DOI: 10.1002/adsc.200800615

Highly Active and Recyclable Heterogeneous Iridium Pincer Catalysts for Transfer Dehydrogenation of Alkanes

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Received: October 8, 2008; Published online: January 2, 2009

Abstract: Pincer-ligated iridium complexes have proven to be highly effective catalysts for the dehydrogenation and transfer-dehydrogenation of alkanes. Immobilization onto a solid support offers significant potential advantages in the application of such catalysts particularly with respect to catalyst separation and recycling. We describe three approaches toward such immobilization: (i) covalent attachment to a Merrifield resin, (ii) covalent bonding to silica *via* a pendant alkoxysilane group, and (iii) adsorption on γ-alumina (γ-Al_2O_3), through basic functional groups on the *para*-position of the pincer ligand. The simplest of these approaches, adsorption on γ-Al_2O_3, is also found to be the most effective, yielding catalysts that are robust, recyclable, and comparable to or even more active than the corresponding species in solution. Spectroscopic evidence (NMR, IR) and studies of catalytic activity support the hypothesis that binding occurs at the *para*-substituent and that this has only a relatively subtle and indirect influence on catalytic behavior.

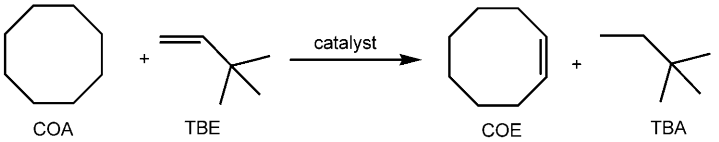
Keywords: alkanes; alumina; dehydrogenation; iridium; pincer ligands; supported catalysts

Introduction

Catalytic alkane dehydrogenation is carried out industrially on an enormous scale for the conversion of inexpensive saturated hydrocarbon feedstocks to higher-value olefins and arenes. Heterogeneous catalysts are used in these cracking and reforming processes which typically operate at high temperatures (400–600 °C), resulting in low product selectivities and poor energy efficiency.[1]

While numerous homogeneous catalytic alkane dehydrogenation systems have been reported,[2] iridium pincer complexes have been shown to be the most productive. Two examples of such systems are shown in Figure 1. The iridium bis(phosphine) ($^{t\text{-Bu}}$PCP) complex, **1a**,[3] has been investigated by Jensen, Kaska and Goldman,[3] while the bis(phosphinite) ($^{t\text{-Bu}}$POCOP) complexes, **2a–e**, have been studied by Brookhart.[4,5] Other related iridium pincer systems have also shown good activity in alkane dehydrogenation.[6] Operating under relatively mild conditions (100–200 °C), these iridium pincer complexes can effect the transfer-dehydrogenation of alkanes, using sacrificial olefins as hydrogen acceptors [as in Eq. (1)], or dehydrogenation in the absence of sacrificial acceptors under conditions where H_2 is allowed to escape from the system.

By comparison with conventional heterogeneous dehydrogenation systems, the iridium pincer catalysts (like other homogeneous dehydrogenation catalysts) show excellent chemoselectivity: "cracking" (C–C bond cleavage side reactions) has never been reported. Even more notably, these complexes have been



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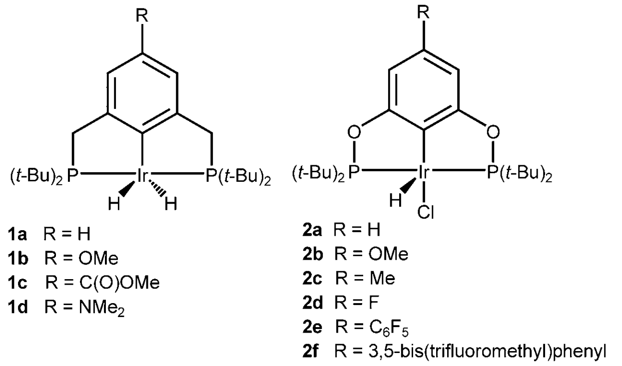


Figure 1. Structures of Ir-PCP and Ir-POCOP complexes.

reported to catalyze dehydrogenation with high regioselectivity for the terminal positions of *n*-alkanes or *n*-alkyl groups. Moreover, in addition to simple alkanes, iridium pincer complexes have been reported to catalyze dehydrogenation of numerous other substrates including amines,[7] alcohols,[8] and polyolefins.[9] Mechanistic details of the dehydrogenations by both iridium PCP and POCOP pincer catalysts have been disclosed.[10]

While the iridium pincer systems are quite robust, the utility of these homogeneous catalysts is limited due to problems of catalyst recyclability and product separation. Heterogeneous iridium pincer systems therefore hold promise for a broad range of applications. In particular, our groups desired such catalysts to combine with heterogeneous olefin metathesis catalysts to generate a fully heterogeneous catalyst system for alkane metathesis.[11]

In this paper we report the results of three strategies for preparing supported iridium pincer complexes: (i) covalent attachment of an iridium complex containing a phenoxide functionality to a Merrifield resin through an S_{N_2} reaction with the chlorobenzyl moieties; (ii) covalent bonding to silica of iridium pincer complexes containing a pendant alkoxysilane group; (iii) adsorption of Ir pincer complexes (particularly those containing basic functional groups) on γ-Al_2O_3 through a Lewis acid/Lewis base interaction. The Merrifield resin-supported iridium POCOP catalyst was found to have low transfer-dehydrogenation activity. The silica-supported iridium POCOP catalyst shows good transfer-dehydrogenation activity at early stages but poor lifetimes. Notably, the γ-Al_2O_3-supported iridium complexes are recyclable and highly active, and in some cases even much more productive than the analogous homogeneous system for transfer dehydrogenation.

Results and Discussion

Alumina-Supported Iridium Pincer Catalyst Systems

The iridium PCP dihydride complexes (**1a–d**) and POCOP ethylene complexes (**3–5**) shown in Figure 1 and Figure 2 were used in the alumina adsorption studies. Complexes **1a, 1b, 1c** and **3** have been previously prepared. Complexes **1d**, **4** and **5**, previously unknown, contain polar groups in the *para* position and were thought to be good candidates for adsorption.

Syntheses of Complexes 1d, 4 and 5

The synthesis of the bis(phosphine) PCP complex **1d** is outlined in Scheme 1.[12] Dimethylation of the commercially available dimethyl 5-aminoisophthalate (**6**) was achieved by adaptation of a method developed by Borch and Hassid.[13] The diester **7** was then reduced to 5-dimethylamino-1,3-benzenedimethanol (**8**) by lithium aluminum hydride in THF.[14] Diol **8** was then treated with PBr_3 in acetonitrile and the resulting dibromide **9** was recrystallized in 77% yield from acetonitrile/water[15] before conversion to Me_2N-PCP-H (**10**) by an adaptation of the method of Moulton and Shaw.[16] Metalation of the free ligand could only be achieved under an H_2 atmosphere; the resulting iridium hydrido chloride was reduced to the iridium dihydride (**1d**) and tetrahydride in analogy with the synthesis of **1a** and the corresponding tetrahydride. Although we were not successful in obtaining crystals of either (Me_2N-PCP)IrH_2 or (Me_2N-PCP)IrH_4, the reaction of this mixture with CO, in analogy with the reaction of the unsubstituted PCP hydrides, gave clean conversion to (Me_2N-PCP)Ir(CO) which was crystallographically characterized.[17] For catalytic

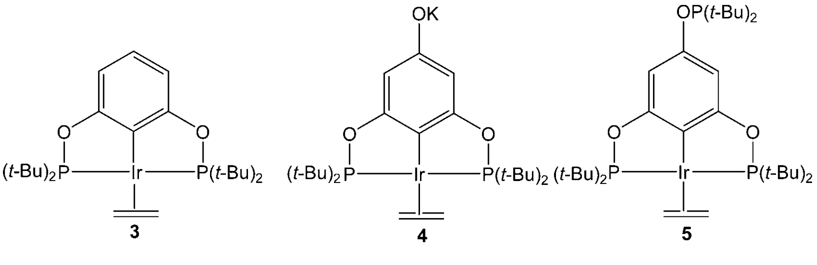
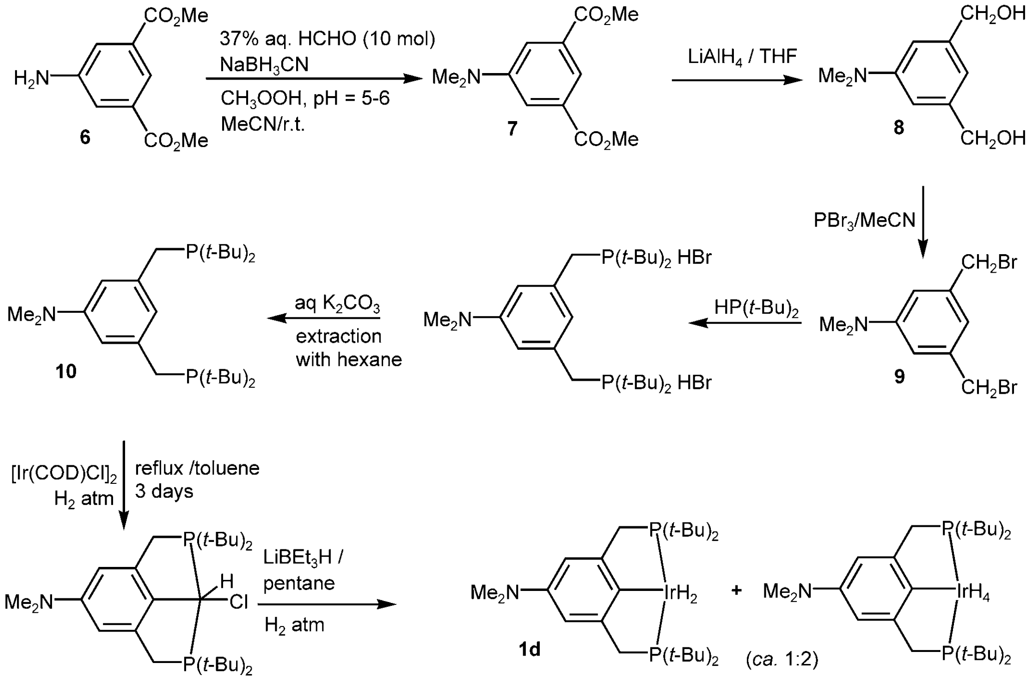
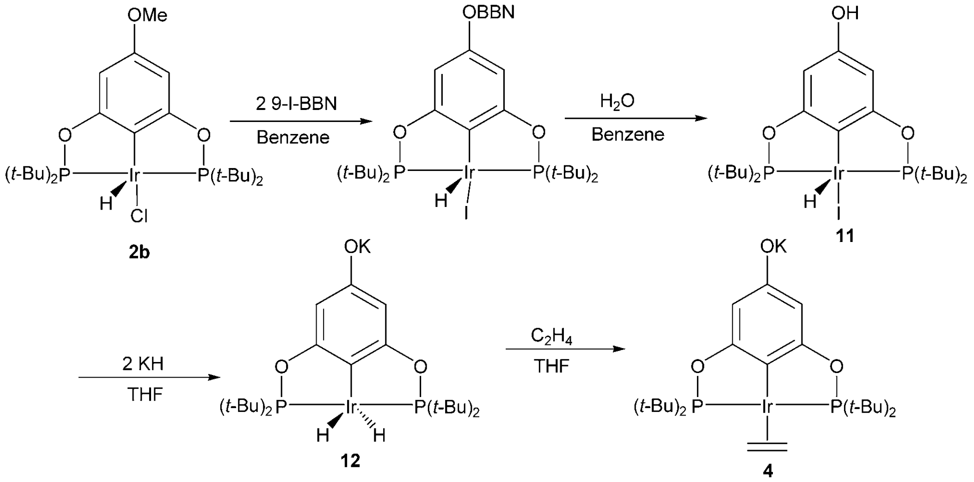


Figure 2. Structures of iridium POCOP complexes used for absorption on γ-alumina.



Scheme 1.

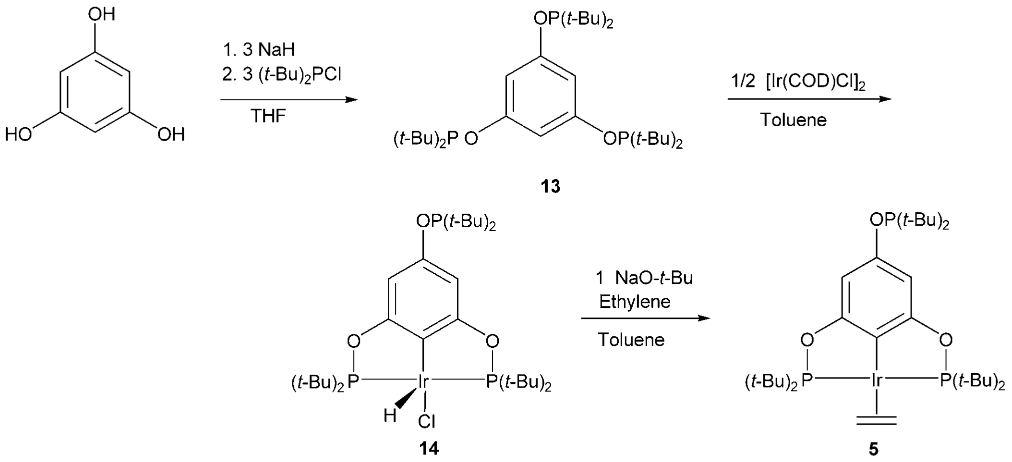


Scheme 2.

runs, **1d** was generally used as a mixture of (Me_2N-PCP)IrH_2 and (Me_2N-PCP)IrH_4 (the iridium PCP and POCOP tetrahydrides readily convert to the dihydrides under catalytic conditions).

The synthesis of complex **4** is outlined in Scheme 2. Deprotection of the methoxy group of the previously reported[4] {*p*-OMe-C_6H_2-2,6-[OP(*t*-Bu)$_2$]$_2$}IrHCl (**2b**) with 9-I-BBN (9-I-BBN = 9-iodo-9-borabicyclo-[3.3.1]nonane, 1 M in hexanes), followed by hydrolysis with water leads to the formation of {4-HO-C_6H_2-2,6-[OP(*t*-Bu)$_2$]$_2$}IrHI (**11**) in 86% yield. Treatment of **11** with 2 equivalents of KH in THF produces Ir dihydride complex, {*p*-KO-C_6H_2-2,6-[OP(*t*-Bu$_2$)]$_2$}Ir(H)$_2$ (**12**) which then reacts with ethylene to form {*p*-KO-C_6H_2-2,6-[OP(*t*-Bu$_2$)]$_2$}Ir(C_2H_4) (**4**) in 70% yield.

The preparation of the tris(phosphinite) Ir pincer complex (**5**) is outlined in Scheme 3. The tris(phosphinite) POCOP ligand (**13**) was synthesized in 89% yield by reaction of 1,3,5-benzenetriol with di-*tert*-butylchlorophosphine and sodium hydride. Ir hydrido chloride complex (**14**) was obtained from the reaction of 0.5 equivalent of [Ir(COD)Cl]$_2$ with the tris(phosphinite) ligand in toluene for 12 h at 130 °C (82% yield). Treatment of the hydrido chloride complex with sodium *tert*-butoxide in the presence of ethylene produced **5** (75% yield).



Scheme 3.

Support of Bisphosphinite (POCOP) Complexes 3 and 4 on γ-Alumina; Transfer-Dehydrogenation Activity

γ-Al_2O_3 has been widely used to support metals or metal oxides for heterogeneous catalysis, with most applications being in the petroleum industry.[18] For example, a γ-Al_2O_3-supported cobalt catalyst has been used in the Fisher–Tropsch process for decades. However, γ-Al_2O_3 is rarely used to support organometallic catalysts. Since alumina contains Lewis acidic sites we considered that iridium pincer complexes containing basic and/or polar functional groups could be strongly adsorbed on this support. We visually examined the effects of adding alumina to cyclooctane solutions of the pincer catalysts, which are orange in color. When 50 mg of γ-Al_2O_3 are added to 1.0 mL of a COA solution containing 2.5 μmol of phenoxide complex **4**, the solution is completely decolorized and the alumina acquires the orange color of the pincer complex. In contrast, a similarly treated solution of **3** retains an orange color. Addition of a further 50 mg alumina results in a nearly colorless solution, suggesting that the parent complex **3** can be adsorbed but that the interaction is weaker than with **4**.

The transfer of hydrogen from COA to *tert*-butylethylene (TBE) as acceptor to yield cyclooctene (COE) and 2,2-dimethylbutane (TBA) [Eq. (1)] is a commonly used "benchmark" reaction;[19] this reaction is thermodynamically favorable by 6 kcal mol^{-1}.[20] Using the iridium PCP complex **1a**, TONs up to 1000 can be achieved at 200 °C but require portionwise addition of TBE which is a strong inhibitor (Figure 3). The iridium POCOP systems, **2a–2f**, are much less subject to inhibition by TBE; TONs up to 2200 have been observed at 200 °C with substrate:catalyst ratios of 3300:1.[4]

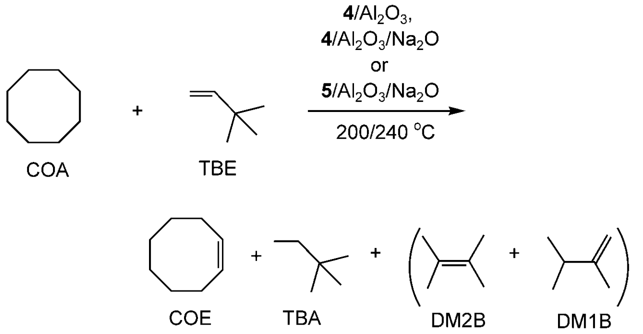


Figure 3. Transfer dehydrogenation of COA and TBE with alumina-supported Ir catalysts.

The γ-Al_2O_3-supported complex **4** was examined for transfer-dehydrogenation activity using the COA/TBE couple. Results are summarized in Table 1. A system containing 2.5 μmol of the iridium catalyst **4** supported on 280 mg of γ-Al_2O_3, 7.5 mmol of COA (3000 equivalents relative to Ir), and 7.5 mmol of TBE, was heated at 200 °C under argon in a sealed glass vessel for 40 h. This process converted 1990

Table 1. Transfer dehydrogenation of COA/TBE using **4** (solution phase) or **4**/γ-Al_2O_3 at 200 °C.[a]

Time	**4**/solution (homogeneous)	**4**/γ-Al_2O_3 (heterogeneous)			
	equiv. TBA	equiv. TBA	DM2B	DM1B	TBE
0.5 h	450	800	280	0	1920
3 h	1450	1290	530	0	1180
15 h	1800	1600	690	40	670
40 h	1970	1990	810	70	130
1st recycle					
40 h	No activity	1420	1150	200	230
2nd recycle					
40 h	No activity	1200	1200	580	20

[a] 1.23 mM iridium catalyst in solution or equivalent amount in the case of supported systems; $[COA]_o = [TBE]_o = 3.7\,M$; 280 mg γ-$Al_2O_3$.

equivalents (relative to Ir) of TBE to TBA, and COA to COE and 1,3-cyclooctadiene (COE/COD ~5/1).[21] The activity is similar to the homogeneous system under identical conditions (1970 TONs, 40 h, Table 1). In the heterogeneous system, part of the TBE was isomerized to form 2,3-dimethyl-2-butene (DM2B, 810 equivalents, 40 h) and 2,3-dimethyl-1-butene (DM1B, 70 equivalents, 40 h). These isomerized olefins were shown to be poor acceptors. For the homogeneous system, no TBE isomerization products were observed.

The homogeneous catalyst **4** gradually decomposed and unidentified black solids precipitated during the transfer dehydrogenation reaction. The catalytic activity was completely lost after evaporation of volatiles and addition of fresh COA and TBE solutions (Table 1). However, when supported on γ-Al_2O_3, **4** can be recycled with only modest loss of activity. Surprisingly, the extent of isomerization of TBE increased after each recycle. After the first run (showing 1990 TONs), the catalyst was isolated and recharged with COA and TBE (3000 equivalents; respectively). After 40 h at 200 °C, 1420 equivalents of TBE were converted to TBA, with the formation of 1150 equivalents of DM2B and 200 equivalents of DM1B. A second recycle exhibited 1200 turnovers (TONs) with 1200 equivalents of DM2B and 580 equivalents of DM1B formed as isomerization products.

The isomerization of TBE decreases the transfer dehydrogenation efficiency since DM2B and DM1B are inefficient hydrogen acceptors. (No 2,3-dimethylbutane, the hydrogenation product of DM2B or DM1B, was observed in the transfer dehydrogenation reaction catalyzed by **4**/γ-Al_2O_3). In control experiments with 280 mg of γ-Al_2O_3 (no Ir), 7.5 mmol of COA, and 7.5 mmol of TBE, 98% of TBE was isomerized at 200 °C to form DM2B (78%) and DM1B (22%) after 6 h. No transfer dehydrogenation products TBA or COE were observed. This result indicates that the isomerization of TBE is catalyzed by the γ-Al_2O_3, presumably by acidic sites on the alumina surface. DM1B and DM2B are well known products of acid-catalyzed rearrangement of TBE.[22]

The supported parent complex **3** (**3**/γ-Al_2O_3; 2.5 μmol of **3** on 280 mg of γ-Al_2O_3) was also investigated for transfer dehydrogenation under similar conditions. Compared to **4**/γ-Al_2O_3, the transfer reaction catalyzed by **3**/γ-Al_2O_3 shows a higher TBE isomerization rate and poorer dehydrogenation activity. After 15 h at 200 °C, 2300 and 480 equivalents of DM2B and DM1B were produced with the **3**/γ-Al_2O_3, and only 190 equivalents of TBA were produced as the transfer dehydrogenation product. The reaction with **4**/γ-Al_2O_3 under the same reaction conditions produced 690 equivalents of DM2B, 40 equivalents of DM1B, and 1600 equivalents of TBA (See Table 1). In contrast to the neutral complex **3**, the basic phenoxide complex **4** must, to a certain extent, "neutralize" the acidity of γ-Al_2O_3, thus decreasing the TBE isomerization rate. Since most of the TBE was isomerized to form DM2B and DM1B with **3**/γ-Al_2O_3, the transfer dehydrogenation efficiency is very low.

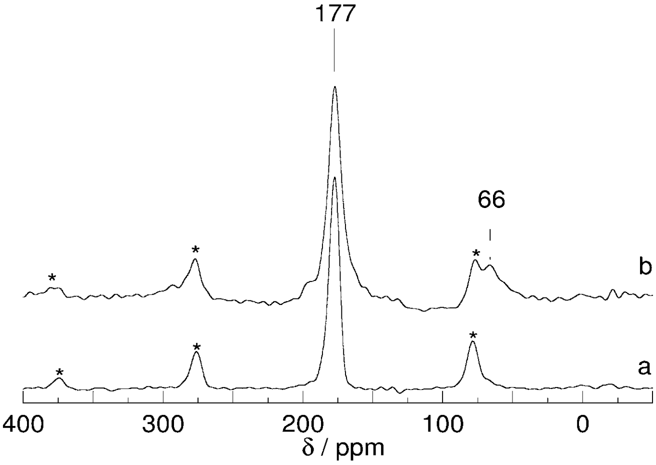


Figure 4. a): Solid-state ^{31}P MAS NMR of fresh **4**/γ-Al_2O_3 (*bottom*) and **b)**: solid-state ^{31}P MAS NMR of **4**/γ-Al_2O_3 after use for catalytic transfer-dehydrogenation (1090 TOs) (*top*). 12 kHz MAS, 20 °C, referenced to 85% H_3PO_4. Starred signals represent spinning sidebands.

Solid-state ^{31}P MAS NMR analysis of the γ-Al_2O_3-supported **4** (5.0 μmol of **4** on 150 mg of γ-Al_2O_3) shows a single species with a ^{31}P NMR shift at 177 ppm which is close to that of complex **4** in solution (170 ppm). After 1090 turnovers in the hydrogen transfer reaction, a new minor (*ca.* 10%) species with a ^{31}P NMR shift of 66 ppm appears (Figure 4.). This shift corresponds to one for the species generated when the supported catalyst is exposed to oxygen and suggests that catalyst decay occurs through oxidation, probably at phosphorus.

Preparation of Basic Alumina and Transfer-Dehydrogenation Activity of Basic Alumina-Supported 4 and 5

As discussed above, the acid-catalyzed isomerization of TBE by γ-Al_2O_3 results in decreased efficiency of COA/TBE transfer dehydrogenation. A variety of commercially available aluminas, including acidic, neutral, and basic were screened as the supports for the iridium catalyst. However, all of these aluminas were found to isomerize TBE rapidly. To decrease the acidity of alumina, an Na_2O-modified γ-Al_2O_3 (2.7 wt% of Na_2O) solid support was synthesized by adding an aqueous solution of NaOH or Na_2CO_3 to γ-Al_2O_3. The solid was calcined at 550 °C for 18 h under a flow of O_2. A control experiment with 310 mg of

Table 2. Transfer dehydrogenation of COA/TBE with solution-phase or supported **4** and **5**.

Time	Homogeneous		Heterogeneous					
	4[a] (200 °C)	**5**[a] (200 °C)	**4**/Al_2O_3/Na_2O[a] (200 °C)		**5**/Al_2O_3/Na_2O[a] (200 °C)		**4**/Al_2O_3/Na_2O[b] (240 °C)	
	TBA (equiv.)	TBA	TBA	DM2B	TBA	DM2B	TBA	DM2B
0.5 h	270	1260	1220	30	980	0	2170	0
3 h	1380	2110	2220	80	2520	0	3620	40
15 h	1830	2540	3490	160	3730	30	6240	130
40 h	1860	2660	4140	180	4310	40	7010	180
	recycle, 200 °C	recycle, 200 °C	recycle, 200 °C		recycle, 200 °C		recycle, 240 °C	
15 h	No activity	No activity	660	60	1520	0	940	50

[a] 0.49 mM iridium catalyst in solution or equivalent amount in the case of supported systems (1.34 μmol supported iridium catalyst); 10.05 mmol COA and TBE, $[COA]_o = [TBE]_o = 3.7$ M; 310 mg γ-Al_2O_3/Na_2O.

[b] 1.34 μmol supported iridium catalyst; 14.74 mmol COA and TBE, $[COA]_o = [TBE]_o = 3.7$ M; 310 mg γ-Al_2O_3/Na_2O.

the Na_2O-modified alumina (Al_2O_3/Na_2O), 7.5 mmol of COA, and 7.5 mmol of TBE, resulted in isomerization of only 1% of the TBE to form DM2B after 48 h at 200 °C.

The Al_2O_3/Na_2O solid (310 mg) was used to support catalyst **4** (1.3 μmol) and was screened for transfer dehydrogenation activity (Table 2). Transfer dehydrogenation of COA and TBE (7500 equivalents relative to Ir) catalyzed by **4**/Al_2O_3/Na_2O results in 4140 turnovers and only 2.4% isomerization of TBE after 40 h at 200 °C. Recycle showed that only 660 TONs were obtained after 15 h (Table 2). It should be noted that the transfer-dehydrogenation activity with the heterogeneous system **4**/Al_2O_3/Na_2O is much higher than the activity with the homogeneous catalyst **4** which exhibited only 1860 TONs after 40 h under the same reaction conditions (Table 2). The homogeneous catalyst **4** decays faster than the heterogeneous system, and no catalytic activity was observed after evaporation of volatiles and addition of fresh COA and TBE solutions (Table 2). Heating at a higher temperature, 240 °C, with the heterogeneous system and 11000 equivalents of COA and TBE gave 7010 turnovers after 40 h, and only 1.6% of TBE was isomerized to form DM2B (Table 2).

One major disadvantage of catalyst **4** is its lengthy and involved synthesis. Complex **5**, readily prepared from 1,3,5-benzenetriol, was found to adsorb strongly on alumina. Analysis of the Al_2O_3/Na_2O-supported **5** (7.6 μmol of **5** on 150 mg of Al_2O_3/Na_2O) by solid-state ^{31}P MAS NMR shows two major phosphorus environments (see Figure 5). The peak at 177 ppm is assigned to the intact, coordinated phosphinite group with a spinning sideband at 275 ppm (the spinning sideband expected at 78 ppm is obscured by the second peak in the spectrum). This constitutes a slight upfield shift from the solution state chemical shift of 181.1 ppm and is a result of complex-support interactions. The peak at 78 ppm is attributed to the phosphinite group not coordinated to Ir, which is shifted far upfield from its solution state chemical shift of 150.8 ppm. The significant upfield shift indicates a reaction between the uncoordinated phosphinite and the alumina. There is a third, minor ^{31}P NMR signal observed at 151 ppm. This signal position is close to the uncoordinated phosphine in solution (150.8 ppm) and is ascribed to some of **5** in which the free phosphinite group is not interacting with alumina.

To investigate the interaction of uncoordinated phosphinite with alumina, the free 1,3,5-tri(di-*tert*-butylphosphinite)benzene ligand and the model compound phenyl di-*tert*-butylphosphinite were supported on Al_2O_3/Na_2O. Analysis of the Al_2O_3/Na_2O-support-

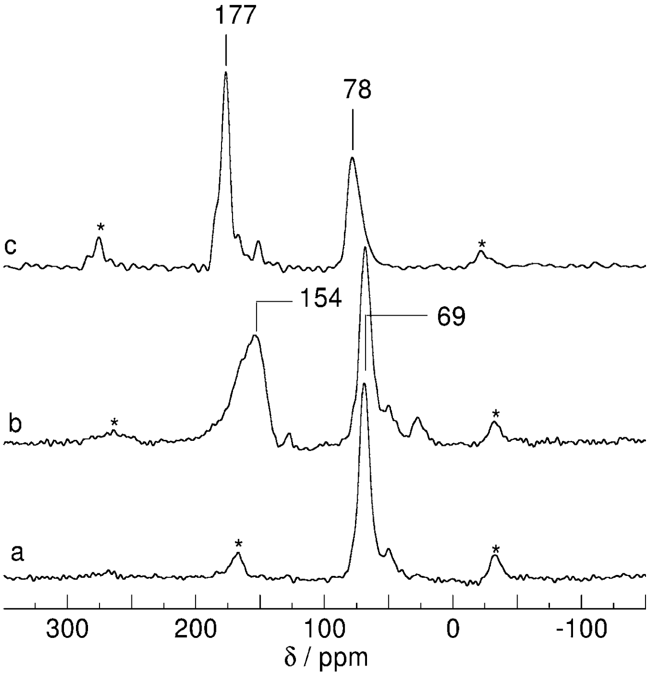


Figure 5. a): Solid-state ^{31}P MAS NMR of phenyl di-*tert*-butylphosphinite/Al_2O_3/Na_2O (*bottom*), **b)**: triphosphinite-benzene/Al_2O_3/Na_2O (*middle*), and **c)**: **5**/Al_2O_3/Na_2O (*top*). 12 kHz MAS, 20 °C, referenced to 85% H_3PO_4. Starred signals represent spinning sidebands.

ed phenyl di-*tert*-butylphosphinite by solid-state ^{31}P MAS NMR shows a large upfield shift from the solution-state chemical shift of 153 ppm to 69 ppm (see Figure 5). Supporting the 1,3,5-tri(di-*tert*-butylphosphinite)benzene results in two major phosphorus environments. The sharp peak at 68.5 ppm is consistent with a phosphinite reacting with the alumina surface as in the phenyl di-*tert*-butylphosphinite sample. The broad peak at 154 ppm is assigned to the phosphinite groups not directly interacting with the surface. The results indicate the uncoordinated phosphinite in complex **5** can indeed react with the alumina surface and this results in a ^{31}P upfield shift by about 70–80 ppm in the ^{31}P MAS NMR spectrum. The nature of this interaction is currently under study.

The Al_2O_3/Na_2O-supported **5** (1.3 μmol **5** on 310 mg Al_2O_3/Na_2O) mirrors the activity of Al_2O_3/Na_2O-supported **4** but recycle of **5**/Al_2O_3/Na_2O is much more efficient. For example, transfer-dehydrogenation of COA and TBE (7500 equivalents each relative to Ir) catalyzed by **5**/Al_2O_3/Na_2O results in 4310 turnovers and less than 1% isomerization of TBE after 40 h at 200 °C. The first recycle exhibited 1520 turnovers after 15 h (Table 2). For the homogeneous system, the conversion at early time (30 min, 1260 TONs) is greater than the heterogeneous system (30 min, 980 TONs), however; after 40 h, the homogeneous system exhibited only 2660 TONs relative to 4310 TONs for the supported system. Attempted recycle of the solution-phase catalyst **5** by evaporation of volatiles and addition of fresh COA and TBE resulted in no additional turnovers, indicating the complete decomposition of **5** under transfer-dehydrogenation condition. Thus the alumina-supported **5** has a much longer lifetime than catalyst **5** in solution.

Leaching Experiments

COA suspensions of **4**/Al_2O_3/Na_2O and **5**/Al_2O_3/Na_2O were filtered at 200 °C. The solid material was extracted twice more with COA at 200 °C and the colorless filtrates were combined and analyzed for iridium content by ICP-MS. The analysis of solutions indicated that only 0.02% of Ir had leached into the solution from the Al_2O_3/Na_2O-supported **4** and only 0.007% from the Al_2O_3/Na_2O-supported **5**. The solutions showed no activity for COA/TBE transfer-dehydrogenation. These results, in combination with the activity of the supported systems being comparable to or even greater than that of the catalysts in solution phase, clearly indicate that the active catalytic species remains bound to the alumina surface during the transfer-dehydrogenation reaction.

Catalytic Activity of Bisphosphine (PCP) Complexes Supported on γ-Alumina

Unlike the bisphosphinite analogues, (PCP)IrH_2 (**1a**) and derivatives react with TBE, if present in high concentration, to give an unidentified, catalytically inactive, decomposition product. Thus we conducted our study of alumina-supported PCP complexes under conditions somewhat different than those applied in studies of the alumina-supported POCOP complexes.

Complexes (MeO-PCP)IrH_2 (**1b**) and [MeOC(O)-PCP]IrH_2 (**1c**) have been previously synthesized.[23] The methoxy-substituted complex **1b** was previously reported to be a more robust alkane dehydrogenation catalyst than the parent complex **1a**,[24] while giving slightly higher rates of acceptorless dehydrogenation (of cyclodecane) but slightly lower rates of *n*-octane/NBE transfer-dehydrogenation. As seen in Table 3 (solution phase), turnover frequencies (TOFs) for COA/TBE transfer-dehydrogenation by **1b** are also somewhat lower than are found for **1a**. The ester-substituted complex **1c** is found to afford slightly greater initial rates for catalytic COA/TBE transfer dehydrogenation than either **1b** or **1a** (Table 3). However **1c** apparently undergoes significant decomposition under the catalytic conditions as indicated by a decrease in catalytic activity. Accordingly, ^{31}P and ^{1}H NMR spectroscopy independently reveal that in the presence of TBE **1c** reacts to give six-coordinate iridium hydride complexes. This decomposition is attributable to inter-

Table 3. COA/TBE transfer-dehydrogenation catalyzed by solution-phase and γ-alumina-supported (PCP)Ir-based complexes at 125 °C.[a]

Catalyst	Time [min]	**Homogeneous** (solution phase) [COE] (mM)	**Heterogeneous** (γ-alumina) [COE] (mM)
(PCP)IrH_2 (**1a**)	15	61	3
	60	164	3
	240	368	4
(MeO-PCP)IrH_2 (**1b**)	15	36	28
	60	115	60
	240	352	84
(MeO_2C-PCP)IrH_2 (**1c**)	15	73	49
	60	155	119
	240	258	354
(Me_2N-PCP)IrH_2 (**1d**)	15	20	42
	60	68	111
	240	200	283

[a] 5 mM iridium catalyst in solution or equivalent amount in the case of supported systems; $[TBE]_o = 0.4$ M, 1 mL COA and 100 mg γ-Al_2O_3.

Table 4. COA/TBE transfer dehydrogenation: recycling catalysts **1c** and **1d**.[a]

Catalyst (5 mM equivalent)	Time [h]	1st cycle	2nd cycle	3rd cycle	4th cycle	5th cycle	6th cycle	7th cycle	8th cycle
(MeO_2C-PCP)IrH_2 (**1c**) heterogeneous (γ-alumina-supported)	1	117	101	27					
	4	331	188	41					
	8	440	259	49					
(Me_2N-PCP)IrH_2 (**1d**) homogeneous (solution phase)	1	75	67	56	47	30	15	9	4
	4	281	222	154	116	70	41	20	11
	8	465	339	246	161	114	65	30	14
(Me_2N-PCP)IrH_2 (**1d**) heterogeneous (γ-alumina-supported)	1	115	91	66	61	46	16	10	6
	4	314	173	135	119	74	43	23	12
	8	464	315	216	197	117	65	31	15

[a] 5 mM iridium catalyst in solution or equivalent amount in the case of supported systems. $[TBE]_o = 0.6$ M, 1 mL COA and 100 mg γ-Al_2O_3.

molecular addition of a C−H bond *ortho* to the ester functionality, in accord with the previously reported reaction of (PCP)Ir with acetophenone.[25]

Upon addition of γ-alumina to a COA (100 mg γ-Al_2O_3 + 1 mL COA) solution of unsubstituted PCP iridium complex **1a** (5 mM) the red solution turned clear and the solid acquired the characteristic red color of the complex. Upon heating to 125 °C the red solid rapidly turned orange, suggesting that decomposition had occurred. Accordingly, very little COA/TBE transfer-hydrogenation occurred in the presence of alumina at 125 °C (less than 5 mM COE formed; Table 3).

Attempts to support (PCP)Ir-based catalysts on alumina were more promising with MeO-PCP complex **1b** than with **1a**, but were still not satisfactory. As in the case of **1a**, upon addition of alumina the solution lost its red color which was acquired by the alumina, but, in contrast to alumina-supported **1a**, no color change was observed even upon heating. After 15 min at 125 °C, **1b** (5 mM) afforded product yields in the presence of alumina only slightly less than in the absence of alumina (28 mM *vs.* 36 mM). But after 240 min the total yield was substantially less than was obtained in the absence of alumina (84 *vs.* 352 mM).

In contrast to results with **1a** and **1b**, the catalyst lifetime and total turnovers effected by ester-substituted complex **1c** were *increased* in the presence of alumina. As with all the bound iridium PCP catalysts, adsorption of **1c** visually appeared to be complete. Although initial rates of COA/TBE transfer-dehydrogenation were slightly lowered by the presence of alumina (49 mM *vs.* 73 mM after 15 min), the yield of COE was appreciably greater after 240 min than was obtained with the solution-phase catalyst (354 mM *vs.* 258 mM). This effect can be rationalized by assuming that adsorption of the catalyst to alumina inhibits the intermolecular catalyst de-activation reaction noted above. However, attempts to recycle the **1c**/γ-alumina catalyst system met with only partial success. The solution was removed from the solid, which was then washed two times with COA (2×2 mL) and a fresh TBE/COA solution was then added. The subsequent catalytic runs showed significantly decreased reactivity (Table 4).

Very promising results were obtained with the new catalyst (Me_2N-PCP)IrH_2 (**1d**). Of the four X-PCP iridium catalysts used in this study, **1d** gave the lowest TOFs for COA/TBE transfer-dehydrogenation in solution (Table 3). Thus it is found that initial COA/TBE solution-phase transfer-dehydrogenation rates increase with decreasing electron-donating ability of the group X: $Me_2N < MeO < H < CO_2Me$. However, when **1d** was adsorbed on γ-alumina, initial rates of COA/TBE transfer-dehydrogenation were greater than obtained by solution-phase **1d**. This is consistent with the correlation with electron-withdrawing ability of X; binding of the Me_2N group to a Lewis acidic surface site would indeed be expected, based on this correlation, to increase catalytic activity.

In addition to the increased TOFs observed upon binding **1d** to alumina, the total TONs effected by the **1d**/γ-alumina system after 4 h were significantly greater than achieved with the homogeneous system (283 *vs.* 200 mM; Table 3). The system proved to be robust and recyclable (Table 4). The solution was removed after 8 h of catalysis at 125 °C and the remaining solid was washed two times with COA; upon addition of fresh TBE/COA solution to the solid, each subsequent run showed only a relatively small decrease in catalytic activity. This process involves extensive exposure of the catalyst (which is sensitive to O_2, H_2O and even N_2) to an imperfect glove-box atmosphere; thus the observed decrease in TOF for each cycle represents only an upper limit of the degree of decomposition that occurred during the actual catalytic run. Recycling of the solution-phase catalyst necessarily involves a different protocol, namely, removal of solvent under vacuum before adding fresh solution. While this presumably involves less exposure to impurities, the loss of activity with each cycle is approximately the same as that observed in the case of the alumina-supported system (Table 4).

The **1d**/γ-alumina system was also effective for the transfer dehydrogenation of *n*-octane, and as was found with COA, more active than solution-phase **1d** (Table 5).

The yield of 1-octene from *n*-octane with this system is much lower than with solution-phase **1d**. We initially assumed that this lower apparent selectivity was due to the isomerization of 1-octene by γ-alumina. Control experiments with γ-alumina, with no iridium present, do indeed show that 1-octene is isomerized under these conditions (Table 6). For example, after *ca.* 60 min, with an initial 1-octene concentration of 29 mM, isomerization is *ca.* 50% complete with *cis*- and *trans*-2-octene being the only major products. However, it does not seem that this level of isomerization activity (half-life of *ca.* 60 min), by itself, could account for the much lower yields of 1-octene obtained from **1d**/γ-alumina *vs.* solution phase **1d** (e.g., 3 mM 1-octene out of 30 mM total octene product *vs.* 9 mM 1-octene out of 22 mM total octene, after only 30 min of catalysis). Further work is ongoing to elucidate the reason for the relatively low yield of terminal alkene, but possible explanations include formation of a minor decomposition product on alumina that acts as a highly active catalyst for isomerization, or perhaps simply increased isomerization activity from **1d** upon binding to alumina (possibly due to decreased electron-density at Ir). It should be noted, however, that even the small yields of 1-octene observed at early reaction times indicate that at least partial selectivity for dehydrogenation at the terminal position is retained upon binding to alumina (even the low 1-octene concentrations observed at early reaction times are much greater than equilibrium values). Furthermore, the predominant internal octenes observed are *cis*- and *trans*-2-octene, with much lower concentrations of 3- and 4-octene (e.g., >80% 2-octene after 60 min); this is indicative of selectivity for the terminal position followed by rapid α-β isomerization and slower further internal isomerization.

To summarize the results in this section, (PCP)IrH_2 (**1a**) shows very rapid loss of catalytic activity in the presence of γ-alumina. All three *para*-substituted complexes investigated in this study underwent decomposition in the presence of γ-alumina far more slowly than **1a**, if at all. Thus *para*-substituent binding appears to inhibit a decomposition reaction of the iridium center with alumina. In the case of complex **1c** the presence of alumina also appears to inhibit the intermolecular decomposition reaction that is observed in the solution phase; this effect is similar to that observed for complexes **4** and **5** as discussed in the preceding section. In the case of catalyst **1b**, deactivation by alumina still occurs, albeit slowly, suggesting that the methoxy group does not bind as strongly as the ester or dimethyl amino groups of **1c** or **1d**, respectively. Electron-withdrawing ability of the *para*-substituent is correlated with catalytic TOFs in solution; consistent with the presumed binding of the Me_2N group to a Lewis acidic surface site, the Me_2N-PCP catalyst **1d** affords increased TOFs when bound to γ-alumina. The **1d**/γ-alumina system is also found to be quite stable under catalytic conditions, and even tolerates multiple cycles of solvent removal, washing, and reuse. In the case of *n*-alkane, the product distribution from the **1d**/γ-alumina system is predominantly 2-octene, but this is likely due to increased rates of α-β isomerization rather than selectivity for dehydrogenation the 2-position of the alkane chain.

Table 5. *n*-Octane/TBE transfer-dehydrogenation by (Me_2N-PCP)IrH_2 (**1d**) at 125 °C.[a]

Time [min]	Homogeneous (solution phase) 1-Octene (mM)	Homogeneous (solution phase) Total octene (mM)	Heterogeneous (γ-alumina-supported) 1-Octene (mM)	Heterogeneous (γ-alumina-supported) Total octene (mM)
15	4	7	2	15
30	9	22	3	30
60	15	43	3	59
120	16	73	4	99
240	16	98	4	130

[a] 5 mM iridium catalyst in solution or equivalent amount in the case of supported systems. $[TBE]_o = 0.4$ M, 1 mL *n*-octane and 100 mg γ-Al_2O_3.

Table 6. Control experiment: isomerization of 1-octene by γ-alumina (no iridium present, 100 mg γ-Al_2O_3 + 1 mL *n*-octane).[a]

Initial [1-octene]	Time [min]	1-Octene (mM)	*trans*-2-Octene (mM)	*cis*-2-Octene (mM)
29 mM	5	27	1	1
	10	26	2	1
	15	24	3	2
	30	20	6	3
	60	14	8	5
427 mM	5	413	8	6
	10	404	14	12
	15	393	22	15
	30	366	46	24
	60	307	88	40

Quantifying the Strength of Binding of the Me_2N-PCP Unit to Alumina

(Me_2N-PCP)IrH_2 (30 mg) was dissolved in 10 mL COA in the presence of 1 g γ-alumina. The mixture was stirred for 15 min and then filtered; the filtrate was then evaporated under vacuum. The residue was analyzed by X-ray fluorescence and the iridium content was found to be below the detection limit of this method, which is estimated as $<1\times10^{-6}$ g, or 0.003% of the initial amount of iridium.

The iridium carbonyl complexes are much more robust than the catalytically active hydrides. For this reason, (Me_2N-PCP)Ir(CO) (**1d-CO**) was used to help quantify, by UV-vis spectroscopy, the strength of binding of the (Me_2N-PCP)Ir unit to alumina. An *n*-hexane solution of **1d-CO** (2.5 mM; 3 mg in 2.0 mL) has an absorbance of 1.58 at $\lambda=493$ nm (1.0 cm pathlength). When 2.0 mL of the same solution was stirred in the presence of 50 mg γ-alumina for 15 min and then filtered, the absorbance at $\lambda=493$ nm was found to be $<1\times10^{-4}$. The concentration of **1d-CO** in solution under these conditions is therefore <0.006% of that present prior to the addition of alumina.

Infrared Spectroscopic Characterization of the Iridium Complexes Supported on γ-Alumina

C–O stretching frequencies act as a valuable [26] indicator of small changes in electron density at the metal center of transition metal carbonyl complexes. In order to probe the nature of the binding of the X-PCP complexes to γ-alumina, we prepared the corresponding (X-PCP)Ir(CO) complexes. All complexes appeared, visually, to be fully adsorbed by γ-alumina. After removal of solvent, nujol mulls of the material were prepared for IR analysis.

Adsorption of (PCP)Ir(CO) (**1a-CO**) on alumina results in a negligible change in C–O stretching frequency as compared with **1a-CO** dissolved in nujol hydrocarbon (1925.9 cm^{-1} *vs.* 1925.3 cm^{-1}; Table 7). The value of ν_{CO} of (MeO-PCP)Ir(CO) in Nujol is *ca.* 3 cm^{-1} red-shifted *versus* solution-phase **1a-CO**, consistent with the electron-donating properties of the *p*-methoxy group. When bound to alumina however, ν_{CO} of **1b-CO** is 5 cm^{-1} greater than solution-phase **1b-CO** and *ca.* 2 cm^{-1} greater than either solution-phase **1a-CO** or **1a-CO/**γ-alumina. These data indicate that **1b-CO** binds to γ-alumina with the *p*-methoxy group acting as a Lewis base toward a Lewis acid surface site; the bound methoxy group is then electron-withdrawing, as might be expected. Likewise, the ν_{CO} value of complex **1d-CO** in solution is 7 cm^{-1} less than that of **1a-CO**; but upon binding to alumina, ν_{CO} is blue-shifted by 10.5 cm^{-1} and is then 3 cm^{-1} higher than that of **1a-CO**/γ-alumina. Thus, as indicated by the relative binding-induced blue shifts, the Me_2N group of **1d-CO** apparently donates significantly more electron density to the alumina than does the MeO group of **1b-CO**; this is in accord with results of the catalytic runs which indicated that **1d** binds more strongly to γ-alumina than does **1b**.

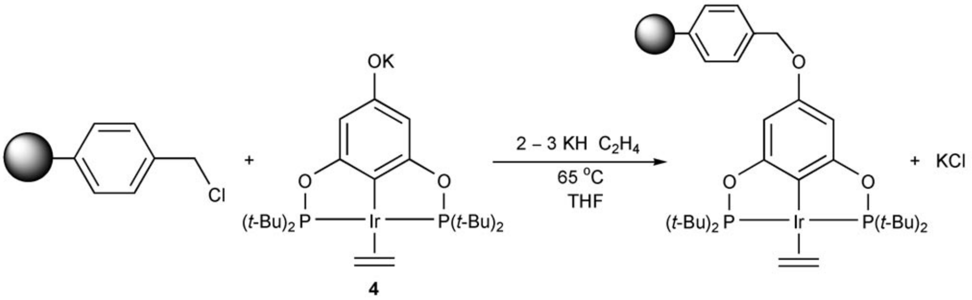
Table 7. C-O stretching frequencies of complexes (X-PCP)Ir(CO) in solution and adsorbed on γ-alumina.

Compound	ν_{CO} [cm^{-1}] (nujol)	ν_{CO} [cm^{-1}] (γ-alumina, nujol)
(PCP)Ir(CO)	1925.3	1925.9
(MeO-PCP)Ir(CO)	1922.6	1927.5
(Me_2N-PCP)Ir(CO)	1918.4	1928.9
(MeO_2C-PCP)Ir(CO)	1931.0	1930.5
(KO-POCOP)Ir(CO)	1945	1945
[(*t*-$Bu)_2$PO-POCOP]Ir(CO)	1934	1945

Ester-substituted complex **1c-CO** shows no significant change in ν_{CO} upon binding to alumina. This may be attributable to a weak interaction with alumina; alternatively, the binding may proceed *via* a trans-esterification type reaction that does not result in a large change in electron density at the iridium center. Likewise, the binding of (KO-POCOP)Ir(CO) to alumina yields no significant change in ν_{CO}; this suggests that the alumina surface exerts an electronic effect similar to that of the K^+ counterion in solution. Finally, [(*t*-$Bu)_2$PO-POCOP]Ir(CO) shows a significant blue shift upon binding to alumina (1934 cm^{-1} to 1945 cm^{-1}). While this large shift is consistent with a strong Lewis acid-base interaction, it may also be noted that the resulting ν_{CO} value is equal to that of alumina-bound (KO-POCOP)Ir(CO). This may suggest that the binding involves cleavage of the (*t*-$Bu)_2$P–O bond to give a species very similar to that obtained from the binding of (KO-POCOP)Ir; this is currently under further investigation.

Synthesis of a Merrifield Resin-Supported Iridium Pincer Complex and Transfer-Dehydrogenation Activity

Complex **4**, which contains a phenoxide functionality, was attached to a Merrifield resin through an S_{N_2} reaction with the chlorobenzyl moieties (Scheme 4). The Merrifield resin (2% cross-linked, 200–400 mesh, 2.25 mmol Cl/g) was swollen in THF-d_8 for 1 h before the coupling reaction. To prevent the possible dissociation of the ethylene ligand, reactions were conducted under *ca.* 1.5 atmosphere of ethylene. Protonation of the phenoxide group of **4** occurred during the reaction although the THF solvent and Merrifield resin were dried before use. With the addition of KH (2–3 equivalents relative to Ir), the conversion to phenol was avoided. When a red THF-d_8 solution of **4** (18 mg, 27 μmol) was treated with a stoichiometric amount of Merrifield resin (12 mg, 27 μmol) (Ir:chlorobenzyl moiety = 1:1) for 15 days at 65 °C, the THF solution was still red indicating incomplete



Scheme 4.

reaction. Analysis of the THF-d_8 solution by ^{1}H NMR spectroscopy indicated that only about 45% of **4** was immobilized on the resin. When **4** was treated with a 7 molar excess of Merrifield resin (Ir:chlorobenzyl moiety = 1:7) in THF, after 7 days at 65 °C the original red solution of complex **4** faded to colorless and the original white resin was now red. Analysis of the THF-d_8 solution by NMR indicated that no **4** remained in solution. The solids were filtered and washed 3 times with THF. To remove the excess KH in the solid mixture, excess *t*-BuOH was added to the solid mixture in THF-d_8 under an ethylene atmosphere (*t*-BuOH has proven to be compatible with the parent complex **3**). Reaction of *t*-BuOH with KH produced KO-*t*-Bu and H_2 which then hydrogenated ethylene to form ethane (ethane was observed by ^{1}H NMR spectroscopy). The red resin was filtered, washed 3 times with THF and H_2O (to remove KCl and KO-*t*-Bu) under argon and then dried under high vacuum overnight.

The polymer-supported iridium catalyst shows poor activity and short lifetimes for transfer dehydrogenation of COA by TBE. A system containing 5.4 μmol of the polymer-supported iridium catalyst, 240 μmol of COA (44 equivalents relative to Ir), 240 μmol of TBE, and 0.3 mL of mesitylene-d_{12} was heated at 175 °C under argon in a J. Young NMR tube. After 2 days, 85% conversion of TBE to TBA (37 TONs) was observed by ^{1}H NMR. The supported catalyst was recovered and recharged with same amount of COA, TBE, and mesitylene. Heating the sample for 2 days at 175 °C resulted in 20% conversion (9 TONs). After the second cycle, the catalyst lost activity completely and the support changed in color from red to black. The decomposition product is unidentified. One possible decomposition pathway could result from reaction of the remaining chlorobenzyl moieties of the Merrifield resin with the Ir center. In light of the low activity of this system, further experiments were not pursued.

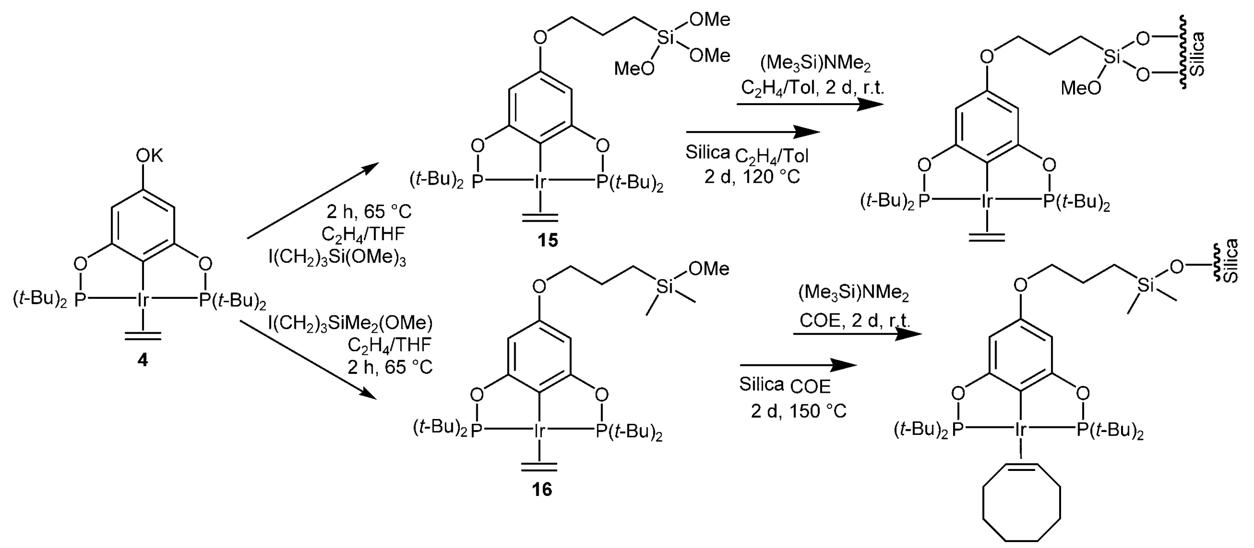
Covalent Attachment of Iridium Pincer Complexes Containing Pendant Alkoxy Silane Groups to Silica and Transfer-Dehydrogenation Activity

Iridium pincer complexes containing either a pendant -Si(OMe)$_3$ group, **15**, or -Si(Me)$_2$OMe group, **16**, were prepared by treating **4** with either 3-iodopropyltrimethoxysilane or 3-iodopropyldimethylmethoxysilane, respectively, in THF under an ethylene atmosphere (Scheme 5).

Attachment of **15** to silica was achieved by heating 300 mg silica (Grace XPO 2402) with 16 mg (20 μmol) **15** in toluene-d_8 at 120 °C under an atmosphere of ethylene to prevent ethylene loss from the Ir center.[27] Periodic analysis of the solution by ^{1}H NMR showed that as the concentration of **15** decreased, methanol and ethane formed and increased in concentration. After 2 days, the original red solution became colorless and the silica acquired a pink color. No detectable **15** remained in solution and *ca.* two equivalents of methanol were produced (relative to Ir) which indicated that on average two methoxy groups of **15** reacted with the silanol groups on silica surface to produce a siloxane linkage and methanol. Excess trimethylsilyldimethylamine was added to cap the remaining silanol groups.[28] This supported catalyst, which contained 63 μmol Ir/g, was isolated, washed with pentane, toluene, and THF three times, respectively, and dried under high vacuum.

Transfer dehydrogenation of COA/TBE with this silica-supported catalyst (50 mg, 3.15 μmol Ir) showed low activity. Reaction with 750 equivalents of COA and TBE at 200 °C gave only 135 turnovers after 24 h. Heating for longer times resulted in no additional turnovers, indicating the decomposition of the catalyst.

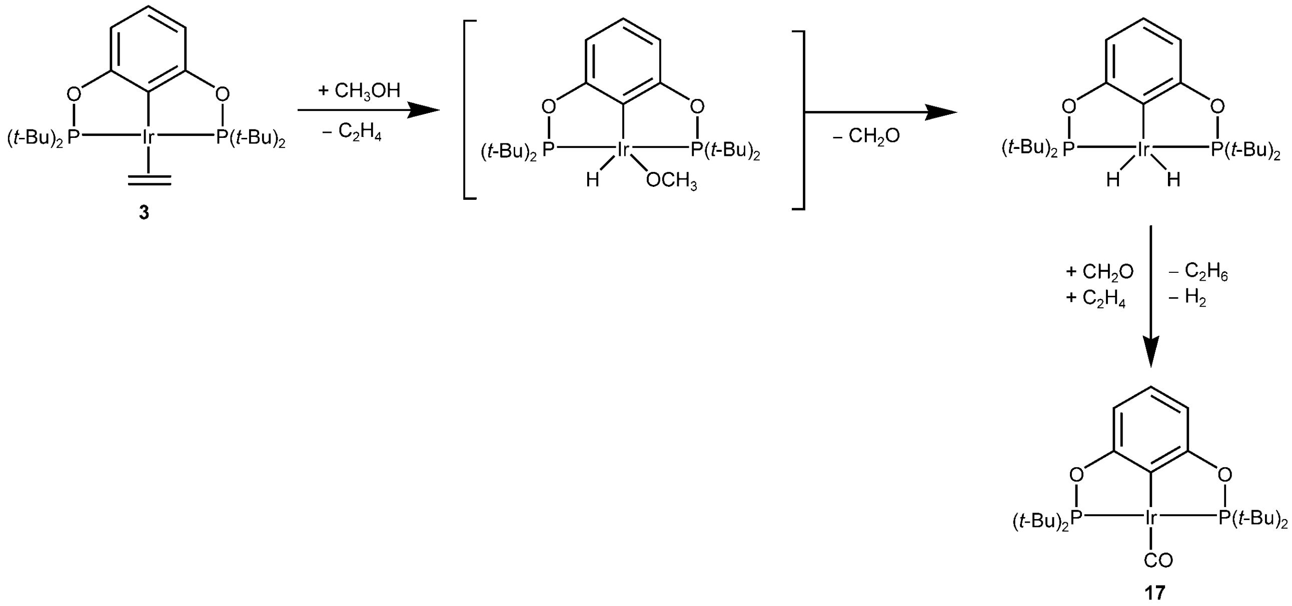
The formation of ethane during the immobilization process indicates that hydrogenation of ethylene occurred. A control experiment was conducted by heating homogeneous complex **3** with 3 equivalents of methanol under an ethylene atmosphere in toluene at 120 °C. Iridium carbonyl complex **17** and ethane were formed as observed by NMR spectroscopy. Production of CO from methanol will produce the hydrogen



Scheme 5.

necessary for the hydrogenation of ethylene (Scheme 6). The formation of ethane during the immobilization process implies conversion of a significant fraction of the Ir ethylene complex to an Ir carbonyl complex which we have shown is inactive for dehydrogenation.

In order to avoid extensive production of an iridium carbonyl complex, reaction conditions and starting material were modified (Scheme 5). The monomethoxy complex **16** was employed to reduce the production of methanol to one equivalent and cyclooctene (COE) was used as the reaction solvent to provide a high concentration of alkene to "protect" the Ir center (we assume under these conditions the ethylene complex will be converted to the COE complex). After reaction of **16** with silica for 2 days at 150 °C in COE, the original red solution became colorless and the silica particles were now red. Excess dimethyl(trimethylsilyl)amine was then added to cap the remaining silanol groups on silica. The solid material was collected and washed with pentane, toluene, and THF three times, respectively, and was dried under high vacuum. The catalyst made by this modified procedure showed improved activity for transfer dehydrogenation. After 15 h, transfer dehydrogenation of COA/TBE (3000 equivalents of COA and



Scheme 6.

TBE) at 200 °C yielded 790 turnovers. However, heating for longer times did not increase the TON (790 after 39 h), which indicates that this silica-supported catalyst is not stable and loses activity at a relatively fast rate.

Conclusions

Three approaches are reported here for constructing iridium pincer-based transfer dehydrogenation catalysts. POCOP iridium catalysts were covalently attached to a Merrifield resin and to silica. These systems showed low to moderate transfer dehydrogenation activity. A third method was developed in which iridium pincer complexes bearing basic functional groups in the *para*-position bind to γ-alumina through a Lewis acid/Lewis base interaction. These alumina-supported complexes have been characterized by solid state ^{31}P NMR and IR spectroscopies which yield information concerning the nature of surface binding. The catalysts are thermally robust and recyclable and display high activities with turnover numbers up to 7000 for transfer of hydrogen from cyclooctane to *tert*-butylethylene. ICP-MS experiments with *para*-phosphinite- and *para*-oxide-supported systems show negligible leaching from alumina under reaction conditions. A number of applications can be envisioned for these catalysts including use in alkane metathesis.[11]

Experimental Section

General Considerations

All manipulations were carried out using standard Schlenk, high-vacuum and glove-box techniques. Tetrahydrofuran (THF) was distilled under a nitrogen atmosphere from sodium benzophenone ketyl prior to use. Pentane and toluene were passed through columns of activated alumina. Water was degassed by purging with argon. Benzene, THF-d_8, and toluene-d_8 were dried with 4 Å molecular sieves and degassed by freeze-pump-thaw cycles. Acetone was dried with 3 Å molecular sieves for 7 h and degassed by freeze-pump-thaw methods. Cyclooctane (COA), 3,3′-dimethyl-1-butene (TBE), *p*-xylene and mesitylene were purchased from Aldrich, dried with $LiAlH_4$ or Na/K, and vacuum transferred into sealed flasks. Complexes **1a**, **1b**, **1c**, **3**,[11] and $[Ir(COD)Cl]_2$[29] were synthesized as previously reported. KH was purchased from Aldrich as 30 wt% in oil and washed with hexanes five times prior to use. $I(CH_2)_3Si(OMe)_3$ and $Cl(CH_2)_3Si(Me)_2(OMe)$ were purchased from Gelest and used as received. $I(CH_2)_3Si(Me)_2(OMe)$ was prepared through the Finkelstein reaction by stirring the mixture of NaI and $Cl(CH_2)_3Si(Me)_2(OMe)$ in dried acetone overnight at 60 °C. γ-Al_2O_3, acidic γ-Al_2O_3, neutral γ-Al_2O_3, and basic γ-Al_2O_3 were purchased from Strem and calcined as noted below. Merrifield resin (2% cross-linked, 200–400 mesh, 2.25 mmol Cl/g) was purchased from Aldrich and dried under high vacuum at 40 °C for 20 h. Silica (Grace XPO 2402) was supplied by DuPont and used as received. All other reagents were purchased from Sigma–Aldrich or Strem and used as received.

NMR spectra were recorded on DRX-400, VANCE-400, Varian-400 and Varian-500 spectrometers. ^{1}H and ^{13}C NMR spectra were referenced to residual protio solvent peaks. ^{31}P NMR chemical shifts were referenced to an external H_3PO_4 standard. The samples for solid-state ^{31}P MAS NMR spectra were packed into 4 mm zirconia solid-state NMR rotors under an argon atmosphere and sealed with tight-fitting rotor caps. Solid-state ^{31}P MAS NMR spectra were recorded on a Bruker Avance DSX300 spectrometer operating at 121.49 MHz with magic angle spinning (MAS) of 12 kHz. The rotors were spun with N_2 in order to keep the samples air-free. All spectra were recorded at room temperature and are referenced to an aqueous 85% H_3PO_4 solution.

UV-visible spectra were recorded on a Varian Cary-50 spectrophotometer. Infrared spectra were recorded on a Thermo Nicolet 360-FT-IR instrument. Elemental analyses were carried out by Robertson Microlit Laboratories, NJ.

GC analyses (FID detection) were performed according to the following methods:

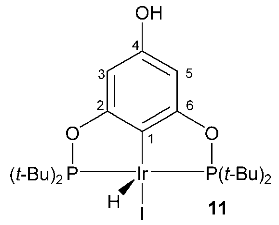
Method A: Agilent 6850 Series GC System fitted with an Agilent HP-1 column (100% dimethylpolysiloxane, 30 m × 0.32 mm i.d., 0.25 μm film thickness). Typical temperature program: 5 min isothermal at 33 °C, 20 °C min^{-1} heat up, 10 min isothermal at 300 °C. Flow rate: 1 mL min^{-1} (He). Split ratio: 400. Inlet temperature: 250 °C. Detector temperature: 250 °C.

Method B: Thermo Electron Corporation Focus GC instrument fitted with an Agilent HP-1 column (100% methyl silicone gum: 100 m × 0.25 mm ID × 0.5 μm film thickness). Typical temperature program: Starting temperature 100 °C, 5 °C min^{-1} up to 230 °C with hold time 10 min, then 5 °C min^{-1} up to ending temperature 250 °C. Flow rate: 1 mL min^{-1} (He). Split ratio: 25. Inlet temperature: 230 °C. Detector temperature: 250 °C.

Method C: As in Method B but with typical temperature program: starting temperature 60 °C with hold time 70 min, 10 °C min^{-1} up to 200 °C with hold time 10 min, then 10 °C min^{-1} up to ending temperature 250 °C.

ICP-MS Analysis was performed on a Varian 820-MS. Sample preparation for ICP-MS: The COA (2 mL × 3) suspension of alumina-supported iridium complex (2.50 μmol Ir on 310 mg of alumina) was filtered through a frit separated double-cell glassware. The COA solution was combined and dried under high vacuum and the residue was digested by a 69.5% HNO_3 solution at 100 °C for 2 h. Finally, the sample was diluted with HNO_3 at 2%. The quantification was carried out using external calibration curves from dilution of a certified ICP-MS Ir standard (Varian). The calibration curves were made as follows: ^{191}Ir and ^{193}Ir: 1000, 500, 250, 50, and 5 ppb. The certified standard was diluted with 2% HNO_3 solution. The quadratic correlation coefficient obtained in the regression line was 0.99997. ^{115}In was used as the internal standard for correcting possible instrumental drifts. Both ^{191}Ir and ^{193}Ir were analyzed. Five replicates were carried out for each isotope analyzed. The RSD mean obtained was 3.0%.

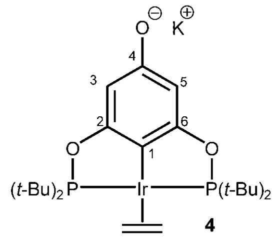
Synthesis of Iridium Complex {*p*-OH-C_6H_2-2,6-[OP(*t*-Bu)$_2$]$_2$}IrHI (11)



11

{*p*-OMe-C_6H_2-2,6-[OP(*t*-Bu)$_2$]$_2$}IrHCl (**2b**) (200 mg, 0.305 mmol) was dissolved in benzene (6 mL) in a flame-dried Schlenk flask and put under a flow of argon. 9-I-BBN (1 M in hexanes, 0.63 mL) was added, and the solution was stirred for 2 h at room temperature. The solvent was removed at room temperature under high vacuum and then the by-product 9-Cl-BBN and the extra 9-I-BBN were removed at 80 °C under high vacuum. A mixture of benzene (3 mL) and degassed water (7 mL) was added into the residue, and the solution was stirred at room temperature overnight. Volatiles were removed under high vacuum. The residue was washed with pentane (3×6 mL) and the resulting red solid was dried under high vacuum overnight to give the pure product; yield: 192 mg (0.262 mmol, 86%). ^{1}H NMR (400 MHz, 23 °C, $CDCl_3$): $\delta = -42.11$ (t, $^2J_{P,H} = 13.0$ Hz, 1H, Ir*H*), 1.36 (virtual triplet, apparent $J = 7.2$ Hz, 36H, 4×*t*-Bu), 4.49 (s, 1H, O*H*), 6.19 (s, 2H, 3- and 5-H); ^{31}P{^{1}H} NMR (162 MHz, 23 °C, $CDCl_3$): $\delta = 181.3$; ^{13}C{^{1}H} NMR (100.6 MHz, 23 °C, $CDCl_3$): $\delta = 28.0$ [CH_3, virtual triplet, apparent $J = 2.8$ Hz, P(*t*-Bu)$_2$], 28.1 [CH_3, virtual triplet, apparent $J = 2.6$ Hz, P(*t*-Bu)$_2$], 40.1 [C_q, virtual triplet, apparent $J = 12.6$ Hz, P(*t*-Bu)$_2$], 43.4 [C_q, virtual triplet, apparent $J = 11.5$ Hz, 2×P(*t*-Bu)$_2$], 93.3 (CH, virtual triplet, apparent $J = 6.0$ Hz, C3 and C5), 111.7 (C_q, m br, C1), 155.3 (C_q, s, C4), 166.9 (C_q, virtual triplet, apparent $J = 6.0$ Hz, C2 and C6); elemental analysis calculated for $C_{22}H_{40}IO_3P_2Ir$ (734.11): C 36.02, H 5.50; found: C 36.87, H 5.31.

Synthesis of Iridium Complex {*p*-OK-C_6H_2-2,6-[OP(*t*-Bu)$_2$]$_2$}Ir(C_2H_4) (4)



4

Complex **11** (160 mg, 0.218 mmol) and KH (22 mg, 0.548 mmol) were weighed into a flame-dried Kontes flask under an argon atmosphere. THF (5 mL) was added to the flask *via* syringe and the resulting suspension was stirred for 2 h at room temperature. The solution was filtered into a Schlenk flask through a 0.2 μm pore size syringe filter (Nalgene 199–2020). Ethylene was bubbled through the solution for 2 h. Volatiles were removed under high vacuum, and the red solid was dried under high vacuum for 4 h to give the pure product; yield: 105 mg (0.156 mmol, 72%). ^{1}H NMR (400 MHz, 23 °C, THF-d_8): $\delta = 1.26$ (virtual triplet, apparent $J = 6.2$ Hz, 36H, 4×*t*-Bu), 2.64 (s, 4H, C_2H_4), 5.67 (s, 2H, 3- and 5-H); ^{31}P{^{1}H} NMR (162 MHz, 23 °C, THF-d_8): $\delta = 170.3$ (s); ^{13}C{^{1}H} NMR (100.6 MHz, 23 °C, THF-d_8): $\delta = 26.5$ [CH_3, m, 2×P(*t*-Bu)$_2$], 28.6 (s, C_2H_4), 38.5 [C_q, apparent $J = 11.1$ Hz, 2 × P(*t*-Bu)$_2$], 91.1 (CH, virtual triplet, apparent $J = 5.5$ Hz, C3 and C5), 134.5 (C_q, m, C1), 168.8 (C_q, virtual triplet, apparent $J = 7.0$ Hz, C2 and C6), 174.4 (C_q, s, C4); elemental analysis calculated for $C_{24}H_{42}O_3P_2IrK$ (672.19): C 42.90, H 6.30; found: C 42.66, H 6.31.

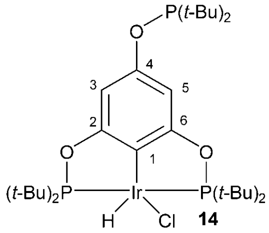
Synthesis of Phenyl Di-*tert*-butylphosphinite

A solution of 10.63 mmol of phenol (1.0 g) in 25 mL of THF was slowly added *via* syringe to a suspension of 10.8 mmol of NaH (259 mg) in 25 mL of THF under a flow of argon (caution: hydrogen evolution). The mixture was heated to reflux for 2 h, di-*tert*-butylchlorophosphine (10.63 mmol, 2.0 g) was then added *via* syringe, and the mixture was refluxed for an additional 8 h. After evaporation of the solvent under high vacuum, the residue was extracted with 3× 40 mL of pentane, and the extract was cannula transferred and filtered through a pad of Celite. After removal of pentane under high vacuum, the flask was heated to 55 °C for 3 h under high vacuum to remove residual amounts of di-*tert*-butylchlorophosphine. Pure product as clear oil was collected; yield: 2.334 g (9.8 mmol, 92%). ^{1}H NMR (400 MHz, 23 °C, $CDCl_3$): $\delta = 1.13$ (d, $^3J_{P,H} = 11.6$ Hz, 18H, 2×*t*-Bu), 6.90 (t, $^3J_{H,H} = 7.2$ Hz, 1H, 4-H), 7.11 (d, $^3J_{H,H} = 7.6$ Hz, 2H, 2- and 6-H), 7.20 (m, 2H, 3- and 5-H); ^{31}P{^{1}H} NMR (162 MHz, 23 °C, $CDCl_3$): $\delta = 153.12$ (s). ^{13}C{^{1}H} NMR (100.6 MHz, 23 °C, $CDCl_3$): $\delta = 27.4$ [CH_3, d, $^2J_{P,C} = 15.1$ Hz, P(*t*-Bu)$_2$], 35.6 [C_q, d, $J_{P,C} = 25.1$ Hz, P(*t*-Bu)$_2$], 118.4 (CH, d, $^3J_{P,C} = 10.1$ Hz, C2 and C6), 121.3 (CH, s, C4), 129.3 (CH, s, C3 and C5), 159.9 (C_q, d, $^2J_{P,C} = 9.0$ Hz, C1).

Synthesis of Pincer Ligand 1,3,5-Tri(di-*tert*-butylphosphinite)benzene (13)

A solution of 10 mmol of 1,3,5-trihydroxybenzene (1.261 g) in 25 mL of THF was slowly added *via* syringe to a suspension of 31 mmol of NaH (782 mg) in 25 mL of THF under a flow of argon (caution: hydrogen evolution). The mixture was heated to reflux for 2 h, di-*tert*-butylchlorophosphine (31.0 mmol, 5.834 g) was then added *via* syringe, and the mixture was refluxed for additional 2 h. After evaporation of the solvent under high vacuum, the residue was extracted with 3×40 mL of pentane, and the extract was cannula transferred and filtered through a pad of Celite. After removal of pentane under high vacuum, the flask was heated to 55 °C for 3 h under high vacuum to remove residual amounts of di-*tert*-butylchlorophosphine. Pure product as clear a waxy solid was collected; yield: 4.972 g (8.9 mmol, 89%). ^{1}H NMR (400 MHz, 23 °C, $CDCl_3$): $\delta = 1.13$ (d, $^3J_{P,H} = 11.6$ Hz, 54H, 6×*t*-Bu), 6.58 (m, 3H, 2-, 4-, and 6-H); ^{31}P{^{1}H} NMR (162 MHz, 23 °C, $CDCl_3$): $\delta = 151.22$ (s); ^{13}C{^{1}H} NMR (100.6 MHz, 23 °C, $CDCl_3$): $\delta = 27.4$ [CH_3, d, $^2J_{P,C} = 16.1$ Hz, 3×P(*t*-Bu)$_2$], 35.6 [C_q, d, $J_{P,C} = 26.1$ Hz, 3×P-(*t*-Bu)$_2$], 100.0 (CH, t, $^3J_{P,C} = 10.6$ Hz, C2, C4, and C6), 161.0 (C_q, d, $^2J_{P-C} = 9.0$ Hz, C1, C3, and C5).

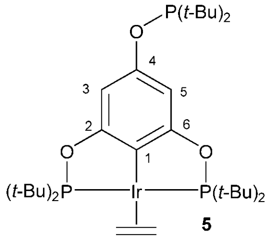
Synthesis of Iridium Vomplex {*p*-OP(*t*-Bu)$_2$-C$_6$H$_2$-2,6-[OP(*t*-Bu)$_2$)]$_2$}IrHCl (14)



14

A Schlenk flask was charged with 1.1 mmol of **13** and 0.5 mmol of [(COD)IrCl]$_2$ and put under a flow of argon. Toluene (5 mL) was added *via* syringe, and the solution was stirred in an oil bath for 15 h at 150 °C. The reaction mixture was cooled to room temperature. Volatiles were removed under high vacuum and the residue was extracted with 10 mL of pentane under ultrasound (10 min). After filtration (no inert gas required), the solid was washed with 3×10 mL of pentane and dried under high vacuum overnight to afford of pure red purple product; yield: 645 mg (0.82 mmol, 82%). ^{1}H NMR (400 MHz, 23 °C, CDCl$_3$): $\delta=-41.91$ (t, $^2J_{\rm P,H}=13.2$ Hz, 1 H, Ir*H*), 1.16 (d, $^3J_{\rm P,H}=12$ Hz, 18 H, 2×*t*-Bu), 1.33 (m, 36 H, 4×*t*-Bu), 6.43 (s, 2 H, 3- and 5-H); ^{31}P{^{1}H} NMR (162 MHz, 23 °C, CDCl$_3$): $\delta=154.2$ [s, uncoordinated P(*t*-Bu)$_2$], 175.8 [s, coordinated 2×P(*t*-Bu)$_2$]; ^{13}C{^{1}H} NMR (100.6 MHz, 23 °C, CDCl$_3$): $\delta=27.5$ [CH$_3$, d, $^2J_{\rm P,C}=16.1$ Hz, uncoordinated P(*t*-Bu)$_2$], 27.6 [CH$_3$, br, coordinated P(*t*-Bu)$_2$], 27.8 [CH$_3$, br, coordinated P(*t*-Bu)$_2$], 35.6 [C$_{\rm q}$, d, $J_{\rm P,C}=25.1$ Hz, uncoordinated P(*t*-Bu)$_2$], 39.5 [C$_{\rm q}$, virtual triplet, apparent $J=12.6$ Hz, coordinated P(*t*-Bu)$_2$], 43.1 [C$_{\rm q}$, virtual triplet, apparent $J=11.1$ Hz, coordinated P(*t*-Bu)$_2$], 96.2 (CH, dvt, apparent $J=4.0$ and 9.0 Hz, C3 and C5), 109.3 (C$_{\rm q}$, m br, C1), 159.4 (C$_{\rm q}$, m br, C4), 166.9 (C$_{\rm q}$, virtual triplet, apparent $J=5.5$, C2 and C6); elemental analysis calculated for C$_{30}$H$_{57}$O$_3$P$_3$ClIr (786.28): C 45.82, H 7.31; found: C 45.58, H 7.04.

Synthesis of Iridium Complex {*p*-OP(*t*-Bu)$_2$-C$_6$H$_2$-2,6-[OP(*t*-Bu)$_2$]$_2$}Ir(C$_2$H$_4$) (5)



5

Complex **14** (500 mg, 0.636 mmol) and NaO-*t*-Bu (64 mg, 0.666 mmol) were weighed into a Schlenk flask and put under a flow of argon. Toluene (20 mL) was added to the flask *via* syringe and ethylene was bubbled through the solution for 2 h. After evaporation of the solvent under high vacuum, the residue was extracted with 3×20 mL of pentane, and the extract was cannula transferred and filtered through a pad of Celite. Pentane was removed under high vacuum, and the red brown solid was dried under high vacuum overnight to give the pure product; yield: 371 mg (0.477 mmol, 75%). ^{1}H NMR (400 MHz, 23 °C, C$_6$D$_6$): $\delta=1.10$ (d, $^3J_{\rm P,H}=8.0$ Hz, 18 H, 2×*t*-Bu), 1.23 (virtual triplet, apparent $J=6.8$ Hz, 36 H, 4×*t*-Bu), 3.11 (s, 4 H, C$_2$*H*$_4$), 7.06 (s, 2 H, 3- and 5-H); ^{31}P{^{1}H} NMR (162 MHz, 23 °C, C$_6$D$_6$): $\delta=150.8$ [s, uncoordinated P(*t*-Bu)$_2$], 181.1 [s, coordinated 2×P-(*t*-Bu)$_2$]; ^{13}C{^{1}H} NMR (100.6 MHz, 23 °C, C$_6$D$_6$): $\delta=27.6$ [CH$_3$, d, $^2J_{\rm P,>C}=15.8$ Hz, uncoordinated P(*t*-Bu)$_2$], 28.7 [CH$_3$, virtual triplet, apparent $J=3.0$ Hz, coordinated 2×P(*t*-Bu)$_2$], 35.6 [C$_{\rm q}$, d, $J_{\rm P,C}=26.8$ Hz, uncoordinated P(*t*-Bu)$_2$], 35.8 (s, *C*$_2$H$_4$), 41.5 [C$_{\rm q}$, virtual triplet, apparent $J=11.0$ Hz, coordinated 2×P(*t*-Bu)$_2$], 94.7 (CH, dvt, apparent $J=5.5$ and 11.1 Hz, C3 and C5), 139.7 (C$_{\rm q}$, m, C1), 161.5 (C$_{\rm q}$, d, $J_{\rm P,C}=10.1$ Hz, C4) 168.8 (C$_{\rm q}$, virtual triplet, apparent $J=8.0$, C2 and C6); elemental analysis calculated for C$_{32}$H$_{60}$O$_3$P$_3$Ir (778.34): C 49.40m H 7.77; found: C 49.60, H 7.60.

Calcination of Alumina

γ-Al$_2$O$_3$, acidic γ-Al$_2$O$_3$, neutral γ-Al$_2$O$_3$, and basic γ-Al$_2$O$_3$ were calcined at 550 °C for 2 h under a flow of O$_2$ and cooled to 135 °C under O$_2$, then cooled to room temperature under high vacuum. The solids were brought into the drybox under high vacuum and stored under argon.

Synthesis of Na$_2$O-Modified Alumina

In a vial, 235 mg (2.22 mmol) of Na$_2$CO$_3$ or 178 mg (4.45 mmol) of NaOH were dissolved in 10 mL of distilled water. The solution was added to 5 g of γ-Al$_2$O$_3$. The suspension was stirred at room temperature until all of the water was absorbed by the alumina. The solid was dried in a 120 °C oven overnight, then calcined at 550 °C for 17 h under a flow of O$_2$ and cooled to 135 °C under O$_2$, and then cooled to room temperature under high vacuum. The solid was brought into the drybox under high vacuum and stored under argon.

Synthesis of Alumina-Supported Iridium Pincer Complexes

The alumina-supported pincer Ir ethylene complexes can be prepared either *in situ* or by using pentane as solvent.

Method A (in situ): Ir complex (1.34–2.50 μmol) was dissolved in alkane (1–3 mL) (cyclooctane or linear alkanes). The solution was added to 280–310 mg (2.74–3.04 mmol) of γ-Al$_2$O$_3$. The suspension was stirred at room temperature. After 10–20 min, the original red solution turned colorless and the alumina acquired a rust-red color. The suspension continued to stir for 2–4 h.

Method B (pentane): Ir complex (1.34–2.50 μmol) was dissolved in pentane (1.5 mL). The solution was added to 280–310 mg (2.74–3.04 mmol) of γ-Al$_2$O$_3$. The suspension was stirred at room temperature for 2–4 h. The original red solution turned colorless and the alumina acquired a rust-red color. The solvent was removed by syringe in the glove-box. The solid was washed with pentane three times. Pentane was evaporated in the glove-box (no vacuum applied) and the rust-red solid was collected.

Synthesis of Alumina-Supported 13 and Phenyl Di-*tert*-butylphosphinite

Compound **13** (26 μmol), or phenyl di-*tert*-butylphosphinite, was dissolved in pentane (1.5 mL). The solution was added to 200 mg (1.96 mmol) of γ-Al_2O_3. The suspension was stirred at room temperature for 2–4 h. The solvent was removed by syringe in the glove-box. The solid was washed with pentane three times. Volatile was evaporated in the glove-box and the white solid was collected.

Hydrogen Transfer from Cyclooctane (COA) to 3,3-Dimethyl-1-butene (TBE) Catalyzed by γ-Al_2O_3-Supported Iridium Pincer Complexes

Complexes **1a–d**: the iridium complex (5 μmol) was dissolved in COA (1 mL) in a Kontes flask. γ-Al_2O_3 (100 mg, 0.98 mmol) was added to the solution and the suspension was stirred at room temperature for 20 min. TBE (95%, 70 μL, 0.54 mmol) was added to the suspension. The flask was sealed tightly with a Teflon plug under an argon atmosphere, and the suspension was stirred in an oil bath at 125 °C. Periodically, the flask was removed from the bath and cooled in an ice bath. An aliquot was removed from the flask, and analyzed by GC (method **B**). Turnover numbers were calculated for each aliquot using mesitylene as a GC standard.

Complexes **3–5**: the iridium complex (1.34–2.50 μmol) was dissolved in COA (0.842–1.655 g, 7.50–14.74 mmol) in a Kontes flask. γ-Al_2O_3 (280–310 mg, 2.74–3.04 mmol) was added to the solution and the suspension was stirred at room temperature for 2–4 h. TBE (95%, 0.664–1.306 g, 7.50–14.74 mmol) was added to the suspension. The procedure was otherwise as described above for complexes **1a–d** but reactions were conducted at 200 or 240 °C and the solution was analyzed by GC using method **A**. Turnover numbers were calculated for each aliquot. Results are summarized in the text.

The heterogeneous catalysts can be recycled. After each cycle, the solution was syringed out and the solid was washed 2–3 times with COA. Fresh COA and TBE were then added.

Hydrogen Transfer from COA or *n*-Octane to TBE Catalyzed by Solution-Phase Iridium Pincer Complexes

A flask was charged with iridium pincer complex **1a**, **1b**, **1c** or **1d** (5 μmol), COA or *n*-octane (1 mL), and TBE (95%, 70 μL, 0.54 mmol). Respective values in the case of complex **4** or **5**: iridium complex, 1.34–2.50 μmol; COA, 0.842–1.655 g, 7.50–14.74 mmol; TBE (95%), 0.664–1.306 g, 7.50–14.74 mmol. The flask was sealed tightly with a Teflon plug under an argon atmosphere, and the solution was stirred in an oil bath at 125 °C (complexes **1a–d**) or 200 °C (complexes **4** and **5**). Periodically, the flask was removed from the bath and cooled in an ice bath. An aliquot was removed from the flask, and analyzed by GC (method **A**, complexes **1a–d**; method **B**, complexes **1a–d**). Turnover numbers were calculated for each aliquot. Recycle of the homogeneous catalysts was obtained by evaporation of under high vacuum and addition of fresh COA and TBE. Results are summarized in the text.

Isomerization of TBE or 1-Octene by Alumina (Control Experiments)

A flask was charged with 280–310 mg of γ-Al_2O_3 or Al_2O_3/Na_2O, 0.842 g of COA (7.50 mmol), and 0.664 g of TBE (7.50 mmol). In the case of 1-octene, a flask was charged with 100 mg of γ-Al_2O_3, COA (1 mL), and 1-octene (4.55 μL, 29 mmol or 67 μL, 427 mmol). The flask was sealed tightly with a Teflon plug under an argon atmosphere, and the solution was stirred in an oil bath at 125 °C (1-octene) or 200 °C (TBE). Periodically, the flask was removed from the bath and cooled in an ice bath. An aliquot was removed from the flask, and analyzed by GC.

Synthesis of a Merrifield Resin-Supported Iridium Pincer Complex

The Merrifield resin (12 mg, 27 μmol chlorobenzyl moiety; or 84 mg, 189 μmol chlorobenzyl moiety when Merrifield resin was used in excess) was swollen in THF-d_8 (0.5 mL) for 1 to 2 h in a thick-walled J. Young tube in the glove-box. Complex **4** (18 mg, 26.8 μmol) and KH (3 mg, 75 μmol) were added to the tube. The THF-d_8 solution was degassed by freeze-pump-thaw cycles. The tube was refilled with ethylene gas at −78 °C. The suspension was heated at 65 °C. The solution was monitored by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy periodically. For the sample with Ir:chlorobenzyl moiety ratios of 1:1, after 15 days, about 45% of **4** was immobilized on the resin (determined by NMR). For the sample with a 7 molar excess of Merrifield resin, after 7 days, no **4** was observed in the solution. The solid was collected by filtration and washed with 3 times of THF (0.5 mL each) in the glove-box. The solid was reloaded into a thick-walled J. Young tube and THF-d_8 (0.5 mL) was added to the tube. Degassed *t*-BuOH (*ca.* 0.2 mL) was added into the J. Young tube by vacuum transfer method (caution, hydrogen evolution). The red resin was filtered, washed with 3 times of THF and H_2O (0.5 mL each) under an argon atmosphere, and then dried under high vacuum overnight.

Hydrogen Transfer from COA to TBE Catalyzed by Merrifield Resin-Supported Iridium Pincer Complex

A J. Young tube was charged with 8 mg of the Merrifield resin supported iridium catalyst (5.4 μmol of Ir), 32 μL of COA (240 μmol), 33 μL of TBE (240 μmol), and 0.3 mL of mesitylene-d_{12}. The tube was sealed tightly under an argon atmosphere, and then heated in an oil bath at 175 °C. The sample was analyzed by NMR spectroscopy periodically. After each cycle, the catalyst was filtered, washed with pentane and dried under high vacuum. Fresh COA, TBE and mesitylene-d_{12} were then added. Results are summarized in the text.

Synthesis of Dimethyl 5-Dimethylaminoisophthalate (7)

The compound was prepared *via* the literature procedure for reductive alkylation of aromatic amines. Sodium cyanoborohydride (5 g, 75.6 mmol) was added to a stirred solution of 5 g (23.4 mmol) of dimethyl 5-aminoisophthalate (**6**) (98%) and 20 mL (269 mmol) of 37% aqueous formaldehyde in 150 mL acetonitrile. This was followed by slow addition (over a period of 20 min) of 3 mL of glacial acetic acid to adjust the pH at 5–6. The resulting solution was stirred at room temperature for 8 h and the solvent was removed under reduced pressure. The wet-solid obtained thereby was washed thoroughly with distilled water and air-dried to give **7** as a light yellowish-white solid; yield: 5.39 g (97%). ^{1}H NMR ($CDCl_3$): $\delta = 8.01$ (s, 1H, *Ar*), 7.56 (s, 2H, *Ar*), 3.94 (s, 6H, CO_2CH_3), 3.05 [s, 6H, $(CH_3)_2N$].

Synthesis of 5-Dimethylamino-1,3-benzenedimethanol (8)

To a stirred suspension of 2.69 g (67.4 mmol) of lithium aluminum hydride (95%) in THF (50 mL) at 0°C under an argon atmosphere was slowly added a THF (100 mL) solution of **7** (5 g, 21.1 mmol). After the addition was complete, the resultant suspension was refluxed for 18 h, diluted with 100 mL tetrahydrofuran and cooled to 0°C. Excess $LiAlH_4$ was quenched by slow addition of a saturated sodium sulfate solution followed by distilled water and the suspension was stirred at 0°C - 5°C for 1 h (until the gray color of $LiAlH_4$ disappeared completely). The suspension was filtered through a pad of anhydrous magnesium sulfate and subsequently washed with ethyl acetate (3×50 mL). The combined filtrates were concentrated under reduced pressure to give a clear colorless oil that crystallized upon standing. The product **8** was recrystallized from THF/heptane system as a white powder; yield: 3.49 g (91%). ^{1}H NMR (DMSO-d_6): $\delta = 6.58$ (s, 1H, *Ar*), 6.56 (s, 2H, *Ar*), 5.03 (t, 2H, O*H*), 4.41 (d, 4H, CH_2), 2.87 [s, 6H, $(CH_3)_2N$].

Synthesis of 1,3-Bis(bromomethyl)-5-dimethylaminobenzene (9)

PBr_3 (10.4 mL, 110 mmol) was added dropwise over a 30-minute period to a stirred solution of **8** (5.0 g, 27.6 mmol) in 140 mL of anhydrous acetonitrile at 0°C under aqn argon atmosphere. The solution was stirred at room temperature for 2 h and then heated to 70°C for an additional 4 h. The reaction was quenched by pouring the solution over ice followed by slow addition of a saturated $NaHCO_3$ solution to adjust pH to ~7. The solution was filtered and the precipitated product was dissolved in acetonitrile. Pure **9** was recrystallized out from acetonitrile/water system to give a white powder; yield: 6.52 g (77%). ^{1}H NMR ($CDCl_3$): $\delta =$ 6.78 (s, 1H, *Ar*), 6.66 (s, 2H, *Ar*), 4.45 (s, 4H, CH_2), 2.99 [s, 6H, $(CH_3)_2N$].

Synthesis of 1,3-Bis[di(*tert*-butyl)phosphinomethyl]-5-dimethylaminobenzene (Me$_2$N-PCP-H) (10)

Synthesis of this ligand and its corresponding iridium hydrido chloride were based on reported syntheses by Shaw for the parent ligand.[16] To 1.0 g of **9** (3.25 mmol) in 20 mL of degassed acetone was added 1.36 mL (7.2 mmol) of di-*tert*-butylphosphine (98%) (Strem) at room temperature. The mixture was heated under reflux with stirring for 24 h under an argon atmosphere, and the solvent was removed under vacuum. The solid was dissolved in degassed deionized water (15 mL) and treated with a solution of potassium carbonate (2.7 g, 19.5 mmol) in degassed deionized water (10 mL). The diphosphine ligand was extracted with degassed *n*-hexane (3×20 mL) and the solvent was evaporated under vacuum, giving the ligand **10** as a white solid; yield: 1.03 g (72%). $^{31}P\{^1H\}$ NMR (C_6D_6): $\delta = 31.03$ (s); ^{1}H NMR (C_6D_6): $\delta = 6.98$ (s, 1H, *Ar*), 6.79 (s, 2H, *Ar*), 2.87 (d, $^2J_{H,P} =$ 2.4 Hz, 4H, CH_2), 2.78 [s, 6H, $(CH_3)_2N$], 1.18 [d, $^3J_{H,P} =$ 10.8 Hz, 36H, $C(CH_3)_3$].

Synthesis of (Me$_2$N-PCP)IrHCl

To 0.51 g of **10** (1.16 mmol) in 30 mL of toluene was added 0.38 g of $[Ir(COD)Cl]_2$ (0.57 mmol) at room temperature and stirred for 30 min under a hydrogen atmosphere. (*note*: the solution changes color from yellow to deep red under the hydrogen atmosphere at room temperature). This mixture was refluxed for three days under the hydrogen with stirring, and the solvent was removed under vacuum giving **4b** as dark-red solid; yield: 0.78 g (94%). $^{31}P\{^1H\}$ NMR (C_6D_6): $\delta = 67.03$ (s); ^{1}H NMR (C_6D_6): $\delta = 6.65$ (s, 2H, *Ar*), 3.16 (dvt, the left part of ABX_2 , $^2J_{H,H} = 17.7$ Hz, $J_{H,P} =$ 3.9 Hz, 2H, CH_2), 3.06 (dvt, the right part of ABX_2 , $^2J_{H,H} =$ 17.7 Hz, apparent $J = 3.9$ Hz, 2H, CH_2), 2.77 [s, 6H, $(CH_3)_2N$], 1.34 [virtual triplet, apparent $J = 6.9$ Hz, 18H, C-$(CH_3)_3$], 1.29 [virtual triplet, apparent $J = 6.9$ Hz, 18H, C-$(CH_3)_3$], −43.11 (t, $^2J_{H,P} = 12.8$ Hz, 1H, Ir-*H*).

Synthesis of (Me$_2$N-PCP)IrH$_4$ and (Me$_2$N-PCP)IrH$_2$ (1d)

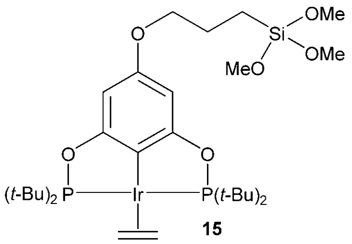
A stream of hydrogen was passed through a solution of 0.73 g of (Me$_2$N-PCP)IrHCl (1.1 mmol) in 300 mL anhydrous pentane for about 30 min. This was followed by a slow dropwise addition of 1.1 mL of 1M $LiBEt_3H$ in THF (1.1 mmol) to this solution with continuous stirring under a hydrogen atmosphere. The solution turned nearly colorless and some white precipitate was formed at the bottom of the flask. After the addition of $LiBEt_3H$ was complete, stirring was continued for 1 h and finally the solution was filtered under argon atmosphere. (*note*: on changing from H_2 to argon atmosphere the solution rapidly turned deep red). The solvent was removed under vacuum, giving **1d** as reddish brown crystals containing *ca.* 10% of (Me$_2$N-PCP)IrH$_4$; yield: 0.55 g (79%). (All the PCP-Ir tetrahydride is quickly converted to the corresponding dihydride under catalytic conditions; accordingly, for catalytic runs, the dihydrides are frequently used containing varying amounts of tetrahydride.)

NMR data for (Me$_2$N-PCP)IrH$_4$: $^{31}P\{^1H\}$ NMR (C_6D_6): $\delta = 72.42$ (s); ^{1}H NMR (C_6D_6): $\delta = 6.73$ (s, 2H, *Ar*), 3.32 (virtual triplet, apparent $J = 3.9$ Hz, 4H, CH_2), 2.79 [s, 6H, $(CH_3)_2N$], 1.24 [virtual triplet, apparent $J = 6.9$ Hz, 36H, C-$(CH_3)_3$], −9.09 (t, $^2J_{H,P} = 9.9$ Hz, 4H, IrH_4).

NMR data for ***1d****:* $^{31}P\{^1H\}$ NMR (C_6D_6): $\delta = 85.48$ (s); 1H NMR (C_6D_6): $\delta = 6.84$ (s, 2H, *Ar*), 3.62 (virtual triplet, apparent $J = 3.6$ Hz, 4H, CH_2), 2.76 [s, 6H, $(CH_3)_2N$], 1.33 [virtual triplet, apparent $J = 6.9$ Hz, 36H, $C(CH_3)_3$], −19.99 (t, $^2J_{H,P} = 8.7$ Hz, 2H, IrH_2).

Synthesis of {*p*-O(CH$_2$)$_3$Si(OMe)$_3$-C$_6$H$_2$-2,6-[OP(*t*-Bu)$_2$]$_2$}Ir(C$_2$H$_4$) (15)

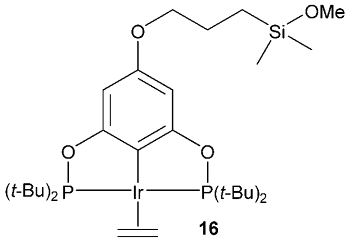
Complex **4** (80 mg, 0.119 mmol), $I(CH_2)_3Si(OMe)_3$ (138 mg, 0.476 mmol), and THF (10 mL) were added to a Kontes flask. The THF solution was degassed by freeze-pump-thaw cycles. The flask was refilled with ethylene gas at −78°C.



15

The mixture was heated at 65 °C for 2 h. NaOMe (22 mg, 0.407 mmol) was then added to the Kontes flask in the glove-box and the flask was refilled with ethylene gas at −78 °C. The mixture was stirred at room temperature for 2 days. NaOMe reacted with the excess of $I(CH_2)_3Si(OMe)_3$ (80 °C/2 mm) to produce NaI and $CH_2{=}CHCH_2Si(OMe)_3$ which is relatively more volatile (bp, 146 °C/760 mm) and easier to remove. Volatiles were then removed under high vacuum. The residue was extracted with 3 × 10 mL of pentane, and the extract was filtered through a 0.2 μm pore size syringe filter (Nalgene 199–2020) into a Schlenk flask. Removal of the solvent under high vacuum afforded of a red waxy solid which contained *ca.* 95% of **11** by NMR and was used without further purification in the next step; yield: 69 mg (0.086 mmol, 73%). ^{1}H NMR (400 MHz, 23 °C, C_6D_6): δ = 0.75 ((m, 2H, CH_2Si), 1.27 (virtual triplet, apparent J = 6.6 Hz, 36H, 4 × *t*-Bu), 1.88 (m, 2H, OCH$_2$CH_2), 3.14 (t, $^3J_{P,H}$ = 2.7 Hz, 4H, C$_2$$H_4$), 3.40, (s, 9H, 3 × OMe), 3.71 (t, $^2J_{H,H}$ = 6.5 Hz, 2H, OCH_2CH$_2$), 6.65 (s, 2H, 3- and 5-H); ^{31}P{^{1}H} NMR (162 MHz, 23 °C, C_6D_6): δ = 181.4.

Synthesis of {*p*-O(CH$_2$)$_3$Si(Me)$_2$(OMe)-C$_6$H$_2$-2,6-[OP(*t*-Bu)$_2$]$_2$}Ir(C$_2$H$_4$) (16)



16

The same synthetic procedure used for **15** was used except that $I(CH_2)_3Si(OMe)_3$ was replaced by $I(CH_2)_3Si(Me)_2(OMe)$ (123 mg, 0.476 mmol), giving a red waxy solid which contained *ca.* 95% of **12** by NMR and was used without further purification in the next step; yield: 63 mg (0.082 mmol, 69%). ^{1}H NMR (400 MHz, 23 °C, C_6D_6): δ = 0.09 [s, 6H, Si-(CH_3)$_2$], 0.56 (m, 2H, CH_2Si), 1.27 (virtual triplet, apparent J = 6.4 Hz, 36H, 4 × *t*-Bu), 1.69 (m, 2H, OCH$_2$CH_2), 3.14 (t, $^3J_{P,H}$ = 2.7 Hz, 4H, C$_2$$H_4$), 3.17, (s, 3H, OMe), 3.71 (t, $^2J_{H,H}$ = 6.4 Hz, 2H, OCH_2CH$_2$), 6.68 (s, 2H, 3- and 5-H); ^{31}P{^{1}H} NMR (162 MHz, 23 °C, C_6D_6): δ = 181.5.

Synthesis of Silica-Supported Iridium Pincer Complex 15

Complex **15** (50 mg, 0.062 mmol), silica (1.5 g), and toluene (10 mL) were added to a Kontes flask. The toluene suspension was degassed by freeze-pump-thaw cycles. The flask was refilled with ethylene gas at −78 °C and the suspension was stirred at 120 °C for 2 days. The flask was cooled to room temperature and ethylene gas was removed by freeze-pump-thaw cycles. Excess trimethylsilyldimethylamine (3 mL, 18.7 mmol) was added in the glove-box and the flask was degassed and refilled with ethylene gas at −78 °C. The suspension was stirred at room temperature for 2 days. This supported catalyst was filtered under argon, and washed with pentane, toluene and THF three times (5 mL each), respectively. The orange solid was dried under high vacuum overnight to give the product; yield: 1.46 g.

Synthesis of Silica-Supported Iridium Pincer Complex 16

Complex **16** (48 mg, 0.062 mmol), silica (1.05 g), and COE (5 mL) were added to a Kontes flask. The COE suspension was stirred at 150 °C for 2 days. The flask was cooled to room temperature and excess trimethylsilyldimethylamine (3 mL, 18.7 mmol) was added in the glove-box. The suspension was stirred at room temperature for 2 days. This supported catalyst was filtered under argon, and washed with pentane, toluene and THF three times (5 mL each), respectively. The light orange solid was dried under high vacuum overnight to give the product; yield: 0.86 g.

Hydrogen Transfer from COA to TBE, Catalyzed by Silica-Supported Iridium Pincer Complexes

The silica-supported complex **15** or **16** (2.0–3.15 μmol), COA (0.265–0.674 g, 2.36–6.0 mmol), and TBE (95%, 0.209–0.532 g, 2.36–6.0 mmol) were added to a Kontes flask. The flask was sealed tightly with a Teflon plug under an argon atmosphere and the suspension stirred in an oil bath at 200 °C. Periodically, the flask was removed from the bath and cooled in an ice bath. An aliquot was removed from the flask, and analyzed by GC (method **A**). Turnover numbers were calculated for each aliquot. Details are summarized in the text.

Acknowledgements

This work is financially supported by the NSF under the auspices of the Center for Enabling New Technologies through Catalysis (CENTC).

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