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Published on Web 01/24/2004

Iridium Bis(phosphinite) *p*-XPCP Pincer Complexes: Highly Active Catalysts for the Transfer Dehydrogenation of Alkanes

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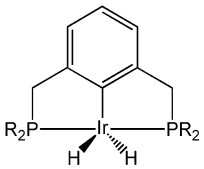
Abstract: A series of new bis(phosphinite) *p*-XPCPIrHCl pincer complexes {[PCP = η^3-5-X−C_6H_2[OP(*t*Bu)$_2$]$_2$-1,3], X = MeO (**4a**), Me (**4b**), H (**4c**), F (**4d**), C_6F_5 (**4e**), and Ar^F [=3,5-bis(trifluoromethyl)phenyl] (**4f**)} have been synthesized. Treatment of compounds **4a**−**f** with Na*t*OBu in cyclooctane (COA)/*tert*-butylethylene (TBE) mixtures generates species with unprecedented catalytic activity for the catalyzed transfer dehydrogenation of COA with TBE as acceptor to form cyclooctene (COE) and *tert*-butylethane (TBA). With substrate:precatalyst ratios of 3030COA:3030TBE:1*p*-XPCPIrHCl (**4**):1.1NaO*t*Bu, turnover numbers (TONs) between 1400 and 2200 (up to 72% conversion in TBE) and initial turnover frequencies (TOFs) between 1.6 and 2.4 s^{-1} have been observed at 200 °C.

Introduction

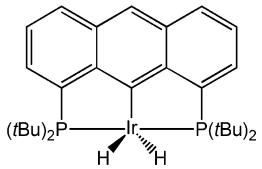
The selective, catalytic functionalization of alkanes remains a challenging and significant goal due to the prospects of transforming inexpensive hydrocarbon feedstocks into more useful, value-added products by low energy processes.[1] In this respect, catalytic alkane dehydrogenation is a potentially significant reaction in that alkanes are converted to olefins which are valuable synthetic intermediates and are used in a variety of industrial processes.

Following early examples of homogeneous dehydrogenations that are substoichiometric in transition metal,[2] a major breakthrough was achieved by Kaska, Jensen et al. who reported that the iridium pincer complex {C_6H_3-2,6-[CH_2P(*t*Bu)$_2$]$_2$}IrH_2 (**1**) (Chart 1) catalyzes the transfer dehydrogenation reaction of cyclooctane (COA) with *tert*-butylethylene (TBE) to form cyclooctene (COE) and *tert*-butylethane (TBA) at 200 °C. While turnover numbers up to 1000 can be achieved, catalyst inhibition by TBE (as well as the COE product) requires periodic addition of TBE to the reaction to achieve such TONs.[1c,3] Subsequently, mechanistic details of these transfer dehydrogenations by means of experimental and computational studies have been disclosed.[4]

Chart 1. Catalysts **1**−**3**



R = *t*Bu (**1**)
R = *i*Pr (**2**)



(**3**)

Transfer dehydrogenation overcomes the thermodynamic (ca. 30−35 kcal/mol endothermic)[5] and kinetic difficulties of hydrogen release but requires an acceptor molecule. To carry out "acceptorless" dehydrogenation, an efficient removal of hydrogen from the reaction mixture is required. Acceptorless dehydrogenation has been achieved using both complex **2**[4j,6] and the even more thermostable anthraphos pincer complex **3** (Chart 1).[7] Turnover numbers (TONs) up to 1000 have been

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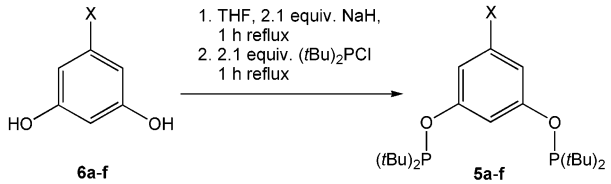
10.1021/ja0385235 CCC: $27.50

Scheme 1. Synthesis of Bis(phosphinite) PCP Pincer Ligands **5a**−**f**



	X	5 [%][a]
5a	MeO	82
5b	Me	87
5c	H	93
5d	F	96
5e	C_6F_5	91
5f	Ar^F	90

[a]NMR purity ca. 95%

achieved for the acceptorless dehydrogenation of cyclodecane at 200 °C with **2** and at 250 °C with **3**, respectively.

Driven by our interest in employing C−H activation reactions in catalytic transformations[8] and the possible advantages of using more electron-deficient iridium pincer complexes, we report here our initial studies of the catalytic properties of resorcinol-derived phosphinite pincer complexes conveniently generated from readily accessible hydridochloride precursors, {*p*-XC_6H_2-2,6-[$OP(tBu)_2]_2$}IrHCl (**4a**−**f**). These species exhibit unprecedented initial turnover frequencies (TOFs) and are less subject to TBE and product inhibition relative to complexes **1**−**3**.

Results and Discussion

(a) Ligand and Complex Synthesis. In analogy to the reported synthesis of {C_6H_3−$P(OiPr_2)_2$-1,3},[9] the bis(phosphinite) PCP ligands [5-$xC_6H_2(OPtBu_2)_2$-1,3] (**5a**−**f**) {x = MeO (**5a**), Me (**5b**), H (**5c**), F (**5d**), C_6F_5 (**5e**), Ar^F [=3,5-bis(trifluoromethyl)phenyl] (**5f**)} under investigation are obtained by diphosphorylation of the respective 5-substituted resorcinols (**6a**−**f**) with *tert*-butyl-chlorophosphine and sodium hydride as a base (Scheme 1). The yields of compounds **5a**−**f** are generally high (82−96%), and the crude products can be used without further purification. 5-Fluororesorcinol (**6d**) was obtained from 1-fluoro-3,5-dimethoxybenzene (**7d**) by deprotection with BCl_3/*n*-Bu_4I according to a literature procedure.[10] Finally, the 5-aryl substituted resorcinols (**6e**,**f**) were obtained in good overall yields (**6e**, 78%; **6f**, 85%) in a Suzuki coupling/deprotection sequence (BCl_3/*n*-Bu_4I-mediated) starting from 3,5-dimethoxybenzene boronic acid (**8**) and pentafluorobromobenzene, or 3,5-bis(trifluoromethyl)bromobenzene, respectively (Scheme 2).[11] Reaction conditions developed by Nolan et al. for the Suzuki coupling of 3,5-bis(trifluoromethyl)bromobenzene using Cs_2CO_3 as base and diimine ligands proved to be useful for the high yield synthesis of **7f**,[12] but gave unsatisfactory yields of compound **7e**.[13] However, excellent yields of compound **7e** could be obtained using KF as base and triphenylphosphine as ligand (Scheme 2).

Complexes **4a**−**f** were obtained in 87−93% isolated yield from reaction of $[(COD)IrCl]_2$ with the respective PCP ligands **5a**−**f** in toluene at 150 °C (Scheme 3). As was confirmed by NMR experiments, formation of complexes **4e**,**f** is complete after 1−2 h at 150 °C in toluene-d_8, whereas formation of **4a**−**d** takes 6−12 h under the same conditions. Unlike the methylene-bridged {4-MeO−C_6H_2−$[CH_2P(tBu)_2]_2$-2,6}IrHCl pincer complex **9**, the oxygen-bridged compound **4a** does not undergo C−H oxidative addition of one of the *tert*-butyl methyl groups and subsequent elimination of hydrogen to form a stable product.[14]

The poor solubility of the products **4a**−**d** in alkane solvents allows a straightforward separation of these complexes by filtration from their pentane suspensions. The more soluble complexes **4e**,**f** were isolated in combined yields by filtration of the solid product and flash chromatography of the remaining pentane filtrate.

Typical spectroscopic features of *p*-XPCPIrHCl (**4**) show two overlapping virtual triplets of the diastereotopic *tert*-butyl groups in the narrow range from 1.3 to 1.4 ppm as well the hydridic IrH resonances appearing as a triplet with $^2J_{PH}$ = 13.0−13.2 Hz in the range of −40.96 (**4f**) to −41.87 ppm (**4a**) in the ^{1}H NMR spectra. The aromatic CH and hydridic resonances of compound **4d** exhibit further splitting due to the ^{19}F nucleus *para* to iridium. The $^{31}P\{^1H\}$ NMR spectra of compounds **4a**−**f** exhibit singlets between 175.8 (**4c**) and 179.1 ppm (**4d**). Acquisition of $^{13}C\{^1H\}$ NMR spectra requires concentrated solutions of compounds **4a**−**f** due to the splitting into virtual triplets of the *tert*-butyl-, C2, C3, C5, and C6 resonances caused by the two equivalent ^{31}P nuclei. In the case of compound **4d**, additional splitting due to ^{19}F is observed for each aromatic ^{13}C nucleus. The Ir−C1 resonances appear as broad multiplets in the range of 108.1 (**4a**) to 121.5 ppm (**4f**) (rather than a triplet), due to incomplete $\{^1H\}$ decoupling of the hydride signal (ca. −41 ppm). Two sets of diastereotopic *tert*-butyl ^{13}C signals are observed at ca. 43.4 and 39.8 ppm for the $C(CH_3)_3$ and ca. 27.8 and 27.6 ppm for the $C(CH_3)_3$ groups for compounds **4a**−**f**. On the basis of these observations and of the reported X-ray structure of the related {4-NO_2−C_6H_2−$[CH_2P(tBu)_2]_2$-2,6}IrHCl pincer complex **10**,[15] we consider complexes **4** as having a square pyramidal geometry with the apical site occupied by the hydride and a mirror plane perpendicular to the plane of the

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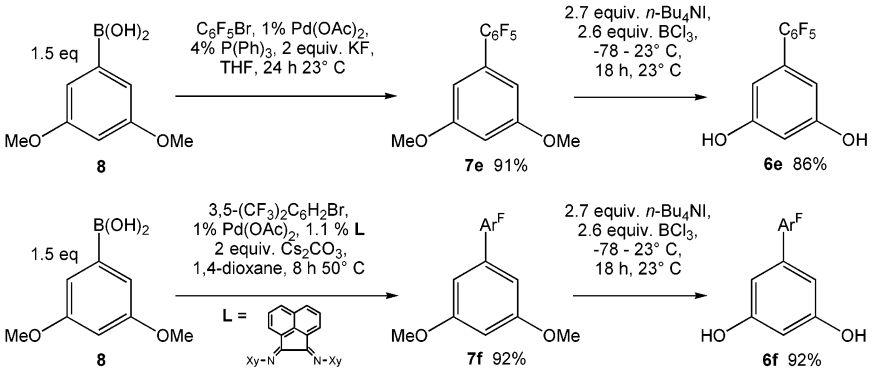
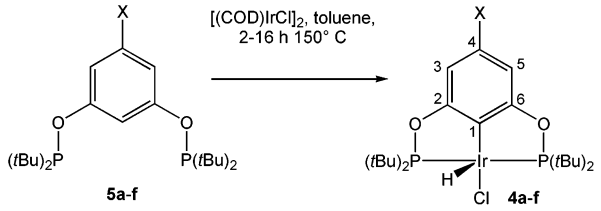
Scheme 2. Synthesis of 5-Arylresorcinols **6e**,**f**



Scheme 3. Synthesis of *p*-XPCPIrHCl Complexes (**4a**−**f**)



	X	4 [%][a]
4a	MeO	89
4b	Me	87
4c	H	93
4d	F	93
4e	C_6F_5	88
4f	Ar^F	93

[a] isolated yield

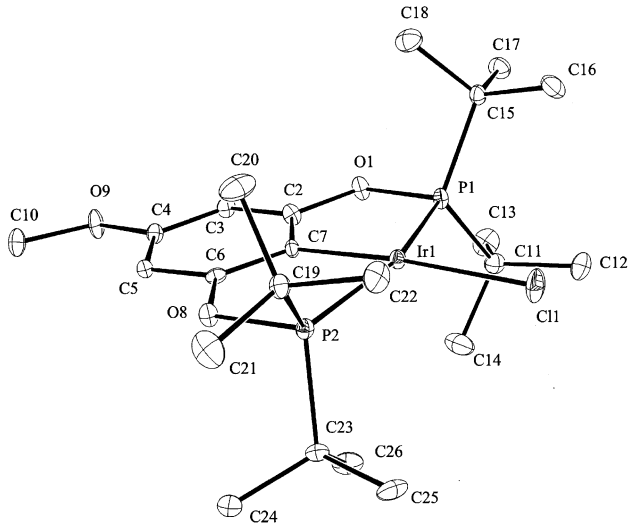


Figure 1. ORTEP plot of compound **4a** with thermal ellipsoids at a 50% probability level. Selected bond lengths (Å) and angles (deg): Ir1−C7 2.004(5), Ir1−P1 2.2949(16), Ir1−P2 2.2889(15), Ir1−Cl 2.4044(14), P1−O1 1.654(4), O1−C2 1.397(6), P2−O8 1.664(4); P1−Ir−P2 159.79(5), P1−Ir−C7 79.91(16), Ir1−P1−O1 104.68(14), P2−Ir−C7 80.07(16), Ir1−P2−O8 104.65(15), Cl1−Ir1−C7 174.75(15).

p-XPCP ligand along the C−Ir−Cl axis. The proposed geometry was confirmed by an X-ray crystal structure analysis of compound **4a** (Figure 1). The most striking feature of this structure as compared to the related methylene-bridged complex **10** is the nearly identical geometry around the Ir center despite the much shorter P1−O1 [1.654(4) Å], P2−O2 [1.664(4)], O1−C2 [1.397(6)], and O8−C6 [1.400(7)] distance. However, as compared to compound **10**, compound **4a** exhibits the shorter C_{aryl}Ir distance Ir1−C7 2.004(5) Å [2.015(3) (**10**)] as well as the smaller P−Ir−P angle 159.79(5)° [166.80(3) (**10**)] and C_{aryl}−Ir−Cl angle 174.75(15)° [179.33(14) (**10**)].

(b) Catalytic Activity of Species Generated from Complexes 4a−f. Kaska and Jensen et al. and Goldman et al. have shown that the iridium PCP pincer complex $\{C_6H_3$-2,6-$[CH_2P(tBu)_2]_2\}IrH_2$ (**1**) is an active dehydrogenation catalyst for several alkanes in both the presence and the absence of a hydrogen acceptor.[3,4j,l,6,16] For the commonly used benchmark reaction of cyclooctane (COA) and *tert*-butylethylene (TBE) to form cyclooctene COE and *tert*-butylethane (TBA) (Scheme 4), turnover numbers (TONs) as high as 720−1000, turnover frequencies (TOFs) as high as 12 min^{-1}, and conversions of 10−25% COA have been reported for complex **1** at 200 °C. However, inhibition of **1** by TBE:**1** ratios >350 is reported, a feature which requires periodic addition of TBE to obtain higher TONs.[1d] Complex **1** is an oxygen- and nitrogen-sensitive compound with high thermal stability obtained in 85% yield after treatment of the $\{C_6H_3$-2,6$[CH_2P(tBu)_2]_2\}$IrHCl (**11**) precursor with $LiBHEt_3$ under an atmosphere of hydrogen and removal of dihydrogen from the formed tetrahydride $\{C_6H_3$-2,6$[CH_2P(tBu)_2]_2\}IrH_4$ at 130 °C.[4l] Unfortunately, as was explicitly noted, the catalytic activity of **1** is very sensitive to boron containing impurities, and thus an in situ generation of catalytic active species was precluded due to the use of $LiBHEt_3$.[1d] The advantage of an in situ generation of the catalytic active species from precursor complex **11** or **4a**−**f**, however, is obvious, because **11** and **4a**−**f** are air stable for at least several months in the solid state and for several weeks in solution.

We have succeeded in generating catalytically active species for the transfer dehydrogenation of COA with TBE starting from either **11** or complexes **4a**−**f**. Thus, simple addition of NaO*t*Bu to mixtures of COA, TBE, and either complexes **4a**−**f** or **11** initiates the generation of TBA and COE according to Scheme 4 upon heating the resulting mixtures to 70−200 °C. Remarkably, we find that precursors **4a**−**f** upon reaction with NaO*t*Bu generate species which are much less subject to inhibition by TBE or product COE than the catalytically active species generated from complex **11** (or catalyst **1**). In an exemplified series of experiments, reaction of COA, TBE, NaO*t*Bu, and **4a**−**f** in a 3030:3030:1.1:1 ratio results in 1480−2070 TONs

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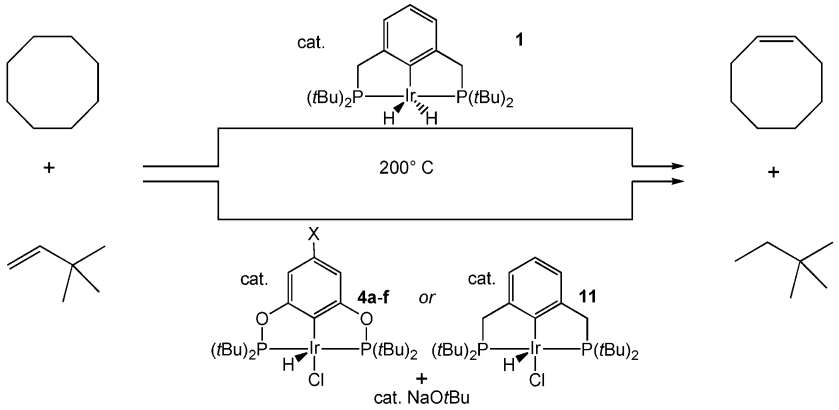
Scheme 4. Transfer Dehydrogenation Catalyzed by **1** or by Hydridochloride Precursors **4a**−**f** or **11** and NaO*t*Bu



(48.8−68.3% conversion of TBE) after 40 h at 200 °C, while 230 TONs are obtained with precatalyst **11** under identical conditions.

More than 50% of the overall TONs for a given precatalyst **4b**−**f** (not **4a**) already occur after 8 min at 200 °C, while >90% of all TONs take place within 40 h (see Table 1). The TONs after 8 min translate into initial average TOFs between 1.6 and 2.4 s^{-1}, which compares to 0.2 s^{-1} for the activity of isolated {C_6H_3-2,6-[$CH_2P(tBu)_2$]$_2$}IrH_2 (**1**).[1d,3] In contrast to the reported catalytic activity of **1**, precatalysts **4a**−**f** give rise to the generation of substantial amounts of 1,3-cyclooctadiene (1,3-COD),[17] as was determined by ^{1}H NMR, with more 1,3-COD produced by the more active systems (Table **1**, entries **4a**,**e**,**f** as compared to **4b**,**c**,**d**).[18]

While a more quantitative analysis of the electronic influence of the *p*-X-substituent in precatalysts **4a**−**f** is underway,[19] σ_p Hammett constants of these *p*-X-substituents identify **4a** [σ_p-(MeO) = −0.27] as the most electron-rich and **4e** [$\sigma_p(C_6F_5)$ = +0.27] [σ_p(Me) = −0.17, σ_p(H) = 0.00, σ_p(F) = +0.06, σ_p-(Ar^F) not reported] as the most electron-deficient systems under investigation.[20] Based on these Hammett constants, a correlation between increasing initial TOFs and increasing electron deficiency of precatalysts **4a**−**f** exists. With respect to the overall TONs, however, this correlation does not persist, because catalysis with **4a** results in nearly as many TOs as with **4e**,**f** and significantly more than with **4b**,**c**,**d** (Table 1). We tentatively ascribe this behavior to the counterbalancing effects of activity and inhibition of active species generated from **4a**−**f**, both increasing with electron deficiency. As was already observed for **1**,[3] the catalytic activity in the reactions described here, for example, with **4c**, is fully restored after evaporation of all volatiles and addition of fresh COA/TBE solutions.

(c) COE Disproportionation into COA and 1,3-COD. Production of Alkylated Benzenes by Further Dehydrogenation of 1,3-COD. As already mentioned, and in striking contrast to catalytically active species derived from {C_6H_3-2,6-[$CH_2P(tBu)_2$]$_2$}IrHCl (**11**), we find substantial amounts of 1,3-COD when catalysts derived from complexes **4a**−**f** are used in the transfer dehydrogenation of COA with TBE. It remained unclear, however, whether TBE serves exclusively as the hydrogen acceptor in these reactions. Therefore, in independent experiments, the possible formation of 1,3-COD and COA via disproportionation COE was probed. No formation of 1,3-COD, however, was observed in neat COE solutions with COE:Ir ratios >1000:1 at 200 °C if precatalyst **4c** was used, thus indicating that TBE likely is the hydrogen acceptor for COE dehydrogenation in COA/TBE mixtures (vide supra). By lowering the COE:Ir ratio to ca. 450:1, however, we could monitor a slow buildup of 1,3-COD and of *o*-xylene and ethylbenzene as higher dehydrogenation products by ^{1}H NMR (cyclooctatriene is not observed). After 192 h at 200 °C, nearly all COE is consumed, and a 4:1-mixture of *o*-xylene:ethylbenzene, as well as COA and 1,2-dimethylcyclohexane (as hydrogenation products), is observed by ^{1}H and ^{13}C NMR, besides traces of 1,3-COD and further unidentified (cyclo)alkanes (ca. 300 TO in COE, 150 COE serve as hydrogen donor, 300 COE serve as hydrogen acceptor). A selective formation of 1,3-COD in nearly quantitative yield (ca. 240 TO in COE) without formation of even traces of *o*-xylene or ethylbenzene, however, was accomplished by reacting a 500:500:1:1.1 mixture of COE, *tert*-butyl alcohol (or cyclohexane), **4c**, and NaO*t*Bu for 48 h at 200 °C. Even after

Table 1. TONs for the Transfer Dehydrogenation of COA and TBE Catalyzed by **4a**−**f** and **11** Plus NaO*t*Bu Obtained at 200 °C and the COE:1,3-COD Product Ratio[a]

	4 (*p*-X=)						
	a MeO	**b** Me	**c** H	**d** F	**e** C_6F_5	**f** Ar^F	**11** H
8 min	806	811	922	840	1150	1162	156
(COE/COD)[b]	(100/0)	(100/0)	(99/1)	(99/1)	(94/6)	(94/6)	(100/0)
31 min	1226	1087	1194	1108	1401	1424	198
(COE/COD)[b]	(93/7)	(95/5)	(93/7)	(93/7)	(90/10)	(89/11)	(100/0)
178 min	1564	1356	1514	1380	1699	1735	216
(COE/COD)[b]	(86/14)	(87/13)	(86/14)	(85/15)	(83/17)	(82/18)	(100/0)
918 min	1674	1413	1512	1465	1863	1893	212
(COE/COD)[b]	(83/17)	(87/13)	(86/14)	(85/15)	(80/20)	(79/21)	(100/0)
2398 min	1904	1484	1583	1530	2041	2070	227
(COE/COD)[b]	(81/19)	(86/14)	(84/16)	(84/16)	(78/22)	(76/24)	(100/0)
6170 min	2017	1488	1609	1605	2175	2186	230
(COE/COD)[b]	(78/22)	(86/14)	(83/17)	(83/17)	(75/25)	(75/25)	(100/0)
20 305 min	2047	1485	1603	1633	2170	2210	230
(COE/COD)[b]	(78/22)	(85/15)	(83/17)	(82/18)	(75/25)	(75/25)	(100/0)

[a] Average of three runs, based on conversion of TBE determined by ^{1}H NMR, 3030 TO = 100% conversion, all reactions performed under an argon atmosphere. [b] Determined by ^{1}H NMR, the sum of COE and COD double bonds equals TON of TBE within 2% difference.

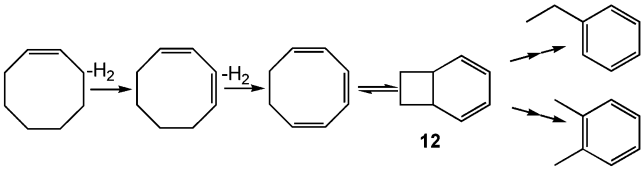
(17) We have not observed formation of 1,4- or 1,5-cyclooctadiene in these reactions. However, while monitoring the synthesis of precatalysts **4a**−**f** from [(COD)IrCl]$_2$ and ligands **5a**−**f** by ^{1}H NMR, we have observed that the 1,5-cyclooctadiene liberated in these reactions isomerizes quantitatively to 1,3-cyclooctadiene even at 150 °C.

(18) We have not been able to resolve COE from 1,3-COD by GC analysis using a Agilent HP-1 column (30 m, 0.32 mm widebore, 0.25 μm film). A 1,3-COD shoulder on the COE signal was resolved at isothermic 70 °C, flow rate 0.2 mL/min.

(19) In preparation.

(20) Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165−195.

Scheme 5. Proposed Pathway for the Formation of Alkylated Benzenes from COE



additional heating to 200 °C (ca. 12−24 h), no buildup of alkylated benzenes was observed. While it remains unclear so far how *tert*-butyl alcohol or cyclohexane are involved in suppressing a further dehydrogenation of 1,3-COD, the formation of *o*-xylene and ethylbenzene in neat COE solvent likely proceeds through the equilibrium disrotatory ring closure of cyclooctatriene to form [4.2.0]octa-2,4-diene **12**,[21] rather than through a Ir-mediated carbon carbon bond cleavage of the eight-membered ring (Scheme 5).

Summary

New bis(phosphinite) *p*-XPCPIrHCl complexes **4a**−**f** have been synthesized. In situ generation of catalytically active species for the transfer dehydrogenation of cyclooctane with *tert*-butylethylene to form cyclooctene and *tert*-butylethane is very easily accomplished by reaction of **4a**−**f** with NaO*t*Bu in the reaction mixture. Under comparable conditions, these new catalysts are roughly 1 order of magnitude more active in terms of TOFs, TONs, and substrate conversion than the benchmark catalyst $\{C_6H_3\text{-}2,6\text{-}[CH_2P(t\text{Bu})_2]_2\}IrH_2$ (**1**), providing TOFs up to 2.4 s^{-1} at 200 °C. A further dehydrogenation of COE to form 1,3-COD is accomplished by transfer dehydrogenation in the presence of TBE at high COE concentration. In the absence of another hydrogen acceptor, COE itself serves as hydrogen acceptor and gives rise to a disproportionation of COE into COA and 1,3-COD, which is further transformed into *o*-xylene and ethylbenzene at temperatures as low as 200 °C. However, disproportionation of COE into 1,3-COD and COA at 200 °C is only operative at relatively low COE to catalyst ratios (ca. 450:1).

Experimental Section

General Considerations. All manipulations were carried out using standard Schlenk, high vacuum, and glovebox techniques. Argon was purified by passage through columns of BASF R3-11 (Chemaolg) and 4 Å molecular sieves. THF was distilled from benzophenone ketyl prior to use. Hexanes, pentane, toluene, diethyl ether, and dichloromethane were passed through columns of activated alumina. Solvents and reagents used in the generation of catalytically active Ir-complexes were thoroughly freed from nitrogen (and oxygen) by several freeze−pump−thaw cycles and stored in an argon atmosphere glovebox. Benzene-d_6 and toluene-d_8 were dried over sodium, degassed, and vacuum transferred prior to use. CD_2Cl_2 was dried over P_2O_5, degassed, and vacuum transferred prior to use. Cyclooctane (COA) was stirred over concentrated H_2SO_4 for several hours until olefin- and arene-free (GC and NMR analysis), then distilled under vacuum, and stored in an argon atmosphere glovebox. *tert*-Butylethylene (TBE) (95%, Aldrich) was degassed, vacuum transferred, and stored in the glovebox prior to use. Resorcinol, 3,5-dihydroxytoluene, 1-fluoro-3,5-dimethoxybenzene, pentafluorobromobenzene, sodium hydride (95%), and di-*tert*-butyl-chlorophosphine (96%) were used as purchased from Aldrich. $[(COD)IrCl]_2$ was used as purchased from Strem or synthesized by a known procedure.[22] 3,5-Dimethoxybenzene boronic acid[11] and 5-fluororesorcinol[10] were synthesized by known procedures. NMR spectra were recorded on Bruker DRX 400 and AMX 300 MHz instruments and are referenced either to residual protio solvent or to TMS as internal standard. ^{31}P chemical shifts are referenced to an external H_3PO_4 standard. ^{19}F chemical shifts have not been referenced. IR spectra were recorded on an ASI ReactIR 1000 spectrometer. Elemental analyses were carried out by Atlantic Microlab, Inc. of Norcross, GA.

General Procedure for the Synthesis of 5-XPCP Pincer Ligands 5. A suspension of 2.1 mmol of NaH in 5 mL of THF was slowly added via syringe to a solution of 1 mmol of the 5-substituted resorcinol in 15 mL of THF (caution: hydrogen evolution). The mixture was heated to reflux for 1 h, a solution of 2.1 mmol of di-*tert*-butyl-chlorophosphine in 5 mL of THF was then added via syringe, and the mixture was refluxed for additional 1 h. After evaporation of the solvent in high vacuum (10^{-3} mbar, 1 h), the residue was extracted with 40 mL of pentane, and the extract was cannula transferred and filtered through a pad of Celite. After removal of pentane under vacuum, the flask was heated to 55 °C for 2 h at high vacuum which removed residual amounts of di-*tert*-butyl-chlorophosphine. The crude products were obtained as colorless viscous oils which occasionally solidified upon standing and generally exhibited ca. 95% purity by NMR. They were used without further purification.

5-MeOPCP (5a). From 140 mg (1 mmol) of 5-methoxyresorcinol (**6a**), 53 mg (2.1 mmol) of NaH, and 395 mg (2.1 mmol) of di-*tert*-butyl-chlorophosphine was obtained 340 mg (0.82 mmol, 82%) of 5-MeOPCP (**5a**) as a colorless oil. ^1H NMR (300 MHz, 23 °C, C_6D_6): δ 7.15 (m, 1H, 2-H), 6.71 (m, 2H, 4- and 6-H), 3.33 (s, 3H, OCH_3), 1.12 [d, $^3J_{P-H}$ = 11.7 Hz, 36H, 2 × P(*t*Bu)$_2$]. $^{31}P\{^1H\}$ NMR (121.5 MHz, 23 °C, C_6D_6): δ 152.0. $^{13}C\{^1H\}$ NMR (75.5 MHz, 23 °C, C_6D_6): δ 162.1 (C_q, d, $^2J_{P-C}$ = 9.4 Hz, C1 and C3), 162.0 (C_q, C5), 101.5 (CH, t, $^3J_{P-C}$ = 11.9 Hz, C2), 98.8 (CH, d, $^3J_{P-C}$ = 11.5 Hz, C4 and C6), 54.8 (OCH_3), 35.6 [C_q, d, $^1J_{P-C}$ = 26.7 Hz, 2 × P(*t*Bu)$_2$], 27.5 [CH_3, d, $^2J_{P-C}$ = 15.8 Hz, 2 × P(*t*Bu)$_2$].

5-MePCP (5b). From 124 mg (1 mmol) of 3,5-dihydroxytoluene (**6b**), 53 mg (2.1 mmol) of NaH, and 395 mg (2.1 mmol) of di-*tert*-butyl-chlorophosphine was obtained 346 mg (0.87 mmol, 87%) of 5-MePCP (**5b**) as an off-white solid. ^1H NMR (300 MHz, 23 °C, C_6D_6): δ 6.70 (m, 1H, 2-H), 6.52 (m, 2H, 4- and 6-H), 2.18 (s, 3H, 4-CH_3), 1.08 [d, $^3J_{P-H}$ = 11.8 Hz, 36H, 2 × P(*t*Bu)$_2$]. $^{31}P\{^1H\}$ NMR (121.5 MHz, 23 °C, C_6D_6): δ 153.1. $^{13}C\{^1H\}$ NMR (75.5 MHz, 23 °C, C_6D_6): δ 160.5 (C_q, d, $^2J_{P-C}$ = 9.0 Hz, C1 and C3), 139.7 (C_q, s, C5), 112.0 (CH, d, $^3J_{P-C}$ = 11.0 Hz, C4 and C6), 105.9 (CH, t, $^3J_{P-C}$ = 10.0 Hz, C2), 35.5 [C_q, d, $^1J_{P-C}$ = 25.3 Hz, 2 × P(*t*Bu)$_2$], 27.3 [CH_3, d, $^2J_{P-C}$ = 15.4 Hz, 2 × P(*t*Bu)$_2$], 21.5 (CH_3, s, C4-Me).

5-HPCP (5c). From 110 mg (1 mmol) of resorcinol (**6a**), 53 mg (2.1 mmol) of NaH, and 395 mg (2.1 mmol) of di-*tert*-butyl-chlorophosphine was obtained 371 mg (0.93 mmol, 93%) of 5-HPCP (**5c**) as a colorless oil which solidified upon standing. ^1H NMR (300 MHz, 23 °C, C_6D_6): δ 7.48 (m, 1H, 2-H), 7.00 (m, 3H, 4−6-H), 1.11 (d, $^3J_{P-H}$ = 11.6 Hz, 2 × P(*t*Bu)$_2$. $^{31}P\{^1H\}$ NMR (121.5 MHz, 23 °C, C_6D_6): δ 153.1. $^{13}C\{^1H\}$ NMR (75.5 MHz, 23 °C, C_6D_6): δ 161.5 (C_q, d, $^2J_{P-C}$ = 9.5 Hz, C1 and C3), 130.1 (CH, C5), 111.8 (CH, d, $^3J_{P-C}$ = 11.3 Hz, C4 and C6), 109.0 (CH, t, $^3J_{P-C}$ = 11.4 Hz, C2), 35.6 [C_q, d, $^1J_{P-C}$ = 26.7 Hz, 2 × P(*t*Bu)$_2$], 27.5 [CH_3, d, $^3J_{P-C}$ = 15.8 Hz, 2 × P(*t*Bu)$_2$].

5-FPCP (5d). From 128 mg (1 mmol) of 5-fluororesorcinol (**6d**), 53 mg (2.1 mmol) of NaH, and 395 mg (2.1 mmol) of di-*tert*-butyl-chlorophosphine was obtained 401 mg (0.96 mmol, 96%) of 5-FPCP (**5d**) as a colorless oil. ^1H NMR (300 MHz, 23 °C, $CDCl_3$): δ 6.78 (m, 1H, 2-H), 6.44 (dm, $^3J_{F-H}$ = 10.5 Hz, 4- and 6-H), 1.07 [d, $^3J_{P-H}$ = 12.0 Hz, 36H, 2 × P(*t*Bu)$_2$]. $^{31}P\{^1H\}$ NMR (121.5 MHz, 23 °C, $CDCl_3$): δ 155.4. $^{19}F\{^1H\}$ NMR (376.5 MHz, 23 °C, $CDCl_3$): δ −111.9. $^{13}C\{^1H\}$ NMR (75.5 MHz, 23 °C, $CDCl_3$): δ 163.5 (C_q, d,

(21) Huisgen, R.; Dahmen, A.; Huber, H. *J. Am. Chem. Soc.* **1967**, *89*, 7130−7131.

(22) Herde, J. L.; Lambert, J. C.; Senoff, C. V. *Inorg. Synth.* **1974**, *15*, 18−19.

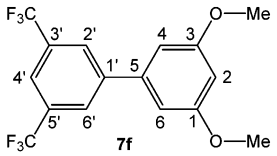
$^1J_{F-C}$ = 243.5 Hz, C5), 161.4 (C_q, dd, $^2J_{P-C}$ and $^3J_{F-C}$ = 10.2 and 14.1 Hz, C1 and C3), 104.3 (CH, dt, $^4J_{F-C}$ = 3.3 Hz, $^3J_{P-C}$ = 10.2 Hz, C2), 99.0 (CH, dd, $^2J_{F-C}$ = 25.0 Hz and $^3J_{P-C}$ = 12.2 Hz, C4 and C6), 35.6 [C_q, d, $^1J_{P-C}$ = 25.8 Hz, 2 × P(*t*Bu)$_2$], 27.3 [CH_3, d, $^2J_{P-C}$ = 15.5 Hz, 2 × P(*t*Bu)$_2$].

5-(C_6F_5)-1,3-$(OMe)_2$Ph (7e). First attempts to synthesize compound **7e** in analogy to compound **7f** resulted in very low yields. An improved synthesis used KF as base: A septum-capped Schlenk flask was charged with 1.365 mg (7.5 mmol) of 3,5-dimethoxyphenylboronic acid (**8**), 1.740 g (30.0 mmol) of KF, 11 mg (0.05 mmol) of $Pd(OAc)_2$, and 55 mg (0.21 mmol) of triphenylphosphine. After evacuation and refill with argon, a solution of 1.235 g (5 mmol) of pentafluorobromobenzene in 5 mL of THF was added, and the slurry was vigorously stirred for 24 h at 23 °C (TLC indicated consumption of pentafluorobromobenzene). The resulting slurry was added to a separatory funnel containing 20 mL of 0.05 M NaOH and extracted with 3 × 25 mL of diethyl ether. The combined organic layers were dried with $MgSO_4$ and filtrated. After removal of the solvent, the resulting solid was separated by column chromotography on silica gel [15 × 1 cm, hexanes:diethyl ether 10:1, R_f = 0.5 (hexanes:diethyl ether 10:1)] to give 1.386 g (4.56 mmol, 91%) of 3,5-dimethoxy-1-(pentafluorophenyl)benzene **(7e)** as a white crystalline solid. ^{1}H NMR (300 MHz, 23 °C, $CDCl_3$): δ 6.42 (m, 3H, 2-, 4-, and 6-H), 3.70 (s, 6H, 2 × OMe). ^{19}F{^{1}H} NMR (376.5 MHz, 23 °C, $CDCl_3$): δ −142.96 (m, 2F, 2′- and 6′-F), −156.25 (t, $^3J_{F-F}$ = 20.9 Hz, 1F, 4′-F), −162.89 (m, 2F, 3′- and 5′-F). ^{13}C{^{1}H} NMR (75.5 MHz, 23 °C, $CDCl_3$): δ 160.8 (C_q, C1 and C3), 144.2, 140.4, and 137.8 (C_q each, dm each, $^1J_{F-C}$ = 247.5, 252.5, and 253.0 Hz, C2′−C6′), 127.8 (C_q, s, C5), 115.9 (C_q, m, C1′), 108.2 (CH, s, C4 and C6), 101.2 (CH, s, C2), 55.3 (CH_3, s, 2 × OMe).

5-C_6F_5Ph$(OH)_2$ (6e). Compound **6e** was synthesized in analogy to a known procedure:[10] To a solution of 1.217 g (4.0 mmol) of 3,5-dimethoxy-1-(pentafluorophenyl)benzene (**7e**) and 3.990 g (10.8 mmol) of tetrabutylammoniumiodide in 35 mL of dichloromethane at −78 °C was added 10.5 mL (10.5 mmol) of a 1.0 M solution of boron trichloride in dichloromethane under stirring in 20 min. The solution was allowed to warm to 23 °C and was stirred for 18 h. Water (50 mL) was added, and the biphasic system was vigorously stirred for 30 min. Dichloromethane was evaporated under reduced pressure (200 mbar, 40 °C), 100 mL of diethyl ether was added to the residue, and the organic layer was extracted with 4 × 50 mL of 1 M HCl (discarded) and finally with 20 mL of 0.5 M NaOH. Dropwise addition of 10 mL of 3 M HCl to the aqueous phase caused precipitation of the crude product which was extracted into 4 × 15 mL of diethyl ether. After the mixture was dried over $MgSO_4$, the solvent was removed under reduced pressure (400 mbar, 40 °C, then 10^{-3} mbar, 23 °C) to yield 948 mg (3.43 mmol, 86%) of a white powder which contained ca. 95% of 5-(pentafluorophenyl)resorcinol (**6e**) by NMR and was used without further purification in the next step. Depending on the solvent used, compound **6e** exhibits tautomerism between the β-ketohydroxy and the dihydroxy form. ^{1}H NMR (400 MHz, 23 °C, acetone-d_6): δ 8.56 (s, 2H, 2 × OH), 6.50 (m, 1H, 2-H), 6.46 (m, 2H, 4- and 6-H). ^{19}F{^{1}H} NMR (376.5 MHz, 23 °C, acetone-d_6): δ −144.67 (m, 2F, 2′- and 6′-F), −159.21 (t, $^3J_{F-F}$ = 20.7 Hz, 1F, 4′-F), −165.29 (m, 2F, 3′- and 5′-F). ^{13}C{^{1}H} NMR (100.6 MHz, 23 °C, acetone-d_6): δ 159.7 (C_q, C1 and C3), 145.2, 141.2, and 138.7 (C_q, each, dm each, $^1J_{F-C}$ = 253.0, 250.9, and 245.8 Hz, C2′−C6′), 128.8 (C_q, C5), 117.3 (C_q, m, C1′), 109.7 (CH, C4 and C6), 104.6 (CH, C2).

5-C_6F_5PCP (5e). From 276 mg (1 mmol) of 5-(pentafluorophenyl)-resorcinol (**6e**), 53 mg (2.1 mmol) of NaH, and 395 mg (2.1 mmol) of di-*tert*-butylchloro-phosphine was obtained 513 mg (0.91 mmol, 91%) of 5-(C_6F_5)PCP (**5e**) as a colorless oil. ^{1}H NMR (400 MHz, 23 °C, Tol-d_8): δ 7.41 (m, 1H, 2-H), 7.08 (m br, 2H, 4- and 6-H), 1.11 [d, $^3J_{P-H}$ = 11.8 Hz, 36H, 2 × P(*t*Bu)$_2$]. ^{31}P{^{1}H} NMR (162 MHz, 23 °C, Tol-d_8): δ 154.9. ^{19}F{^{1}H} NMR (376.5 MHz, 23 °C, Tol-d_8): δ −143.17 (m, 2F, 2′- and 6′-F), −157.00 (t, $^3J_{F-F}$ = 21.4 Hz, 1F, 4′-F), −163.20 (m, 2F, 3′- and 5′-F). ^{13}C{^{1}H} NMR (100.6 MHz, 23 °C, Tol-d_8): δ 161.6 (C_q, d, $^2J_{P-C}$ = 10.0 Hz, C1 and C3), 144.4, 140.5, and 138.0 (C_q each, dm, $^1J_{F-C}$ = 247.1, 253.0, and 251.7 Hz, C2′−C6′), C5 not detected, 115.8 (C_q, m, C1′), 113.7 (CH, d, $^3J_{P-C}$ = 12.5 Hz, C4 and C6), 110.0 (CH, t, $^3J_{P-C}$ = 10.7 Hz, C2), 36.0 [C_q, d, $^1J_{P-C}$ = 26.9 Hz, 2 × P(*t*Bu)$_2$], 27.5 [CH_3, d, $^2J_{P-C}$ = 15.6 Hz, 2 × P(*t*Bu)$_2$].

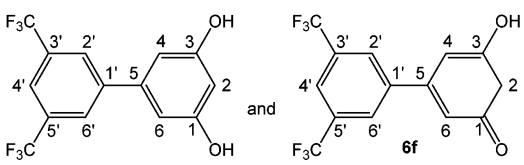
5-Ar^FPh$(OMe)_2$ (7f). This compound was synthesized in analogy to a known procedure:[11] A septum-capped Schlenk flask was charged with 1.365 mg (7.5 mmol) of 3,5-dimethoxyphenylboronic acid (**8**), 6.517 g (20.0 mmol) of Cs_2CO_3, 11 mg (0.05 mmol) of $Pd(OAc)_2$, and 42 mg (0.11 mmol) of *N*,*N*′-1,2-acenaphthylidene-bis(2,6-dimethyl)-benzenamine. After evacuation and refill with argon, a solution of 1.465 g (5 mmol) of 3,5-bis(trifluoromethyl)bromobenzene in 10 mL of 1,4-dioxane was added, and the slurry was vigorously stirred for 8 h at 50 °C (TLC control indicated consumption of 3,5-bis(trifluoromethyl)-bromobenzene). The resulting slurry was added to a separatory funnel containing 20 mL of 0.05 M NaOH and extracted with 3 × 25 mL of diethyl ether. The combined organic layers were dried over $MgSO_4$ and filtered. After removal of the solvent, the resulting solid was separated by column chromotography on silica gel [15 × 1 cm, hexanes: diethyl ether 10:1, R_f = 0.6 (hexanes:diethyl ether 5:1)] to give 1.613 g (4.61 mmol, 92%) of 3,5-dimethoxy-1-[3,5-bis(trifluoromethyl)-phenyl]benzene (**7f**) as a white crystalline solid.



7f

^{1}H NMR (300 MHz, 23 °C, C_6D_6): δ 7.77 (s, 2H, 2′- and 6′-H), 7.73 (s, 1H, 4′-H), 6.50 (s, 2H, 4- and 6-H), 3.29 (s, 6H, 2 × OMe). ^{19}F{^{1}H} NMR (376.5 MHz, 23 °C, C_6D_6): δ −62.88. ^{13}C{^{1}H} NMR (75.5 MHz, 23 °C, C_6D_6): δ 161.9 (C_q, C1 and C3), 144.0 and 140.0 (C_q, each, C5 and C1′), 132.2 (C_q, q, $^2J_{F-C}$ = 33.1 Hz, C3′ and C5′), 127.5 (CH, m, C2′ and C6′), 123.9 (C_q, q, $^1J_{F-C}$ = 273.0 Hz, 3′- and 5′-CF_3), 121.1 (CH, m, C4′), 105.9 (CH, C4 and C6), 100.9 (CH, C2), 54.9 (2 × OCH_3).

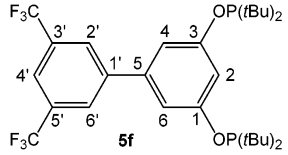
5-Ar^FPh$(OH)_2$ (6f). Synthesis of compound **6f** was accomplished in analogy to a published procedure:[10] To a solution of 1.401 g (4.0 mmol) of 3,5-dimethoxy-1-[3,5-bis(trifluoromethyl)phenyl]benzene (**7f**) and 3.990 g (10.8 mmol) of tetrabutylammoniumiodide in 35 mL of dichloromethane at −78 °C was added 10.5 mL (10.5 mmol) of a 1.0 M solution of borontrichloride in dichloromethane under stirring in 20 min. The solution was allowed to warm to 23 °C and stirred for 18 h. Water (50 mL) was added, and the biphasic system was vigorously stirred for 30 min. Dichloromethane was evaporated under reduced pressure (200 mbar, 40 °C), 100 mL of diethyl ether was added to the residue, and the organic layer was extracted with 4 × 50 mL of 1 M HCl (discarded) and finally with 20 mL of 0.5 M NaOH. Dropwise addition of 10 mL of 3 M HCl to the aqueous phase caused precipitation of the crude product which was extracted into 4 × 15 mL of diethyl ether. Removal of the solvent under reduced pressure (400 mbar, 40 °C, then 10^{-3} mbar, 23 °C) yielded 1.189 g (3.69 mmol, 92%) of a white powder which contained ca. 95% of 5-[3,5-bis(trifluoromethyl)-phenyl]resorcinol (**6f**) by NMR and was used without further purification in the next step. Depending on the solvent used, compound **6f** exhibits tautomerism between the β-ketohydroxy- and the dihydroxy form.



6f

^{1}H NMR [400 MHz, 23 °C, acetone-d_6, dynamic mixture of two isomers, second isomer in {}]: δ 8.54 (s, 1H, OH), 8.14 {8.14} (s, 2H, 2′- and 6′-H), 7.98 {7.98} (s, 1H, 4′-H), 6.73 {6.71} (d, $^4J_{H-H}$ = 2.1 Hz, 2H, 4- and 6-H), 6.49 {3.92} (t, $^4J_{H-H}$ = 2.1 Hz, 1H, 2-H {s, 2H, 2-H$_2$}). ^{1}H NMR (300 MHz, 23 °C, $CDCl_3$, only dihydroxy form): δ 7.96 (s, 2H, 4′- and 6′-H), 7.86 (s, 1H, 2′-H), 6.67 (s, 2H, 4- and 6-H), 6.45 (s, 1H, 2-H), 5.56 (s, 2H, 2 × OH). ^{19}F{^{1}H} NMR (376.5 MHz, 23 °C, acetone-d_6): δ −63.72. ^{13}C{^{1}H} NMR [100.6 MHz, 23 °C, acetone-d_6, second isomer in {}]: δ 160.1 {160.2 and 210.2} (C$_q$, C1 and C3), 144.6 and 140.7 {144.6 and 140.7} (C$_q$ each, C5 and C1′), 132.5 {132.5} (C$_q$, q, $^2J_{F-C}$ = 33.1 Hz, C3′ and C5′), 128.1 {128.1} (CH, m br, C2′ and C6′), 124.5 {124.5} (C$_q$, q, $^1J_{F-C}$ = 272.1 Hz, 3′- and 5′-CF$_3$), 121.6 (CH, m, C4′), 106.7 {106.8 and 104.1} (CH, C4 and C6), 104.0 {69.5 br} (CH {CH$_2$}, C2).

5-Ar^{F}PCP (5f). From 322 mg (1 mmol) of 5-[3,5-bis(trifluoromethyl)phenyl]resorcinol (**6f**), 53 mg (2.1 mmol) of NaH, and 395 mg (2.1 mmol) of di-*tert*-butyl-chlorophosphine was obtained 550 mg (0.90 mmol, 90%) of 5-(Ar^F)PCP (**5f**) as a colorless oil.



^{1}H NMR (300 MHz, 23 °C, C_6D_6): δ 7.78 (s, 2H, 2′- and 6′-H), 7.65 (s, 1H, 4′-H), 7.17 (s, 2H, 4- and 6-H), 7.08 (s, 1H, 2-H), 1.13 [d, $^3J_{P-H}$ = 12.0 Hz, 2 × P(*t*Bu)$_2$]. ^{31}P{^{1}H} NMR (121.5 MHz, 23 °C, C_6D_6): δ 154.8. ^{19}F{^{1}H} NMR (376.5 MHz, 23 °C, $CDCl_3$): δ −62.82. ^{13}C{^{1}H} NMR (75.5 MHz, 23 °C, C_6D_6): δ 162.1 (C$_q$, d, $^2J_{P-C}$ = 10.2 Hz, C1 and C3), 143.8 and 140.9 (C$_q$ each, C5 and C1′), 132.1 (C$_q$, q, $^2J_{F-C}$ = 33.1 Hz, C3′ and C5′), 127.7 (CH, C2′ and C6′), 123.8 (C$_q$, q, $^1J_{F-C}$ = 272.7 Hz, 3′- and 5′-CF$_3$), 121.1 (CH, m, C4′), 111.1 (CH, d, $^3J_{P-C}$ = 9.5 Hz, C4 and C6), 108.8 (CH, t, $^3J_{P-C}$ = 14.1 Hz, C2), 35.8 [C$_q$, d, $^1J_{P-C}$ = 26.7 Hz, 2 × P(*t*Bu)$_2$], 27.4 [CH$_3$, d, $^2J_{P-C}$ = 15.7 Hz, 2 × P(*t*Bu)$_2$].

General Procedure for the Synthesis of Complexes *p*-XPCPIrHCl (4a−f). A rubber septum-capped Schlenk flask was charged with 0.5 equiv of [(COD)IrCl]$_2$ and 1.1 equiv of the respective 5-XPCP ligand (**5a**−**f**). The flask was evacuated and refilled with argon. A small amount of toluene was added via syringe, and the solution was stirred in an oil bath for 1−16 h at 150 °C while the products **4a**−**d** started to precipitate. The reaction mixture was rapidly cooled to 30 °C. The solvent and free (1,3)-COD were removed in a vacuum (10^{-3} mbar, 30 °C), and the residue was extracted with a small amount of pentane under ultrasound (10 min). After filtration (no inert gas required), the solid was washed with small amounts of pentane and dried under high vacuum (10^{-3} mbar) to yield analytically pure samples. For higher solubility, it is desirable to obtain the products as microcrystalline solids when used for further transformations. In the case of compounds **4e**,**f**, the remaining mother liquors were flash chromatographed on neutral alumina to yield an additional crop of compounds **4e**,**f**.

***p*-MeOPCPIrHCl (4a).** Using the general procedure, we heated 168 mg (0.25 mmol) of [(COD)IrCl]$_2$ and 236 mg (0.55 mmol) of 5-MeOPCP (**5a**) for 16 h at 150 °C in 3 mL of toluene to yield 293 mg (0.45 mmol, 89%) of compound **4a** as a dark red microcrystalline solid that is virtually insoluble in pentane. ^{1}H NMR (300 MHz, 23 °C, $CDCl_3$): δ 6.27 (s, 2H, 3- and 5-H), 3.78 (s, 3H, OCH$_3$), 1.37 [m, 36H, 2 × P(*t*Bu)$_2$], −41.87 (t, $^2J_{P-H}$ = 13.2 Hz, IrH). ^{31}P{^{1}H} NMR (121.5 MHz, 23 °C, $CDCl_3$): δ 177.6. ^{13}C{^{1}H} NMR (75.5 MHz, 23 °C, $CDCl_3$): δ 167.3 (C$_q$, vt, J_{P-C} = 6.0 Hz, C2 and C6), 159.6 (C$_q$, C4), 108.1 (C$_q$, m br, C1), 91.9 (CH, t, $^2J_{P-C}$ = 5.1 Hz, C3 and C5), 55.4 (OCH$_3$), 43.0 and 39.5 [C$_q$ each, vt each, J_{P-C} = 22.6 and 25.3 Hz, 2 × P(*t*Bu)$_2$], 27.7 and 27.5 [CH$_3$, each vt, each, J_{P-C} = 3.2 and 3.1 Hz, 2 × P(*t*Bu)$_2$]. IR (CH_2Cl_2, cm^{-1}): 2944, 2904, 2871, 1595, 1563, 1475, 1370. Elemental analysis calcd for $C_{23}H_{42}O_3P_2ClIr$ (656.21): C, 42.09; H, 6.45. Found: C, 41.90; H, 6.33. X-ray structure analysis of compound **4a** (−100 °C): space group and cell dimensions, orthorhombic *Pbcn*, *a* 34.8215(7), *b* 10.49720(20), *c* 14.3434(3) Å, volume 5242.92(18) Å^3, empirical formula, $C_{23}H_{41}O_3P_2IrCl$. Cell dimensions were obtained from 7667 reflections with 2θ angle in the range 5.00−56.00°. Crystal dimensions: 0.35 × 0.15 × 0.05 mm, FW = 655.19, Z = 8, F(000) = 2611.51, ρ_{calc} 1.660 Mg/m^3, μ 5.35 mm^{-1}, λ 0.71073 Å, 2θ (max) 56.0°. The intensity data were collected on a Bruker SMART 1K diffractometer, using the ω scan mode. The *h*,*k*,*l* ranges used during structure solution and refinement are H$_{min,max}$ 0, 46; K$_{min,max}$ 0, 13; L$_{min,max}$ 0, 18. No. of reflections measured 25 346, no. of unique reflections 6337, no. of reflections with Inet > 2.5σ (Inet) 4687. Merging R-value on intensities 0.041. Correction was made for absorption using SADABS. Details of the last least squares cycle: 71 atoms, 272 parameters full-matrix on F_o counter wts (k 0.000050). The residuals are as follows: significant reflections, 4682 R_F 0.036, R_W 0.037; all reflections, 6337 R_F 0.058, R_W 0.041; included reflections, 4682 R_F 0.036, R_W 0.037; GOF 1.6181, where $R_F = \sum(F_o - F_c)/\sum(F_o)$, $R_W = [\sum(w(F_o - F_c)^2)/\sum(wF_o^2)]^{1/2}$ and GOF = $[\sum(w(F_o - F_c)^2)/(\text{no. of reflns} - \text{no. of params.})]^{1/2}$. The maximum shift/sigma ratio was 0.000. Last D-map: minimum density −2.540 e/Å^3, maximum density 1.440 e/Å^3. Secondary ext. coeff. 0.2050 μm sigma 0.0463.

***p*-MePCPIrHCl (4b).** Using the general procedure, we heated 168 mg (0.25 mmol) of [(COD)IrCl]$_2$ and 227 mg (0.55 mmol) of 5-MePCP (**5b**) for 12 h at 150 °C in 3 mL of toluene to yield 279 mg (0.44 mmol, 87%) of compound **4b** as a red brown microcrystalline solid slightly soluble in pentane. ^{1}H NMR (400 MHz, 23 °C, CD_2Cl_2): δ 6.42 (s, 2H, 3- and 5-H), 2.26 (s, 3H, 4-CH$_3$), 1.35 (m, 36H, 4 × *t*Bu), −41.63 (t, $^2J_{P-H}$ = 13.1 Hz, 1H, IrH). ^{31}P{^{1}H} NMR (162 MHz, 23 °C, CD_2Cl_2): δ 176.1. ^{13}C{^{1}H} NMR (100.6 MHz, 23 °C, CD_2Cl_2): δ 1167.6 (C$_q$, vt, J_{P-C} = 5.9 Hz, C2 and C6), 136.3 (C$_q$, C4), 114.4 (C$_q$, m br, C1), 106.0 (CH, vt, J_{P-C} = 5.3 Hz, C3 and C5), 43.3 and 39.7 [C$_q$ each, vt each, J_{P-C} = 11.5 and 12.7 Hz, 2 × P(*t*Bu)$_2$], 27.8 and 27.6 [CH$_3$ each, vt each, J_{P-C} = 3.1 and 3.1 Hz, 2 × P(*t*Bu)$_2$], 21.5 (4-CH$_3$). IR (CH_2Cl_2, cm^{-1}): 2945, 2904, 2871, 1596, 1557, 1475, 1392. Elemental analysis calcd for $C_{23}H_{42}O_2P_2ClIr$ (640.21): C, 43.15; H, 6.61. Found: C, 43.89; H, 6.70.

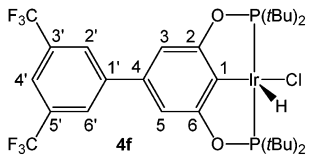
***p*-HPCPIrHCl (4c).** Using the general procedure, we heated 336 mg (0.5 mmol) of [(COD)IrCl]$_2$ and 438 mg (1.1 mmol) of 5-HPCP (**5c**) for 12 h at 150 °C in 3 mL of toluene to yield 585 mg (0.93 mmol, 93%) of compound **4c** as a red brown microcrystalline solid virtually insoluble in pentane. ^{1}H NMR (400 MHz, 23 °C, CD_2Cl_2): δ 6.76 (t, $^3J_{H-H}$ = 8.0 Hz, 1H, 4-H), 6.54 (d, $^3J_{H-H}$ = 8.0 Hz, 2H, 3- and 5-H), 1.35 (m, 36H, 4 × *t*Bu), −41.39 (t, $^2J_{P-H}$ = 13.1 Hz, 1H, IrH). ^{31}P{^{1}H} NMR (162 MHz, 23 °C, CD_2Cl_2): δ 175.8. ^{13}C{^{1}H} NMR (100.6 MHz, 23 °C, CD_2Cl_2): δ 167.7 (C$_q$, vt, J_{P-C} = 5.9 Hz, C2 and C6), 125.7 (CH, C4), 118.5 (C$_q$, m br, C1), 105.0 (CH, C3 and C5), 43.3 and 39.7 [C$_q$, each, vt each, J_{P-C} = 11.5 and 12.7 Hz, 2 × P(*t*Bu)$_2$], 27.8 and 27.6 [CH$_3$ each, vt each, J_{P-C} = 3.1 and 3.1 Hz, 2 × P(*t*Bu)$_2$]. IR (CH_2Cl_2, cm^{-1}): 2945, 2904, 2871, 1579, 1562, 1475, 1371. Elemental analysis calcd for $C_{22}H_{40}O_2P_2ClIr$ (626.18): C, 42.19; H, 6.44. Found: C, 42.40; H, 6.42.

***p*-FPCPIrHCl (4d).** Using the general procedure, we heated 168 mg (0.25 mmol) of [(COD)IrCl]$_2$ and 229 mg (0.55 mmol) of 5-FPCP (**5d**) for 8 h at 150 °C in 3 mL of toluene to yield 300 mg (0.47 mmol, 93%) of compound **4d** as a red brown microcrystalline solid virtually insoluble in pentane. ^{1}H NMR (400 MHz, 23 °C, CD_2Cl_2): δ 6.37 (d, $^3J_{F-H}$ = 9.5 Hz, 2H, 3- and 5-H), 1.34 (m, 36H, 4 × *t*Bu), −41.61 (t, $^2J_{P-H}$ = 13.1 Hz, 1H, IrH). ^{31}P{^{1}H} NMR (162 MHz, 23 °C, CD_2Cl_2): δ 179.1. ^{19}F{^{1}H} NMR (376.5 MHz, 23 °C, CD_2Cl_2): δ −119.01. ^{13}C-{^{1}H} NMR (75.5 MHz, 23 °C, CD_2Cl_2): δ 167.0 (C$_q$, dvt, $^3J_{F-C}$ = 14.8 Hz, J_{P-C} = 5.8 Hz, C2 and C6), 162.7 (C$_q$, d, $^1J_{F-C}$ = 237.0 Hz, C4), 112.5 (C$_q$, m br, C1), 93.4 (CH, dvt, $^2J_{F-C}$ = 26.0 Hz, J_{P-C} = 5.6 Hz, C3 and C5), 43.4 and 39.8 [C$_q$ each, vt each, J_{P-C} = 11.3 and 12.5 Hz, 2 × P(*t*Bu)$_2$], 27.7 and 27.6 [CH$_3$ each, vt each, J_{P-C} = 3.1 and 3.1 Hz, 2 × P(*t*Bu)$_2$]. IR (CH_2Cl_2, cm^{-1}): 2946, 2904, 2871, 1594,

1581, 1475, 1371. Elemental analysis calcd for $C_{22}H_{39}O_2P_2FClIr$ (644.17): C, 41.02; H, 6.10. Found: C, 40.44; H, 5.92.

***p*-C_6F_5PCPIrHCl (4e).** Using the general procedure, we heated 168 mg (0.25 mmol) of $[(COD)IrCl]_2$ and 311 mg (0.55 mmol) of 5-(C_6F_5)-PCP (**5e**) for 2 h at 150 °C in 3 mL of toluene to yield 313 mg (0.40 mmol, 79%) of compound **4e** as an orange microcrystalline solid moderately soluble in pentane. An additional 34 mg (0.04 mmol, 9%) of compound **4e** was obtained by column chromatography (8 × 0.3 cm, hexanes:diethyl ether 20:1, R_f = 0.6 hexanes:diethyl ether 10:1) of the collected filtrates (88% overall yield). ^{1}H NMR (400 MHz, 23 °C, $CDCl_3$): δ 6.63 (s, 2H, 3- and 5-H), 1.40 (m, 36H, 4 × *t*Bu), −41.06 (t, $^2J_{P-H}$ = 13.0 Hz, 1H, IrH). ^{31}P{^{1}H} NMR (162 MHz, 23 °C, $CDCl_3$): δ 177.4. ^{19}F{^{1}H} NMR (376.5 MHz, 23 °C, $CDCl_3$): δ −143.02 (m, 2F, 2′- and 6′-F), −157.13 (t, $^3J_{F-F}$ = 42.2 Hz, 1F, 4′-F), −163.22 (m, 2H, 3′- and 5′-F). ^{13}C{^{1}H} NMR (100.6 MHz, 23 °C, $CDCl_3$): δ 167.7 (C_q, vt, J_{P-C} = 6.0 Hz, C2 and C6), 144.7, 140.3, and 138.3 (C_q each, dm each, $^1J_{F-C}$ = 246.1, 252.5, and 249.9 Hz, C2′−C6′), 123.2 and 121.9 (C_q each, C4 and C1′), 116.9 (C_q, m, C1), 106.9 (CH, m br, C3 and C5), 43.4 and 39.8 [C_q each, vt each, J_{P-C} = 11.3 Hz, 2 × P(*t*Bu)$_2$], 27.8 and 27.7 [CH_3 each, vt each, 3.0 and 3.0 Hz, 2 × P(*t*Bu)$_2$]. IR (CH_2Cl_2, cm^{-1}): 2926, 2906, 2871, 1545, 1523, 1493, 1475. Elemental analysis calcd for $C_{28}H_{39}O_2P_2F_5ClIr$ (792.23): C, 42.45; H, 4.96. Found: C, 42.92; H, 5.04.

***p*-Ar^{F}PCPIrHCl (4f).** Using the general procedure, we heated 336 mg (0.5 mmol) of $[(COD)IrCl]_2$ and 672 mg (1.1 mmol) of 5-Ar^{F}PCP (**5f**) for 2 h at 150 °C in 3 mL of toluene to yield 764 mg (0.91 mmol, 91%) of compound **4f** as an orange red microcrystalline solid moderately soluble in pentane. An additional 20 mg (0.02 mmol, 2%) of compound **4f** was obtained by column chromatography (8 × 0.3 cm, hexanes:diethyl ether 20:1, R_f = 0.5 hexanes:diethyl ether 10:1) of the collected filtrates (93% overall yield).



4f

^{1}H NMR (400 MHz, 23 °C, CD_2Cl_2): δ 8.10 (s, 2H, 2′- and 6′-H), 7.83 (s, 1H, 4′-H), 6.91 (s, 2H, 3- and 5-H), 1.39 (m, 36H, 4 × *t*Bu), −40.96 (t, $^2J_{P-H}$ = 13.0 Hz, 1H, IrH). ^{31}P{^{1}H} NMR (162.5 MHz, 23 °C, CD_2Cl_2): δ 177.8. ^{19}F{^{1}H} NMR (376.5 MHz, 23 °C, CD_2Cl_2): δ −63.58. ^{13}C{^{1}H} NMR (100.6 MHz, 23 °C, CD_2Cl_2): δ 168.5 (C_q, vt, J_{P-C} = 5.9 Hz, C2 and C6), 143.8 and 136.0 (C_q each, C4 and C1′), 132.2 (C_q, q, $^2J_{F-C}$ = 33.0 Hz, C3′ and C5′), 127.1 (CH, m C2′ and C6′), 124.0 (C_q, q, $^1J_{F-C}$ = 272.6 Hz, 2 × CF_3), 121.5 (C_q, m, C1), 120.6 (CH, m, C4′), 103.9 (CH, vt, J_{P-C} = 5.3 Hz, C3 and C5), 43.5 and 40.0 [C_q, each, vt each, J_{P-C} = 11.3 Hz, 2 × P(*t*Bu)$_2$], 27.8 and 27.7 [CH_3 each, vt each, J_{P-C} = 3.1 and 3.0 Hz]. IR (CH_2Cl_2, cm^{-1}): 2945, 2904, 2871, 1619, 1593, 1545, 1476, 1373. Elemental analysis calcd for $C_{30}H_{42}O_2P_2F_6ClIr$ (838.27): C, 42.98; H, 5.05. Found: C, 43.02; H, 5.14.

General Procedure for the Transfer Dehydrogenation of Cyclooctane with *tert*-Butylethylene. A stock solution prepared from 3.400 g of cyclooctane (30.31 mmol), 2.690 g of *tert*-butylethylene (30.36 mmol based on 95% purity), 10 μmol of the respective *p*-XPCPIrHCl (**4a**−**f**), and 1.1 mg of NaO*t*Bu was occasionally shaken and aged for at least 2 h in the glovebox. Next, 1.5 mL aliquots of these stock solutions were transferred into 4 mL thick walled Kontes reactors closed with Teflon screw caps, and the reactors were placed in the cavities of a heated aluminum block at 200 °C. After the desired reaction time, the Kontes reactors were removed from the aluminum block and cooled by a stream of air. GC analysis (Agilent, HP-1, 30 m, 0.32 mm widebore, 0.25 μm film) of the reaction mixtures even under isothermic low temperature (70 °C) and low flow rate (0.2 mL/min) conditions was hampered due to identical retention times of COE and 1,3-COD. Therefore, aliquots of the reaction mixtures were taken in the glovebox and analyzed by ^{1}H NMR. An average of three runs (all from the same stock solution) was taken to determine the TONs at a given time. TONs were extracted from the ratio of both the integrals of the olefinic COE, 1,3-COD, and TBE signals and the integrals of the *tert*-butyl resonance of TBE (s, 9H) and the overlapping methyl resonances of TBA (s and t, 12H). The ratio of COE and 1,3-COD was extracted from the two overlapping olefinic signals of COE and 1,3-COD (2,3-H) and the isolated olefinic 1,3-COD signal (1,4-H). Except for the 5% impurity in the commercially available TBE, which was proven to be unreactive with a mesitylene capillary standard in a deuterium free NMR tube experiment at 200 °C (and which therefore can be used as an internal standard), no signals other than COA, COE, 1,3-COD, TBE, and TBA were detected in these reaction mixtures. The number of COE and 1,3-COD double bonds equaled the number of produced TBA molecules within <2% deviation in each experiment.

COE Disproportionation into COA and 1,3-COD. 1,3-COD Dehydrogenation To Form Alkylbenzenes. To 6.3 mg (10 μmol) of precatalyst **4c** and 1.1 mg (11 μmol) of NaO*t*Bu in a J. Young tube was added 496 mg (4.5 mmol) of COE under argon. The tube was then immersed in a sand bath at 200 °C for 192 h. Periodically, ^{1}H NMR spectra were recorded which indicated the formation of 1,3-COD, and subsequently (but already at an early stage of the reaction) the formation of *o*-xylene and ethylbenzene besides COA, 1,2-dimethylcyclohexane, and trace amounts of further unidentified (cyclo)alkanes. The formation of *o*-xylene, ethylbenzene, COA, 1,2-dimethylcyclohexane, and 1,3-COD was unambiguously proven by comparing ^{1}H and ^{13}C NMR spectra of the final product mixture after 192 h at 200 °C with authentic samples (1,2-dimethylcyclohexane as received from Aldrich was a mixture of the *cis*- and *trans*-isomer). When stock solutions prepared from 6.3 mg (10 μmol) of precatalyst **4c**, 1.1 mg (11 μmol) of NaO*t*Bu, 550 mg (5.0 mmol) of COE, and 421 mg (5.0 mmol) of cyclohexane [or 370 mg (5.0 mmol) of *tert*-butyl alcohol] were heated in a J. Young tube for 48−72 h at 200 °C, exclusive formation of 1,3-COD and COA in nearly quantitative yield as based on the ^{1}H NMR spectra was observed, while cyclohexane (or *tert*-butyl alcohol) remained unreacted.

Acknowledgment. We gratefully acknowledge funding by the National Institutes of Health (grant no. GM 28938) and the Deutsche Akademie der Naturforscher Leopoldina (grant no. BMBF-LPD 9901/8-60 to I.G.-S.). We thank Alan Goldman for fruitful discussions.

Supporting Information Available: Crystallographic data of compound **4a**. This material is available free of charge via the Internet at http://pubs.acs.org.

JA0385235