, 24.0, 23.7, 2.48. The signal for the N≡CCH_3 carbon, expected at ∼116 ppm by analogy to **4-Mes** and **4-dtbp**, was too weak to identify unambiguously. Anal. Calcd. for $C_{46}H_{49}ClIrN_5$: C, 61.42; H, 5.49; N, 7.79. Found: C, 61.22; H, 5.30; N, 7.61.

Transfer-Dehydrogenation of *n*-Octane. In an argon-filled glovebox, a 15 mL, medium-pressure screw-cap tube was charged with a stir bar, an iridium complex (4.0 μmol), sodium *tert*-butoxide (3.8 mg, 40 μmol), norbornene (75 mg, 0.80 mmol), and 4.0 mL of *n*-octane. The tube was capped, removed from the glovebox, and heated to 150 °C in an oil bath for 20 h. The mixture was cooled to room temperature, and a 100 μL aliquot was transferred to 700 μL of a standard solution of 1,3,5-trimethoxybenzene in $CDCl_3$. Only internal isomers of octene were observed. The total quantity of octene was determined by integrating the ^{1}H NMR signals against the standard.

Isomerization of 1-Hexene. In an argon-filled glovebox, a 15 mL medium-pressure screw-cap tube was charged with a stir bar, iridium complex **4-Mes** (3.3 mg, 4.0 μmol), sodium *tert*-butoxide (0.77 mg, 8 μmol), 1-hexene (500 μL, 4.0 mmol), and 3.5 mL of *n*-octane. The tube was capped, removed from the glovebox, and heated to 150 °C in an oil bath for either 15 or 60 min. The mixture was cooled to room temperature, and a 100 μL aliquot was transferred to 700 μL of a standard solution of 1,3,5-trimethoxybenzene in $CDCl_3$. The conversion of 1-hexene to internal isomers was determined by integrating the ^{1}H NMR signals against the standard. Separately, a 100 μL aliquot of the reaction mixture was added to 2 mL of toluene, filtered, and analyzed by GC-MS to determine the ratios of internal hexene isomers formed.

Isomerization of 1-Octene. In an argon-filled glovebox, a vial was charged with a stir bar, an iridium complex (5.0 μmol), 1-octene (392 μL, 2.5 mmol), 1.6 mL toluene, and optionally sodium *tert*-butoxide (4.8 mg, 50 μmol). The vial was capped and heated in the glovebox while stirring. At the time points indicated, aliquots were removed for analysis. A 50 μL aliquot was transferred to 700 μL of a standard solution of 1,3,5-trimethoxybenzene in $CDCl_3$. The conversion of 1-octene to internal isomers was determined by ^{1}H NMR integration against the standard. Separately, a 50 μL aliquot was added to 2 mL of toluene, filtered, and analyzed by GC-MS to determine the ratios of internal octene isomers formed.

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.[42] Direct methods structure solution was accomplished using SIR92,[43] and full-matrix least-squares refinement was carried out using CRYSTALS.[44] All non-hydrogen atoms were refined anisotropically. Unless otherwise noted, hydrogen atoms were placed in calculated positions, and their positions were initially refined using distance and angle restraints. All hydrogen positions were fixed in place for the final refinement cycles.

X-ray Structure Determination of 4-tBu. X-ray quality crystals of **4-tBu** were grown by slow evaporation of a solution in CH_2Cl_2 and hexanes. One molecule of dichloromethane was present in the asymmetric unit. The iridium-bound chloride was disordered over two positions. The site occupancy was freely refined, and no geometric restraints were employed. The occupancy of the major component was 0.782; the structural data listed in Figure 3 refer to this component. The iridium-bound hydride, also expected to be disordered over two positions, was not located in the difference map.

X-ray Structure Determination of 4-Ad. X-ray quality crystals of **4-Ad** grew directly from a slowly cooled crude reaction mixture. The iridium-bound hydride was located in the difference map, and its position was refined freely before being fixed in place for the final refinement cycles.

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X-ray Structure Determination of 4-dipp. X-ray quality crystals of **4-dipp** were grown by slow evaporation of a solution in CH_2Cl_2 and hexanes. A molecule of dichloromethane was present in the asymmetric unit. The iridium-bound hydride was located in the difference map, and its position was refined freely before being fixed in place for the final refinement cycles.

■ ASSOCIATED CONTENT

Supporting Information

CIF file giving crystallographic data for complexes **4-tBu**, **4-Ad**, and **4-dipp**; detailed NMR assignments for complexes **4-tBu**, **4-Ad**, and **4-dipp**; and complete experimental procedures for ligand synthesis and characterization. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Bellina, F.; Rossi, R. *Chem. Rev.* **2010**, *110*, 1082−1146. (b) Colby, D. A.; Bergman, R. G.; Ellman, J. A. *Chem. Rev.* **2010**, *110*, 624−655. (c) Dobereiner, G. E.; Crabtree, R. H. *Chem. Rev.* **2010**, *110*, 681−703. (d) Doyle, M. P.; Duffy, R.; Ratnikov, M.; Zhou, L. *Chem. Rev.* **2010**, *110*, 704−724. (e) Lyons, T. W.; Sanford, M. S. *Chem. Rev.* **2010**, *110*, 1147−1169. (f) Mkhalid, I. A. I.; Barnard, J. H.; Marder, T. B.; Murphy, J. M.; Hartwig, J. F. *Chem. Rev.* **2010**, *110*, 890−931. (g) Willis, M. C. *Chem. Rev.* **2010**, *110*, 725−748. (h) Goldberg, K. I., Goldman, A. S., Eds. *Activation and Functionalization of C−H Bonds*; ACS Symposium Series 885; American Chemical Society: Washington, DC, 2004.

(2) Choi, J.; MacArthur, A. H. R.; Brookhart, M.; Goldman, A. S. *Chem. Rev.* **2011**, *111*, 1761−1779.

(3) (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. *J. Chem. Soc., Chem. Commun.* **1980**, 1243−1244.

(4) (a) *Dalton Trans.* **2011**, *40* (themed issue on pincers and other hemilabile ligands). (b) Morales-Morales, D., Jensen, C. M., Eds. *The Chemistry of Pincer Compounds*; Elsevier: Amsterdam, 2007.

(5) (a) Gupta, M.; Hagen, C.; Flesher, R. J.; Kaska, W. C.; Jensen, C. M. *Chem. Commun.* **1996**, 2083−2084. (b) Gupta, M.; Hagen, C.; Kaska, W. C.; Cramer, R. E.; Jensen, C. M. *J. Am. Chem. Soc.* **1997**, *119*, 840−841.

(6) (a) Liu, F. C.; Goldman, A. S. *Chem. Commun.* **1999**, 655−656. (b) Kundu, S.; Choliy, Y.; Zhuo, G.; Ahuja, R.; Emge, T. J.; Warmuth, R.; Brookhart, M.; Krogh-Jespersen, K.; Goldman, A. S. *Organometallics* **2009**, *28*, 5432−5444.

(7) Haenel, M. W.; Oevers, S.; Angermund, K.; Kaska, W. C.; Fan, H. J.; Hall, M. B. *Angew. Chem., Int. Ed.* **2001**, *40*, 3596−3600.

(8) (a) Göttker-Schnetmann, I.; White, P.; Brookhart, M. *J. Am. Chem. Soc.* **2004**, *126*, 1804−1811. (b) Zhu, K. M.; Achord, P. D.; Zhang, X. W.; Krogh-Jespersen, K.; Goldman, A. S. *J. Am. Chem. Soc.* **2004**, *126*, 13044−13053. (c) Huang, Z.; Brookhart, M.; Goldman, A. S.; Kundu, S.; Ray, A.; Scott, S. L.; Vicente, B. C. *Adv. Synth. Catal.* **2009**, *351*, 188−206.

(9) Morales-Morales, D.; Redon, R.; Yung, C.; Jensen, C. M. *Inorg. Chim. Acta* **2004**, *357*, 2953−2956.

(10) Kuklin, S. A.; Sheloumov, A. M.; Dolgushin, F. M.; Ezernitskaya, M. G.; Peregudov, A. S.; Petrovskii, P. V.; Koridze, A. A. *Organometallics* **2006**, *25*, 5466−5476.

(11) Adams, J. J.; Arulsamy, N.; Roddick, D. M. *Organometallics* **2012**, *31*, 1439−1447.

(12) Gruver, B. C.; Adams, J. J.; Warner, S. J.; Arulsamy, N.; Roddick, D. M. *Organometallics* **2011**, *30*, 5133−5140.

(13) Bauer, E. B.; Andavan, G. T. S.; Hollis, T. K.; Rubio, R. J.; Cho, J.; Kuchenbeiser, G. R.; Helgert, T. R.; Letko, C. S.; Tham, F. S. *Org. Lett.* **2008**, *10*, 1175−1178.

(14) Raynal, M.; Pattacini, R.; Cazin, C. S. J.; Vallee, C.; Olivier-Bourbigou, H.; Braunstein, P. *Organometallics* **2009**, *28*, 4028−4047.

(15) (a) Zhang, X. W.; Emge, T. J.; Goldman, A. S. *Inorg. Chim. Acta* **2004**, *357*, 3014−3018. (b) Pelczar, E. M.; Emge, T. J.; Goldman, A. S. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **2007**, *63*, M323−M326.

(16) Zuo, W. W.; Braunstein, P. *Organometallics* **2010**, *29*, 5535−5543.

(17) (a) Zuo, W. W.; Braunstein, P. *Organometallics* **2012**, *31*, 2606−2615. (b) Zuo, W. W.; Braunstein, P. *Dalton Trans.* **2012**, *41*, 636−643.

(18) Schultz, K. M.; Goldberg, K. I.; Gusev, D. G.; Heinekey, D. M. *Organometallics* **2011**, *30*, 1429−1437.

(19) Chianese, A. R.; Mo, A.; Lampland, N. L.; Swartz, R. L.; Bremer, P. T. *Organometallics* **2010**, *29*, 3019−3026.

(20) Rivas, F. M.; Riaz, U.; Giessert, A.; Smulik, J. A.; Diver, S. T. *Org. Lett.* **2001**, *3*, 2673−2676.

(21) (a) Gründemann, S.; Kovacevic, A.; Albrecht, M.; Faller Robert, J. W.; Crabtree, H. *Chem. Commun.* **2001**, 2274−2275. (b) Chianese, A. R.; Kovacevic, A.; Zeglis, B. M.; Faller, J. W.; Crabtree, R. H. *Organometallics* **2004**, *23*, 2461−2468. (c) Albrecht, M. *Chem. Commun.* **2008**, 3601−3610.

(22) Abbreviations: DPEPHOS = bis(2-diphenylphosphinophenyl) ether; BINAP = 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl; CyPF-*t*Bu = (*R*)-(-)-1-[(*S*)-2-dicyclohexylphosphino)ferrocenyl]ethyldi-*t*-butylphosphine; dba = dibenzylideneacetone.

(23) (a) Shen, Q.; Ogata, T.; Hartwig, J. F. *J. Am. Chem. Soc.* **2008**, *130*, 6586−6596. (b) Shen, Q. L.; Shekhar, S.; Stambuli, J. P.; Hartwig, J. F. *Angew. Chem., Int. Ed.* **2005**, *44*, 1371−1375.

(24) Diez-Gonzalez, S.; Marion, N.; Nolan, S. P. *Chem. Rev.* **2009**, *109*, 3612−3676.

(25) Hahn, F. E.; Jahnke, M. C. *Angew. Chem., Int. Ed.* **2008**, *47*, 3122−3172.

(26) Poyatos, M.; Mata, J. A.; Peris, E. *Chem. Rev.* **2009**, *109*, 3677−3707.

(27) Gusev, D. G. *Organometallics* **2009**, *28*, 6458−6461.

(28) Lee, H. S.; Lee, G. Y. *Bull. Korean Chem. Soc.* **2005**, *26*, 461−462.

(29) (a) Cramer, R.; Lindsey, R. V. *J. Am. Chem. Soc.* **1966**, *88*, 3534−3544. (b) Alper, H.; LePort, P. C.; Wolfe, S. *J. Am. Chem. Soc.* **1969**, *91*, 7553−7554. (c) Casey, C. P.; Cyr, C. R. *J. Am. Chem. Soc.* **1973**, *95*, 2248−2253. (d) Mayer, M.; Welther, A.; von Wangelin, A. J. *ChemCatChem* **2011**, *3*, 1567−1571.

(30) (a) Roos, L.; Orchin, M. *J. Am. Chem. Soc.* **1965**, *87*, 5502−5504. (b) Casey, C. P.; Cyr, C. R. *J. Am. Chem. Soc.* **1971**, *93*, 1280−1282. (c) Taylor, P.; Orchin, M. *J. Am. Chem. Soc.* **1971**, *93*, 6504−6506. (d) Casey, C. P.; Cyr, C. R. *J. Am. Chem. Soc.* **1973**, *95*, 2240−2247.

(31) Tolman, C. A. *J. Am. Chem. Soc.* **1972**, *94*, 2994−2999.

(32) Hanessian, S.; Giroux, S.; Larsson, A. *Org. Lett.* **2006**, *8*, 5481−5484.

(33) Morrill, T. C.; D'Souza, C. A. *Organometallics* **2003**, *22*, 1626−1629.

(34) Baxendale, I. R.; Lee, A. L.; Ley, S. V. *Synlett* **2001**, 2004−2004.

(35) McGowan, K. P.; Abboud, K. A.; Veige, A. S. *Organometallics* **2011**, *30*, 4949−4957.

(36) Scarso, A.; Colladon, M.; Sgarbossa, P.; Santo, C.; Michelin, R. A.; Strukul, G. *Organometallics* **2010**, *29*, 1487−1497.

(37) Larsen, C. R.; Grotjahn, D. B. *J. Am. Chem. Soc.* **2012**, *134*, 10357−10360.

(38) Grotjahn, D. B.; Larsen, C. R.; Gustafson, J. L.; Nair, R.; Sharma, A. *J. Am. Chem. Soc.* **2007**, *129*, 9592.

(39) Biswas, S.; Huang, Z.; Choliy, Y.; Wang, D. Y.; Brookhart, M.; Krogh-Jespersen, K.; Goldman, A. S. *J. Am. Chem. Soc.* **2012**, *134*, 13276−13295.
(40) Alberty, R. A.; Gehrig, C. A. *J. Phys. Chem. Ref. Data* **1985**, *14*, 803−820.
(41) Lin, Y.; Nomiya, K.; Finke, R. G. *Inorg. Chem.* **1993**, *32*, 6040−6045.
(42) *CrysAlisPro Software System*, Version 1.171.32; Oxford Diffraction Ltd.: Abingdon, U.K., 2007.
(43) Altomare, A.; Cascarano, M.; Giacovazzo, C.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli, M. *J. Appl. Crystallogr.* **1994**, *27*, 435−436.
(44) Betteridge, P. W.; Carruthers, J. R.; Cooper, R. I.; Prout, K.; Watkin, D. J. *J. Appl. Crystallogr.* **2003**, *36*, 1487.