ACS Catalysis

Research Article

pubs.acs.org/acscatalysis

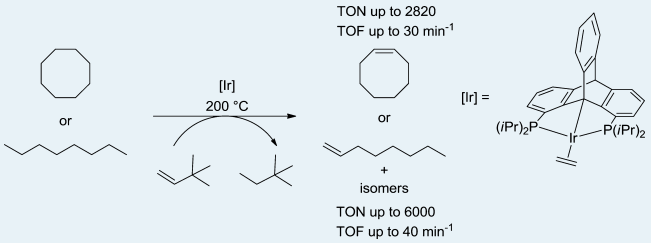
Applications of PC(sp^3)P Iridium Complexes in Transfer Dehydrogenation of Alkanes

David Bézier and Maurice Brookhart*

Department of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27599-3290, United States

Supporting Information

ABSTRACT: Iridium ethylene complexes based on the PC(sp^3)P pincer-type triptycene ligand have been synthesized. Complexes bearing various substituents on the phosphines have been investigated as catalysts in transfer dehydrogenation of alkanes. The complex **8a**, which bears isopropyl groups, has demonstrated high stability and activity when used as a catalyst in the disproportionation of 1-hexene at 180 °C and in the transfer dehydrogenation of linear and cyclic alkanes with *tert*-butylethylene as a hydrogen acceptor at 200 °C. A similar complex bearing a CH_2NMe_2 group, **33**, allowed support of the catalyst on γ-alumina for operation in a heterogeneous mode.



KEYWORDS: *pincer complexes, iridium, C−H activation, dehydrogenation, alkanes, supported catalyst*

INTRODUCTION

The selective cleavage and functionalization of C−H bonds has been a widely studied topic in organometallic chemistry in recent years.[1] The dehydrogenation of alkanes transforms inexpensive hydrocarbon feedstocks into olefins, which are valuable intermediates in the synthesis of fine chemicals and polymers. Industrially, catalytic alkane dehydrogenation is carried out on large scales using heterogeneous systems at high temperatures, which results in low product selectivities.[2]

The first use of homogeneous catalysts for transfer dehydrogenation of alkanes was reported independently by Crabtree and Felkin.[3] Turnover numbers (TONs) were limited due to catalyst decomposition at high temperatures. A major advance was the discovery of the robust and effective iridium pincer catalyst ($^{t\text{-Bu}}$PCP)IrH$_2$ **1a** (Figure 1) initially reported by

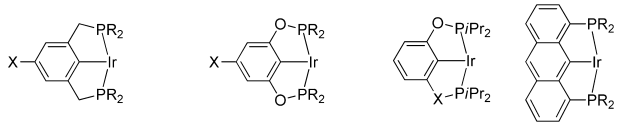


Figure 1. Examples of active PCP iridium pincer complexes for alkane dehydrogenation.

Kaska and Jensen and later studied extensively by Goldman.[4] Derivatives of this complex were further developed by modifying substituents on the phosphine (**1b**−**1d**),[4e,5] adding functional groups to the aromatic backbone (**1e**−**1g**),[6] replacing the phosphines by phosphinite groups (**2a**−**2d**),[7] creating hybrid complexes (**3a**,[8] **3b**[9]), and incorporating an anthracenyl group in the backbone (**4a**, **4b**).[8a,b,10]

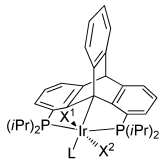
Many of these modifications provided improvement of the stability and the activity of the catalysts for the dehydrogenation of linear and cyclic alkanes.[11] These pincer complexes allowed the development of other significant applications such as alkane metathesis,[8c,12] alkane dehydroaromatization,[8a] and the synthesis of *p*-xylene from ethylene.[8b] New pincer complexes such as metallocene-based (PCP)Ir complexes,[13] (CCC)Ir carbene complexes,[14] (^{CF3}PCP)Ru complexes,[15] and 7−6−7 ring-based iridium complexes[16] have also demonstrated catalytic activity for alkane dehydrogenation.

The immobilization on solid supports of PCP and POCOP iridium complexes was reported by our group in collaboration with the Goldman group. Catalysts bearing basic functional groups (**1g**, **2c**, and **2d**) were successfully supported on alumina. The **2c**/Al_2O_3 system showed particularly high activity and recyclability for alkane dehydrogenation[17] and alkane metathesis.[12b]

In the quest for developing highly thermally stable catalysts for alkane dehydrogenation, we have been interested by the development of the PC(sp^3)P−Ir complexes.[18] The synthesis and applications of aliphatic C(sp^3)-metalated pincer complexes are far less common than their C(sp^2) analogues. These types of complexes often suffer from instability due to the presence of easily abstractable α- and β-hydrogens. Recently, dibenzobarrelene-based PC(sp^3)P−M pincer complexes (M = Ir,[19] Ru,[19b,h] Pt,[19b,20] Ni,[20a] Pd,[20] Rh[19g]) were described by Gelman and co-workers. In this family, iridium complexes based on the PC(sp^3)P triptycene ligand (Figure 2)[19a−d]

Received: June 23, 2014
Revised: August 20, 2014
Published: August 21, 2014

   dx.doi.org/10.1021/cs500892p | ACS Catal. 2014, 4, 3411−3420



X^1 = H, X^2 = Cl: L = PPh_3 (**5a**), CH_3CN (**5b**), CO (**5c**)
X^1 = H, X^2 = H: L = PPh_3 (**5d**)
X^1 = CO, X^2 = Cl: L = Cl (**5e**)

Figure 2. Iridium triptycene-based pincer complexes developed by Gelman.

showed interesting properties. The strong σ-donation of the metalated bridgehead sp^3 hybridized carbon combined with the lack of labile α- and β-hydrogens allowed robustness and stability of these complexes. The complexes **5c** and **5e** were found to be highly active when used as catalysts for the transfer hydrogenation of ketones in isopropanol.[19a,b] The transfer dehydrogenation of alcohols to form ketones was also demonstrated by using complex **5e** as a catalyst.[19c]

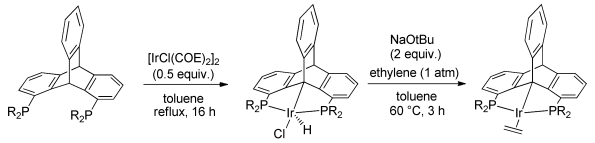
Particularly interested by this family of complexes and the possibility that they will exhibit high stabilities and turnover numbers, we decided to investigate their use as catalysts for alkane transfer dehydrogenation.

We report here the synthesis of a variety of iridium triptycene bis(phosphine) ethylene complexes bearing different alkyl substituents on the phosphine atoms and their use as catalysts in transfer dehydrogenation of alkanes. We also report the synthesis of complexes bearing basic functional groups, which allowed their support on γ-alumina for operation in a heterogeneous mode.

RESULTS AND DISCUSSION

Synthesis of Iridium Triptycene Bis(phosphine) Ethylene Complexes. Following the procedure developed by Gelman,[21] we synthesized 1,8-bis(phosphino)triptycene ligands by varying the group R carried on the phosphine (R = *i*Pr (**6a**), Cy (**6b**), Cp (**6c**), Scheme 1). These bis(phosphines) were

Scheme 1. Synthesis of Iridium Triptycene Bis(phosphine) Ethylene Complexes

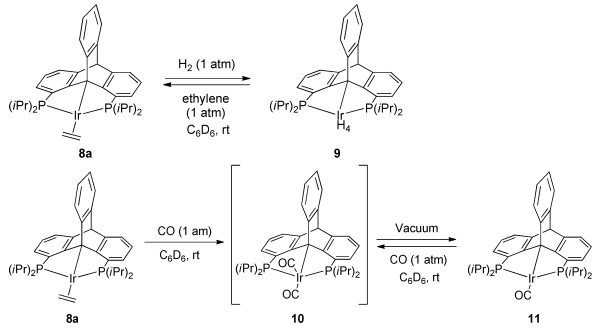


R = *i*Pr (**6a**), Cy (**6b**), Cp (**6c**) R = *i*Pr (**7a**), Cy (**7b**), Cp (**7c**) R = *i*Pr (**8a**), Cy (**8b**), Cp (**8c**)

treated with $[Ir(COE)_2Cl]_2$ at reflux in toluene to generate the corresponding hydridochloride iridium complexes 7**a**–7**c**. The structure of the complex **7a** has been confirmed by X-ray crystallography (see Supporting Information). Deprotonation with NaO*t*-Bu followed by addition of ethylene yielded the ethylene complexes (R = *i*Pr (**8a**), R = Cy (**8b**), R = Cp (**8c**)).

The ethylene complex **8a** ($^{31}P\{^1H\}$ NMR: δ = 62.54 (s)) can be reversibly transformed to the tetrahydride iridium complex **9** ($^{31}P\{^1H\}$ NMR: δ = 56.70 (s); ^1H NMR: −9.34 (t, J = 9.8 Hz, 4H)) by addition of H_2 (Scheme 2). The addition of CO to the complex **8a** allowed the in situ observation of the dicarbonyl complex **10**, which was converted to the monocarbonyl complex **11** ($^{31}P\{^1H\}$ NMR: δ = 56.70 (s); IR ν(CO) = 1946 cm^{-1}) under vacuum.

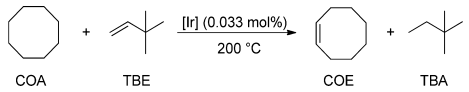
Scheme 2. Transformation of the Iridium Ethylene Complex 8a to the Tetrahydride and Carbonyl Complexes



8a **9** **8a** **10** **11**

Use of Iridium Bis(phosphine) Triptycene Ethylene Complexes as Catalysts for Transfer Dehydrogenation of Alkanes. The complexes **8a**, **8b**, and **8c** were first tested as catalysts for transfer dehydrogenation of cyclooctane (COA) with *tert*-butylethylene (TBE) as the hydrogen acceptor. Results are summarized in Table 1. A system containing 1.3

Table 1. TONs for the Transfer Dehydrogenation of COA and TBE Catalyzed by Complexes 8a, 8b, and 8c[a]



COA TBE COE TBA

entry	t [h]	8a	8b	8c
1	0.5	910		
2	1	1410		
3	2	2250		
4	4	2590		
5	6	2650		
6	24	2820	35	40

[a]TONs were calculated based on conversion of TBE determined by GC analysis. COA (15.2 mmol), TBE (15.2 mmol), [Ir] (0.005 mmol).

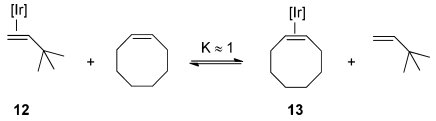
mM (5 μmol, 0.03 mol %) of iridium catalyst (**8a**, **8b**, or **8c**), COA (3.9 M, 15.2 mmol, 3030 equiv relative to Ir), and TBE (3.9 M, 15.2 mmol), was heated at 200 °C under argon in a sealed vessel. We found that the catalyst **8a** was highly active for the COA/TBE dehydrogenation. TONs of 910 and 2590 have been obtained after 30 min and 4 h, respectively (entry 1, 4). A total of 93% of the TBE was converted to TBA after 24 h (2820 turnovers with a ratio of COE/1,3-cyclooctadiene = 3:1). By comparison under similar conditions, the catalytic system ($^{t\text{-Bu}}$POCOP)IrHCl/NaO*t*-Bu is reported to yield a maximum TON of 1880.[9]

We also tested complexes **8b** and **8c** in similar conditions. Surprisingly, they demonstrated extremely low activities (TONs ≈ 40 after 24 h, entry 6).[22]

By monitoring the in situ reaction employing **8a**, the initially observed species was the Ir-TBE complex, **12** ($^{31}P\{^1H\}$ NMR: δ = 50.25 (d, J_{PP} = 320 Hz), 46.35 (d, J_{PP} = 320 Hz)) (Scheme 3). As the reaction proceeds and product COE accumulates, the Ir-COE complex **13** begins to appear ($^{31}P\{^1H\}$ NMR: δ = 57.06 (s)). Thus, like the (POCOP)Ir catalyst **2a**, the resting state(s) of the catalyst are the olefin complexes. It is noteworthy that the Ir(III) vinyl hydride, Ir(H)[CH=CHC-$(CH_3)_3$], generated from the oxidative addition of the TBE vinylic C–H bond, has never been detected in this system.[23] By

dx.doi.org/10.1021/cs500892p | ACS Catal. 2014, 4, 3411–3420

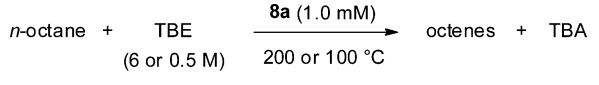
Scheme 3. Resting States of the Transfer Dehydrogenation of COA and TBE Catalyzed by 8a



carrying out competition experiments, we determined that the binding affinities of TBE and COE are the same (Scheme 3). In the case of Ir(POCOP) catalyst **2a**, the binding affinity of COE is much greater than TBE, and thus, catalysis is significantly inhibited as the concentration of COE builds.[7b] This is not the case here since TBE and COE exhibit similar binding affinities.

Next, we investigated the catalytic activity of **8a** for the transfer dehydrogenation of linear alkanes (Table 2). A solution

Table 2. Transfer Dehydrogenation of *n*-Octane with TBE Catalyzed by 8a[a]



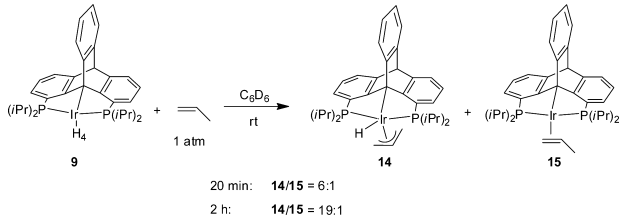
entry	*t* [min]	TON	1-octene [mM]	1-octene fraction [%][b]	*trans*-2-octene [mM]	*cis*-2-octene [mM]
1[c]	5	62	10	16	36	11
	10	135	10	7	57	28
	30	1205	27	2	302	41
	600	6000	6	0.1	487	163
2[d]	60	34	9	27	13	8
	120	91	18	19	46	13
	1740	500	6	1	192	55

[a]TONs were calculated based on conversion of TBE determined by GC analysis. [b]The fraction of 1-octene relative to the total of octenes. [c]Ir (1.0 mM), TBE (6 M), 200 °C. [d]Ir (1.0 mM), TBE (0.5 M), 100 °C.

of *n*-octane containing **8a** (1.0 mM, 3 μmol) and TBE (6.0 M, 18 mmol) was heated at 200 °C under argon (entry 1). After 5 min, 62 TONs were obtained in which 1-octene represented 16% of the total of octenes. The catalytic system has shown high activity (TOF up to 40 min^{-1}) and stability (TON = 6000 after 10 h) at 200 °C. By decreasing the reaction temperature to 100 °C with 0.5 M of TBE, the 1-octene represented up to 27% of the octenes after 1 h of reaction (TON = 34). Under these conditions, full conversion of TBE to TBA (TON = 500) was obtained after 29 h. From data in Table 2, it is clear that olefin isomerization occurs readily under these conditions. Because higher fractions of 1-octene are observed at lower TONs, it seems likely this olefin is the initially formed product and internal olefin isomers follow from rapid isomerization.[24]

The olefin isomerization mechanism by iridium pincer catalysts has been recently shown to proceed via a π-allyl mechanism involving a η^3-allyl iridium hydride intermediate.[25] In a previous study, the (POCOP)Ir system was shown to thermodynamically favor the η^2-olefin complex over the η^3-allyl hydride complex. After formation of the ($^{t\text{-Bu}}$POCOP)Ir(η^3-propenyl)(H) at −88 °C, this complex rapidly converts to the ($^{t\text{-Bu}}$POCOP)Ir(η^2-propene) at −58 °C. An important difference was observed when using the PC(sp^3)P−Ir system (Scheme 4). By exposing the PC(sp^3)P-IrH_4 **9** to 1 atm of propylene at room temperature, we observed the favored formation of the complex Ir(η^3-propenyl)(H) **14** ($^{31}P\{^1H\}$ NMR: δ 38.12 (d, J_{PP} = 338 Hz), 35.82 (d, J_{PP} = 338 Hz); ^1H NMR: −13.58 (dd, *J* = 22.4 Hz, *J* = 16.7 Hz, 1H)) over the Ir(η^2-propene) **15** ($^{31}P\{^1H\}$ NMR: δ 57.69 (d, J_{PP} = 300 Hz), 53.61 (d, J_{PP} = 300 Hz)) with a ratio **14**/**15** = 6:1 after 20 min and 19:1 after 2 h.[26]

Scheme 4. Formation of Ir(η^3-propenyl)(H) 14 and Ir(η^2-propene) 15



Recently, we reported the synthesis of *para*-xylene using ethylene as the sole feedstock. The important step of this reaction is the conversion of 1-hexene to 2,4-hexadiene by catalytic disproportionation. The catalytic activity of PC(sp^3)P−Ir **8a** in this reaction has been explored. The kinetic profile of 1-hexene disproportionation catalyzed by **8a** (0.04 mol %, 180 °C) was followed by GC (Figure 3). Under these

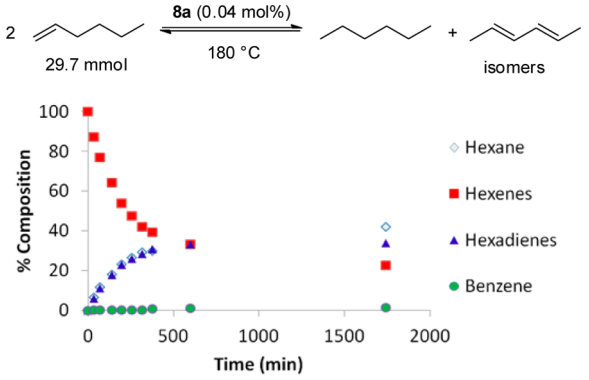


Figure 3. 1-Hexene disproportionation profile with **8a**.

conditions, 1-hexene is rapidly converted to a mixture of hexenes prior to significant hydrogen transfer and the hexadienes produced appear as the thermodynamic ratio of dienes. The reaction reaches equilibrium after 10 h under these conditions. The product distribution after 29 h is reported in Figure 4 and shows the formation of the (2*E*, 4*E*), (2*Z*-4*E*)-hexadienes and hexane as major products. In our previous report,[8b] we found that when using catalysts ($^{i\text{-Pr}}$POCCP)Ir **3a**

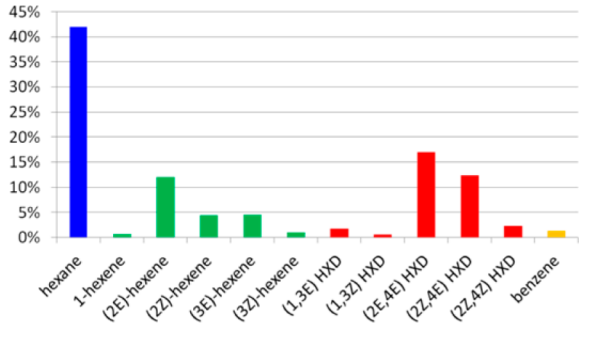
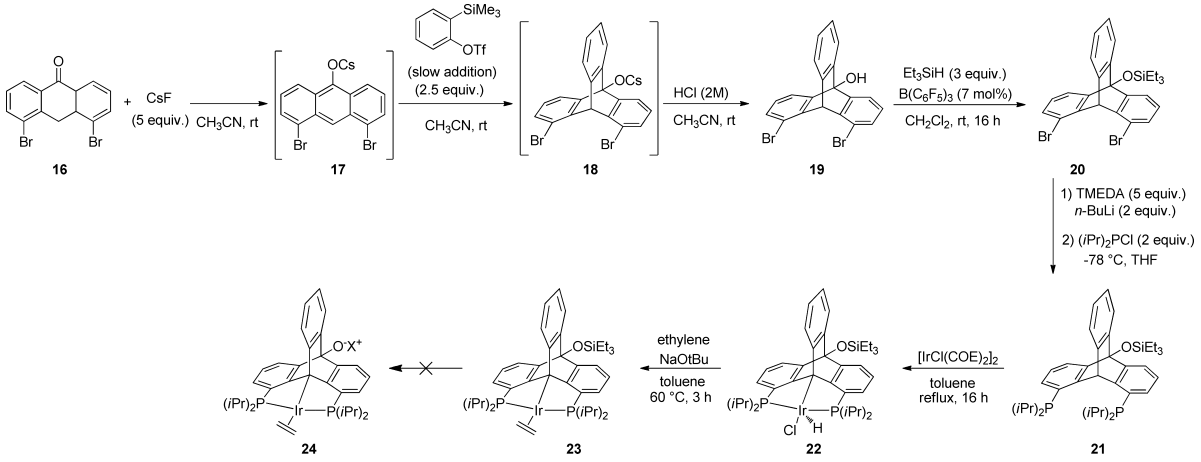


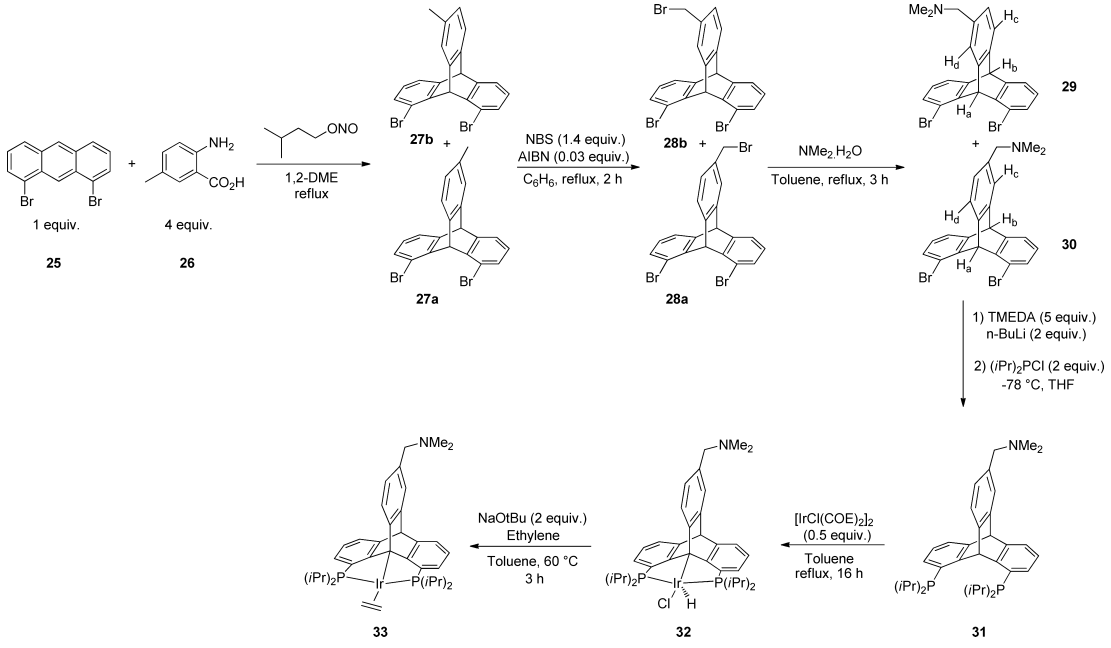
Figure 4. Product distribution after 29 h from disproportionation of 1-hexene with **8a**.

dx.doi.org/10.1021/cs500892p | ACS Catal. 2014, 4, 3411−3420

Scheme 5. Attempt of the Synthesis of the Alkoxide PC(sp^3)P−Ir Complex 24



Scheme 6. Synthesis of the Me$_2$NCH$_2$−PC(sp^3)P−Ir Complex 33



and anthraphos iridium complex **4b** under similar conditions, equilibrium was achieved after ca. 13 and 3.5 h, respectively. The catalysts ($^{t\text{-Bu}}$PCP)Ir **1a** and ($^{t\text{-Bu}}$POCOP)Ir **2a** have shown very low activity for this reaction. Complex PC(sp^3)P−Ir **8a** is a little less active than complex **4b** but demonstrates similar activity to complex **3a** in the disproportionation of 1-hexene.

Synthesis of Iridium Bis(phosphine) Triptycene Complexes Bearing a Basic Functional Group for Support on Alumina. Encouraged by the high activity and stability of the PC(sp^3)P−Ir complex **8a** as a catalyst for transfer dehydrogenation of alkanes, the synthesis of similar complexes bearing a basic functional group on the backbone of the triptycene has been investigated. We previously reported the highly active and recyclable heterogeneous system (OK-POCOP)IrH$_2$ (**2c**)/Al$_2$O$_3$ as a catalyst for alkane metathesis[12b] and transfer dehydrogenation of cyclooctane.[17]

Inspired by these results, we targeted the synthesis of the alkoxide PC(sp^3)P−Ir **24** (Scheme 5). Deprotonation of the 1,8-dibromoanthrone **16** with CsF in acetonitrile formed the 1,8-dibromoanthracene alkoxide **17** which reacted with benzyne (generated in situ from the reaction between the 2-(trimethylsilyl)phenyl trifluoromethanesulfonate and excess CsF) to form the dibromotriptycene alkoxide **18**. After protonation and protection with Et$_3$SiH/B(C$_6$F$_5$)$_3$, the dibromotriptycene triethylsilylether **20** was isolated. Lithium halogen exchange and addition of the diisopropylchlorophosphine generated the bis(diisopropylphosphine) derivative **21**, which was successfully converted to the iridium hydridochloride complex **22**. After addition of ethylene and NaO*t*-Bu, the ethylene complex **23** (^{31}P{^{1}H} NMR: δ = 62.30 ppm (s)) was isolated. However, all attempts to deprotect the triethylsilyl ether group to generate the alkoxide compound **24** have been unsuccessful, thwarting the ability to support the complex on alumina.

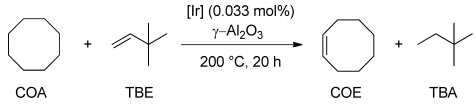
Noting our previous report showing that Me$_2$N-PCP-Ir **1g** could be supported on alumina,[17] we decided to explore an alternate strategy and incorporate a −NMe$_2$ group on the triptycene backbone. The synthesis of the complex Me$_2$NCH$_2$−PC(sp^3)P−Ir, **33**, is outlined in Scheme 6. Starting from the dibromoanthracene **25**, the reaction with the methylbenzyne

dx.doi.org/10.1021/cs500892p | ACS Catal. 2014, 4, 3411−3420

(generated in situ from the reaction between the 2-amino-5-methylbenzoic acid **26** and the oxidant) formed the two isomers of dibromo(methyl)triptycene **27a** and **27b** in a 1:1 ratio. Bromination, followed by nucleophilic substitution with dimethylamine yielded the two amines, **29** and **30**, which were separated by chromatography on silica gel. NOESY experiments allowed easy distinction between the two amines by the observation of an NOE enhancement between the protons H_a–H_d and H_b–H_c in **29** and **30**. The amine **30** was transformed to the corresponding bis(diisopropylphosphine)triptycene **31** which was further converted to the iridium ethylene complex **33** ($^{31}P\{^1H\}$ NMR: δ = 62.59 ppm (s)).

Supported Iridium Bis(phosphine) Triptycene 33 as a Catalyst for the Transfer Dehydrogenation of Alkanes. Various types of γ-aluminas (basic, Na_2CO_3 modified, acidic, neutral, low soda) were screened as the supports for the iridium catalyst. We used our previously reported conditions[17] to support in situ the iridium complex **33** on γ-Al_2O_3. By mixing the iridium complex (5 μmol) **33** in cyclooctane, an orange solution was obtained. When 250 mg of γ-Al_2O_3 was added, the solution was completely decolorized, and the alumina acquired the orange color of the iridium complex. In contrast, a similarly treated solution of **8a** retained the orange color. After addition of TBE, the reaction was heated at 200 °C and monitored by GC (Table 3).

Table 3. Transfer Dehydrogenation of COA and TBE Catalyzed by 33/Al_2O_3[a]



		TON	
entry	γ-Al_2O_3	NMe_2CH_2– $PC(sp^3)P$–Ir **33**	$PC(sp^3)P$–Ir **8a**
1		2040	2800
2	basic	185	20
3	Na_2CO_3- modified	235	
4	neutral	1230	
5	low soda	1250	20
6	acidic	70	

[a]TONs were calculated based on conversion of TBE determined by GC analysis. COA (15.2 mmol), TBE (15.2 mmol), Ir (0.005 mmol).

By first comparing the activity of the catalyst **33** with the catalyst **8a** in a homogeneous mode (without γ-Al_2O_3), we observed similar activities for the two catalysts (TONs = 2040 and 2800, respectively, entry 1). The supported systems (**33**/γ-Al_2O_3) were investigated, and modest catalytic activities were obtained due to the fast decomposition of the catalytic systems. Best results were achieved with TONs of 1230 and 1250 by using neutral and low soda γ-Al_2O_3, respectively (entry 4, 5). Very low TONs were obtained when other types of γ-Al_2O_3 were used. Test reactions were conducted by mixing the complex **8a** with basic and low soda γ-Al_2O_3. TONs of 20 have been achieved in both cases demonstrating direct inhibition of the catalytic activity in the presence of γ-Al_2O_3. Consequently, by supporting the complex **33** on γ-Al_2O_3 (neutral and low soda), we stabilized the catalytic system by limiting direct interaction between the alumina and the iridium center. However, the stabilization was not sufficient to achieve a highly stable, recyclable heterogeneous catalytic system.

CONCLUSIONS

Syntheses of new $PC(sp^3)P$–Ir(ethylene) pincer complexes based on the triptycene ligand have been achieved. The iridium ethylene complex **8a** bearing isopropyl substituents on phosphorus shows exceptionally high activity and stability as a catalyst for the transfer dehydrogenation of linear and cyclic alkanes at 200 °C and for the disproportionation of 1-hexene at 180 °C. The synthesis of similar complexes bearing basic functionalities in the backbone has been described. The complex bearing a NMe_2CH_2– substituent, **33**, has been successfully supported on γ-alumina. Modest catalytic activity has been observed for the transfer dehydrogenation of alkanes when using this supported catalyst, but the catalyst lifetime is limited due to degradation by reaction with the alumina support. Other types of supports are now under investigation in our laboratories in an effort to circumvent this problem.

EXPERIMENTAL SECTION

General Considerations. All manipulations were carried out under an argon atmosphere using standard Schlenk, high-vacuum, and glovebox techniques. Argon was purified by passing through columns of BASF R3–11 catalyst (Chemalog) and 4 Å molecular sieves. Benzene-d_6, toluene-d_8, *p*-xylene-d_{10}, CD_2Cl_2, and $CDCl_3$ (Cambridge Isotope Laboratories) were used without purification. THF, *n*-hexane, *n*-pentane, and toluene were distilled from sodium, then degassed by three freeze–pump–thaw cycles and stored in an argon atmosphere glovebox. Cyclooctane (COA) (99%), *tert*-butylethylene (TBE) (98.5%), *n*-octane (99%), and 1-hexene were purchased from Aldrich and dried over Na overnight. These reagents were then distilled under vacuum and stored in an argon atmosphere glovebox prior to use. Acidic, neutral, low soda, and basic γ-Al_2O_3 were purchased from Strem, calcined at 400 °C under a flow of oxygen for 16 h, and stored under argon. 1,8-Dibromoanthracene,[21] 1,8-dibromotriptycene,[21] and $[Ir(COE)_2Cl]_2$[27] were prepared according to previously reported procedures. All other reagents and solvents mentioned in this text were purchased from commercial sources and used as received. NMR spectra were recorded on Bruker spectrometers (DRX-400, AVANCE-400, AVANCE-500, and AVANCE-600). ^1H and ^{13}C NMR spectra were referenced to residual solvent peaks. ^{31}P NMR chemical shifts were referenced to an external H_3PO_4 standard. Gas chromatographic analysis of reactions was conducted on an Agilent Technologies 6850 GC instrument fitted with a fused silica capillary column (100 m length × 0.25 mm ID × 0.50 μm film thickness) using the following parameters: FID detector: temperature = 300 °C, initial temperature: 40 °C, final temperature: 250 °C, oven program: 40 °C, hold for 20 min, ramp 1:85 °C/min to 150 °C, hold for 5 min, ramp 2:10 °C/min to 250 °C, hold for 20 min. Calibration curves were prepared using standard samples. Products were confirmed using authentic samples and calibrated with an internal standard (mesitylene). High-resolution mass spectrometer (HRMS) analyses were carried out by the Mass Spectrometry Facility at UNC. Elemental analyses were carried out by Atlantic Microlab, Inc. of Norcross, GA. X-ray diffraction studies were conducted on a Bruker-AXS SMART APEXII diffractometer. Crystals were selected and mounted using Paratone oil on a MiteGen Mylar tip. Complexes **7b**, **7c**, **8b**, **8c**, and **32** are highly soluble in hydrocarbon solvents, unable to be crystallized, and are not stable to column chromatography, and therefore, inevitably

dx.doi.org/10.1021/cs500892p | ACS Catal. 2014, 4, 3411–3420

they contain some solvent as an impurity and do not pass elemental analysis. However, all of these complexes show a single ^{31}P resonance for symmetrical structures and only two ^{31}P signals in one case where two isomers are present (**7c**).

General Procedure for the Synthesis of 1,8-Bis(phosphino)triptycene 6a−6c. The bis(phosphines) were synthesized following the procedure reported by Gelman.[21] To a cold stirred solution (−78 °C) of 1,8-dibromotriptycene (1.5 g, 3.64 mmol) and TMEDA (2.8 mL, 18.2 mmol) in dry THF (18 mL) was added *n*-BuLi (1.6 M, 4.6 mL, 7.28 mmol) over a period of 30−35 min. The solution was stirred for an additional 15 min, and the chlorophosphine (7.28 mmol) solution in THF (1 mL) was added dropwise. The solution was allowed to reach room temperature and then refluxed for 1 h. After cooling to room temperature, ethyl acetate (20 mL) was added under air; the organic phase was successively washed with sodium bicarbonate and water, dried on Na_2SO_4, and evaporated. The white solid was washed three times with MeOH, affording the product as a white powder.

1,8-Bis(diisopropylphosphino)triptycene ***6a.*** Following the general procedure, 1.06 g (2.18 mmol, 60%) of compound **6a** was obtained from 1.2 mL (7.28 mmol) of diisopropylchlorophosphine. The product was obtained as described previously.[21]

1,8-Bis(dicyclohexylphosphino)triptycene ***6b.*** Following the general procedure, 1.70 g (2.62 mmol, 72%) of compound **6b** was obtained from 1.6 mL (7.28 mmol) of dicyclohexylchlorophosphine. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): δ −16.67 (s). ^1H NMR ($CDCl_3$, 400 MHz): δ 7.50 (t, J = 6.3 Hz, 1H), 7.37−7.33 (m, 4H), 7.11 (d, J = 7.7 Hz, 2H), 6.97−6.93 (m, 4H), 5.37 (s, 1H), 2.05−1.99 (m, 6H), 1.83−1.80 (m, 4H), 1.65−1.49 (m, 11H), 1.43.1.05 (m, 19H), 0.95−0.83 (m, 6H). HRMS (m/z): $[M + H]^+$ calcd for $C_{44}H_{56}P_2$, 647.3936; found, 647.3926.

1,8-Bis(dicyclopentylphosphino)triptycene ***6c.*** Following the general procedure, 0.97 g (1.64 mmol, 45%) of compound **6c** was obtained from 1.4 mL (7.28 mmol) of dicyclopentylchlorophosphine. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): δ −17.80 (s). ^1H NMR ($CDCl_3$, 400 MHz): δ 7.53−7.51 (m, 1H), 7.39−7.34 (m, 4H), 7.16 (m, 2H), 6.99−6.96 (m, 4H), 5.37 (s, 1H), 2.28 (m, 2H), 1.98 (m, 6H), 1.71 (m, 6H), 1.58−1.40 (m, 18H), 1.28 (m, 4H). HRMS (m/z): $[M + H]^+$ calcd for $C_{40}H_{48}P_2$, 591.3310; found, 591.3293.

General Procedure for the Synthesis of PC(sp^3)P−Ir(H)(Cl) 7a−7c. $[IrCl(COE)_2]_2$[27] (0.255 g, 0.28 mmol) was added to a solution of 1,8-bis(phosphino)triptycene **6a−6c** (0.59 mmol) in 10 mL of toluene. The contents were stirred at reflux overnight. After evaporation of the solvent, the orange residue was washed six times with 15 mL of cold pentane and dried under vacuum to afford the product as an orange solid.

$^{i\text{-Pr}}$PC(sp^3)P−Ir(H)(Cl) 7a. Following the general procedure, 0.180 g (0.252 mmol, 45%) of compound **7a** was obtained from 0.286 g (0.59 mmol) of 1,8-bis(diisopropylphosphino)-triptycene **6a**. $^{31}P\{^1H$ NMR (C_6D_6, 162 MHz): δ 63.93 (s). ^1H NMR (C_6D_6, 600 MHz): δ 7.83 (d, J = 7.0 Hz, 1H), 7.14−7.10 (m, 2H), 6.94 (dd, J = 7.3 Hz, J = 1.3 Hz, 1H), 6.85−6.84 (m, 4H), 6.78 (td, J = 7.5 Hz, J = 1.3 Hz, 1H), 6.62 (td, J = 7.5 Hz, J = 1.2 Hz, 1H), 5.18 (s, 1H), 2.67−2.63 (m, 2H), 2.48−2.45 (m, 2H), 1.48 (q, J = 7.5 Hz, 6H), 1.11 (q, J = 7.8 Hz, 6H), 1.00 (q, J = 7.4 Hz, 6H), 0.88 (q, J = 7.2 Hz, 6H), −35.12 (t, J = 15.1 Hz, 1H). ^{13}C NMR (C_6D_6, 151 MHz): δ 168.8 (t, J = 15.8 Hz, 2C), 153.4, 146.8, 145.3 (t, J = 6.6 Hz, 2C), 134.8 (t, J = 23.0 Hz, 2C), 126.2 (2C), 125.8, 125.1 (t, J = 3.2 Hz, 2C), 124.7, 124.6 (2C), 123.8, 122.5, 54.7, 33.7 (d, J = 5.5 Hz, 1C), 28.8 (t, J = 12.1 Hz, 2C), 25.5 (t, J = 16.2 Hz, 2C), 20.5 (2C), 19.6 (t, J = 2.6 Hz, 2C), 19.5 (t, J = 2.6 Hz, 2C), 19.1 (2C). Anal. Calcd for $C_{32}H_{40}ClIrP_2$: C, 53.81; H, 5.64. Found: C, 53.95; H, 5.75.

^{Cy}PC(sp^3)P−Ir(H)(Cl) 7b. Following the general procedure, 0.210 g (0.241 mmol, 43%) of compound **7b** was obtained from 0.381 g (0.59 mmol) of 1,8-bis(dicyclohexylphosphino)-triptycene **6b**. The product was washed one time with cold pentane. $^{31}P\{^1H\}$ NMR (C_6D_6, 162 MHz): δ 56.76 (s). ^1H NMR (C_6D_6, 400 MHz): δ 7.90 (d, J = 7.3 Hz, 1H), 7.12−7.01 (m, 2H), 6.97−6.88 (m, 5H), 6.79−6.76 (t, J = 7.4 Hz, 1H), 6.68−6.64 (t, J = 7.4 Hz, 1H), 5.20 (s, 1H), 2.65 (m, 2H), 2.50−2.46 (m, 2H), 2.36−2.33 (m, 4H), 2.18−2.07 (m, 3H), 1.83 (m, 2H), 1.62−1.49 (m, 6H), 1.45−1.37 (m, 4H), 1.32−1.09 (m, 14H), 1.00−0.76 (m, 7H), −34.64 (t, J = 15 Hz, 1H).

^{Cp}PC(sp^3)P−Ir(H)(Cl) 7c. Following the general procedure, 0.325 g (0.241 mmol, 71%) of compounds were obtained as a mixture of two isomers **7c′** and **7c″** with a ratio 1:1 from 0.349 g (0.59 mmol) of 1,8-bis(dicyclopentylphosphino)triptycene **6c**. The products were not washed with cold pentane due to their high solubility in this solvent. Characteristic signals: **7c′**: $^{31}P\{^1H\}$ NMR (C_6D_6, 162 MHz): δ 54.10 (s). ^1H NMR (C_6D_6, 400 MHz): δ −34.64 (t, J = 15.5 Hz, 1H). **7c″**: $^{31}P\{^1H\}$ NMR (C_6D_6, 162 MHz): δ 31.90 (s). ^1H NMR (C_6D_6, 400 MHz): δ −28.56 (t, J = 15.6 Hz, 1H).

General Procedure for the Synthesis of PC(sp^3)P−Ir−ethylene 8a−8c. One equivalent (0.189 mmol) of the respective PC(sp^3)P−Ir(H)(Cl) (**7a-7c**) and 2.3 equiv of NaO-*t*-Bu (0.042 g, 0.435 mmol) were dissolved in toluene (10 mL) in a Kontes Flask, filled with 1 atm of ethylene, and stirred at 60 °C for 48 h. The solvent was evaporated under high vacuum, and the Kontes flask was transferred to the glovebox, pentane was added, and the solution was filtered through a 0.2 μm pore size syringe filter (Nalgene 199−2020) into another Schlenk flask. The solvent was removed in vacuo to afford the corresponding PC(sp^3)P−Ir−ethylene complexes **8a−8c** as orange powders.

$^{i\text{-Pr}}$PC(sp^3)P−Ir−ethylene 8a. Following the general procedure, 0.124 g (0.176 mmol, 93%) of compound **8a** was obtained from 0.135 g (0.189 mmol) of ^{ipr}PC(sp^3)P−Ir(H)(Cl) **7a**. $^{31}P\{^1H\}$ NMR (C_6D_6, 162 MHz): δ 62.54 (s). ^1H NMR (C_6D_6, 400 MHz): δ 7.78 (d, J = 7.3 Hz, 1H), 7.30 (d, J = 6.9 Hz, 2H), 7.13 (m, 1H, overlapping the residual C_6D_5H peak), 7.04−7.01 (m, 2H), 6.94 (t, J = 7.3 Hz, 2H), 6.85 (d, J = 7.3 Hz, 1H), 6.71 (t, J = 7.3 Hz, 1H), 5.30 (s, 1H), 2.77 (t, J = 2.5 Hz, 4H), 2.61−2.56 (m, 2H), 2.42−2.38 (m, 2H), 1.12 (q, J = 7.0 Hz, 6H), 0.90−0.82 (m, 18H). ^{13}C NMR (C_6D_6, 151 MHz): δ 168.4 (t, J = 19.6 Hz, 2C), 158.1, 148.2, 147.0 (t, J = 7.9 Hz, 2C), 135.4 (t, J = 20.1 Hz, 2C), 130.4, 125.9 (2C), 124.8 (t, J = 2.8 Hz, 2C), 124.8 (2C), 123.6, 123.0, 122.8, 67.9 (t, J = 5.3 Hz, 1C), 54.9, 34.4, 29.8 (t, J = 11.7 Hz, 2C), 28.8 (t, J = 1.7 Hz, 4C), 25.9 (t, J = 17.6 Hz, 2C), 22.7, 20.4 (t, J = 3.3 Hz, 1C), 19.6, 18.8, 18.8 (2C), 14.2. Anal. Calcd for $C_{34}H_{43}IrP_2$: C, 57.85; H 6.14. Found: C, 58.05; H, 6.25.

^{Cy}PC(sp^3)P−Ir−ethylene 8b. Following the general procedure, 0.150 g (0.174 mmol, 92%) of compound **8b** was obtained from 0.165 g (0.189 mmol) of ^{Cy}PC(sp^3)P−Ir(H)(Cl) **7b**. $^{31}P\{^1H\}$ NMR (C_6D_6, 202 MHz): δ 57.55 (s). ^1H NMR (C_6D_6, 600 MHz): δ 7.77 (d, J = 7.4 Hz, 1H), 7.34 (d, J = 7.0 Hz, 2H), 7.17−7.13 (m, 3H, overlapping the residual C_6D_5H peak), 7.01 (t, J = 7.4 Hz, 2H), 6.84 (t, J = 7.5 Hz, 1H), 6.73 (t, J = 7.3 Hz, 1H), 5.33 (s, 1H), 2.82 (t. J = 2.4 Hz, 4H),

dx.doi.org/10.1021/cs500892p | ACS Catal. 2014, 4, 3411−3420

2.55−2.53 (m, 2H), 2.35 (t, J = 12.5 Hz, 2H), 2.21 (d, J = 12.7 Hz, 2H), 2.10−2.08 (m, 2H), 1.67 (t, J = 12.2 Hz, 4H), 1.59 (m, 3H), 1.55−1.52 (m, 4H), 1.48−1.36 (m, 15H), 1.08−1.05 (m, 6H), 0.76−0.62 (m, 4H). NMR (C_6D_6, 151 MHz): δ 168.8 (t, J = 20.2 Hz, 2C), 158.2, 148.3, 147.1 (t, J = 7.6 Hz, 2C), 135.6 (t, J = 20.0 Hz, 2C), 130.4, 126.2 (2C), 124.9 (2C), 124.7 (2C), 123.5, 123.1, 123.0, 67.8 (t, J = 6.0 Hz, 1C), 55.0, 39.7 (t, J = 11.4 Hz, 2C), 36.1 (t, J = 17.3 Hz, 2C), 31.4 (2C), 30.8 (2C), 30.2 (2C), 29.6 (4C), 29.4 (2C), 27.8 (t, J = 6.4 Hz, 2C), 27.7 (t, J = 5.2 Hz, 2C), 27.6 (2C), 27.4 (t, J = 6.2 Hz, 2C), 27.0 (2C), 26.5 (2C).

^{Cp}PC(sp^3)P−Ir−ethylene 8c. Following the general procedure, 0.127 g (0.157 mmol, 83%) of compound **8c** was obtained from 0.156 g (0.189 mmol) of the mixture of the two compounds 7c′ and 7c″. $^{31}P\{^1H\}$ NMR (C_6D_6, 162 MHz): δ 50.80 (s). ^1H NMR (C_6D_6, 400 MHz): δ 7.82 (d, J = 7.2 Hz, 1H), 7.31 (d, J = 7.0 Hz, 2H), 7.16−7.12 (m, 3H, overlapping the residual C_6D_5H peak), 6.98 (t, J = 7.3 Hz, 2H), 6.88 (t, J = 7.5 Hz, 1H), 6.73 (t, J = 7.4 Hz, 1H), 5.32 (s, 1H), 2.81 (t, J = 2.4 Hz, 4H), 2.71−2.66 (m, 4H), 1.88−1.85 (m, 4H), 1.80−1.78 (m, 3H), 1.70−1.59 (m, 6H), 1.54−1.50 (m, 8H), 1.44−1.42 (m, 5H), 1.31−1.24 (m, 6H). ^{13}C NMR (C_6D_6, 151 MHz): δ 167.9 (t, J = 19.9 Hz, 2C), 158.3, 148.1, 146.8 (t, J = 7.9 Hz, 2C), 137.3 (t, J = 21.0 Hz, 2C), 130.0, 126.0 (2C), 125.1 (t, J = 2.9 Hz, 2C), 124.7 (2C), 123.8, 123.2, 123.0, 67.7 (t, J = 5.5 Hz, 1C), 54.9, 43.1 (t, J = 12.7 Hz, 2C), 38.6 (t, J = 18.7 Hz, 2C), 32.5, 30.4 (t, J = 2.9, 4C), 30.1, 29.9 (2C), 29.9 (2C), 29.3, 28.1, 26.8 (t, J = 4.6 Hz, 2C), 26.3 (t, J = 4.6 Hz, 2C), 25.9 (t, J = 4.9 Hz, 2C), 25.7 (t, J = 4.8 Hz, 2C).

In Situ Generation of $^{i\text{-Pr}}$PC(sp^3)P-IrH$_4$ 9. To a C_6D_6 solution of 5 mg of $^{i\text{-Pr}}$PC(sp^3)P−Ir−ethylene **8a** (7.1 μmol) in a J-Young tube was added 1 atm of H_2. An immediate color change from orange to colorless was observed. The resulting complex **9** was quantitatively generated and characterized by NMR. $^{31}P\{^1H\}$ NMR (C_6D_6, 162 MHz): δ 56.70 (s). ^1H NMR (C_6D_6, 400 MHz): δ 8.10 (d, J = 7.6 Hz, 1H), 7.22 (d, J = 7.0 Hz, 2H), 7.16−7.14 (m, 1H, overlapping the residual C_6D_5H peak), 6.95 (t, J = 7.4 Hz, 1H), 6.87 (t, J = 7.3 Hz, 2H), 6.83−6.80 (m, 2H), 6.77 (t, J = 7.3 Hz, 1H), 5.31 (s, 1H), 2.08−2.06 (m, 2H), 1.58−1.55 (m, 2H), 1.18 (q, J = 7.5 Hz, 6H), 0.89 (q, J = 7.2 Hz, 6H), 0.83 (q, J = 7.5 Hz, 6H), 0.73 (q, J = 7.2 Hz, 6H), −9.34 (t, J = 9.8 Hz, 4H).

In Situ Generation of $^{i\text{-Pr}}$PC(sp^3)P−Ir(CO)$_2$ 10 and synthesis of $^{i\text{-Pr}}$PC(sp^3)P−Ir(CO) 11. To a C_6D_6 solution of 10 mg of $^{i\text{-Pr}}$PC(sp^3)P−Ir−ethylene **8a** (14.2 μmol) in a J-Young tube was added 1 atm of CO. An immediate color change from orange to pale yellow was observed. The resulting complex **$^{i\text{Pr}}$PC(sp^3)P−Ir(CO)$_2$ 10** was quantitatively generated and characterized by NMR. This complex cannot be isolated as a solid due to loss of CO. $^{31}P\{^1H\}$ NMR (C_6D_6, 162 MHz): δ 57.93 (s). ^1H NMR (C_6D_6, 400 MHz): δ 8.63 (d, J = 7.6 Hz, 1H), 7.16−7.12 (m, 3H, overlapping the residual C_6D_5H peak), 6.99 (t, J = 7.6 Hz, 1H), 6.85−6.76 (m, 5H), 5.18 (s, 1H), 2.42−2.40 (m, 2H), 1.89−1.87 (m, 2H), 1.13−1.07 (m, 12H), 0.91−0.88 (m, 6H), 0.65−0.63 (m, 6H). ^{13}C NMR (C_6D_6, 151 MHz): δ 184.4 (t, J = 11.2 Hz, CO), 184.0 (CO), 167.5 (t, J = 18.1 Hz, 2C), 154.9, 146.9 (t, J = 8.2 Hz, 2C), 145.9, 134.2 (t, J = 20.9 Hz, 2C), 130.0, 125.3 (t, J = 3.0 Hz, 2C), 124.9 (3C), 124.8 (2C), 124.7, 123.2, 62.2 (t, J = 3.4 Hz, 1C), 55.4, 30.6 (t, J = 17.0 Hz, 2C), 28.1 (t, J = 11.7 Hz, 2C), 19.7 (2C), 19.6 (t, J = 2.2 Hz, 2C), 19.4 (t, J = 3.1 Hz, 2C), 18.4 (2C). The solvent was removed under vacuum, and the resulting complex **$^{i\text{Pr}}$PC(sp^3)P−Ir(CO) 11** was isolated and characterized by NMR and IR (9 mg, 13.5 μmol, 95%). $^{31}P\{^1H\}$ NMR (C_6D_6, 162 MHz): δ 74.21 (s). ^1H NMR (C_6D_6, 600 MHz): δ 7.82 (d, J = 7.3 Hz, 1H), 7.29−7.28 (m, 2H), 7.12 (d, J = 7.2 Hz, 1H), 6.91−6.89 (m, 5H), 6.69 (t, J = 7.4 Hz, 1H), 5.21 (s, 1H), 2.59−2.55 (m, 2H), 2.08−2.06 (m, 2H), 1.35 (q, J = 7.5 Hz, 6H), 1.08−1.03 (m, 12H), 0.81 (q, J = 7.3 Hz, 6H). ^{13}C NMR (C_6D_6, 151 MHz): δ 193.7 (t, J = 7.9 Hz, CO), 166.5 (t, J = 18.2 Hz, 2C), 158.9, 149.8, 148.1 (t, J = 7.1 Hz, 2C), 134.4 (t, J = 22.3 Hz, 2C), 129.8, 126.5 (2C), 125.9 (2C), 125.3 (t, J = 3.2 Hz, 2C), 124.2, 123.5, 123.4, 75.2 (t, J = 3.6 Hz, 1C), 55.0, 30.3 (t, J = 11.9 Hz, 2C), 26.2 (t, J = 17.5 Hz, 2C), 20.6 (t, J = 3.2 Hz, 2C), 19.9 (2C), 19.7 (2C), 19.1 (2C). IR (hexanes, cm^{-1}): 1946 ν(CO).

In Situ Generation of $^{i\text{-Pr}}$PC(sp^3)P−Ir(TBE) 12. To a C_6D_6 solution of 5 mg of $^{i\text{-Pr}}$PC(sp^3)P−Ir−ethylene **8a** (7.1 μmol) in a J-Young tube was added 1 atm of H_2. After 5 min of stirring, TBE (9 μL, 73 μmol) was added. An immediate color change from colorless to orange was observed. The resulting complex **12** was quantitatively generated and characterized by NMR. $^{31}P\{^1H\}$ NMR (C_6D_6, 162 MHz): δ 50.25 (d, J = 320 Hz, 1P), 46.35 (d, J = 320 Hz, 1P). ^1H NMR (C_6D_6, 400 MHz): δ 8.15 (d, J = 7.2 Hz, 1H), 7.30 (d, J = 6.7 Hz, 2H), 7.19−7.16 (m, 1H, overlapping the residual C_6D_5H peak), 6.98−6.90 (m, 5H), 6.74 (t, J = 7.4 Hz, 1H), 5.28 (s, 1H), 4.77−4.66 (m, 1H), 3.46 (t, J = 11.4 Hz, 1H), 3.00 (m, 1H), 2.69 (m, 1H), 2.54 (m, 1H), 2.22 (m, 1H), 1.96 (d, J = 7.9 Hz, 1H), isopropyl, and *t*-butyl protons are overlapped with the excess of TBE and 2,2-dimethylbutane.

In Situ Generation of $^{i\text{-Pr}}$PC(sp^3)P−Ir(COE) 13. To a C_6D_6 solution of 5 mg of $^{i\text{-Pr}}$PC(sp^3)P−Ir−ethylene **8a** (7.1 μmol) in a J-Young tube was added 1 atm of H_2. After 5 min of stirring, COE (9 μL, 73 μmol) was added. An immediate color change from colorless to orange was observed. The resulting complex **13** was quantitatively generated and characterized by NMR. $^{31}P\{^1H\}$ NMR (C_6D_6, 162 MHz): δ 57.06 (s). ^1H NMR (C_6D_6, 400 MHz): δ 7.95 (d, J = 7.3 Hz, 1H), 7.29 (d, J = 6.9 Hz, 2H), 7.20−7.16 (m, 1H, overlapping the residual C_6D_5H peak), 7.02−6.98 (m, 3H), 6.92 (t, J = 7.3 Hz, 2H), 6.78 (t, J = 7.3 Hz, 1H), 5.31 (s, 1H), 3.81−3.79 (m, 2H), 2.65−2.58 (m, 6H), 1.99−1.84 (m, 6H), 1.67−1.64 (m, 2H), 1.25−1.20 (q, J = 7.6 Hz, 6H), 1.01−0.97 (m, 6H), 0.92−0.85 (m, 8H), 0.67 (q, J = 7.8 Hz, 6H).

In Situ Generation of Ir(η^3-propenyl)(H) 14 and Ir(η^2-propene) 15. To a C_6D_6 solution of 5 mg of $^{i\text{-Pr}}$PC(sp^3)P−Ir−ethylene **8a** (7.1 μmol) in a J-Young tube was added 1 atm of H_2. After 5 min of stirring, 1 atm of propylene was added. After 20 min, we observed a ratio **14**/**15** = 6:1 and 19:1 after 2 h. The resulting complexes **14** and **15** were quantitatively generated and characterized by NMR. **14**: $^{31}P\{^1H\}$ NMR (C_6D_6, 162 MHz): δ 38.12 (d, J = 338 Hz, 1P), 35.82 (d, J = 338 Hz, 1P). ^1H NMR (C_6D_6, 600 MHz): δ 8.54 (d, J = 7.5 Hz, 1H), 7.23−7.21 (m, 1H), 7.19 (d, J = 7.2 Hz, 1H), 7.16−7.13 (m, 1H, overlapping the residual C_6D_5H peak), 7.01 (td, J = 7.5 Hz, J = 1.2 Hz, 1H), 6.90−6.88 (m, 1H), 6.86 (td, J = 7.3 Hz, J = 1.8 Hz, 1H), 6.81 (td, J = 7.4 Hz, J = 1.2 Hz, 1H), 6.78−6.76 (m, 1H), 5.29 (s, 1H), 4.65−4.58 (m, 1H, H_2), 3.48 (d, J = 6.4 Hz, 1H, H_{syn}), 2.85 (d, J = 6.0 Hz, 1H, H_{syn}), 2.56−2.47 (m, 2H), 2.16−2.14 (m, 1H, H_{anti}), 1.89−1.85 (m, 1H), 1.83 (t, J = 9.7 Hz, 1H, H_{anti}), 1.73−1.70 (m, 1H), 1.14−1.11 (m, 3H), 1.00−0.97 (m, 3H), 0.92−0.88 (m, 6H), 0.78−0.74 (m, 6H), 0.64−0.61 (m, 3H), 0.44−0.40 (m, 3H), −13.58 (dd, J = 22.4 Hz, J = 16.7 Hz, 1H). **15**: $^{31}P\{^1H\}$ NMR (C_6D_6, 162 MHz): δ 57.69 (d, J = 300 Hz, 1P), 53.61 (d, J = 300 Hz, 1P).

dx.doi.org/10.1021/cs500892p | ACS Catal. 2014, 4, 3411−3420

Synthesis of 1,8-Dibromotriptycene−OH 19. 1,8-Dibromoanthrone **16**[21,28] (2 g, 5.68 mmol) and CsF (4.32 g, 28.4 mmol) were mixed in 80 mL of acetonitrile at room temperature for 30 min. A fast color change from yellow to red was observed. A solution containing 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (2.72 mL, 11.36 mmol) in 16 mL of acetonitrile was slowly added for 1 h to the reaction mixture and stirred another 2 h. Forty milliliters of aqueous HCl (2M) was added dropwise followed by 150 mL of ethyl acetate. The organic layer was separated, and the aqueous layer was extracted with EtOAc (2 × 80 mL). The combined organic layers were washed with H_2O (2 × 60 mL), dried on $MgSO_4$, and the solvent was evaporated. The crude product was purified by chromatography on silica gel (hexane−EtOAc, 10:1 to 10:3) affording **19** as a white powder (1.35 g, 55%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.53 (d, J = 7.1 Hz, 2H), 7.47 (d, J = 7.4 Hz, 2H), 7.26−7.24 (m, 2H, overlapping the residual $CHCl_3$ peak), 7.16−7.08 (m, 2H), 6.96 (t, J = 7.7 Hz, 2H), 6.40 (s, 1H), 3.30 (s, 1H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 148.5 (2C), 145.4, 142.5 (2C), 141.9, 129.5 (2C), 126.9 (2C), 126.2, 125.9, 124.4 (2C), 119.5, 119.3, 118.4 (2C), 81.1, 50.9. HRMS (m/z): $[M + H]^+$ calcd for $C_{20}H_{12}Br_2O$, 426.9333; found, 426.9325.

Synthesis of 1,8-Dibromotriptycene-OSiEt$_3$ 20. To a solution of dichloromethane (15 mL) containing 1,8-dibromotriptycene−OH **19** (1.23 g, 2.87 mmol) and $B(C_6F_5)_3$ (0.103 g, 0.20 mmol) was added Et_3SiH (1.40 mL, 8.61 mmol) at room temperature and mixed for 16 h. After evaporation of volatile compounds, the crude product was purified by chromatography on silica gel (hexane−EtOAc, 10:0.2) affording **20** as a white powder (1.32 g, 85%). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.54 (d, J = 7.5 Hz, 1H), 7.50 (d, J = 7.2 Hz, 1H), 7.46 (d, J = 7.5 Hz, 2H), 7.23 (d, J = 8.1 Hz, 2H), 7.12 (t, J = 7.5 Hz, 1H), 7.08 (t, J = 7.4 Hz, 1H), 6.93 (t, J = 7.8 Hz, 2H), 6.37 (s, 1H), 1.17 (t, J = 7.9 Hz, 9H), 1.06−1.02 (m, 6H). ^{13}C NMR ($CDCl_3$, 151 MHz): δ 149.6 (2C), 146.4, 142.2 (2C), 141.6, 129.2 (2C), 126.6 (2C), 125.9, 125.6, 124.2 (2C), 120.7, 119.6 (2C), 119.4, 85.3, 50.8, 8.5 (3C), 7.8 (3C).

Synthesis of 1,8-Bis(diisopropylphosphino)-triptycene-OSiEt$_3$ 21. Following the same procedure as for **6a**, 1.06 g (1.72 mmol, 65%) of coumpond **21** was obtained as a white powder from 1,8-dibromotriptycene-OSiEt$_3$ **20** (1.16 g, 2.13 mmol), diisopropylchlorophosphine (0.68 mL, 4.26 mmol), n-BuLi (2.7 mL, 4.26 mmol) and TMEDA (1.61 mL, 10.66 mmol) in 11 mL of THF. ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): δ −9.00 (s). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.54 (d, J = 7.4 Hz, 2H), 7.51 (d, J = 7.5 Hz, 1H), 7.46 (t, J = 5.1 Hz, 1H), 7.37 (d, J = 7.3 Hz, 1H), 7.11 (d, J = 7.6 Hz, 1H), 7.04−7.00 (m, 3H), 6.95 (t, J = 7.0 Hz, 1H), 2.21−2.17 (m, 2H), 2.08−2.04 (m, 2H), 1.22−1.19 (m, 15H), 1.09−1.05 (m, 6H), 1.02−0.99 (m, 6H), 0.91−0.88 (m, 6H), 0.78−0.75 (m, 6H). HRMS (m/z): $[M + H]^+$ calcd for $C_{38}H_{54}OP_2Si$, 617.3497; found, 617.3511.

Synthesis of (OSiEt$_3$)-$^{i\text{-Pr}}$PC(sp^3)P−Ir(H)(Cl) 22. Following the same procedure as for **7a**, 0.149 g (0.176 mmol, 51%) of compound **22** was obtained from 0.213 g (0.345 mmol) of 1,8-bis(diisopropylphosphino)triptycene-OSiEt$_3$ **21** and 0.154 g (0.173 mmol) of $[IrCl(COE)_2]_2$ in 10 mL of toluene. ^{31}P{^{1}H NMR (C_6D_6, 243 MHz): δ 64.19 (s). ^{1}H NMR (C_6D_6, 600 MHz): δ 7.83 (d, J = 7.3 Hz, 1H), 7.67 (d, J = 7.3 Hz, 2H), 7.48 (d, J = 7.3 Hz, 1H), 6.97 (t, J = 7.5 Hz, 2H), 6.87−6.85 (m, 2H), 6.79 (t, J = 7.4 Hz, 1H), 6.75 (t, J = 7.4 Hz, 1H), 2.68−2.65 (m, 2H), 2.47−2.45 (m, 2H), 1.49 (q, J = 7.6 Hz, 6H), 1.16 (t, J = 7.9 Hz, 9H), 1.10 (q, J = 7.9 Hz, 6H), 1.05−0.89 (m, 12H), 0.89 (q, J = 7.0 Hz, 6H), −35.34 (t, J = 14.9 Hz, 1H). ^{13}C NMR (C_6D_6, 151 MHz): δ 167.4 (t, J = 15.7 Hz, 2C), 151.4, 149.0, 146.8 (t, J = 6.0 Hz, 2C), 134.5 (t, J = 22.9 Hz, 2C), 126.5 (2C), 125.3, 124.9 (2C), 124.8, 123.6, 121.5 (2C), 119.3, 85.9, 32.4, 28.9 (t, J = 12.0 Hz, 2C), 25.6 (t, J = 16.3 Hz, 2C), 20.5 (2C), 19.6 (2C), 19.5 (2C), 19.2 (2C), 8.8 (3C), 7.9 (3C). Anal. Calcd for $C_{38}H_{54}ClIrOP_2Si$: C, 54.04; H, 6.44. Found: C, 54.13; H, 6.49.

Synthesis of (OSiEt$_3$)-$^{i\text{-Pr}}$PC(sp^3)P−Ir−ethylene 23. Following the same procedure as for **8a**, 0.124 g (0.176 mmol, 93%) of compound **23** was obtained from 0.100 g (0.118 mmol) of (OSiEt$_3$)-$^{i\text{-Pr}}$PC(sp^3)P−Ir(H)(Cl) **22** and 0.026 g (0.272 mmol) of NaO-t-Bu in 6 mL of toluene. ^{31}P{^{1}H} NMR (C_6D_6, 162 MHz): δ 62.30 (s). ^{1}H NMR (C_6D_6, 400 MHz): δ 7.83−7.79 (m, 3H), 7.65 (d, J = 6.3 Hz, 1H), 7.08−7.01 (m, 4H), 6.88−6.81 (m, 2H), 2.67 (t, J = 2.5 Hz, 4H), 2.61−2.55 (m, 2H), 2.42−2.36 (m, 2H), 1.20 (t, J = 7.6 Hz, 9H), 1.14−1.05 (m, 15H), 0.90−0.81 (m, 15H). ^{13}C NMR (C_6D_6, 151 MHz): δ 167.0 (t, J = 19.8 Hz, 2C), 156.2, 150.1, 148.3 (t, J = 7.7 Hz, 2C), 135.2 (t, J = 20.4 Hz, 2C), 130.0, 126.3 (2C), 124.7 (t, J = 2.8 Hz, 2C), 123.7, 122.9, 121.6 (2C), 119.6, 85.9, 66.5, 31.3, 29.9 (t, J = 11.8 Hz, 2C), 29.0 (t, J = 1.7 Hz, 4C), 26.0 (t, J = 17.7 Hz, 2C), 22.8, 20.4 (t, J = 3.3 Hz, 1C), 19.7, 18.9, 18.9 (2C), 14.3, 9.0 (3C), 8.0 (3C). Anal. Calcd for $C_{34}H_{43}IrP_2$: C, 57.46; H, 6.87. Found: C, 57.12; H, 7.07.

Synthesis of 1,8-Dibromotriptycene-CH$_3$ 27a and 27b. The protocol developed by Gelman[29] was modified as follows: 1,8-dibromoanthracene (1.12 g, 3.33 mmol) in 12 mL of 1,2-dimethoxyethane and isopentyl nitrite (0.76 mL, 5.66 mmol) were placed in a 100 mL three-necked round-bottomed flask fitted with a reflux condenser and a mechanical stirrer. The mixture was heated to reflux, and the solution of 2-amino-5-methylbenzoic acid (1.01 g, 6.66 mmol) in 7 mL of 1,2-dimethoxyethane was added slowly over 40 min by means of a syringe pump. The mixture was cooled to room temperature and an additional portion of isopentyl nitrite (0.76 mL, 5.66 mmol) was added at once. After resuming reflux, another portion of 2-amino-5-methylbenzoic acid (1.01 g, 6.66 mmol) in 7 mL of 1,2-dimethoxyethane was added over 30 min. The mixture was cooled to room temperature, and 3 mL of methanol along with 50 mL of 10% sodium hydroxide were added. The solution was cooled to ca. 0 °C, mixed for 10 min, and filtered. The residue was washed with 3 portions of chilled methanol/water (4/1) and the powder was air-dried overnight. The products **27a** and **27b** were obtained as a mixture of two isomers with a ratio 1:1 and a conversion of 86%. The crude material was used without further purification.

Synthesis of 1,8-Dibromotriptycene-CH$_2$Br 28a and 28b. The crude material **27a−b** (3.9 g, 86% pure, 6.24 mmol), N-Bromosuccinimide (1.55 g, 8.74 mmol) and AIBN (0.031 g, 0.187 mmol) were dissolved in 300 mL of benzene and heated at reflux for 3 h. The solution was cooled to room temperature, filtered, and the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2 (50 mL), the combined organic layers were dried over $MgSO_4$, and the solvent was evaporated. After addition of CCl_4 (60 mL), the solution was heated at reflux and cooled to −15 °C. The solution was filtered to separate the succinimide. The solvent was evaporated and the white powder was air-dried overnight. Subsequently, 3.33 g of crude materials **28a** and **28b** were obtained as a mixture of two isomers with a ratio 1:1 with full conversion of the starting

dx.doi.org/10.1021/cs500892p | ACS Catal. 2014, 4, 3411−3420

material **27a−b**. The crude material was used without further purification.

Synthesis of 1,8-Dibromotriptycene-CH_2NMe_2 29, 30. The crude material **28a−b** (3.33 g, 6.59 mmol) and dimethylamine (40 wt % in H_2O, 12.5 mL, 99 mmol) were dissolved in 13 mL of toluene, and the solution was heated at reflux for 3 h. After cooling to room temperature, 60 mL of HCl 2N was added. The organic layer was washed with Et_2O (3 × 50 mL), and 120 mL of NaOH (2N) was added dropwise. The aqueous layer was extracted with CH_2Cl_2 (4 × 50 mL), the combined organic layers were dried on $MgSO_4$, and the solvent was evaporated. The crude product was purified by chromatography on silica gel (EtOAc-NEt_3, 10:0.5) affording **29** (0.97 g, 2.06 mmol, 32%) and **30** (1.00 g, 2.12 mmol, 33%) as white powders. NOESY experiments allowed easy distinction between the two amines by observation of an NOE enhancement between the protons H_a−H_d and H_b−H_c. **29**: ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.50 (d, J = 1.6 Hz, 1H, H_d), 7.34 (d, J = 7.5 Hz, 1H, H_c), 7.30 (d, J = 7.3 Hz, 2H), 7.20 (dd, J = 8.0 Hz, J = 1.0 Hz, 2H), 6.97 (dd, J = 7.5 Hz, J = 1.6 Hz, 1H), 6.86 (dd, J = 8.1 Hz, J = 7.3 Hz, 2H), 6.39 (s, 1H, H_a), 5.41 (s, 1H, H_b), 3.35 (s, 2H), 2.21 (s, 6H). ^{13}C NMR ($CDCl_3$, 151 MHz): δ 147.8 (2C), 144.3 (2C), 143.7, 143.5, 136.9, 129.2 (2C), 127.0 (2C), 126.5, 125.4, 123.5, 122.7 (2C), 119.7 (2C), 64.3, 54.6, 52.4, 45.7 (2C). HRMS (m/z): $[M + H]^+$ calcd for $C_{23}H_{19}Br_2N$, 467.9963; found, 467.9965. **30**: ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.45 (d, J = 7.4 Hz, 1H, H_d), 7.41 (d, J = 1.6 Hz, 1H, H_c), 7.28 (d, J = 7.3 Hz, 2H), 7.20 (dd, J = 8.1 Hz, J = 1.0 Hz, 2H), 6.98−6.93 (m, 1H), 6.86 (dd, J = 8.1 Hz, J = 7.3 Hz, 2H), 6.39 (s, 1H, H_a), 5.40 (s, 1H, H_b), 3.33 (s, 2H), 2.19 (s, 6H). ^{13}C NMR ($CDCl_3$, 151 MHz): δ 147.7 (2C), 145.1, 144.2 (2C), 142.1, 137.0, 129.1 (2C), 127.0 (2C), 126.4, 124.6, 124.3, 122.9 (2C), 119.6 (2C), 64.3, 54.9, 52.2, 45.6 (2C). HRMS (m/z): $[M + H]^+$ calcd for $C_{23}H_{19}Br_2N$, 467.9963; found, 467.9965.

Synthesis of 1,8-Bis(diisopropylphosphino)-triptycene-CH_2NMe_2 31. Following the same procedure as for **6a**, 0.85 g (1.56 mmol, 73%) of compound **31** was obtained as a white powder from 1,8-dibromotriptycene-CH_2NMe_2 **30** (1.00 g, 2.13 mmol), diisopropylchlorophosphine (0.68 mL, 4.26 mmol), n-BuLi (2.7 mL, 4.26 mmol) and TMEDA (1.6 mL, 10.66 mmol) in 10 mL of THF. ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): δ −8.59 (s). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.45 (t, J = 4.8 Hz, 1H), 7.34−7.30 (m, 4H), 7.10−7.08 (m, 2H), 6.96 (t, J = 7.5 Hz, 2H), 6.83 (dd, J = 7.4 Hz, J = 1.6 Hz, 1H), 5.34 (s, 1H), 3.29 (s, 2H), 2.20−2.17 (m, 8H), 2.10−2.01 (m, 2H), 1.24−1.19 (m, 6H), 1.03−0.98 (m, 6H), 0.92−0.87 (m, 6H), 0.78−0.74 (m, 6H). HRMS (m/z): $[M + H]^+$ calcd for $C_{35}H_{47}NP_2$, 544.3262; found, 544.3292.

Synthesis of (NMe_2CH_2)-$^{i\text{-}Pr}$PC(sp^3)P−Ir(H)(Cl) 32. Following the same procedure as for **7a**, 0.160 g (0.207 mmol, 38%) of compound **32** was obtained from 0.300 g (0.551 mmol) of 1,8-bis(diisopropylphosphino)triptycene-CH_2NMe_2 **31** and 0.247 g (0.276 mmol) of $[IrCl(COE)_2]_2$ in 12 mL of toluene. ^{31}P{^{1}H} NMR (C_6D_6, 243 MHz): δ 63.68 (s). ^{1}H NMR (C_6D_6, 600 MHz): δ 7.79 (d, J = 7.5 Hz, 1H), 7.22 (m, 1H), 7.13−7.11 (m, 3H), 6.85−6.81 (m, 4H), 5.23 (s, 1H), 3.10 (s, 2H), 2.67 (m, 2H), 2.48−2.46 (m, 2H), 1.94 (s, 6H), 1.50−1.49 (m, 6H), 1.15−1.11 (m, 6H), 1.02−0.99 (m, 6H), 0.92−0.90 (m, 6H), −35.09 (t, J = 14.9 Hz, 1H).

Synthesis of (NMe_2CH_2)-$^{i\text{-}Pr}$PC(sp^3)P−Ir−ethylene 33. Following the same procedure as for **8a**, 0.142 g (0.186 mmol, 90%) of compound **33** was obtained from 0.160 g (0.207 mmol) of (NMe_2CH_2)-$^{i\text{-}Pr}$PC(sp^3)P−Ir(H)(Cl) **32** and 0.040 g (0.415 mmol) of NaO-t-Bu in 12 mL of toluene. ^{31}P{^{1}H} NMR (C_6D_6, 162 MHz): δ 62.59 (s). ^{1}H NMR (C_6D_6, 600 MHz): δ 7.73 (d, J = 7.5 Hz, 1H), 7.34 (d, J = 1.6 Hz, 1H), 7.30−7.28 (m, 2H), 7.04−7.01 (m, 2H), 6.94−6.91 (m, 3H), 5.33 (s, 1H), 3.20 (s, 2H), 2.77 (t, J = 2.4 Hz, 4H), 2.60−2.58 (m, 2H), 2.43−2.41 (m, 2H), 1.99 (s, 6H), 1.13 (q, J = 7.0 Hz, 6H), 0.91−0.85 (m, 18H). ^{13}C NMR (C_6D_6, 151 MHz): δ 168.6 (t, J = 19.7 Hz, 2C), 156.8, 148.3, 147.1 (t, J = 7.9 Hz, 2C), 135.4 (t, J = 20.2 Hz, 2C), 134.3, 129.9, 125.9 (2C), 124.9 (t, J = 2.9 Hz, 2C), 124.9 (2C), 123.9, 123.4, 67.8 (t, J = 5.2 Hz, 1C), 64.6, 55.1, 45.1, 34.5, 29.8 (t, J = 11.6 Hz, 2C), 28.8 (t, J = 1.8 Hz, 4C), 25.9 (t, J = 17.6 Hz, 2C), 22.7, 20.5 (t, J = 3.2 Hz, 1C), 19.7, 18.9, 18.9 (2C), 14.3. Anal. Calcd for $C_{37}H_{50}IrNP_2$: C, 58.25; H, 6.61; N, 1.84. Found: C, 57.32; H, 7.10; N, 1.64.

General Procedure for Transfer Dehydrogenation of COA with TBE Catalyzed by 8a. In an argon-filled glovebox, a 4 mL Kontes vial equipped with a Teflon screw-cap was charged with the complex **8a** (3.5 mg, 5.0 μmol) and dissolved in a solution of COA (1.7 g, 15.15 mmol) and TBE (1.278 g, 15.15 mmol), sealed, and heated in a preheated oil-bath at 200 °C. At regular intervals, the tube was cooled to room temperature, and a sample was analyzed by gas chromatography.

General Procedure for Transfer Dehydrogenation of *n*-Octane with TBE Catalyzed by 8a. In an argon-filled glovebox, a 4 mL Kontes vial equipped with a Teflon screw-cap was charged with the complex **8a** (2.1 mg, 3.0 μmol, 1 mM) and dissolved in a solution of n-octane (2.113 g, 3 mL, 18.5 mmol) and TBE (1.515 g, 18 mmol, 6M), sealed, and heated in a preheated oil-bath at 200 °C. At regular intervals, the tube was cooled to room temperature, and a sample was analyzed by gas chromatography.

General Procedure for the Disproportionation of 1-Hexene Catalyzed by 8a. In an argon-filled glovebox, a 4 mL Kontes vial equipped with a Teflon screw-cap was charged with the complex **8a** (9.5 mg, 13.5 μmol) and dissolved in n-hexane (2.5 g, 29.7 mmol), sealed, and heated in a preheated oil-bath at 180 °C. At regular intervals, the tube was cooled to room temperature, and a sample was analyzed by gas chromatography. An aliquot of 90 μL of solution was combined with 10 μL of mesitylene as an internal standard.

General Procedure for Transfer Dehydrogenation of COA with TBE Catalyzed by γ-Al_2O_3-Supported Complex 33. In an argon-filled glovebox, a 4 mL Kontes vial equipped with a Teflon screw-cap was charged with the complex **33** (3.9 mg, 5.0 μmol) and dissolved in a solution of COA (1.7 g, 15.15 mmol). γ-Al_2O_3 (250 mg) was added to the solution, and the suspension was stirred at room temperature for 2−4 h. After a few seconds of stirring, the solution was completely decolorized, and the alumina acquired the orange color of the pincer complex. TBE (1.278 g, 15.15 mmol) was added to the suspension, and the vial was sealed and heated in a preheated oil-bath at 200 °C. At regular intervals, the tube was cooled to room temperature, and a sample was analyzed by gas chromatography.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Images of NMR spectra for all new compounds and X-ray crystallographic file in CIF format of the complex **7a**. This material is available free of charge via the Internet at http://pubs.acs.org.

dx.doi.org/10.1021/cs500892p | ACS Catal. 2014, 4, 3411−3420

AUTHOR INFORMATION

Corresponding Author

*E-mail: mbrookhart@unc.edu.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We gratefully acknowledge the financial support of the National Science Foundation as part of the Center for Enabling New Technologies through Catalysis (CENTC, CHE-1205189).

REFERENCES

(1) *Activation and Functionalization of C−H Bonds*; Goldman, A. S., Goldberg, K. I., Eds.; ACS Symposium Series *885*; American Chemical Society: Washington, DC, 2004.

(2) Weissermel, K.; Arpe, H.-J. Olefins. In *Industrial Organic Chemistry*; Wiley-VCH Verlag GmbH: Weinheim, 2008; pp 59−89.

(3) (a) Burk, M. J.; Crabtree, R. H.; Parnell, C. P.; Uriarte, R. J. *Organometallics* **1984**, *3*, 816−817. (b) Felkin, H.; Fillebeen-Khan, T.; Holmes-Smith, R.; Lin, Y. *Tetrahedron Lett.* **1985**, *26*, 1999−2000. (c) Burk, M. J.; Crabtree, R. H. *J. Am. Chem. Soc.* **1987**, *109*, 8025−8032.

(4) (a) Gupta, M.; Hagen, C.; Flesher, R. J.; Kaska, W. C.; Jensen, C. M. *Chem. Commun.* **1996**, 2083−2084. (b) Xu, W.; Rosini, G. P.; Gupta, M.; Jensen, C. M.; Kaska, W. C.; Krogh-Jespersen, K.; Goldman, A. S. *Chem. Commun.* **1997**, 2273−2274. (c) Gupta, M.; C. Kaska, W.; M. Jensen, C. *Chem. Commun.* **1997**, 461−462. (d) Lee, D. W.; Kaska, W. C.; Jensen, C. M. *Organometallics* **1998**, *17*, 1−3. (e) Liu, F.; Pak, E. B.; Singh, B.; Jensen, C. M.; Goldman, A. S. *J. Am. Chem. Soc.* **1999**, *121*, 4086−4087.

(5) (a) 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. (b) Punji, B.; Emge, T. J.; Goldman, A. S. *Organometallics* **2010**, *29*, 2702−2709. (c) Adams, J. J.; Arulsamy, N.; Roddick, D. M. *Organometallics* **2012**, *31*, 1439−1447.

(6) (a) Krogh-Jespersen, K.; Czerw, M.; Zhu, K.; Singh, B.; Kanzelberger, M.; Darji, N.; Achord, P. D.; Renkema, K. B.; Goldman, A. S. *J. Am. Chem. Soc.* **2002**, *124*, 10797−10809. (b) Zhu, K.; Achord, P. D.; Zhang, X.; Krogh-Jespersen, K.; Goldman, A. S. *J. Am. Chem. Soc.* **2004**, *126*, 13044−13053. (c) Ray, A.; Zhu, K.; Kissin, Y. V.; Cherian, A. E.; Coates, G. W.; Goldman, A. S. *Chem. Commun.* **2005**, 3388−3390.

(7) (a) Goettker-Schnetmann, I.; White, P.; Brookhart, M. *J. Am. Chem. Soc.* **2004**, *126*, 1804−1811. (b) Gottker-Schnetmann, I.; Brookhart, M. *J. Am. Chem. Soc.* **2004**, *126*, 9330−9338. (c) Göttker-Schnetmann, I.; White, P. S.; Brookhart, M. *Organometallics* **2004**, *23*, 1766−1776. (d) Morales-Morales, D.; Redón, R. o.; Yung, C.; Jensen, C. M. *Inorg. Chim. Acta* **2004**, *357*, 2953−2956.

(8) (a) Ahuja, R.; Punji, B.; Findlater, M.; Supplee, C.; Schinski, W.; Brookhart, M.; Goldman, A. S. *Nat. Chem.* **2011**, *3*, 167−171. (b) Lyons, T. W.; Guironnet, D.; Findlater, M.; Brookhart, M. *J. Am. Chem. Soc.* **2012**, *134*, 15708−15711. (c) Nawara-Hultzsch, A. J.; Hackenberg, J. D.; Punji, B.; Supplee, C.; Emge, T. J.; Bailey, B. C.; Schrock, R. R.; Brookhart, M.; Goldman, A. S. *ACS Catal.* **2013**, *3*, 2505−2514.

(9) Yao, W.; Zhang, Y.; Jia, X.; Huang, Z. *Angew. Chem., Int. Ed.* **2014**, *53*, 1390−1394.

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

(11) (a) Choi, J.; MacArthur, A. H. R.; Brookhart, M.; Goldman, A. S. *Chem. Rev.* **2011**, *111*, 1761−1779. (b) Choi, J.; Goldman, A., Ir-Catalyzed Functionalization of C−H Bonds. In *Iridium Catalysis*; Andersson, P. G., Ed. Springer: Berlin, Heidelberg, 2011; Vol. *34*, pp 139−167. (c) Haibach, M. C.; Kundu, S.; Brookhart, M.; Goldman, A. S. *Acc. Chem. Res.* **2012**, *45*, 947−958.

(12) (a) Goldman, A. S.; Roy, A. H.; Huang, Z.; Ahuja, R.; Schinski, W.; Brookhart, M. *Science* **2006**, *312*, 257−261. (b) Huang, Z.; Rolfe, E.; Carson, E. C.; Brookhart, M.; Goldman, A. S.; El-Khalafy, S. H.; MacArthur, A. H. R. *Adv. Synth. Catal.* **2010**, *352*, 125−135.

(13) 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.

(14) (a) Chianese, A. R.; Mo, A.; Lampland, N. L.; Swartz, R. L.; Bremer, P. T. *Organometallics* **2010**, *29*, 3019−3026. (b) Zuo, W.; Braunstein, P. *Organometallics* **2011**, *31*, 2606−2615. (c) Chianese, A. R.; Drance, M. J.; Jensen, K. H.; McCollom, S. P.; Yusufova, N.; Shaner, S. E.; Shopov, D. Y.; Tendler, J. A. *Organometallics* **2014**, *33*, 457−464.

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

(16) Shi, Y.; Suguri, T.; Dohi, C.; Yamada, H.; Kojima, S.; Yamamoto, Y. *Chem.—Eur. J.* **2013**, *19*, 10672−10689.

(17) Huang, Z.; Brookhart, M.; Goldman, A. S.; Kundu, S.; Ray, A.; Scott, S. L.; Vicente, B. C. *Adv. Synth. Catal.* **2009**, *351*, 188−206.

(18) (a) Gelman, D.; Musa, S. *ACS Catal.* **2012**, *2*, 2456−2466. (b) Gelman, D.; Romm, R. In *Organometallic Pincer Chemistry*; van Koten, G., Milstein, D., Eds. Springer: Berlin, Heidelberg, 2013; Vol. *40*, pp 289−317.

(19) (a) Azerraf, C.; Gelman, D. *Chem.—Eur. J.* **2008**, *14*, 10364−10368. (b) Azerraf, C.; Gelman, D. *Organometallics* **2009**, *28*, 6578−6584. (c) Levy, R.; Azerraf, C.; Gelman, D.; Rueck-Braun, K.; Kapoor, P. N. *Catal. Commun.* **2009**, *11*, 298−301. (d) Musa, S.; Romm, R.; Azerraf, C.; Kozuch, S.; Gelman, D. *Dalton Trans.* **2011**, *40*, 8760−8763. (e) Musa, S.; Shaposhnikov, I.; Cohen, S.; Gelman, D. *Angew. Chem., Int. Ed.* **2011**, *50*, 3533−3537. (f) Oded, K.; Musa, S.; Gelman, D.; Blum, J. *Catal. Commun.* **2012**, *20*, 68−70. (g) Musa, S.; Filippov, O. A.; Belkova, N. V.; Shubina, E. S.; Silantyev, G. A.; Ackermann, L.; Gelman, D. *Chem.—Eur. J.* **2013**, *19*, 16906−16909. (h) Musa, S.; Ackermann, L.; Gelman, D. *Adv. Synth. Catal.* **2013**, *355*, 3077−3080.

(20) (a) Azerraf, C.; Shpruhman, A.; Gelman, D. *Chem. Commun.* **2009**, 466−468. (b) Musa, S.; Shpruhman, A.; Gelman, D. J. *Organomet. Chem.* **2012**, *699*, 92−95.

(21) Grossman, O.; Azerraf, C.; Gelman, D. *Organometallics* **2006**, *25*, 375−381.

(22) A reviewer has suggested that impurities in **8b** and **8c** could be responsible for the low activities seen. A single ^{31}P signal is seen for each of these complexes; the impurities are largely hydrocarbon solvents which should not retard catalysis. Nevertheless, we cannot unequivocally rule out this possibility.

(23) In the case of ($^{t\text{-Bu4}}$PCP)IrH_2 (**1**), Ir(H)[CH═CHC$(CH_3)_3$ is the resting state of the reaction in presence of high concentration of TBE, decreasing the rate of the reaction.

(24) Liu, F.; Pak, E. B.; Singh, B.; Jensen, C. M.; Goldman, A. S. *J. Am. Chem. Soc.* **1999**, *121*, 4086−4087.

(25) 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.

(26) Similar results have been observed when using 2-*trans*-octene instead of propene with the formation of two isomers Ir(η^3-octenyl)(H) complexes showing two hydride signals at −13.36 ppm (dd, J = 21.3 Hz; J = 17.9 Hz, 1H) and −15.53 ppm (t, J = 18.9 Hz, 1H).

(27) Herde, J. L.; Lambert, J. C.; Senoff, C. V.; Cushing, M. A.. In *Inorganic Syntheses*; John Wiley & Sons, Inc.: Hoboken, NJ, 2007; pp 18−20.

(28) Goichi, M.; Segawa, K.; Suzuki, S.; Toyota, S. *Synthesis* **2005**, 2116−2118.

(29) Grossman, O.; Gelman, D. *Org. Lett.* **2006**, *8*, 1189−1191.