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Characterization and Reactivity Studies of Dinuclear Iridium Hydride Complexes Prepared from Iridium Catalysts with N,P and C,N Ligands under Hydrogenation Conditions

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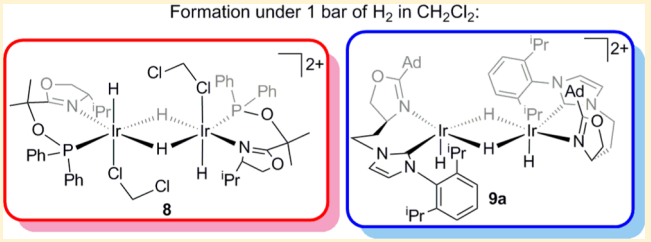
Supporting Information

ABSTRACT: The dinuclear iridium hydride complexes $[IrH(CH_3CN)(L1)(\mu\text{-}H)]_2(BAr_F)_2$ (**7**; L1 = (*S*)-2-(2-((diphenylphosphanyl)oxy)propan-2-yl)-4-isopropyl-4,5-dihydrooxazole, BAr_F = tetrakis[3,5-bis(trifluoromethyl)phenyl]-borate), $[IrH(CH_2Cl_2)(L1)(\mu\text{-}H)]_2(BAr_F)_2$ (**8**), $[IrH(L2)(\mu\text{-}H)]_2(BAr_F)_2$ (**9a**; L2 = (*S*)-1-[2-(2-adamantan-2-yl-4,5-dihydrooxazol-4-yl)-ethyl]-3-(2,6-diisopropylphenyl)-1,2-dihydroimidazol-2-ylidene), and $[IrH(L3)(\mu\text{-}H)]_2(BAr_F)_2$ (**9b**; L3 = (*S*)-1-[2-(2-*tert*-butyl-4,5-dihydrooxazol-4-yl)-ethyl]-3-(2,6-diisopropylphenyl)-1,2-dihydroimidazol-2-ylidene) were prepared from the corresponding mononuclear $[Ir(COD)(L)]BAr_F$ precursors by treatment with H_2 and characterized by 2D NMR spectroscopy and X-ray diffraction. Conversion to a trinuclear iridium hydride complex, which is usually observed for N,P iridium hydride complexes, is inhibited by addition of 0.5 equiv of $[H(OEt_2)_2]BAr_F$ or acetonitrile. Reactions with acetonitrile or 6,6′-bi-2-picoline afforded the mononuclear iridium dihydride complexes $[Ir(H)_2(CH_3CN)_2(L1)]BAr_F$ (**5**), $[Ir(H)_2(CH_3CN)_2(L3)]BAr_F$ (**10**), or $[Ir(H)_2(6,6'\text{-bi-2-picoline})(L3)]BAr_F$ (**11**). The CH_3CN complexes **7** and **10** are inactive as hydrogenation catalysts. In contrast, the coordinatively unsaturated dinuclear complexes **9a** and **9b** are active catalysts for the hydrogenation of (*E*)-1,2-diphenyl-1-propene at 50 bar hydrogen pressure.



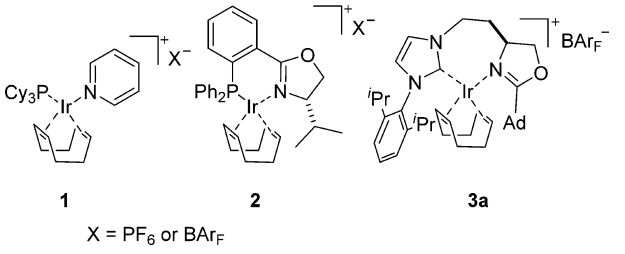
INTRODUCTION

Iridium catalysts based on chiral N,P or C,N ligands have considerably enhanced the scope of asymmetric hydrogenation of olefins. In contrast to rhodium- or ruthenium-diphosphine catalysts, they do not require a coordinating group next to the C=C bond and, therefore, perform well with a wide range of structurally diverse olefins.[1] Despite the large number of iridium catalysts and successful applications reported in the literature, experimental data on the reaction mechanism are still scarce.[2]

On the basis of DFT calculations, the groups of Andersson[2d,3] and Burgess[4] proposed a catalytic cycle involving an Ir(III) olefin complex containing two hydride ligands and a side-on coordinated dihydrogen molecule, which, after migratory insertion and concomitant oxidative addition of dihydrogen, forms an Ir(V) trihydride complex. These computational studies indicated that an Ir(III)−Ir(V) cycle is preferred over an Ir(I)−Ir(III) cycle going through an iridium(III) dihydride complex, which reacts with the substrate through migratory insertion, followed by reductive elimination, to yield the hydrogenation product and an Ir(I) complex. On the other hand, experimental studies of Dietiker and Chen[2c] have shown that, at least in the gas phase, an Ir(I)−Ir(III) cycle is possible.

Obviously, iridium hydrides play a central role as intermediates in the catalytic cycle. However, the high reactivity of iridium hydride complexes makes it difficult to study their chemistry and to characterize such species as intermediates in catalytic reactions.

Chart 1. Selection of Iridium Hydrogenation Catalysts



Previous studies[5] have shown that Crabtree's catalyst, $[Ir(COD)(PCy_3)(py)]PF_6$ (**1**), forms trimeric and tetrameric iridium hydride clusters under hydrogenation conditions. Brown and co-workers[5d] have suggested that trimerization is a consequence of ligand lability, in particular due to dissociation of the Ir−N bond. The chiral hydrogenation catalyst $[Ir(COD)(PHOX)]PF_6$ (**2**) as well forms a trinuclear iridium hydride complex upon treatment with hydrogen gas (see eq

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1).[6] All of these iridium polyhydride clusters are inactive as hydrogenation catalysts.[7]

$$3\ [Ir(COD)(PHOX)]PF_6 \xrightarrow[-\ 3\ C_8H_{16}\ -\ HPF_6]{1\ bar\ H_2,\ MeOH} [Ir_3(H)_6(PHOX)_3(\mu_3\text{-}H)](PF_6)_2 \quad (1)$$

The rate of conversion to trinuclear hydride complexes depends on the anion. With hexafluorophosphate, iridium cluster formation competes with hydrogenation, and therefore, catalyst deactivation is a serious problem. In contrast, the corresponding BAr_F salts (BAr_F = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate) show a much lower tendency to form inactive iridium clusters. Thus, much higher turnover numbers of >5000 become possible with iridium complexes with BAr_F or related very weakly coordinating anions.[2a]

The cationic C,N complex **3a**, developed by Burgess and co-workers,[8] was also reported to form inactive iridium hydride species when treated with dihydrogen in the absence of substrate. However, the structures of the components in the resulting complex product mixtures were not elucidated.[9]

In addition to a trinuclear hydride complex, three mononuclear Ir(III) dihydride complexes derived from precatalyst **2** have been characterized by low-temperature NMR experiments in THF-D_8.[10] Treatment of **2** with H_2 at −40 °C led to a single stereoisomer of $[Ir(H)_2(COD)(PHOX)]BAr_F$, which reacted at 0 °C to give two isomers of $[Ir(H)_2(PHOX)]BAr_F$ and cyclooctane. At room temperature, formation of trinuclear hydride complexes was observed. A coordinating solvent, such as THF, had to be used in these experiments, because it stabilizes these labile hydride complexes. However, THF is not suited for hydrogenation as it inhibits the catalyst. Analogous experiments in dichloromethane, commonly used as a hydrogenation solvent, led to complex mixtures of unidentified hydride species. Moreover, attempts to identify further intermediates in the reaction sequence leading to trinuclear complexes or to detect catalytic intermediates under hydrogenation conditions failed so far. Thus, further studies of iridium hydride complexes will be necessary for a better understanding of the mechanism of C=C bond hydrogenation and catalyst deactivation.

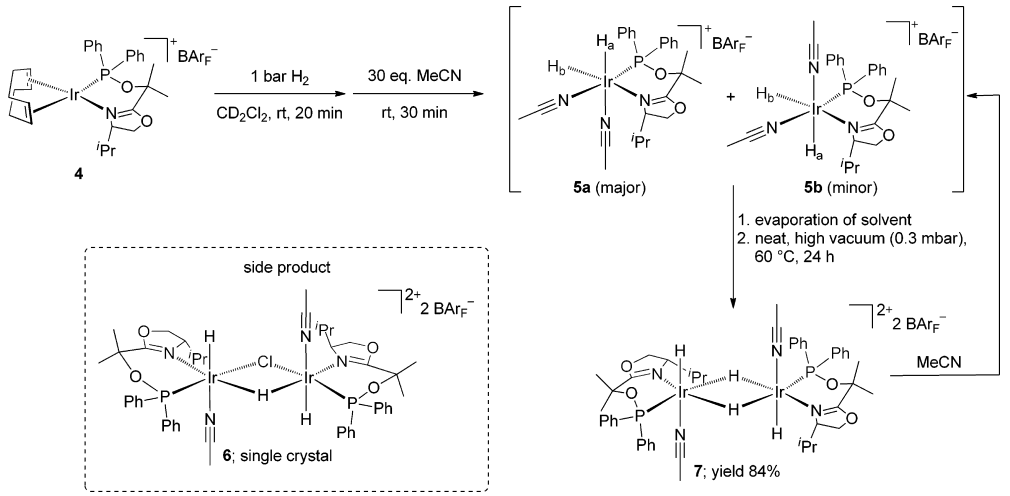
Here, we report the identification, synthesis, and characterization of a series of new dinuclear iridium hydride complexes that are formed under hydrogenation conditions. Furthermore, we discuss the activity of these new complexes as catalysts for the hydrogenation of (*E*)-1,2-diphenyl-1-propene.

RESULTS AND DISCUSSION

(SimplePHOX)Ir(III)(H)$_2$(CH$_3$CN)$_2$ Complexes. On the basis of initial experiments with several N,P iridium complexes, we chose the SimplePHOX complex **4** for our studies. Catalyst **4** had been previously fully characterized (including X-ray analysis) and successfully used for the hydrogenation of various olefins.[11] Treatment of iridium complex **4** with 1 bar of hydrogen gas at room temperature in CD_2Cl_2 for 20 min, followed by the addition of 30 equiv of MeCN and stirring for 30 min, cleanly afforded a mixture of two iridium species.[12] 2D NMR analyses revealed the formation of two stereoisomeric bis-acetonitrile *cis*-dihydride complexes **5a** and **5b** in a ratio of 5:1 (Scheme 1). Because of the stabilizing effect of the coordinated acetonitrile molecules, the complexes proved to be sufficiently stable, even at room temperature, to allow proper characterization. The two isomers differ in the position of H_a relative to the isopropyl group of the SimplePHOX ligand. In the ^{1}H NMR spectrum, the two hydrides appeared as two doublets of doublets at −19.64 and −21.41 ppm for the major isomer and at −18.95 and −21.85 ppm for the minor isomer, respectively. The ^2J(H,P) values of 20−24 Hz for both isomers confirmed that both hydrides were located *cis* to the phosphorus atom.[13] Similar results had been previously obtained by treating iridium complex **2** with H_2 in THF-D_8.[10a] However, the resulting dihydride complexes were not stable above 0 °C and conversion remained incomplete. The observed electronically favored formation of an Ir−H bond *trans* to the coordinated N atom is consistent with previous studies by Crabtree and co-workers[14] and Mazet et al.[10a]

Identification and Characterization of New Dinuclear N,P Iridium Hydride Complexes. Attempts to isolate the two stereoisomeric iridium complexes **5a** and **5b** from the reaction mixture by evaporation of the solvent afforded new products. The ^{1}H NMR spectrum of the redissolved crude material in CD_2Cl_2 showed the appearance of several new hydride signals. Attempts to purify the crude product by

Scheme 1. Formation of Dinuclear Iridium(III) Hydride Complexes under Substrate-Free Hydrogenation Conditions



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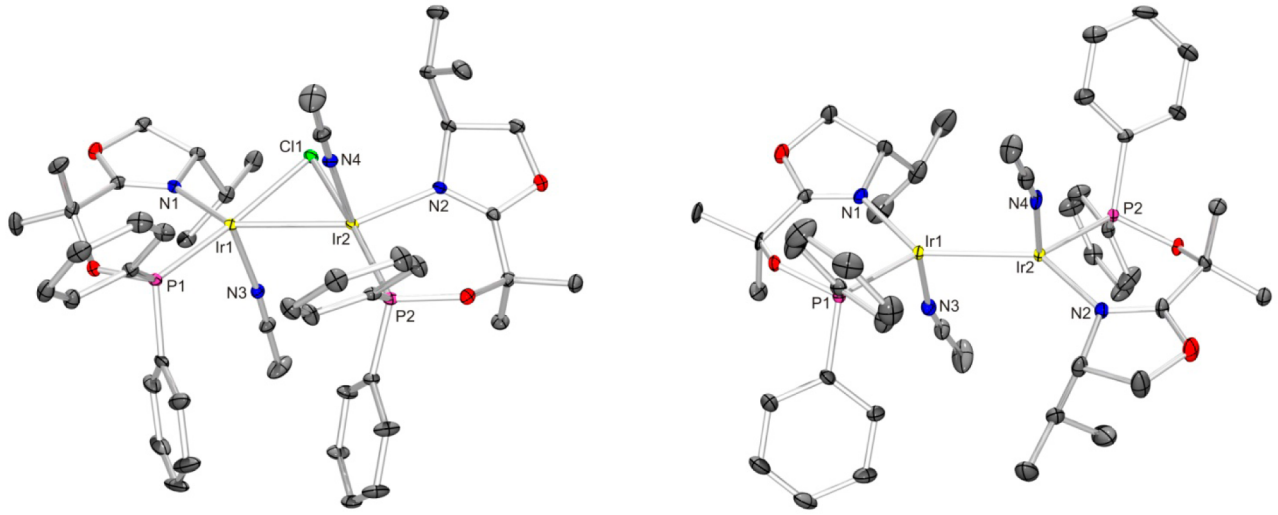

Figure 1. ORTEP view of the cations of salts **6** (left) and **7** (right). Hydrogen atoms and solvent molecules are omitted for clarity, and thermal ellipsoids are set to 30% probability. Selected bond lengths (Å) for cation **6**: Ir1−Ir2, 2.82334(14); Ir1−Cl1, 2.4343(5); Ir2−Cl1, 2.4346(5); Ir1−N3, 2.168(2); Ir2−N4, 2.168(2). Bond angle (deg) for Ir1−Cl−Ir2 in cation **6**: 70.884(15). Selected bond lengths (Å) for cation **7**: Ir1−Ir2, 2.67849(11); Ir1−N3, 2.164(4); Ir2−N4, 2.163(5).

crystallization from a dichloromethane/hexane solution afforded a few single crystals suitable for X-ray analysis. X-ray diffraction of these crystals showed that an unexpected hydride- and chloro-bridged dinuclear Ir(III) complex **6** had formed as a side product (Scheme 1). Figure 1 (left) shows the cation of this complex with selected bond lengths in the caption. The solid-state structure reveals a bridging μ-chloride atom *trans* to the phosphorus atoms P1 and P2. The hydride ligands were not located in the final difference density map, but two apparent vacant sites in the coordination spheres of Ir1 and Ir2 *trans* to N3 and N4 were presumed to be the positions for two terminal hydrides, while a bridging hydride was tentatively positioned *trans* to N1 and N2. To verify this result, we redissolved a single crystal in CD_2Cl_2 and analyzed the compound by ^1H NMR spectroscopy. The spectrum showed two hydride signals, one as a doublet of doublets at −23.68 ppm (terminal hydrides) and the other as a multiplet at −28.70 ppm (bridging hydride) with a ratio of 2:1. The $^{31}P\{^1H\}$ NMR spectrum exhibited only one singlet at 82.8 ppm. The $^2J(H,P)$ values of <20 Hz clearly indicate that none of the three hydrides is located *trans* to a phosphorus atom. The NMR and crystal structure data are in agreement with the C_2 symmetric structure of **6** shown in Scheme 1. The bridging hydride and chloride atoms can be viewed to form 3-center 2-electron and 3-center 4-electron units, respectively. The Ir−Ir distance of 2.82 Å is consistent with a reported structure of a dinuclear Ir(I)/Ir(III) complex containing an $Ir_2(\mu\text{-}H)(\mu\text{-}Cl)$ fragment.[15] The bridging μ-chloride atom presumably arises from dichloromethane used for crystallization. Oxidative addition of dichloromethane with a mononuclear iridium(I) complex has been described by Tejel and co-workers.[16]

To avoid formation of the chloro-bridged complex **6**, we performed the hydrogenation of precatalyst **4** in acetonitrile at 50 bar hydrogen pressure. Evaporation of the solvent and subsequent ^1H NMR analysis of the crude material showed partial formation of a new dinuclear iridium(III) hydride complex **7** (Scheme 1). The crude material was dried at 0.3 mbar at 60 °C for 24 h, and after washing with hexane/dichloromethane, the dinuclear complex **7** was isolated in 84% yield. ^1H NMR studies in CD_2Cl_2[17] showed that complex **7** does not react with dichloromethane. Nevertheless, upon standing for 8 h at room temperature in CD_2Cl_2, partial decomposition with concomitant back reaction to the isomeric mixture of **5a** and **5b** was observed. Addition of acetonitrile to a CD_2Cl_2 solution of complex **7** induced rapid conversion to **5a** and **5b** within <5 min. Crystals of the dinuclear complex **7** suitable for X-ray diffraction were obtained from a hexane/dichloromethane solution. The crystal structure of this complex is shown in Figure 1 (right) with selected bond lengths in the caption. The hydride ligands were not located in the final difference density map, but two apparent vacant sites in the coordination sphere *trans* to the nitrogen atoms N3 and N4 represent the positions of two terminal hydrides,. The Ir−Ir distance of 2.68 Å is consistent with literature values for dinuclear Ir(III)/Ir(III) complexes containing an $Ir_2(H)_2(\mu\text{-}H)_2$ fragment.[18] Comparison of solid-state structures **6** and **7** reveals that, in the former, the phosphorus atoms are oriented *syn*, whereas, in the latter, they adopt an *anti* arrangement. In contrast to complex **6**, complex **7** does not possess C_2 symmetry, consistent with the solution structure analyzed by NMR spectroscopy. The two isopropyl groups of the SimplePHOX ligand are on the same side of the plane defined by these six atoms, Ir1, P1, N1, Ir2, P2, and N2. Consequently, the terminal hydrides H1 and H2 are nonequivalent and appear as separate signals at −20.04 and −20.24 ppm. The $^{31}P\{^1H\}$ NMR spectrum as well shows two different phosphorus signals at 71.1 and 67.8 ppm. A signal at −17.89 ppm is observed for the two bridging hydrides. The $^2J(H,P)$ values of 20 Hz for the terminal hydrides and 55 Hz for the bridging hydrides fully support the structure drawn in Scheme 1 (for full characterization, see the Experimental Section and the Supporting Information).

The Ir_2 core of the dinuclear complex possesses a 32-electron configuration with the bridging hydrides forming two 3-center 2-electron units. The bond order between the two Ir centers in hydride-bridged complexes of this type has been discussed controversially.[18] Structures with an Ir═Ir double bond as well as structures without a bond between the two metal centers have been formulated.

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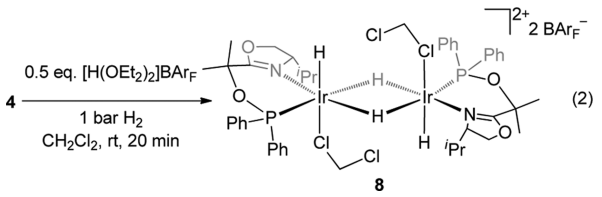
Treatment of iridium complex **4** with hydrogen gas (1 bar) at room temperature in the presence of 0.5 equiv of $[H(OEt_2)_2]$-BAr_F[19] in dichloromethane for 20 min, followed by evaporation of the solvent and washing with hexane/dichloromethane, led to a new hydride complex (see eq 2). The ^1H NMR spectrum



(2)

of the crude product showed that complex **4** had been fully consumed and converted almost quantitatively (>95%) to a single species that displayed two hydride signals at −16.14 and −26.45 ppm in a 1:1 ratio. The $^{31}P\{^1H\}$ NMR spectrum showed a singlet at 72.0 ppm. Single crystals suitable for X-ray diffraction were obtained from a hexane/dichloromethane solution. The solid-state structure of **8** shows an *anti* orientation of the phosphorus atoms similar to that found for complex **7** (Figure 2). Two terminal and two bridging hydride

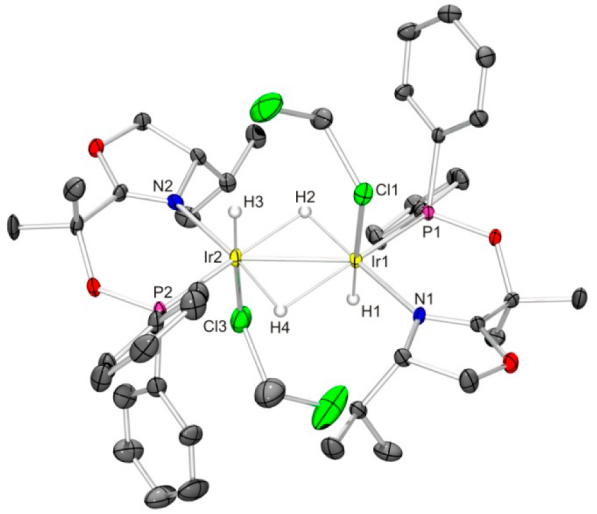


Figure 2. ORTEP view of the cation of salt **8**. Hydrogen atoms are omitted for clarity except the hydrides and ellipsoids are set to 30% probability. The dichloromethane molecule coordinated to Ir2 is disordered over two sites with occupancy factors of approximately 50% for each site. One of the disordered CH_2Cl_2 molecules (not shown) is too far from Ir2 to form a bond. Selected bond lengths (Å): Ir1−Ir2, 2.6443(2); Ir1−Cl1, 2.6121(14); Ir2−Cl3, 2.519(6); Ir1−H1, 1.51; Ir1−H2, 1.76; Ir1−H4, 2.09; Ir2−H2, 1.96; Ir2−H3, 1.50; Ir2−H4, 1.73.

ligands were located in the final difference density map. The Ir−Ir distance of 2.64 Å is similar to that found for complex **7**. Each of the two Ir centers bears a coordinated dichloromethane molecule. The CH_2Cl_2 molecule at Ir2 is disordered over two sites (occupancy factors ∼ 50% for each site). One of the disordered solvent molecules forms an axial Ir−Cl bond, whereas the other is too distant to coordinate to the metal center. Complex **8** represents a rare example of a solid-state structure with an iridium bound dichloromethane molecule.[20] The relatively long Ir−Cl bonds in complex **8** with 2.61 and 2.52 Å indicate that the dichloromethane molecules are only weakly bound.

The ^1H NMR spectrum of a dissolved crystal was identical to that of the crude material. The dinuclear complex **8** is dynamic in solution. The ^1H NMR spectrum shows broadened signals consistent with a time-averaged symmetrical structure. We assume that the coordinated dichloromethane molecules exchange rapidly with the solvent.

When the reaction shown in eq 2 was repeated under the same conditions, but in the absence of $[H(OEt_2)_2]BAr_F$, ^1H NMR analysis revealed that ca. 20% of a trinuclear complex $[Ir_3(H)_6(L1)_3(\mu_3\text{-}H)]^{2+}$ had formed.[21] In the reaction sequence leading to the trinuclear complex, one proton is liberated (eq 1), which explains why addition of acid inhibits its formation.

Identification and Characterization of New Dinuclear C,N Iridium Hydride Complexes. On the basis of the results obtained with the N,P iridium complex **4**, we carried out analogous experiments with C,N iridium complexes **3a** and **3b** developed by Burgess et al.[8] When complex **3a** was treated with hydrogen gas at 1 bar in dichloromethane at room temperature for 30 min, followed by evaporation of the solvent, a new complex was obtained in >95% yield. On the basis of extended 2D NMR studies, elemental analysis, and ESI-MS data structure, **9a** was proposed.

The ESI mass spectrum of complex **9a** showed a signal at *m/z* 654.3027 ($[C_{60}H_{86}N_6O_2Ir_2]^{2+}$ calcd 654.3031) consistent with a dinuclear species charged +2, as evidenced by the *m/z* difference of 0.5 between the isotopomers. The ^1H NMR spectrum displayed two singlets for the bridging and terminal hydrides at −18.40 and −36.85 ppm, respectively. The very low frequency shift of the terminal hydrides is consistent with literature values[22] reported for iridium complexes of this type with a vacant coordination site or a C−H agostic interaction *trans* to a terminal hydride. The $^{13}C\{^1H\}$ spectrum exhibits a very characteristic low-frequency singlet at 133.4 ppm for the iridium-bound C atom of the N-heterocyclic carbene (NHC) unit.[23] Figure 3 shows two segments of the 2D NOESY spectrum of complex **9a** at room temperature, in which the contacts from the hydrides to the various protons of the C,N ligands are visible. This measurement allows to distinguish between the terminal and bridging hydrides H_t and H_μ. For example, H_μ shows a strong cross-peak to H22, whereas there is no interaction between H_t and H22.

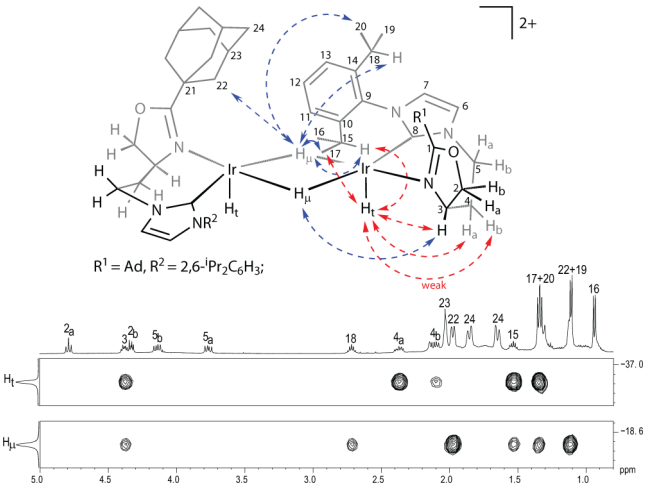


Figure 3. Section of the 2D NOESY spectrum for salt **9a**, showing the contacts from the hydrides (H_μ (blue) and H_t (red)) to the various protons of the C,N ligands.

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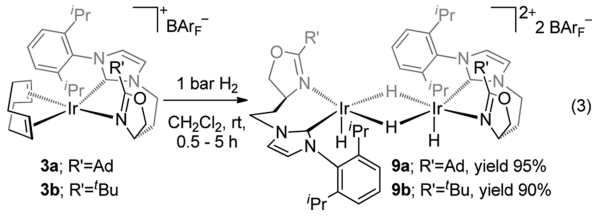
Although we were unable to produce crystals of complex **9a** for X-ray analysis, a related crystalline complex **9b** was obtained in high yield by hydrogenation of the ^{t}Bu analogue **3b** (eq 3).



(3)

The ^{1}H NMR spectrum showed broad resonances in dichloromethane at room temperature, but the signals became sufficiently sharp at −30 °C to allow determination of the solution structure, which closely corresponds to that of **9a** (see the Experimental Section and the Supporting Information). The low-temperature ^{1}H 2D exchange spectrum of **9b** reveals two further minor components in equilibrium with structure **9b**. Crystallization from hexane/dichloromethane led to crystals that were used for structure determination by X-ray diffraction (Figure 4). The hydride ligands were not located in the final

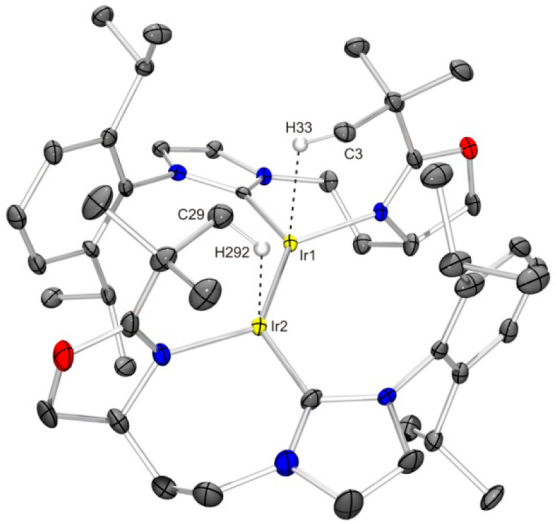


Figure 4. ORTEP view of the cation of salt **9b**. Hydrogen atoms are omitted for clarity except H33 and H292. Only one orientation of the disordered isopropyl group is shown, and thermal ellipsoids are set to 30% probability. Selected bond lengths (Å) and distances (Å): Ir1−Ir2, 2.6012(2); Ir1−H33, 2.17; Ir2−H292, 2.13; Ir1−C3, 2.77; Ir2−C29, 2.79.

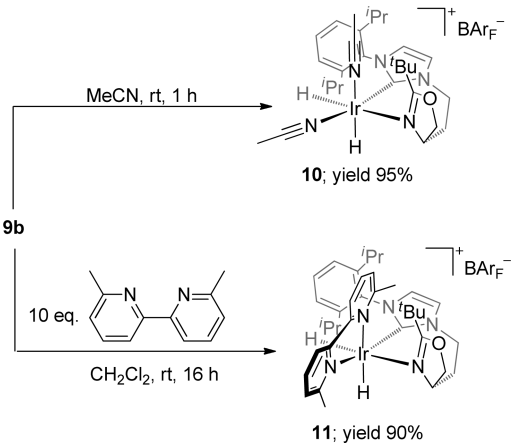
difference density map, but the coordination geometry of the two Ir centers is in agreement with the structure deduced by NMR spectroscopy in which the two terminal hydrides are located on the same side of the Ir$_2$(μ-H)$_2$ plane (see eq 3). The structure possesses C_2 symmetry with the two NHC units oriented *anti*. The Ir−Ir distance is 2.60 Å, somewhat shorter than the Ir−Ir bond in the N,P complex **8** (2.64 Å) The two Ir centers are coordinatively unsaturated with two vacant coordination sites *trans* to the terminal hydrides. The 14-electron configuration of the two Ir centers is stabilized by agostic interactions with the *tert*-butyl methyl groups, as evidenced by the short Ir(1)−C(3), Ir(1)−H(33), Ir(2)−C(29), and Ir(2)−H(292) distances, which are in agreement with literature values.[22a,b,24] We assume that the dinuclear complex **9a** is stabilized in a similar fashion by agostic interactions with the adamantyl groups.

Both complexes **9a** and **9b** are stable for several hours in CD_2Cl_2 at room temperature under a hydrogen atmosphere at 1 bar. However, at 50 bar hydrogen pressure, a complex mixture of products is formed, showing a multitude of hydride signals in the ^{1}H NMR spectrum.

Apparently, the dinuclear hydride C,N complexes **9a** and **9b** are stable under 1 bar of H_2 in a noncoordinating environment, in contrast to analogous N,P ligand complexes, which are converted to trinuclear hydride complexes in the absence of stabilizing additives, such as coordinating ligands or [H(OEt$_2$)$_2$]BAr$_F$. Consistent with these observations, attempts to form a C,N-based trinuclear iridium hydride complex from **3a** under the conditions previously used for iridium N,P complexes (eq 1) failed.[25] These findings may be explained by the stronger σ-donation of NHC ligands resulting in lower acidity of C,N compared to N,P iridium hydride complexes,[26] rendering the deprotonation step required for the conversion to a trinuclear complex (see eq 1) more difficult.

The presence of two vacant coordination sites in complex **9b** led us to examine its reactivity toward nitrogen-based ligands. Stirring an acetonitrile solution of **9b** for 1 h at room temperature cleanly led to the mononuclear complex **10** in almost quantitative yield (Scheme 2). The ^{1}H NMR spectrum

Scheme 2. Synthesis of New Mononuclear Iridium Hydride Complexes 10 and 11



showed two hydride signals as doublets at −21.93 and −26.12 ppm and the ^{13}C{^{1}H} spectrum a singlet at 154.2 ppm for the iridium-bound NHC C atom. An analogous product **11** was obtained by stirring a dichloromethane solution of complex **9b** in the presence of 6,6′-bi-2-picoline for 16 h in 90% yield (Scheme 2). Complex **11** can be also prepared by treating a dichloromethane solution of **3b** and 6,6′-bi-2-picoline with hydrogen gas for 4 h. The ^{1}H NMR spectrum of this complex shows two hydride signals as doublets at −21.92 and −28.62 ppm. The ^{13}C signal of the iridium-bound NHC C atom appears at 158.2 ppm. It is noteworthy that the sterically demanding 6,6′-bi-2-picoline is capable of coordination in the presence of the bulky C,N iridium fragment. Structures **10** and **11** indicate that the formation of an Ir−H bond *trans* to the NHC ligand is electronically disfavored[27] and that the stereoisomers with hydrides *trans* to the oxazoline and acetonitrile/picoline N atoms are thermodynamically preferred.

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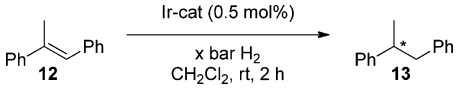
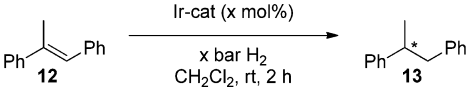
Table 1. Hydrogenation of (*E*)-1,2-Diphenyl-1-propene Catalyzed by Different N,P Iridium Complexes



entry	cat.	molarity (M)	pressure (bar)	**13** (%)[a]	ee **13** (%)[b]	byproduct (%)[a]
1[c]	**4**[d]	0.2	50	>99[e]	85 (*R*)	
2[f]	**7**	0.2	1	<1	n.d.	
3[f]	**7**	0.2	50	4	n.d.	
4[f]	**7**	2.0	50	6	n.d.	
5[f]	**8**	0.2	1	<1	n.d.	24
6[f]	**8**	0.2	50	<1	n.d.	42
7[f]	**8**	0.2	100	<1	n.d.	61
8[f]	**8**	2.0	1	5	n.d.	13
9[f]	**8**	2.0	50	57	71 (*R*)	11
10[f]	**8**	2.0	100	71	79 (*R*)	13

[a]Yields were determined by ^{1}H NMR. [b]Enantioselectivities were determined by HPLC on a chiral stationary phase. [c]Result reported in ref 11. [d]1 mol % cat. [e]Yield was determined by GC analysis. [f]Average values of at least two experiments.

Table 2. Hydrogenation of (*E*)-1,2-Diphenyl-1-propene Catalyzed by Different C,N Iridium Complexes



entry	cat.	cat. loading (mol %)	molarity (M)	pressure (bar)	**13** (%)[a]	ee **13** (%)[b]
1[c]	**3a**	0.6	2.0	50	>99	98 (*S*)
2[c]	**3b**	0.6	2.0	50	81	50 (*S*)
3	**10**	0.6	2.0	50	3	n.d
4[d]	**9a**	0.3	2.0	1	16	97 (*S*)
5[d]	**9a**	0.3	2.0	50	95	97 (*S*)
6[d]	**9a**	0.3	2.0	90	96	97 (*S*)
7[d]	**9b**	0.3	2.0	1	<1	n.d.
8[d]	**9b**	0.3	2.0	50	62	96 (*S*)
9[d]	**9b**	0.3	2.0	90	77	96 (*S*)
10	**3a**	0.6	2.0	1	>99	99 (*S*)
11[d]	**3a**	0.6	2.0	50	>99	98 (*S*)
12	**3b**	0.6	2.0	1	>99	99 (*S*)
13[d]	**3b**	0.6	2.0	50	>99	98 (*S*)
14[d]	**3a**	0.6	0.2	50	26	63 (*S*)
15[d]	**3b**	0.6	0.2	50	24	68 (*S*)
16[d]	**3a**	0.1	2.0	50	39	86 (*S*)

[a]Yields were determined by GC analysis. [b]Enantioselectivities were determined by HPLC on a chiral stationary phase. [c]Results reported in ref 8b. [d]Average values of at least two experiments.

In summary, these results demonstrate that the NHC-based complexes **3a**,**3b** are converted to dinuclear hydride-bridged iridium complexes under hydrogenation conditions in the absence of hydrogenation substrates. In contrast to their counterparts derived from N,P ligands, they show no tendency to form trinuclear complexes.

Hydrogenation Reactions. With these new iridium hydride complexes in hand, we decided to examine their reactivity as hydrogenation catalysts. Catalyst **4** has been previously reported to hydrogenate (*E*)-1,2-diphenyl-1-propene (**12**) with full conversion and an enantiomeric excess of 85% (entry 1 of Table 1).[11] The dinuclear iridium complex **7** showed almost no conversion to the corresponding alkane **13** under the same reaction conditions at 1 or 50 bar hydrogen pressure and 0.2 and 2.0 M substrate concentrations (entries 2−4). This was expected, since acetonitrile is a relatively strong ligand, and coordinating species are known to strongly inhibit catalysts of this type.[1c] Monitoring CD_2Cl_2 solutions of complex **7** under 1 bar hydrogen gas or in the presence of **12** (1 equiv) by ^{1}H NMR spectroscopy showed no change in the hydride region after 16 h. Next, we tested the dinuclear iridium complex **8** prepared according to eq 2, in which the two acetonitrile ligands were replaced by more weakly bound dichloromethane molecules. Under standard conditions (0.2 M) at 1, 50, and 100 bar, no conversion to the alkane was observed. However, significant amounts of byproducts were formed, which resulted from acid-catalyzed dimerization of alkene **12** (entries 5−7).[28] These side reactions were likely caused by proton transfer from acidic iridium hydride species[26] present in the reaction mixture. When the substrate concentration was increased to 2.0 M, the dinuclear iridium complex **8** showed some weak activity at 1 bar. However, at 50 and 100 bar, it afforded the alkane in 57% and 71% yield with 71% and 79% ee, respectively (entries 8−10). At this concentration, less than 13% byproducts were formed. Apparently, the dinuclear iridium complex **8** was converted to an active catalyst under these conditions. However, the

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conversion and enantioselectivity were lower than those in hydrogenations with the mononuclear precatalyst **4**.

Burgess and co-workers[8b] reported full conversion and 98% ee for this hydrogenation reaction using their catalyst **3a**, whereas complex **3b**, with a *tert*-butyl instead of an adamantyl substituent in the oxazoline ring, gave significantly lower conversion and ee (Table 2, entries 1 and 2). As expected, the bis-acetonitrile complex **10** showed almost no activity (entry 3). On the other hand, the dinuclear complex **9a** with two vacant coordination sites proved to be an active and highly enantioselective catalyst. Whereas, at 1 bar hydrogen pressure, only 16% conversion was observed after the standard reaction time of 2 h, almost full conversion with the same ee of 97% was achieved at 50 and 90 bar (entries 4−6). The analogous complex **9b** with a *tert*-butyl instead of an adamantyl group was inactive at 1 bar hydrogen pressure, but led to 77% conversion with 96% ee at 90 bar (entries 7−9). Surprisngly, the enantioselectivity induced by the dinuclear complex **9b** was much higher than the reported value for the corresponding mononuclear complex **3b** (entries 2 and 8). This prompted us to reinvestigate the hydrogenation of **12** with complexes **3a** and **3b** at 1 and 50 bar hydrogen pressure. In all reactions, we consistently observed full conversion and >98% ee (entries 10−13).[29] Remarkably, the performance strongly depended on the substrate concentration. A decrease in the alkene concentration from 2 to 0.2 M resulted in a much lower conversion and enantioselectivity (entries 14−15). Similar results were obtained for the dinuclear iridium hydride complexes **9a** and **9b** (see the Supporting Information, Table S6). Lowering the catalyst loading of complex **3a** to 0.1 mol % also decreased the conversion and enantiomeric excess (entry 16, Table 2).

CONCLUSIONS

Previous studies of iridium hydrides derived from phosphinooxazoline complexes were carried out in THF,[10] which stabilizes these reactive species by coordination. However, for catalytic hydrogenations, weakly coordinating solvents, such as dichloromethane, have to be used, because coordinating solvents or additives deactivate the catalyst. We have shown here that iridium hydride complexes can be prepared in dichloromethane under hydrogenation conditions in the absence of substrate and characterized by NMR and X-ray analysis. In contrast to the mononuclear dihydride complexes obtained in THF, dinuclear complexes with two bridging hydrides and two terminal hydride ligands are formed in CH_2Cl_2. These complexes prepared from the N,P ligand complex **4** and analogous NHC-based catalysts, developed by Burgess et al.,[8] are coordinatively unsaturated (28-electron configuration of the Ir_2 core) with a vacant coordination site at each Ir center. In the case of the N,P ligand complexes, the two vacant coordination sites are occupied by two weakly bound CH_2Cl_2 molecules in the crystal structure, whereas the NHC-based analogues are stabilized by agostic interactions between these sites and adjacent alkyl groups of the C,N ligand.

Both the N,P and the C,N hydride complexes show catalytic activity in the hydrogenation of (*E*)-1,2-diphenyl-1-propene, with enantioselectivities similar to those recorded for the corresponding mononuclear Ir(COD) precursors. While it seems unlikely that the dinuclear hydride complexes are the actual catalysts, our results indicate that they are converted to an active (presumably mononuclear) species under the reaction conditions.

The C,N dinuclear hydride complexes proved to be remarkably stable despite their coordinatively unsaturated 28-electron Ir_2 core. In contrast to analogous N,P complexes, they were cleanly formed in high yields upon treatment of the Ir(COD) precursors **3a** and **3b** with H_2 in pure CH_2Cl_2, whereas the hydrogenation of the N,P analogue **4** gave substantial amounts of a stable catalytically inactive trinuclear hydride complex. The conversion to Ir_3 hydride clusters is a known deactivation pathway for N,P iridium catalysts, presumably proceeding through dinuclear hydride complexes of the type described in this work. Notable in this context is our finding that formation of a trinuclear complex can be suppressed by addition of the strong Brønsted acid $[H(OEt_2)_2]BAr_F$. In continuation of this work, we are currently exploring the reactivity of iridium hydride complexes toward olefins, with the aim of identifying potential hydrogenation intermediates.

EXPERIMENTAL SECTION

General Information. All reactions and manipulations with air- or moisture-sensitive materials were carried out under an atmosphere of argon using standard Schlenk techniques. Schlenk tubes were heated in an oven (120 °C) and then dried under high vacuum. CH_2Cl_2 was dried over CaH_2 and then distilled under argon. CH_3CN and pentane were dried and degassed using a solvent purification system (PureSolv, Innovation Technology Inc.). Dry hexane was purchased in septum-sealed bottles from Aldrich and stored over 4 Å molecular sieves under argon. CD_2Cl_2 was distilled (bulb-to-bulb) over CaH_2, degassed by three freeze−pump−thaw cycles, and stored over 4 Å molecular sieves under argon. All commercially available starting materials were purchased from commercial sources and used as received. [Ir(L1)(COD)]BAr_F (**4**),[11] [Ir(L2)(COD)]BAr_F (**3a**),[8b] Ir(L3)(COD)]BAr_F (**3b**),[8b] and $[H(OEt_2)_2]BAr_F$[30] were synthesized according to literature procedures.^{1}H, ^{13}C, ^{31}P, and 2D NMR spectra were recorded with a Bruker Advance 400 (400 MHz) and a Bruker Advance DRX-500 (500 MHz) spectrometer. Chemical shifts (δ) are given in parts per million and referenced relative to TMS for ^{1}H and ^{13}C NMR spectra and H_3PO_4 for ^{31}P NMR spectra. ^{1}H 2D NOESY spectra were acquired using a standard three-pulse sequence and a mixing time of 700 ms.

X-ray Analyses. Data sets were obtained using a Bruker Kappa Apex2 diffractometer (graphite monochromated Mo Kα radiation, λ = 0.71073 Å) at 123 K. The structures were solved by direct methods using the program SIR92.[31] CRYSTALS[32] was used for structure refinement. The crystallographic data and *R* values of the full-matrix least-squares refinements are given in Tables S7 (**6**), S8 (**7**), S9 (**8**), and S10 (**9b**), respectively (see the Supporting Information). All atoms except hydrogen atoms and atoms of disordered molecules were refined with anisotropic displacement parameters. In general, H atoms were placed at calculated positions based on stereochemical considerations and refined according to the riding model. The crystallographic data of complexes **6** (CCDC 943439), **7** (CCDC 943440), **8** (CCDC 943442), and **9b** (CCDC 943441) can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis of [IrH(CH_3CN)(L1)(μ-H)]$_2$(BAr_F)$_2$ (7). Iridium complex **4** (150 mg, 99 μmol) was added to a 4 mL vial and dissolved in CH_3CN (1.0 mL), and the vial was placed into an autoclave. The autoclave was purged with hydrogen for 30 s, pressurized to 50 bar of hydrogen, and sealed. The reaction mixture was stirred at 900 rpm for 2 h at room temperature. After release of hydrogen, the solution was transferred into a Schlenk tube. The solvent was completely evaporated under vacuum, and the residue was dried at 0.3 mbar for 1 h. The colorless residue was dissolved in CH_2Cl_2 (1 mL). The solvent was then completely evaporated under vacuum, and the residue was dried at 0.3 mbar at 333 K for 8 h. This procedure was repeated two times. The resulting yellow residue was washed with a mixture of CH_2Cl_2/hexane (3/1, 2 × 0.7 mL) and dried under vacuum

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to afford complex **7** as a yellow solid (121 mg, 84%). A CH_2Cl_2 solution (0.5 mL) of this solid (10 mg) was layered with hexane (2 mL) and stored at 4 °C, to afford crystals of **7** suitable for X-ray diffraction. ^{1}H NMR (500 MHz, CD_2Cl_2, 233 K): δ 7.70−7.60 (m, 20H, BAr_F-*H* + $H_{arom.}$), 7.54−7.39 (m, 22H, BAr_F-*H* + $H_{arom.}$), 7.29−7.25 (m, 2H, $H_{arom.}$), 4.57 (t, 1H, *J* = 10 Hz, C-5-H_a), 4.49−4.38 (m, 3H, C-5′-H_a, C-5-H_b + C-5′-H_b), 3.94−3.92 (m, 1H, C-1-*H*), 3.75−3.73 (m, 1H, C-1′-*H*), 2.38−2.34 (m, 2H, C-2-*H* + C-2′-*H*), 1.91 (s, 3H, C-11-*H*), 1.78 (s, 3H, C-11′-*H*), 1.76 (s, 3H, C-9′-*H*), 1.73 (s, 3H, C-9-*H*), 1.45 (s, 3H, C-8-*H*), 1.37 (s, 3H, C-8′-*H*), 0.77 (d, 3H, *J* = 6.5 Hz, C-3′-*H*), 0.68−0.66 (m, 6H, C-4′-*H* + C-4-*H*), 0.54 (d, 3H, *J* = 6.6 Hz, C-3-*H*), −17.77−(−18.00) (m, 2H, Ir-H'_μ + Ir-H_μ), −20.04 (d, 1H, *J* = 18.7 Hz, Ir-H'_t), −20.24 (dd, 1H, *J* = 19.7 Hz, *J* = 3.2 Hz, Ir-H_t). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2, 295 K): δ 169.8 (d, $^3J_{CP}$ = 5 Hz, *C*-6′), 169.1(d, $^3J_{CP}$ = 5 Hz, *C*-6), 162.1 (q, $^1J_{CB}$ = 50 Hz, *C*-BAr_F), 136.9 ($C_{arom.}$), 136.2 ($C_{arom.}$), 135.8 ($C_{arom.}$), 135.3 ($C_{arom.}$), 135.2 (*C*-BAr_F), 134.0−130.0 (9 × $C_{arom.}$), 129.3 (q, $^2J_{CF}$ = 32 Hz, *C*-BAr_F), 129.2−128.6 (3 × $C_{arom.}$), 125.0 (q, $^1J_{CF}$ = 272 Hz, *C*-BAr_F), 121.0 (d, $^3J_{CP}$ = 10 Hz, *C*-10), 120.8 (d, $^3J_{CP}$ = 10 Hz, *C*-10′), 117.9 (br s, *C*-BAr_F), 80.7 (d, $^2J_{CP}$ = 7 Hz, *C*-7′), 80.6 (d, $^2J_{CP}$ = 7 Hz, *C*-7), 78.5 (*C*-1′), 74.2 (*C*-1), 70.1 (*C*-5), 70.0 (*C*-5′), 29.6 (*C*-2), 28.5 (*C*-2′), 27,6 (d, $^3J_{CP}$ = 7 Hz, *C*-9′), 27.4 (d, $^3J_{CP}$ = 6 Hz, *C*-9), 26.4 (d, $^3J_{CP}$ = 3 Hz, *C*-8), 26.3 (d, $^3J_{CP}$ = 3 Hz, *C*-8′), 18.8 (*C*-4′), 18.4 (*C*-4), 13.6 (*C*-3′), 12.7 (*C*-3), 3.0 (*C*-11), 2.3 (*C*-11′). ^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2, 295 K): 71.1 (*P*-B), 67.8 (*P*-A). Anal. Calcd for $C_{110}H_{86}B_2F_{48}Ir_2N_4O_4P_2$: C, 45.44; H, 2.98, N, 1.93. Found: C, 45.32; H, 2.95, N, 1.93. ESI-MS (CH_2Cl_2, 323 K): *m*/*z* 591 ([M − 2 × BAr_F]$^{2+}$).

[IrH(CH_2Cl_2)(L1)(μ-H)]$_2$(BAr_F)$_2$ (8). Iridium complex **4** (15 mg, 9.9 μmol, 1.0 equiv) and [H(OEt_2)$_2$][BAr_F] (100 mg, 4.3 μmol, 0.5 equiv) were added to a Schlenk tube and dissolved in CH_2Cl_2 (0.5 mL). The Schlenk tube was placed in liquid N_2 until the yellow solution froze. The Schlenk tube was then evacuated and purged with hydrogen gas (balloon), and the solution was allowed to warm up to room temperature. After stirring for 20 min at that temperature, the solvent was completely evaporated. The remaining yellow solid was washed with a mixture of CH_2Cl_2/pentane (3/1, 3 × 0.5 mL) and dried at 0.3 mbar for 16 h. ^{1}H NMR spectroscopy of this material indicates formation of one major species (>95%). A CH_2Cl_2 solution (0.5 mL) of this solid (10 mg) was layered with hexane (2 mL) and stored at 4 °C, to afford crystals of **7** suitable for X-ray diffraction. The ^{1}H NMR spectrum of a dissolved crystal in CD_2Cl_2 showed two hydride signals at −16.15 and −26.46 ppm and the ^{31}P{^{1}H} NMR spectrum one signal at 72.0 ppm (see the Supporting Information).

Synthesis of [IrH(L2)(μ-H)]$_2$(BAr_F)$_2$ (9a). Iridium catalyst **3a** (100 mg, 62 μmol) was added to a Schlenk tube and dissolved in CH_2Cl_2 (4.0 mL). The Schlenk tube was placed in liquid N_2 until the yellow solution froze. The Schlenk tube was then evacuated and purged with hydrogen gas (balloon), and the solution was allowed to warm up to room temperature. After stirring for 30 min at room temperature, the solvent was completely evaporated under vacuum. The resulting yellow foam was washed with hexane (3 × 1.5 mL) and dried at 0.3 mbar for 16 h to afford complex **9a** as a yellow solid (93 mg, 95%). ^{1}H NMR (500 MHz, CD_2Cl_2, 295 K): δ 7.73 (br s, 16H, BAr_F-*H*), 7.57 (br s, 8H, BAr_F-*H*), 7.38 (t, 2H, *J* = 7.7 Hz, C-12-*H*), 7.28 (dd, 2H, *J* = 7.8 Hz, *J* = 1.2 Hz, C-13-*H*), 7.14 (dd, 2H, *J* = 7.8 Hz, *J* = 1.2 Hz, C-11-*H*), 6.96 (d, 2H, *J* = 2.0 Hz, C-7-*H*), 6.95 (d, 2H, *J* = 2.0 Hz, C-6-*H*), 4.76 (dd, 2H, *J* = 9.7 Hz, *J* = 9.7 Hz, C-2-H_a), 4.37−4.33 (m, 2H, C-3-*H*), 4.30 (dd, 2H, *J* = 9.3 Hz, *J* = 5.8 Hz, C-2-H_b), 4.11 (dd, 2H, *J* = 15.2 Hz, *J* = 8.2 Hz, C-5-H_b), 3.74 (dd, 2H, *J* = 15.2 Hz, *J* = 9.2 Hz, C-5-H_a), 2.73−2.65 (m, 2H, C-18-*H*), 2.37−2.31 (m, 2H, C-4-H_a), 2.10−2.05 (m, 2H, C-4-H_b), 2.00 (br s, 6H, C-23-*H*), 1.95 (br d, 6H, C-22-*H*), 1.83 (br d, 6H, C-24-*H*), 1.62 (br d, 6H, C-24-*H*), 1.52−1.48 (m, 2H, C-15-*H*), 1.32 (d, 6H, *J* = 6.8 Hz, C-17-*H*), 1.30 (d, 6H, *J* = 6.8 Hz, C-20-*H*), 1.10−1.07 (m, 12H, C-22-*H* + C-19-*H*), 0.92 (d, 6H, *J* = 6.8 Hz, C-16-*H*), −18.40 (s, 2H, Ir-H_μ), −36.85 (s, 2H, Ir-H_t). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2, 295 K): δ 181.6 (*C*-1), 162.2 (q, $^1J_{CB}$ = 50 Hz, *C*-BAr_F),147.5 (*C*-10), 145.5 (*C*-14), 137.6 (*C*-9), 135.2 (*C*-BAr_F), 133.4 (*C*-8), 130.3 (*C*-12), 129.3 (q, $^2J_{CF}$ = 32 Hz, *C*-BAr_F), 126.7 (*C*-6), 125.0 (q, $^1J_{CF}$ = 272 Hz, *C*-BAr_F), 124.6 (*C*-7), 124.4 (*C*-11), 124.3 (*C*-13), 117.9 (br s, *C*-BAr_F), 74.1 (*C*-2), 66.9 (*C*-3), 46.0 (*C*-5), 37.2 (*C*-21), 36.3 (*C*-22), 35.8 (*C*-24), 34.6 (*C*-4), 29.9 (*C*-18), 29.1 (*C*-15), 27.7 (*C*-23), 25.9 (*C*-19), 25.8 (*C*-16), 23.8 (*C*-20), 22.3 (*C*-17). Anal. Calcd for $C_{124}H_{110}B_2F_{48}Ir_2N_6O_2$: C, 49.08; H, 3.65, N, 2.77. Found: C, 49.26; H, 3.72; N, 2.83. HR ESI-MS (CH_2Cl_2, 333 K) Calcd *m*/*z* for ($[C_{60}H_{86}N_6O_2Ir_2]^{2+}$: 654.3031. Found: 654.3027.

Synthesis of [IrH(L3)(μ-H)]$_2$(BAr_F)$_2$ (9b). Iridium catalyst **3b** (100 mg, 65 μmol) was added to a Schlenk tube and dissolved in CH_2Cl_2 (2.0 mL). The Schlenk tube was placed in liquid N_2 until the yellow solution froze. The Schlenk tube was then evacuated and purged with hydrogen gas (balloon), and the solution was allowed to warm up to room temperature. After stirring for 5 h at room temperature, the solvent was completely evaporated under vacuum. The resulting yellow foam was washed with hexane (3 × 1 mL) to afford a yellow solid, which was dissolved in CH_2Cl_2 (1.5 mL) and layered with hexane (5 mL). The yellow crystals formed during 48 h at −4 °C were separated from the mother liquor and dried at 0.3 mbar for 16 h to afford complex **9b** (84 mg, 90%). These crystals were used for X-ray analysis. ^{1}H NMR (500 MHz, CD_2Cl_2, 243 K): δ 7.71 (br s, 16H, BAr_F-*H*), 7.55 (br s, 8H, BAr_F-*H*, 7.37 (t, 2H, *J* = 7.6 Hz, C-12-*H*), 7.23 (d, 2H, *J* = 7.6 Hz, C-13-*H*), 7.17 (d, 2H, *J* = 7.6 Hz, C-11-*H*), 6.97 (br s, 4H, C-6-*H* + C-7-*H*), 4.82 (dd, 2H, *J* = 10.0 Hz, *J* = 10.0 Hz, C-2-H_a), 4.50−4.45 (m, 2H, C-3-*H*), 4.40 (dd, 2H, *J* = 9.5 Hz, *J* = 6.1 Hz, C-2-H_b), 4.20 (dd, 2H, *J* = 15.0 Hz, *J* = 8.2 Hz, C-5-H_b), 3.69 (dd, 2H, *J* = 15.0 Hz, *J* = 10.0 Hz, C-5-H_a), 2.73−2.67 (m, 2H, C-4-H_a), 2.37−2.31 (m, 2H, C-18-*H*), 2.08−2.03 (m, 2H, C-4-H_b), 1.78−1.72 (m, 2H, C-15-*H*), 1.22 (d, 6H, *J* = 6.8 Hz, C-17-*H*), 1.19 (d, 6H, *J* = 6.8 Hz, C-20-*H*), 1.01 (d, 6H, *J* = 6.8 Hz, C-19-*H*), 0.88 (d, 6H, *J* = 6.8 Hz, C-16-*H*), 0.80 (s, 18H, C-22-*H*), −18.90 (s, 2H, Ir-H_μ), −34.45 (s, 2H, Ir-H_t). In addition, the spectrum shows weak signals of minor isomers, which are in equilibrium with the major component according to the ^{1}H 2D exchange spectrum (see the Supporting Information).^{13}C{^{1}H} NMR (125 MHz, CD_2Cl_2, 243 K): δ 181.4 (*C*-1), 161.8 (q, $^1J_{CB}$ = 50 Hz, *C*-BAr_F), 147.3 (*C*-10), 145.0 (*C*-14), 136.9 (*C*-9), 134.8 (*C*-BAr_F), 132.2 (*C*-8), 130.3 (*C*-12), 128.8 (q, $^2J_{CF}$ = 32 Hz, *C*-BAr_F), 126.2 (*C*-6), 124.6 (q, $^1J_{CF}$ = 272 Hz, *C*-BAr_F), 124.3 (*C*-13), 123.8 (*C*-7 + C-11), 117.6 (br s, *C*-BAr_F), 73.9 (*C*-2), 66.1 (*C*-3), 45.7 (*C*-5), 34.2 (*C*-21), 32.5 (*C*-4), 28.9 (*C*-18), 28.4 (*C*-15), 26.0 (*C*-19), 25.5 (*C*-16), 23.4 (*C*-22), 22.3 (*C*-17), 22.0 (*C*-20). Anal. Calcd for $C_{112}H_{98}B_2F_{48}Ir_2N_6O_2$: C, 46.74; H, 3.43, N, 2.92. Found: C, 46.46; H, 3.34, N, 3.03. ESI-MS (CH_2Cl_2, 323 K): *m*/*z* 576 ([M − 2×BAr_F]$^{2+}$).

Synthesis of [Ir($H)_2$($CH_3CN)_2$(L3]BAr_F (10). Iridium catalyst **9b** (30.0 mg, 10.4 μmol) was added to a Schlenk tube and dissolved in CH_3CN (1.0 mL). The resulting solution was stirred for 1 h at room temperature, and the solvent was evaporated under vacuum. The residue was dissolved in CH_2Cl_2 (1.0 mL), and the solvent was completely removed at 0.3 mbar. This procedure was repeated two times. The resulting residue was dried at 0.3 mbar for 16 h to afford complex **10** as a pale yellow solid (31 mg, 95%). ^{1}H NMR (500 MHz, CD_2Cl_2, 263 K): δ 7.72 (br s, 8H, BAr_F-*H*), 7.56 (br s, 4H, BAr_F-*H*), 7.46 (t, 1H, *J* = 7.8 Hz, C-12-*H*), 7.26 (dd, 1H, *J* = 7.8 Hz, *J* = 1.2 Hz, C-11-*H*), 7.24 (dd, 1H, *J* = 7.8 Hz, *J* = 1.2 Hz, C-13-*H*), 6.98 (d, 1H, *J* = 1.9 Hz, C-6-*H*), 6.87 (d, 1H, *J* = 1.9 Hz, C-7-*H*), 4.53 (dt, 1H, *J* = 13.7 Hz, *J* = 3.3 Hz, C-5-H_a), 4.13−4.05 (m, 2H, C-2-H_a + C-3-*H*), 4.01 (br d, 1H, *J* = 7.5 Hz, C-2-H_b), 3.90 (dd, 1H, *J* = 13.7 Hz, *J* = 2.9 Hz, C-5-H_b), 2.29 (s, 3H, C-3′-*H*), 2.27−2.21 (m, 5H, C-15-*H*, C-18-*H* + C-1′-*H*), 2.04−1.97 (m, 1H, C-4-H_a), 1.74−1.68 (m, 1H, C-4-H_b), 1.35 (s, 9H, C-22-*H*), 1.24 (d, 3H, *J* = 6.9 Hz, C-17-*H*), 1.22 (d, 3H, *J* = 6.9 Hz, C-20-*H*), 1.03 (d, 3H, *J* = 6.9 Hz, C-16-*H*), 1.00 (d, 3H, *J* = 6.9 Hz, C-19-*H*), −21.93 (d, 1H, *J* = 7.3 Hz, Ir-H_a), −26.12 (d, 1H, *J* = 7.3 Hz, Ir-H_b). ^{13}C{^{1}H} NMR (125 MHz, CD_2Cl_2, 263 K): δ 179.4 (*C*-1), 161.9 (q, $^1J_{CB}$ = 50 Hz, *C*-BAr_F), 154.2 (*C*-8), 146.0 (*C*-14), 145.6 (*C*-10), 138.0 (*C*-9), 134.9 (*C*-BAr_F), 129.7 (*C*-12), 128.9 (q, $^2J_{CF}$ = 32 Hz, *C*-BAr_F), 124.7 (q, $^1J_{CF}$ = 272 Hz, *C*-BAr_F), 124.1 (*C*-13), 124.0 (*C*-11), 123.2 (*C*-7), 120.6 (*C*-6), 119.8 (*C*-4′), 118.1 (*C*-2′), 117.7 (br s, *C*-BAr_F), 71.9 (*C*-2), 70.7 (*C*-3), 45.6 (*C*-5), 36.2 (*C*-4), 34.9 (*C*-21), 28.7 (*C*-15), 28.6 (*C*-18), 27.9 (*C*-22), 25.3 (*C*-16), 25.1 (*C*-19), 22.1 (*C*-17), 21.9 (*C*-20), 4.6 (*C*-3′), 3.4 (*C*-1′). Anal. Calcd for $C_{60}H_{55}BF_{24}IrN_5O$: C, 47.38; H, 3.64; N, 4.60. Found: C,

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47.42; H, 3.66; N, 4.91. ESI-MS (CH_2Cl_2, 323 K): m/z 617 ([M − BAr_F − CH_3CN]$^+$).

Synthesis of [Ir(H)$_2$(L3)(6,6′-Bi-2-picoline)]BAr$_F$ (11). *Method A.* Iridium complex **3b** (50.0 mg, 32.4 μmol, 1.0 equiv) and 6,6′-dimethyl-2,2′-bipyridine (59.6 mg, 323.5 μmol, 10.0 equiv) were added to a Schlenk tube and dissolved in CH_2Cl_2 (2.5 mL). The Schlenk tube was placed in liquid N_2 until the yellow solution froze. The Schlenk tube was then evacuated and purged with hydrogen gas (balloon), and the solution was allowed to warm up to room temperature. After stirring for 4 h at that temperature, the solvent was removed under vacuum. The residue was washed with hexane (3 × 6 mL) and dried at 0.3 mbar to afford complex **11** as an orange solid (46 mg, 87%).

Method B. Iridium complex **9b** (10.0 mg, 3.5 μmol, 1.0 equiv) and 6,6′-dimethyl-2,2′-bipyridine (6.4 mg, 34.7 μmol, 10.0 equiv) were added to a Schlenk tube and dissolved in CH_2Cl_2 (1.0 mL). After stirring at room temperature for 16 h, the solvent was evaporated under vacuum. The residue was washed with hexane (3 × 2 mL) and dried at 0.3 mbar for 16 h to afford complex **11** as an orange solid (10 mg, (90%). ^{1}H NMR (500 MHz, CD_2Cl_2, 295 K): δ 7.93−7.90 (m, 2H, C-5′-*H* + C-8′-*H*), 7.80−7.75 (m, 2H, C-4′-*H* + C-9′-*H*), 7.73 (br s, 8H, BAr_F-*H*), 7.56 (br s, 4H, BAr_F-*H*), 7.43−7.42 (m, 2H, C-3′-*H* + C-10′-*H*), 7.28 (t, 1H, J = 7.8 Hz, C-12-*H*), 7.13 (dd, 1H, J = 7.8 Hz, J = 1.2 Hz, C-11-*H*), 7.10 (d, 1H, J = 1.9 Hz, C-6-*H*), 6.98 (dd, 1H, J = 7.8 Hz, J = 1.2 Hz, C-13-*H*), 6.91 (d, 1H, J = 1.9 Hz, C-7-*H*), 4.88−4.80 (m, 2H, C-3-*H* + C-5-H_a), 4.19 (dd, 1H, J = 8.7 Hz, J = 7.2 Hz, C-2-H_a), 4.09 (dd, 1H, J = 8.7 Hz, J = 1.2 Hz, C-2-H_b), 4.02 (ddd, 1H, J = 13.6 Hz, J = 6.2 Hz, J = 3.0 Hz, C-5-H_b), 2.76 (s, 3H, C-1′-*H*), 2.65 (s, 3H, C-12′-*H*), 2.40−2.33 (m, 1H, C-18-*H*), 2.29−2.21 (m, 2H, C-4-H_a + C-15-*H*), 1.82 (ddt, 1H, J = 13.6 Hz, J = 11.3 Hz, J = 2.8 Hz, C-4-H_b), 1.32 (d, 3H, J = 6.9 Hz, C-17-*H*), 1.06 (d, 3H, J = 6.9 Hz, C-16-*H*), 0.96 (d, 3H, J = 6.9 Hz, C-19-*H*), 0.59 (s, 9H, C-22-*H*), 0.34 (d, 3H, J = 6.9 Hz, C-20-*H*), −21.92 (d, 1H, J = 7.3 Hz, Ir-H_a), −28.62 (d, 1H, J = 7.3 Hz, Ir-H_b). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2, 295 K): δ: 180.7 (*C-1*), 162.0 (q, $^1J_{CB}$ = 50 Hz, *C*-BAr_F), 162.2 (*C-2′*), 161.5 (*C-11′*), 159.6 (*C-6′*), 158.4 (*C-7′*), 158.2 (*C-8*), 146.4 (*C-10*), 145.3 (*C-14*), 138.5 (*C-9*), 138.2 (*C-4′*), 137.7 (*C-9′*), 135.2 (*C*-BAr_F), 129.6 (*C-12*), 129.0 (q, $^2J_{CF}$ = 32 Hz, *C*-BAr_F), 127.3 (*C-10′*), 126.9 (*C-3′*), 125.0 (q, $^1J_{CF}$ = 272 Hz, *C*-BAr_F), 124.6 (*C-11*), 123.9 (*C-7*), 123.8 (*C-13*), 121.5 (*C-5′*), 121.1 (*C-6*), 120.9 (*C-8′*), 117.9 (br s, *C*-BAr_F), 73.7 (*C-3*), 72.9 (*C-2*), 46.6 (*C-5*), 36.3 (*C-4*), 34.5 (*C-21*), 30.8 (*C-1′*), 28.9 (*C-18*), 28.9 (*C-15*), 27.3 (*C-22*), 26.6 (*C-12′*), 25.3 (*C-16*), 24.7 (*C-19*), 22.8 (*C-17*), 21.4 (*C-20*). Anal. Calcd for $C_{68}H_{61}BF_{24}IrN_5O$: C, 50.32; H, 3.79; N, 4.31. Found: C, 50.22; H, 4.02; N, 4.24. ESI-MS (CH_2Cl_2, 323 K): m/z 760 ([M − 2×BAr_F]$^{2+}$).

Hydrogenation Reactions. The hydrogenation experiments were performed as previously described for the corresponding catalysts **4**[11] and **3a**.[8b]

■ ASSOCIATED CONTENT

Supporting Information

Additional spectroscopic data and complete labeling of the complexes is given. Crystallographic data for **6**, **7**, **8**, and **9b** in CIF format. 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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■ ABBREVIATIONS

L1 = (*S*)-1-[2-(2-adamantan-2-yl-4,5-dihydrooxazol-4-yl)-ethyl]-3-(2,6-diisopropylphenyl)-1,2-dihydroimidazol-2-ylidene; L2 = (*S*)-1-[2-(2-adamantan-2-yl-4,5-dihydrooxazol-4-yl)-ethyl]-3-(2,6-diisopropylphenyl)-1,2-dihydroimidazol-2-ylidene; L3 = (*S*)-1-[2-(2-*tert*-butyl-4,5-dihydrooxazol-4-yl)-ethyl]-3-(2,6-diisopropylphenyl)-1,2-dihydroimidazol-2-ylidene; COD = 1,5-cyclooctadiene; Cy = cyclohexyl; py = pyridine; BAr_F = tetrakis[3,5-bis(trifluoromethyl)phenyl]-borate; NHC = N-heterocyclic carbene; n.d. = not determined

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