ORGANOMETALLICS

Synthesis and Characterization of Iridium(I) and Iridium(III) Complexes Containing Dialkylbiphenylphosphines

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Supporting Information

ABSTRACT: The synthesis and characterization of iridium complexes containing the PCy₂biPh ligand (PCy₂biPh = 2-(dicyclohexylphosphino)biphenyl), is described. Chloride abstraction from (COD)Ir(PCy₂biPh)Cl with Na(BAr_F)₄ affords [(COD)Ir(PCy₂biPh)][B(Ar_F)₄] (1, Ar_F = 3,5bis(trifluoromethyl)phenyl). Heating 1 in benzene results in dehydrogenation of one of the cyclohexyl groups on the phosphine ligand with COD serving as the hydrogen acceptor, leading to the new complex 2, with benzene coordinated in an η^6 fashion to the metal center. Complex 1 reacts with H₂ to produce the Ir(III) dihydride complex [(PCy₂biPh)IrH₂][B(Ar_F)₄] (3). Initial studies of transfer dehydrogenation and attempts at benzene hydrogenation using 1 and 3 are described.



T he use of iridium complexes to catalyze hydrogenation and dehydrogenation reactions is well documented in the literature.¹ Typically, the iridium catalysts employed contain phosphine ligands and one or more weakly coordinating ligands that can be readily displaced, allowing for substrate binding. The use of arenes as labile ligands has been investigated for a variety of transition metals, including Rh,^{2–5} Ag,⁶ Ru,^{7–9} Pd,¹⁰ Ni,¹¹ and Ir.¹² More recently, Werner and Oro reported an Ir(III) dihydride complex containing a bulky phosphine ligand with an alkyl aryl group, which can coordinate to iridium in an η^6 fashion and is less labile than nonchelating arenes.¹³ This type of combination ligand is potentially useful for catalytic hydrogenation.

Dialkylbiarylphosphine ligands have been extensively used in palladium-catalyzed coupling reactions.¹⁴ It is proposed that the Pd catalyst stability is enhanced by metal—arene interactions with the pendent ring.¹⁵ Although these ligands have been widely utilized in Pd-catalyzed amination chemistry,¹⁶ the application of this class of ligand toward other metal-catalyzed processes has remained underexplored.^{17–20}

We are interested in exploring whether the arene stabilization observed in Pd complexes could be utilized at other metal centers. A few reports have detailed the synthesis of dialkyl biaryl phosphine Ir complexes and the applications of these complexes in catalysis. In 2009, Tsuji reported the addition of aromatic acyl chlorides to terminal alkynes using an iridium catalyst and a biarylphosphine ligand.²¹ Dahlenburg described a neutral Ir(I) COD complex containing a (di-*tert*-butylphosphino)-2-methylbiphenyl (^tBu₂PbiPh^{Me}) ligand. Aryl cyclometalation was observed, yielding a four-membered iridacycle species, consistent with DFT calculations.²² Previously, we reported the synthesis of Rh(I) and Rh(III) complexes containing dialkylbiarylphosphines.²³ The rhodium complexes were not thermally stable; decomposition was observed upon heating at 60 °C. To date there have been limited reports of iridium complexes containing the PCy_2biPh ($PCy_2biPh = 2$ -(dicyclohexylphosphino)biphenyl) ligand.²⁴ In an effort to synthesize more robust arene-stabilized complexes for hydrogenation reactions, we report the synthesis and characterization of new iridium compounds containing the PCy_2biPh ligand.

RESULTS AND DISCUSSION

Synthesis of $[(COD)Ir(PCy_2biPh)][B(Ar_F)]_4$ (1). Reaction of $(COD)Ir(PCy_2biPh)Cl^{24}$ with $Na(BAr_F)_4$ in CH_2Cl_2 led to removal of the chloride ligand and yielded compound 1 as a red powder (eq 1).



X-ray quality red block crystals of 1 were obtained by vapor diffusion of pentane into a concentrated CH_2Cl_2 solution and the molecular structure of 1 was determined by X-ray diffraction (Figure S1, Supporting Information). The coordination geometry about iridium is approximately square planar, with coordination of both olefin bonds in COD, phosphorus, and an η^2 -arene moiety. The last group is evidenced by close contacts of the C1 and C6 aryl carbons with the iridium center

Received: March 30, 2013 Published: July 1, 2013 (Ir–C₁ = 2.49 Å and Ir–C₆ = 2.44 Å). A similar η^2 coordination mode has been reported in related Pd complexes^{25,26} and was observed in the analogous complex (COD)Rh(PCy₂biPh)⁺. Notably the aryl carbon distances to the metal are shorter for Ir in comparison to Rh (2.53 and 2.60 Å).²³ Longer Ir–C_{olefin} bond distances are observed for the olefin of COD that is trans to phosphorus (2.24 and 2.23 Å) relative to those trans to the η^2 -aryl (2.14 and 2.15 Å) due to the stronger trans influence of phosphorus.

Two broad singlets (2H each) at 3.88 and 3.36 ppm are observed for the olefinic hydrogens of the bound COD ligand. The upfield shift of the doublet (2H) at 6.86 ppm (${}^{3}J_{H-H} = 5.0$ Hz) in the aromatic region suggests arene coordination. The upfield resonance at 119.7 ppm in the 13 C NMR also indicates that the arene moiety is coordinated η^{2} to Ir. The 31 P NMR spectrum of complex 1 exhibits a singlet at 33.7 ppm. In contrast to the Rh analogue, there is no indication of dynamic behavior of the COD moiety.²³

Thermolysis of Complex 1 in Aromatic Solvents. New products are observed when complex 1 is heated in benzene or toluene (eq 2). Complex 1 is sparingly soluble in nonpolar



aromatic solvents at room temperature but is soluble at higher temperatures. Heating a solution of 1 in C₆H₆ for 5 h at 100 °C leads to a color change from deep red to pale yellow. After the volatiles were removed under vacuum and the residue was redissolved in CD₂Cl₂, the ¹H NMR spectrum exhibited a singlet at 6.55 ppm (6H). This signal can be attributed to the symmetric coordination of benzene to iridium. Two multiplets were observed at 4.26 (1H) and 4.20 (1H) ppm, which were assigned to the olefinic hydrogen atoms of the dehydrogenated cyclohexyl group coordinated to the metal. No hydride signals were visible, and a new singlet at 56.2 ppm was evident in the ³¹P NMR spectrum. The NMR data are consistent with dehydrogenation of a cyclohexyl ring and trapping of an unsaturated Ir center with benzene. Hydrogen obtained from the cyclohexyl group was transferred to the COD ligand and was released as COE. Formation of COE was clearly evident in the ¹H NMR spectrum when the reaction was performed in benzene- d_6 and was also verified by GC-MS. A similar complex with an η^6 -bound toluene was observed when complex 1 was heated to 100 °C in toluene. Full characterization of benzene complex 2 and the corresponding toluene complex can be found in the Supporting Information.

X-ray-quality crystals of **2** were grown at room temperature from a benzene solution. The molecular structure of **2** was determined by X-ray crystallography (Figure 1). η^2 coordination of the alkene moiety is identified by close Ir₁ to C₄₁ and C₄₂ contacts (2.14 and 2.15 Å, respectively). The C₄₁-C₄₂ bond length (1.43 Å) is shortened relative to the other C-C distances in the cyclohexene ring (1.49–1.54 Å). The other ligands coordinated to the iridium center are the phosphine and an η^6 -benzene. The pendent aromatic ring on the phosphine ligand is uncoordinated. The Ir-C_{benzene} bond lengths are in the range of 2.25–2.32 Å.

Dehydrogenation of a cyclohexyl moiety has precedent with PCy₃-containing metal complexes. Weller observed dehydro-



Figure 1. ORTEP drawing of the cationic portion of complex 2. H atoms have been omitted for clarity.

genation of a cyclohexyl ring in $\{H_2RhPCy_3\}(closo-CB_{11}H_6Br_6)$,²⁷ and Sabo-Etienne observed dehydrogenation of the cyclohexyl group of PCy₃ in Ru hydride complexe.²⁸ Vrieze observed dehydrogenation of a cyclohexyl ring of PCy₃ in an iridium complex.²⁹ In complex **1**, the bulky biphenyl moiety positions a cyclohexyl ring close to the metal, with a close contact between the iridium center and a C–H bond $(Ir_1-H_{28B} = 2.84 \text{ Å})$. This interaction may facilitate the dehydrogenation reaction.

Reaction of Cationic Complex 1 with H₂. Reaction of 1 with H₂ in CD_2Cl_2 at room temperature resulted in a rapid color change from red to pale yellow. In the ¹H NMR spectrum, the signals for bound COD were no longer observed and the formation of cyclooctane was seen (1.53 ppm). A doublet at -14.1 ppm (²J_{P-H} = 23 Hz) was observed, indicative of a metal hydride complex. Removal of the solvent under vacuum allowed isolation of complex 3 as an air-stable solid (eq 3).



The dihydride complex 3 was fully characterized. In the ¹H NMR spectrum, three distinct signals at 6.93 (2H, t, ${}^{3}J_{H-H} = 6.0$ Hz), 6.46 (1H, t, ${}^{3}J_{H-H} = 6.0$ Hz), and 6.37 (2H, d, ${}^{3}J_{H-H} = 6.1$ Hz) ppm, shifted upfield in the aromatic region, were observed, while the remaining aromatic signals were downfield in the range of 7.45–7.70 ppm. In the ¹³C NMR spectrum, three resonances attributed to a coordinated arene were observed at 103.8 (s), 96.7 (s), and 86.8 (d, $J_{P-C} = 8.8$ Hz) ppm. These chemical shifts are consistent with those of other η^{6} -arene complexes.¹³ A singlet at 55.1 ppm was observed in the ³¹P NMR spectrum.

The solid-state structure of compound **3** was determined by X-ray crystallography (Figure 2). X-ray-quality crystals were grown by vapor diffusion of pentane into a dichloromethane solution of **3** at -21 °C. Two molecules of **3** were contained within the unit cell with nearly identical structures. Complex **3** exhibits a three-legged piano-stool geometry, in which the arene moiety of the phosphine biphenyl group is coordinated in an η^6 fashion to Ir. A similar geometry was proposed for the previously reported cationic Rh(III) dihydride analogue on the basis of NMR spectroscopy.²³ The observed geometry is also



Figure 2. ORTEP drawing of the cationic portion of complex 3. Carbon-bound H atoms and solvent are omitted for clarity.

analogous to an Ir(I) η^6 -coordinated arene complex reported by Werner.¹³ The arene ring of complex 3 remains nearly planar. The Ir–C_{arene} distances range from 2.20 to 2.31 Å, in the typical range of η^6 -arene coordination to Ir.^{13,30} Additionally, the Ir–P bond length has shortened to 2.24 Å in comparison to the Ir–P bond length (2.31 Å) of 1, wherein the iridium is formally Ir(I). The stronger Ir–P bond in 3 highlights the electrophilic nature of the cationic Ir(III) complex.

Reactivity of Ir(III) Dihydride Complex 3. Thermal Stability. The thermal stability of the iridium dihydride complex 3 was evaluated in a variety of solvents. Heating a sample of 3 at 60 °C in CD_2Cl_2 resulted in no change. Heating complex 3 in $C_2D_4Cl_2$ to at 130 °C resulted in slight decomposition after 5 days. New aromatic resonances indicate counteranion decomposition, but no other products were identified.

Transfer Dehydrogenation. Complexes 1 and 3 were screened for transfer dehydrogenation of cyclooctane with TBE as a hydrogen acceptor (eq 4). At 155 °C, 13 turnovers were achieved after 5 days with 0.2 mol % of complex 3 as a catalyst. With complex 1, 22 turnovers were observed after 5 days at 155 °C.



Arene Hydrogenation. Heating a CD_2Cl_2 solution of 3 (7.4 mol % loading) in the presence of C_6H_6 resulted in only 5% conversion to cyclohexane after 3 days at 60 °C. After 3 days the sample darkened substantially to an orange-brown from near colorless but no precipitate was observed. The major species observed by ¹H NMR was the dihydride complex 3. Heating a neat solution of anisole at 125 °C with 1.7 or 0.8 mol % loading of 3 under 90 psi of H₂ resulted in no change in the ¹H NMR spectrum. Complex 3 is still present in solution after 2.5 days at 125 °C, as identified by ¹H NMR spectroscopy. Decomposition of complex 3 was observed after 1 day upon raising the temperature to 145 °C. Arene coordination prevents the generation of open coordination sites at the metal center.

The synthesis and characterization of Ir(I) and Ir(III) complexes containing the ligand PCy₂biPh have been described. The structure of the cationic Ir(I) complex 1 includes an η^2 interaction of a pendent phenyl ring. Dehydrogenation of one of the cyclohexyl rings is observed upon heating 1 in benzene to yield the new Ir(I) complex 2, which exhibits a three-legged piano-stool geometry. Addition of

 H_2 to complex 1 yields the Ir(III) dihydride complex 3 with hydrogenation of COD. Complexes 1 and 3 catalyze COA dehydrogenation to COE in the presence of an H_2 acceptor. It is likely that the arene moiety of 3 is strongly bound to the metal center and is difficult to displace, impeding further reactivity with H_2 .

EXPERIMENTAL SECTION

General procedures and materials are found in the Supporting Information. (COD)Ir(PCy₂biPh)Cl was previously reported.²⁴ All ¹H NMR spectra were measured in CD₂Cl₂ at 25 °C (500 MHz).

[(COD)Ir(PCy₂biPh)][B(Ar_F)₄] (1). A flask was charged with (COD)Ir(PCy₂biPh)Cl (100 mg, 0.15 mmol) in air. NaB(Ar_F)₄ (140 mg, 0.16 mmol) was added in a glovebox. The solids were dissolved in CH₂Cl₂ (10 mL), generating a dark red solution with a precipitate. The sample was stirred for 1 h and then filtered in air. The solvent was removed, yielding 1 as a red powder (230 mg, 0.15 mmol, 100%). ¹H NMR: δ 7.61 (t, J_{H-H} = 6.9 Hz, 1H), 7.51 (m), 6.88 (m, 1H), 6.84 (d, ³J_{H-H} = 7.1 Hz, 2H), 3.88 (br s, 2H, COD HC=), 3.36 (br s, 2H, COD HC=), 2.34 (br q, J_{H-H} = 9.7 Hz), 2.02 (m), 1.87 (m), 1.75 (m), 1.58 (m), 1.33 (m), 1.18 (m). Anal. Calcd for C₆₄H₅₅BF₂₄IrP: C, 50.74; H, 3.66. Found: C, 50.04; H, 3.50.

Thermolysis of 1 in Benzene. In air, a J. Young style NMR tube was charged with 6 mg of 1, and then benzene (420 mg) was added by vacuum transfer. The dark red suspension was degassed and heated (100 °C) overnight, affording a pale yellow solution. The solvent was removed to yield a pale yellow powder. COE was detected by NMR and GC-MS. Characteristic ¹H NMR signals for **2**: δ 8.46 (ddd, *J* = 18 Hz, *J* = 6 Hz, *J* = 3 Hz, 1H), 7.48–7.15 (Ar of biphenyl, 6H), 6.53 (s, bound C₆H₆), 5.61 (COE), 4.25 (m, 1H, olefinic), 4.21 (m, 1H, olefinic), 2.67 (m), 1.45 (COE), 2.13–0.64 (m, Cy).

[H₂Ir(PCy₂biPh)][B(Ar_F)₄] (3). (COD)Ir(PCy₂biPh)Cl (100 mg, 0.15 mmol) was added to a dry flask in air. Na(BAr_F)₄ (150 mg, 0.17 mmol) was added in the drybox. The solids were dissolved in dry CH₂Cl₂ (6.0 mL), yielding a red solution with a precipitate. H₂ was then bubbled through the sample for 15 min, giving a near-colorless solution. The solvent was removed to yield a pale yellow powder, which was dissolved in a minimal amount of CH₂Cl₂ and filtered in air to give a pale yellow powder (210 mg, 0.15 mmol, 100%). ¹H NMR: *δ* 7.70 (overlapping with Ar_F H_{*o*}, 1H), 7.64 (br t, ³J_{H-H} = 7.4 Hz, 1H), 7.59 (overlapping with Ar_F H_{*p*} 1H), 7.47 (t, ³J_{H-H} = 8.1 Hz, 1H), 6.93 (t, ³J_{H-H} = 6.0 Hz, 2H, H₂), 6.46 (t, ³J_{H-H} = 6.0 Hz, 1H, H₁), 6.37 (t, ³J_{H-H} = 6.1 Hz, 2H, H₃), 2.11 (m, 2H), 1.85 (br m, 4H), 1.76 (br m, 2H, Cy), 1.68 (br m, 2H), 1.48 (br m, 2H), 1.37–1.14 (m, 8H), 0.99 (m, 2H), -14.1 (d, 2H, ²J_{P-H} = 23 Hz, H₄). Anal. Calcd for C₅₆H₄₅F₂₄BPIr: C, 47.77; H, 3.22. Found: C, 47.71; H, 3.09.

ASSOCIATED CONTENT

S Supporting Information

Text, tables, figures, and CIF files giving experimental details, X-ray crystallographic data for complexes 1-3, and details of crystallographic data collection. 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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