Synthesis and Properties of Iridium Bis(phosphinite) Pincer Complexes (*p*-XPCP)IrH_2, (*p*-XPCP)Ir(CO), (*p*-XPCP)Ir(H)(aryl), and {(*p*-XPCP)Ir}$_2${μ-N_2} and Their Relevance in Alkane Transfer Dehydrogenation

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A series of bis(phosphinite) (*p*-XPCP)IrH_2 pincer complexes {[PCP = η^3-5-X-C_6H_2[OP(*t*Bu)$_2$]$_2$-1,3], X = MeO (**6a**), Me (**6b**), H (**6c**), F (**6d**), C_6F_5 (**6e**), and Ar^F [=3,5-bis(trifluoromethyl)phenyl] (**6f**)} have been synthesized by dehydrochlorination of (*p*-XPCP)IrHCl precursor complexes **4a**−**f** with NaO*t*Bu in the presence of hydrogen. Dehydrochlorination of **4f** in the presence of nitrogen yields {(*p*-Ar^FPCP)Ir}$_2${μ-N_2} (**11f**), which was analyzed by X-ray diffraction. Complexes **6a**−**f** exhibit identical catalytic activity in the transfer dehydrogenation of cyclooctane (COA) with *tert*-butylethylene (TBE) when compared to mixtures of precatalysts **4a**−**f** and NaO*t*Bu. The electronic properties of the fragments (*p*-XPCP)Ir (**Aa**−**f**) are discussed on the basis of the ν_{CO} of (*p*-XPCP)Ir(CO) complexes (**8a**−**f**) as well as on $^1J_{HD}$ coupling constants of monodeuterated complexes (*p*-XPCP)Ir*HD* (**6a**−**f**-d_1). Reaction of **4a**−**f** with NaO*t*Bu in arene solvents generates (*p*-XPCP)Ir(aryl)(H) complexes (**9** and **10**), which undergo rapid arene exchange on the NMR time scale. Exchange rates are zero-order in free arene, implying a dissociative exchange mechanism. More electron-deficient complexes, e.g., (*p*-C_6F_5PCP)Ir(*m*-xylyl)(H) (**10e**) or (*p*-Ar^FPCP)Ir(*m*-xylyl)(H) (**10f**), reductively eliminate *m*-xylene significantly faster than the more electron-rich complexes, e.g., (*p*-MeOPCP)Ir(*m*-xylyl)(H) (**10a**), on the basis of the line widths $\Delta\nu_{1/2}$(0 °C) of the hydridic NMR resonances of (*p*-XPCP)Ir(*m*-xylyl)(*H*) complexes **10a**−**f**. The same correlation with substituent effects applies to the catalytic activity (initial turnover frequencies) of complexes **6a**−**f** in the transfer dehydrogenation of COA with TBE.

Introduction

The selective functionalization of unactivated alkanes remains a challenging task in organic chemistry, especially considering homogeneous catalyzed reactions.[1] Among the known alkane functionalization processes[2−5] alkane dehydrogenation[6] provides access to olefins and arenes that are valuable feedstocks for conversion to higher value materials. Industrial alkane dehydrogenations are restricted to heteregenous catalysts and operate at high temperatures (ca. 400−600 °C);[7] thus effective homogeneous alkane dehydrogenation under relatively low-temperature conditions is a desirable process.

In 1996 Kaska, Jensen, et al. reported that the {C_6H_3-[CH_2P(*t*Bu)$_2$]$_2$-2,6}IrH_2 pincer complex (**1**) catalyzes the

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(1) For recent reviews on this topic: (a) Kakiuchi, F.; Chatani, N. *Adv. Synth. Catal.* **2003**, *345*, 1077−1101. (b) Labinger, J. A.; Bercaw, J. E. *Nature* **2002**, *417*, 507−514. (c) Crabtree, R. H. *J. Chem. Soc., Dalton Trans.* **2001**, 2437−2450. (d) Jia, C.; Kitamura, T.; Fujiwara, Y. *Acc. Chem. Res.* **2001**, *34*, 633−639. (e) Jensen, C. M. *Chem. Commun.* **1999**, 2443−2449. (f) Sen, A. *Acc. Chem. Res.* **1998**, *31*, 550−557. (g) Shilov, A. E.; Shul'pin, G. B. *Chem. Rev.* **1997**, *97*, 2879−2932. For leading reviews on the functionalization of sp and sp^2 C−H bonds: (h) Ritleng, V.; Sirlin, C.; Pfeffer, M. *Chem. Rev.* **2002**, *102*, 1731−1769. (i) Guari, Y.; Sabo-Etienne, S. *Eur. J. Inorg. Chem.* **1999**, 1047−1055. (j) Dyker, G. *Angew. Chem., Int. Ed.* **1999**, *38*, 1699−1712.

(2) Alkane oxidation: (a) Gol'dschleger, N. F.; Es'kova, V. V.; Shilov, A. E.; Shteinman, A. A. *Zh. Fiz. Khim* **1972**, *42*, 1353−1354 (Engl. transl.) **1972**, *46*, 785−786. A comprehensive review featuring the mechanistic details inter alia disclosed by the Bercaw group has been published by: (b) Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *Angew. Chem., Int. Ed.* **1998**, *37*, 2180−2192. Further progress was disclosed by the Catalytica and related systems: (c) Periana, R. A.; Taube, D. J.; Gamble, S.; Taube, H.; Satoh, T.; Fujii, H. *Science* **1998**, *280*, 560−564. (d) Matsumoto, T.; Taube, D. J.; Periana, R. A.; Taube, Yoshida, H. *J. Am. Chem. Soc.* **2000**, *122*, 7414−7415. (e) Periana, R. A.; Liu, X. Y.; Bhalla, G. *Chem. Commun.* **2002**, 3000−3001.

(3) For the borylation of alkanes see: (a) Smith, M. R., III; Iverson, C. N. *J. Am. Chem. Soc.* **1999**, *121*, 7696−7697. (b) Chen, H.; Schlecht, S.; Semple, T. C.; Hartwig, J. F *Science* **2000**, *287*, 1995−1997. (c) Kondo, Y.; Garcia-Cuadrado, D.; Hartwig, J. F.; Boaen, N. K.; Wagner, N. L.; Hillmyer, M. A. *J. Am. Chem. Soc.* **2002**, *124*, 1164−1165.

(4) Carboxylation of alkanes: (a) Fujiwara, Y.; Jintoku, T.; Uchida, Y. *New J. Chem.* **1989**, *13*, 649−650. (b) Fujiwara, Y.; Takaki, K.; Uchida, Y.; Taniguchi, H. *Chem. Lett.* **1989**, 1687−1688. (c) Lin, M.; Hogan, T. E.; Sen, A. *J. Am. Chem. Soc.* **1996**, *118*, 4574−4580. (d) Periana, R. A.; Mironov, O.; Taube, D.; Bhall, G.; Jones, C. J. *Science* **2003**, *301*, 814−818.

(5) Aminomethylation of alkanes: Taniguchi, Y.; Horie, S.; Takaki, K.; Fujiwara, Y. *J. Organomet. Chem.* **1995**, *504*, 137−141.

(6) (a) Crabtree, R. H.; Mihelcic, J. M.; Quirk, J. M. *J. Am. Chem. Soc.* **1979**, *101*, 7738−7740. (b) Baudry, M. J.; Ephritikine, M.: Felkin, H.; Holmes-Smith, R. *J. Chem. Soc., Chem. Commun.* **1983**, 788−789. (c) Baudry, M. J.; Crabtree, R. H.; Parnell, C. P.; Uriarte, R. J. *Organometallics*, **1984**, *3*, 816−817. For some further catalytic examples: (d) Burk, M. W.; Crabtree, R. H. *J. Am. Chem. Soc.* **1987**, *109*, 8025−8032. (e) Maguire, J. A.; Goldman, A. S. *J. Am. Chem. Soc.* **1991**, *113*, 6706−6708. (f) Maguire, J. A.; Petrillo, A.; Goldman, A. S. *J. Am. Chem. Soc.* **1992**, *114*, 9492−9498. (g) Belli, J.; Jensen, C. M. *Organometallics* **1996**, *15*, 1532−1534.

(7) (a) Wieseman, P. *Petrochemicals*; Ellis Horwood: Chichester, England, 1986; pp 90−91. (b) Weissermel, K.; Arpel, H.-J. *Industrial Organic Chemistry*; Wiley-VCH: Weinheim, 2003; pp 59−89.

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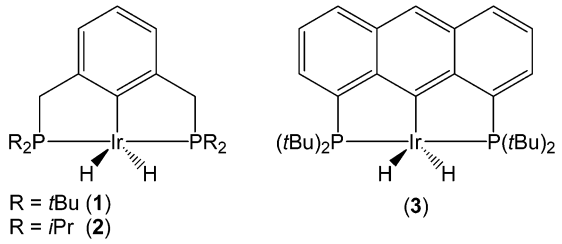
Chart 1. PCP Iridum Pincer Complexes 1−3



transfer dehydrogenation of cyclooctane (COA) with *tert*-butylethylene (TBE) in neat substrate solution to form cyclooctene (COE) and *tert*-butylethane (TBA). TBE is used as hydrogen acceptor in this reaction to overcome the thermodynamic difficulty caused by the highly endergonic dehydrogenation of COA (ca. 23.3 kcal/mol).[8] A high thermal stability of the Ir catalyst and up to 1000 turnovers (TON) have been observed at 200 °C.[1e,9] In further studies the similar $\{C_6H_3\text{-}[CH_2P(i\text{Pr})_2]_2\text{-}2,6\}IrH_2$ (**2**) derivative proved to be the first homogeneous catalyst for the efficient thermal acceptorless dehydrogenation of, for example, refluxing cyclodecane (ca. 1000 TON).[10] Since these initial reports, extensive experimental and theoretical investigations have been conducted to amplify the scope and gain a better understanding of the acceptor and acceptorless dehydrogenations using PCP iridium pincer catalysts.[11] An "anthraphos"-based (PCP)IrH_2 pincer complex (**3**) despite its lower activity at 200 °C has been proven to dehydrogenate cyclodecane effectively without an acceptor, since it operates at 250 °C without decomposition.[12] Recently, complex **1** was shown to catayze the transfer dehydrogenation of secondary and tertiary amines to form imines[13a] and enamines,[13b] respectively.

Electronic tuning by substitution of the original ligand backbone in **1** has been reported, but not yet been tested for catalytic performance.[11c,14] Driven by the remarkable reactivity of these catalysts and our ongoing interest in exploiting C−H activation in catalytic reactions,[15] we investigated the synthesis of a series of bis(phosphinite) (*p*-XPCP)IrHCl complexes $\{4\text{-X-}C_6H_2\text{-}[OP(t\text{Bu})_2]_2\text{-}2,6\}$-IrHCl {X = MeO (**4a**), Me (**4b**), H (**4c**), F (**4d**), C_6F_5 (**4e**), and Ar^F [=3,5-bis(trifluoromethyl)phenyl] (**4f**)}, which we expected to be much more electron-deficient than $\{C_6H_3\text{-}[CH_2P(t\text{Bu})_2]_2\text{-}2,6\}IrH_2$ (**1**). Treatment of complexes **4a**−**f** with NaO*t*Bu results in in situ generation of catalysts with unprecedented activity for transfer dehydrogenation in terms of TON, TOF, and substrate conversion.[16] We now wish to report on the sequential synthesis of the catalytically active dihydride complexes $\{4\text{-X-}C_6H_2\text{-}[OP(t\text{Bu})_2]_2\text{-}2,6\}IrH_2$ (**4a**−**f**), as well as on some electronic features relevant to the catalytic activities of the parent fragments $\{4\text{-X-}C_6H_2\text{-}[OP(t\text{Bu})_2]_2\text{-}2,6\}$-Ir (**Aa**−**f**).

Results and Discussion

(a) Generation of Bis(phosphinite) PCP Iridum Trihydrides (*p*-XPCP)$IrH_3^-Na^+$ (5a,c,f) and Synthesis of Iridium Dihydrides (*p*-XPCP)IrH_2 (6a−f) and Tetrahydrides (*p*-XPCP)IrH_4 (7a−f). Kaska and Jensen et al. and Goldman et al. have shown that the iridium PCP pincer complex $\{C_6H_3\text{-}2,6\text{-}[CH_2P(t\text{Bu})_2]_2\}$-$IrH_2$ (**1**) is an active dehydrogenation catalyst for several alkanes in both the presence and absence of a hydrogen acceptor.[9−11] Complex **1** is an oxygen- and nitrogen-sensitive compound obtained in 85% yield after treatment of the $\{C_6H_3\text{-}2,6[CH_2P(t\text{Bu})_2]_2\}$IrHCl precursor with $LiBHEt_3$ under an atmosphere of hydrogen and removal of dihydrogen from the formed tetrahydride $\{C_6H_3\text{-}2,6[CH_2P(t\text{Bu})_2]_2\}IrH_4$ at 130 °C.[11l] An alternative protocol for the generation of related (PCP)IrH_2 pincer complexes using either KH under ca. 2 atm of hydrogen[11c] or NaH under 1 atm of hydrogen has been reported.[12] Treatment of, for example, $\{C_6H_3\text{-}2,6\text{-}[OP(t\text{Bu})_2]_2\}$IrHCl (**4c**) with NaH (or KH) under an atmosphere of hydrogen in THF-d_8 generates the anionic trihydride $\{C_6H_3\text{-}2,6\text{-}[OP(t\text{Bu})_2]_2\}IrH_3Na(K)$ [**5c-Na(K)**] as the major species on the basis of the ^1H and $^{31}P\{^1H\}$ NMR spectra. Addition of a catalytic amount of a mild Brønsted acid such as phenol or Brønsted base such as NaO*t*Bu greatly accelerates the reaction, and the anionic trihydrides **5** are the only Ir-containing products formed (Scheme 1).

The most characteristic feature of complexes **5a**,**c**,**f** is the appearance of a multiplet and a doublet of triplets in the hydridic region of the ^1H NMR spectra at δ = −13.35 (**5a**)$\{-13.33$ (**5c**), −13.12 (**5f**)$\}$ and −13.65 (**5a**) $\{-13.55$ (**5c**), −13.32 (**5f**)$\}$ in a 1:2 ratio. Upon ^{31}P decoupling, the hydride resonances **5a**−**f** assigned *trans*

(8) The dehydrogenation enthalpy of COA (23.3 kcal/mol) is among the lowest known for alkanes, which makes it an even more suitable substrate for alkane dehydrogenation: NIST Standard Reference Database Number 69, March 2003 Release, http://webbook.nist.gov/chemistry/.

(9) Gupta, M.; Hagen, C.; Flesher, R. J.; Kaska, W. C.; Jensen, C. M. *Chem. Commun.* **1996**, 2083−2084.

(10) (a) Xu, W.-W.; Rosini, G. P.; Gupta, M.; Jensen, C. M.; Kaska, W. C.; Krogh-Jespersen, K.; Goldman, A. S. *Chem. Commun.* **1997**, 2273−2274. (b) Liu, F.; Goldman, A. S. *Chem. Commun.* **1999**, 655−656.

(11) (a) Renkema, K. B.; Kissin, Y. V.; Goldman, A. S. *J. Am. Chem. Soc.* **2003**, *125*, 7770−7771. (b) Krogh-Jespersen, K.; Czerw, M.; Summa, N.; Renkema, K. B.; Achord, P. D.; Goldman, A. S. *J. Am. Chem. Soc.* **2002**, *124*, 11404−11416. (c) Krogh-Jespersen, K.; Czerw, M.; Zhu, K.; Singh, B.; Kanzelberger, M.; Darji, N.; Achord, P. D.; Renkema, K. B.; A.Goldman, A. S. *J. Am. Chem. Soc.* **2002**, *124*, 10797−10809. (d) Li, S.; Hall, M. B. *Organometallics* **2001**, *20*, 2153-2160. (e) Morales-Morales, D.; Lee, D. W.; Wang, Z.; Jensen, C. M. *Organometallics* **2001**, *20*, 1144−1147. (f) Krogh-Jespersen, K.; Czerw, M.; Kanzelberger, M.; Goldman, A. S. *J. Chem. Inf. Comput. Sci.* **2001**, *41*, 56−63. (g) Kanzelberger, M.; Singh, B.; Czerw, M.; Krogh-Jespersen, K.; Goldman, A. S. *J. Am. Chem. Soc.* **2000**, *122*, 11017−11018. (h) Liu, F.; Pak, E. B.; Singh, B.; Jensen, C. M.; Goldman, A. S. *J. Am. Chem. Soc.* **1999**, *121*, 4086−4087. (i) Niu, S.; Hall, M. B. *J. Am. Chem. Soc.* **1999**, *121*, 3992−3999. (j) Liu, F.; Goldman, A. S. *Chem. Commun.* **1999**, 655−656. (k) Lee, D. W.; Kaska, W. C.; Jensen, C. M. *Organometallics* **1998**, *17*, 1−3. (l) Gupta, M.; Hagen, C.; Kaska, C. W.; Cramer, R. E.; Jensen, C. M. *J. Am. Chem. Soc.* **1997**, *119*, 840−841.

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

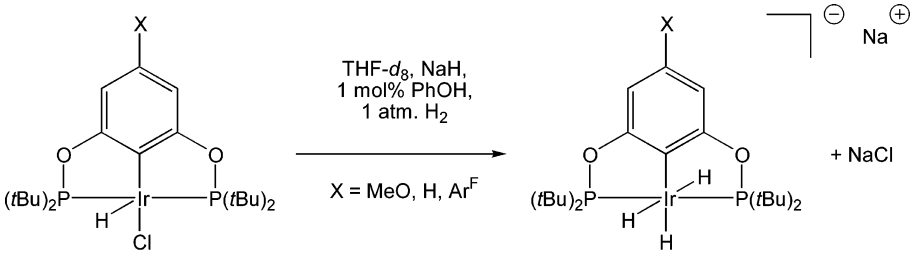
(13) (a) Gu, X.-Q.; Chen, W.; Morales-Morales, D.; Jensen, C. M. *J. Mol. Catal. A* **2002**, *189*, 119−124. (b) Zhang, X.; Fried, A.; Knapp, S.; Goldman, A. S. *Chem. Commun.* **2003**, 2060−2061.

(14) (a) Mohammad, H. A. Y.; Grimm, J. C.; Eichele, K.; Mack, H.-G.; Speiser, B.; Novak, F.; Quintañilla, M. G.; Kaska, W. C.; Mayer, H. A. *Organometallics* **2002**, *21*, 5775−5784. (b) Grimm, J. C.; Nachtigal, C.; Mack, H.-G.; Kaska, W. C.; Mayer, H. A. *Inorg. Chem. Commun.* **2000**, *3*, 511−514.

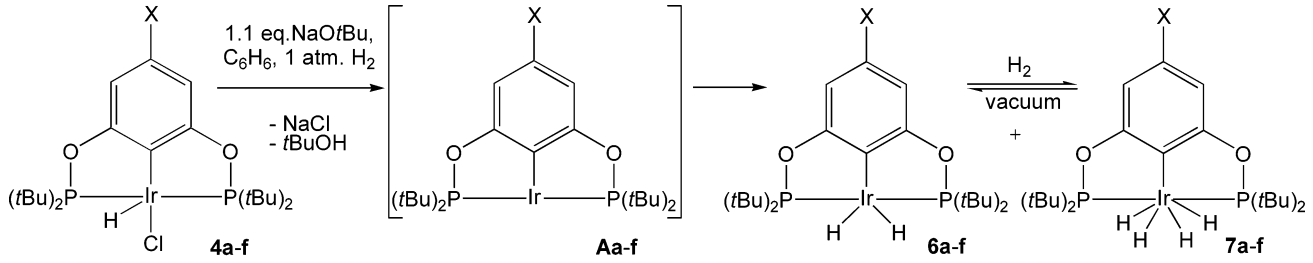
(15) (a) Diaz-Requejo, M. M.; DiSalvo, D.; Brookhart, M. *J. Am. Chem. Soc.* **2003**, *125*, 2038−2039. (b) Reinartz, S.; White, P. S.; Brookhart, M.; Templeton, J. *J. Am. Chem. Soc.* **2001**, *123*, 12724−12725. (c) Reinartz, S.; White, P. S.; Brookhart, M.; Templeton, J. *Organometallics* **2001**, *20*, 1709−1712. (d) Lenges, C. P.; Brookhart, M. *J. Am. Chem. Soc.* **1999**, *121*, 6616−6623. (e) Lenges, C. P.; White, P. S.; Brookhart, M. *J. Am. Chem. Soc.* **1999**, *121*, 4385−4396. (f) Lenges, C. P.; Brookhart, M.; Grant, B. *J. Organomet. Chem.* **1997**, *528*, 199−203.

(16) Göttker-Schnetmann, I.; White, P. S.; Brookhart, M. *J. Am. Chem. Soc.* **2004**, *126*, 1804−1811.

Scheme 1. Generation of Anionic (*p*-XPCP)IrH$_3$− Complexes (5a,c,f)



Scheme 2. Generation of (*p*-XPCP)IrH$_2$ (6a−f) and (*p*-XPCP)IrH$_4$ (7a−f) by Dehydrochlorination of 4a−f in the Presence of H$_2$



4	a	b	c	d	e	f
X	MeO	Me	H	F	C_6F_5	Ar^F
6 [%][a]	91	86	95	87	90	93

[a] isolated yield.

to carbon appear as a triplet, while the two hydrides *trans* to each other appear as a doublet ($^2J_{cis\mathrm{H-H}} = 4.8$ Hz for **5a**,**c**, 4.9 Hz for **5f**).

On the basis of these observations we assumed that reaction of hydridochloro complexes **4a**−**f** with a base rather than a hydride donor in the presence of dihydrogen would also be suitable for generation of the iridium dihydrides **6a**−**f**, via dehydrochlorination of **4a**−**f**, to form the respective 14e$^-$ fragment (*p*-XPCP)Ir (**Aa**−**f**) followed by H_2 addition.[17] Indeed, reaction of complexes **4** with 1.1 equiv of NaO*t*Bu in aromatic solvents under 1 atm of hydrogen generates mixtures of dihydrides **6** and tetrahydrides **7**[18] within 30−60 min at 23 °C. In an improved procedure the reaction is carried out in benzene: after sublimation of the frozen solvent and formed *t*BuOH at 0 °C and subsequent extraction with pentane, pure (*p*-XPCP)IrH$_2$ complexes (**6**) are obtained in 86−95% yield (Scheme 2). We have not been able to isolate pure tetrahydrides **7a**−**f**; these complexes lose dihydrogen to form pure complexes **6a**−**f** much easier than complex {C$_6$H$_3$-2,6-[CH$_2$P(*t*Bu)$_2$]$_2$}IrH$_4$.[19] Thus heating a solution of **7f** under 1.2 atm of H_2 in toluene-d_8 in a J. Young tube from 23 to 100 °C causes the gradual broadening and downfield shifting of the ^{31}P NMR resonance of the IrH$_4$ complex **7f** at 186.0 ppm (23 °C). Upon further temperature increases, this band broadens into the baseline and then becomes sharper again at ca. 203 ppm (90 °C), which is already very close to the 206.9 ppm shift observed for the pure IrH$_2$ complex **6f**. We therefore suggest a rapid interconversion of **6a**−**f** with **7a**−**f** via reductive elimination/oxidative addition of H_2 with a temperature-dependent equilibrium favoring the dihydride species at higher temperatures. Even at 23 °C nearly colorless solutions of **7f** turn red-brown after a few seconds under vacuum, indicating formation of **6f**. Finally, treatment of solid **6f** with 1 atm of hydrogen results in immediate color change from red-brown to pale yellow, indicating formation of **7f**, which loses H_2 upon purging with argon. Characteristic spectroscopic features of the IrH$_2$ complexes **6** are ^{31}P{^{1}H} NMR resonances in the range of 204.9 (**6c**) to 208.4 ppm (**6d**), and IrH$_2$ resonances between −17.55 (**6a**) and −16.13 ppm (**6f**) resolved as one triplet in each case with $^2J_{\mathrm{P-H}} = 8.1$−8.5 Hz.

On the basis of the equivalency of the hydridic sites and the *tert*-butyl groups of complexes **6** as well as on calculations on d^6-L$_2$L′MH$_2$ fragments in general,[20] and on calculations of the {C$_6$H$_3$-2,6-[CH$_2$P(*t*Bu)$_2$]$_2$}IrH$_2$ geometry in particular,[11c,f,i] a distorted trigonal bipyramidal ground state geometry of complexes **6** is assumed.

(b) Electronic Properties of the Fragments (*p*-XPCP)Ir (Aa−f). A sensitive tool for determining the electronic influence of the *p*-substituent in the (*p*-XPCP)-Ir fragments is the ν_{CO} stretching frequency of the respective carbonyl complex (*p*-XPCP)Ir(CO) (**8a**−**f**).

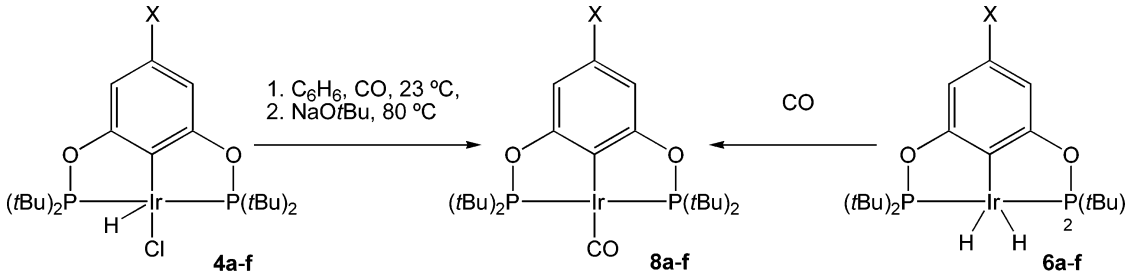
(17) Several base-induced dehydrochlorination reactions of transition metal complexes have been reviewed: Grushin, V. V. *Acc. Chem. Res.* **1993**, *26*, 279−286, and references herein.

(18) During review, one referee pointed out that complexes **7** are probably not Ir(V) tetrahydrides but rather Ir(III) dihydride/dihydrogen adducts. We totally agree, on the basis of the observations made for the Ir(III) dihydride complexes **6**: These complexes already exhibit (nonclassical) dihydrogen binding character (and likewise Ir(I) character) due to the substantial $^1J_{\mathrm{HD}}$ coupling constants in their **6**-d_1 isotopomers (vide infra). However, for the sake of simplicity and the lack of hard experimental evidence we will refer to complexes **7** in a "stoichiometric" way as tetrahydrides. A more detailed discussion of the binding mode in the dihydride complexes **6** will be published elsewhere.

(19) The {C$_6$H$_3$-2,6-[CH$_2$P(*t*Bu)$_2$]$_2$}IrH$_4$ complex can easily be obtained by reaction of the precursor {C$_6$H$_3$-2,6-[CH$_2$P(*t*Bu)$_2$]$_2$}IrHCl with hydrogen and 1.1 equiv of NaO*t*Bu in analogy with the procedures described here.

(20) Riehl, J.-F.; Jean, Y.; Eisenstein, O.; Péllssier, M. *Organometallics* **1992**, *11*, 729−737.

Scheme 3. Generation of Carbonyl Complexes 8a−f from 4 or 6 and ν_{CO} of Complexes 8



8 X	a MeO	b Me	c H	d F	e C_6F_5	f Ar^F
[%][a]	94	91	95	96	84	92
ν_{CO} [cm^{-1}]	1947	1947	1949	1953	1955	1955

[a] isolated yield from *in situ* generated complexes **6** and CO

Generation of complexes **8a**−**f** was achieved in quantitative yield by displacement of hydrogen in complexes **6a**−**f** by CO. An alternative synthesis is based on addition of CO to complexes **4a**−**f** and subsequent dehydrochlorination with NaO*t*Bu at 80 °C (Scheme 3).

The ν_{CO} stretching frequencies obtained for complexes **8a**−**f** in pentane solution (Scheme 3) compare to 1925.5 cm^{-1} for {4-MeO−C_6H_2-2,6-[$CH_2P(tBu)_2$]$_2$}Ir(CO), 1927.7 cm^{-1} for {C_6H_3-2,6-[$CH_2P(tBu)_2$]$_2$}Ir(CO),[21] and 1930.0 cm^{-1} obtained for {4-[$CH_3O(O)C$]-C_6H_2-2,6-[$CH_2P(tBu)_2$]$_2$}Ir(CO).[11c] As jugded by the significant blue shift of ca. 20 cm^{-1} for the bis(phosphinite) PCP complexes **8**, their (*p*-XPCP)Ir fragments (**Aa**−**f**) are distinctively more electron deficient than the respective methylene-bridged {4-X-C_6H_2-2,6-[$CH_2P(tBu)_2$]$_2$}Ir pincer fragments.

Further information about the electronic properties of the (*p*-XPCP)Ir fragments (**A**) has been extracted from isotopic labeling studies of complexes **6a**−**f**: The isotopomers **6a**−**f**-d_1 have been shown to exhibit inter alia $^1J_{HD}$ couplings that are sensitive to the *p*-X substituent of the PCP ligand backbone. At 23 °C in pentane the $^1J_{HD}$ values are 6.5 Hz (**6a**-d_1), 7.7 Hz (**6b**,**c**-d_1), 8.0 Hz (**6c**-d_1), and 9.0 Hz (**6e**,**f**-d_1). An increasing $^1J_{HD}$ in transition metal (poly)hydrides is indicative of a decreasing H−D distance, finally resulting in complete reductive elimination of HD at $^1J_{HD} = 43$ Hz.[22] While a detailed report on the structural implications of the spectroscopic properties of deuterium-labeled compounds **6** will be published elsewhere, the observed $^1J_{HD}$ for **6a**−**f**-d_1 suggest r_{HH} between 1.33 and 1.27 Å for **6f** and between 1.41 and 1.31 Å for **6a**,[23] which justifies their classification as "elongated" dihydrogen complexes.

The degree of π-back-donation from a given ligand−metal fragment to the antibonding σ^*−H_2 (H−D, respectively) orbital has been shown to govern the observed r_{HH}, r_{HD} distance along a putative reaction coordinate going from a classical dihydride complex (strong π-back-donation) through an "elongated" dihydrogen complex to a nonclassical dihydrogen complex (weak π-back-donation).[22] We therefore concluded that the higher the $^1J_{HD}$ in complexes **6a**−**f**-d_1, the weaker the π-back-donation from the (*p*-XPCP)Ir fragments (**Aa**−**f**).

By comparing the electronic effects based on the ν_{CO} of complexes **8** and the $^1J_{HD}$ of complexes **6**-d_1 we find a good correlation except for the (*p*-FPCP)Ir fragment (**Ad**). Whereas ν_{CO} of (*p*-FPCP)Ir(CO) (**8d**) (1953 cm^{-1}) is significantly blue-shifted with respect to **8b**,**c** (1947, 1949 cm^{-1}), the 7.7 Hz $^1J_{HD}$ observed for **6d** compares to 7.7 Hz (**6b**) and 8.0 Hz (**6c**). Considering that the observed ν_{CO} for complexes **8** reflect both the σ-acceptor as well as the π-donor abilities of the fragments (*p*-XPCP)Ir (**A**), whereas the $^1J_{HD}$ is governed by the π-donor abilities of **A**, we can qualitatively rationalize this discrepancy on the basis of the strong σ-acceptor and significant π-donor abilities of the F-substituent in complexes **8d** and **6d**-d_1.

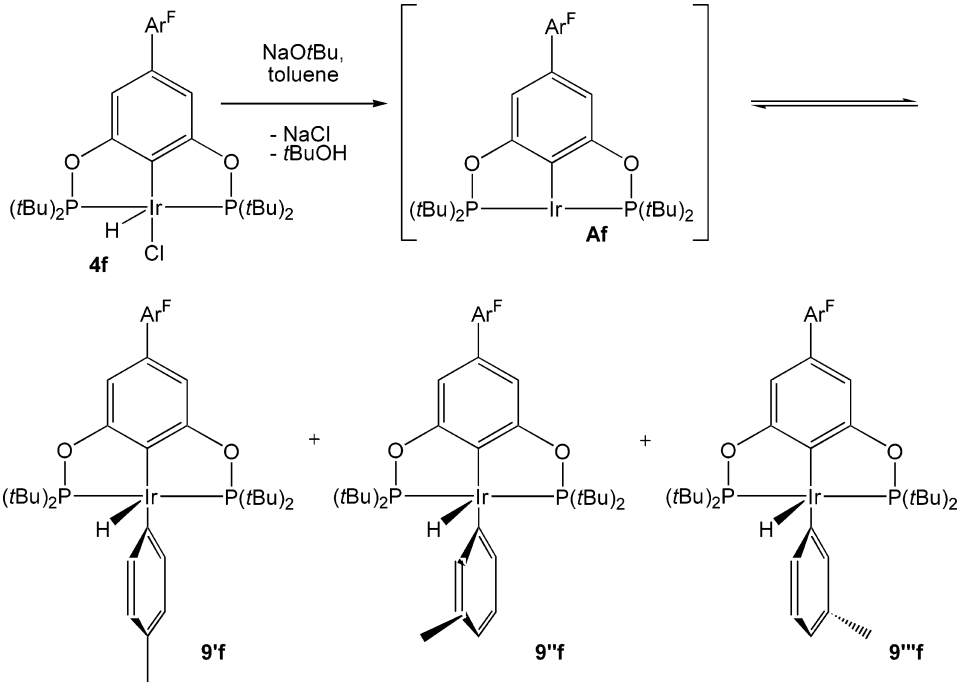
(c) Aromatic C−H Activation, Dissociative Arene Exchange, and (*p*-XPCP)Ir-Dependent Arene Exchange Rates. Generation of complexes **6a**−**f** can be accomplished in a sequential manner starting from complexes **4a**−**f** and NaO*t*Bu in aromatic solvents. In a typical experiment after ca. 30−60 min at 23 °C in benzene-d_6 the starting complex **4f** is completely consumed, as judged by ^{1}H and ^{31}P NMR, and the appearance of one new resonance at 182.0 ppm is observed by $^{31}P\{^1H\}$ NMR. The ^{1}H NMR spectrum shows one set of signals for the aromatic ligand backbone as well as one triplet for the *tert*-butyl groups of the new reaction intermediate. Addition of hydrogen to this reaction mixture leads to formation of **6f** and **7f** within a few minutes at 23 °C. When toluene-d_8 is used as solvent, the ^{1}H NMR spectrum looks essentially identical at 23 °C, while the ^{31}P NMR resonance appears at 181.9 ppm. Considering that oxidative addition of arenes to the {C_6H_3-2,6-[$CH_2P(tBu)_2$]$_2$}Ir fragment has been reported,[11g] these results are indicative of aryl C−D oxidative addition to the respective fragment **Af**. We therefore decided to monitor the reaction of **4f**, NaO*t*Bu, and toluene-h_8 by low-temperature NMR spectroscopy. Upon cooling the reaction mixture obtained after ca. 60 min at 23 °C to −30 °C, three overlapping triplets at −43.22 ppm can be detected by ^{1}H NMR experiments, which broaden with increasing

(21) A differing value of $\nu_{CO} = 1913$ cm^{-1} in KBr is reported by: Morales-Morales, D.; Redón, R.; Wang, Z.; Lee, D. W.; Yung, C.; Magnuson, K.; Jensen, C. M. *Can. J. Chem.* **2001**, *79*, 823−829.

(22) Kubas, G. J. *J. Organomet. Chem.* **2001**, *635*, 37−68.

(23) (a) Heinekey, D. M.; Luther, T. A. *Inorg. Chem.* **1996**, *35*, 4396−4399. (b) Maltby, P. A.; Schlaf, M.; Steinbeck, M.; Lough, A. J.; Morris, R. H.; Klooster, W. T.; Koetzle, T. F.; Srivastava, R. C. *J. Am. Chem. Soc.* **1996**, *118*, 5396−5407. (c) Hush, N. S. *J. Am. Chem. Soc.* **1997**, *119*, 1717−1719. (d) Gründemann, S.; Limbach, H. H.; Buntkowsky, G.; Sabo-Etienne, S.; Chaudret, B. *J. Phys. Chem. A* **1999**, *103*, 4752−4754.

Scheme 4. Generation of (Tolyl)hydrido Complexes 9f from Complexes 4f and NaO*t*Bu in Neat Toluene



temperature and are no longer detectable above 10 °C. A ^{2}D NMR experiment in toluene-d_8 at −30 °C shows one broad signal at −43.22 ppm without detectable splitting, while three overlapping signals at 181.9−182.0 ppm are observed in in the ^{31}P NMR spectrum. When reaction mixtures of **4f**, NaO*t*Bu, and *m*-xylene (or *o*-xylene) are cooled to −30 (−20) °C, the appearance of one triplet at ca. −43.03 (−43.10) ppm in the ^{1}H NMR as well as one singlet at 181.6 (181.2) ppm in the ^{31}P-{^{1}H} NMR can be observed. On the basis of the formation of only one C−H activation product in *m*- or *o*-xylene we attribute the appearance of three isomers in the case of toluene to one *p*-tolyl isomer (**9′f**) and two *m*-tolyl rotamers with the tolyl-methyl group *cisoid*-(**9″f**) or *transoid* (**9‴f**) to the hydride at Ir (Scheme 4). The ^{1}H NMR chemical shift of the hydridic sites in the range of −43 ppm for all aryl C−H activation products suggests a square pyramidal geometry at iridium with the hydride in the apical position.[24] On the basis of calculations this geometry was also proposed for the analogous complex {C_6H_3-2,6-[$CH_2P(tBu)_2$]$_2$}Ir(H)(Ph), which undergoes a fast dissociative arene exchange and shows decoalescence on the NMR time scale at low temperatures.[11c,g]

To obtain more information about an associative versus dissociative arene exchange by the (*p*-XPCP)Ir fragments (**Aa**−**f**) we have reacted the respective (*p*-XPCP)IrHCl precursors (**4a**−**f**) with 1.1 equiv of NaO*t*Bu and initially 2−3 equiv of *m*-xylene in mesitylene-d_{12}. Generation of the respective (3,5-dimethylphenyl)hydrido complexes **10a**−**f** is complete after 30−60 min at 23 °C. However traces of iridium dihydrides **6a**−**f** and one uncharacterized iridum complex in each case can be detected by ^{31}P NMR (not by ^{1}H NMR), presumably formed due to impurities in the commercially available mesitylene-d_{12}. As exemplified for **10f**, two broadened singlets (7.28 and 6.43 ppm, 2:1 H) and the hydridic resonance split into a triplet (−43.02 ppm) are observed by ^{1}H NMR at −30 °C for the oxidatively added *m*-xylene in addition to 2 equiv of free *m*-xylene. Further temperature-dependent ^{1}H{^{31}P} NMR experiments on this sample between 23 and −40 °C reveal a minimum line width $\Delta\nu_{1/2}(\text{min}) = 5.5 \pm 0.1$ Hz of the hydridic resonance of **10f** at −30 °C. At −0 °C the ^{31}P decoupled hydridic resonance of **10f** exhibits a line width $\Delta\nu_{1/2}(0\ °C) = 43$ Hz in the presence of 2 equiv of free *m*-xylene. In the presence of 11 and 30 equiv of free *m*-xylene $\Delta\nu_{1/2}(0\ °C) = 42$ and 41 Hz, respectively. Finally we find $\Delta\nu_{1/2}(0\ °C) = 38.0$ Hz in neat protio *m*-xylene (ca. 330 equiv) compared with $\Delta\nu_{1/2}(\text{min}_{-30\ °C}) = 3.6 \pm 0.1$ Hz in neat *m*-xylene. On the basis of these findings the exchange of *m*-xylene is clearly zero-order in *m*-xylene and supports a dissociative mechanism involving a 14e$^-$ fragment **Af** (which could exist as the agostic complex **Bf** or the oxidative addition product derived thereof) (Scheme 5). Under identical experimental conditions similar results have been obtained for the *m*-xylene exchange of complexes **10a**−**e**. Significantly, $\Delta\nu_{1/2}(0\ °C)$ of complexes **10a**−**f** is quite *p*-substituent dependent, spanning a range from $\Delta\nu_{1/2}(0\ °C) = 14.3$ Hz (in neat *m*-xylene) for the most electron-rich **10a** to 38 Hz for the most electron-deficient system **10f**. Using the slow exchange approximation $k = (\pi \times \Delta(\Delta\nu_{1/2}))/2^{1/2}$ and the lower limit $\Delta\nu_{1/2}$ in neat *m*-xylene, we have obtained *p*-substituent-dependent rate constants $k_{\text{red.el}}$(**10a**−**f**) for the reductive elimination of *m*-xylene from complexes **10a**−**f**, which translate into free activation energies $\Delta G^{\ddagger}_{0\ °C}$ between 14.2 kcal/mol for the most electron-rich complex **10a** and 13.6 kcal/mol for the most electron-deficient complex **10f** (Table 1).

On the basis of the $^1J_{HD}$ of complexes **6a**−**f** and ν_{CO} of **8a**−**f** the reductive elimination of *m*-xylene is significantly enhanced for the more electron-deficient com-

(24) The hydridochloro precursors **4a**−**f** exhibit hydridic resonances between −40.9 and −41.9 ppm. In addition an X-ray structure analysis of **4a** indicates that the hydride occupies the apical position; see ref 16.

Scheme 5. Dissociative Exchange of *m*-Xylene in Complexes 10a−f

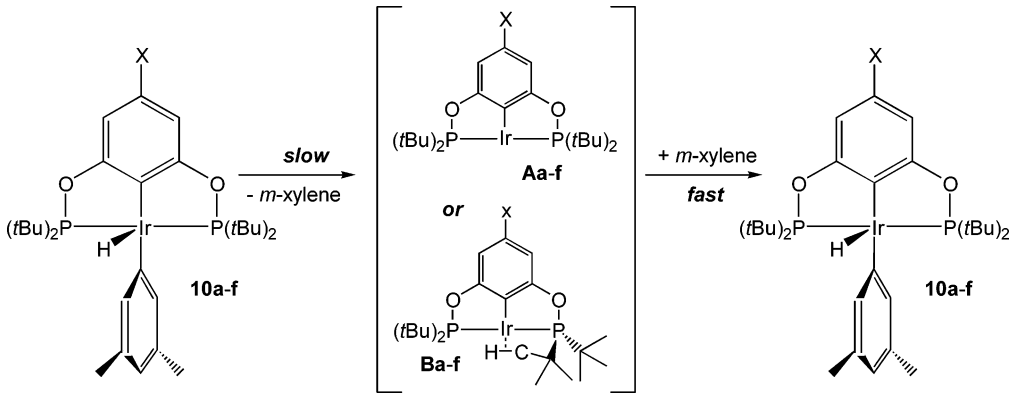


Table 1. Temperature- and [*m*-Xylene]-Dependent Line Width ($\Delta\nu_{1/2}$) of the ^{31}P-Decoupled Hydridic Resonance of (*p*-XPCP)Ir(*m*-xylyl)(H) (10a−f)

		equiv of free *m*-xylene				
		2−3	28−30	330 neat *m*-xylene	$k_{red.el.}$(0 °C),[a] neat *m*-xylene	$\Delta G^{\ddagger}_{0\,°C}$
10	X	$\Delta\nu_{1/2}$(0 °C)/[Hz]			[s^{-1}]	[kcal/mol]
a	MeO	17.2	16.7	14.3	24	14.2
b	Me	18.4	18.1	17.1	31	14.1
c	H	18.6	18.2	17.6	32	14.1
d	F	17.1	16.1	15.1	26	14.2
e	C_6F_5	33	30	28	55	13.8
f	Ar^F	43	41	38	77	13.6

[a] Rates are based on $\Delta(\Delta\nu_{1/2}) = \Delta\nu_{1/2}(0\ °C) - \Delta\nu_{1/2}(\text{min})$ in neat *m*-xylene. The minimum line width values $\Delta\nu_{1/2}$(min) for compounds **10** are 3.4 (**10a**), 3.3 (**10b**), 3.3 (**10c**), 3.6 (**10d**), 3.3 (**10e**), and 3.6 Hz (**10f**) in neat *m*-xylene at −30 °C in each case.

plexes **10e**,**f**, while π-donation by the MeO and F substituents in **10a**,**d** results in the lowest rates of reductive elimination.

(d) Generation of the μ-N_2 Iridium Dimer {(*p*-Ar^FPCP)Ir}$_2$(μ-N_2} (11f). We have observed the formation of {(*p*-Ar^FPCP)Ir}$_2$(μ-N_2} (**11f**) by reacting **4f** with NaO*t*Bu in toluene-d_8 saturated with N_2. The formation of the similar {C_6H_3-2,6(CH_2P*t*Bu_2)$_2$Ir}$_2$(μ-N_2} dimer (**12**) has been reported and is known to inhibit the catalytic activity of the {C_6H_3-2,6(CH_2-P*t*Bu_2)$_2$}Ir fragment.[11k] However, upon exposing suspensions of isolated **11f** to an atmosphere of H_2 in an NMR tube, we have observed dissociation of the dimer and quantitative formation of mixtures of the di- and tetrahydride **6f** and **7f**, respectively, by ^{1}H and ^{31}P NMR.

Compound **11f**, even in low concentrations, crystallizes as a toluene adduct out of these solutions, while a minor uncharacterized product remains in solution. The X-ray structure analysis of compound **11f** shows a very similar geometry at the Ir center when compared to **12**. However, the C−Ir distance is shorter in **11f** [2.001(4) Å] than in **12** [2.053(12) Å], as is the Ir−N distance [1.982(3) Å (**11f**), 2.007(11) Å (**12**)] and the N−N distance [1.119(6) Å (**11f**), (1.176(13) Å **12**)], which is close to the reported value in free N_2 (1.098 Å).[25] Additionally the P−Ir−P angle is smaller [154.86(3)° (**11f**), 160.22(10)° (**12**)].

(e) Catalytic Activity of Complexes 6a−f and 11f in the Transfer Dehydrogenation of Cyclooctane (COA) with *tert*-Butylethylene (TBE). By comparing the catalytic activity of complexes **6a**−**f** with the activity of species generated from **4a**−**f** and NaO*t*Bu in the benchmark transfer dehydrogenation of COA with TBE,[9] we see no advantage in using complexes **6a**−**f**. Neither the initial turnover frequencies (TOFs) for entries 1−6 nor the turnover numbers (TONs) after 40 h at 200 °C differ substantially under identical conditions (Table 2). We also find virtually identical product ratios of cyclooctene to 1,3-cyclooctadiene in these reactions. Noteworthy, the dinitrogen complex **11f** exhibits nearly the same activity as catalyst **6f** or precatalyst **4f** plus NaO*t*Bu on a per iridium basis, when the reaction is conducted under an argon atmosphere. Even under an atmosphere of nitrogen, however, the catalytic activity of complex **11f** is not totally quenched (Table 2, entry 8).

Summary

Catalytically active dihydride complexes **6a**−**f** for the transfer dehydrogenation of COA with TBE have been synthesized by dehydrochlorination of complexes **4a**−**f** in arene solvents in the presence of hydrogen. In the absence of hydrogen the formation of highly fluxional Ir(aryl)(hydrido) complexes **9** and **10** has been observed, which upon addition of hydrogen furnish complexes **6a**−**f**. The aryl hydrido moieties in complexes **9** and **10** exhibit rapid exchange with free arene. Rate measurements establish this reaction is zero-order in free arene and provide evidence either for 14e$^-$ fragments **Aa**−**f** or for species derived from the agostic complexes **Ba**−**f** as reaction intermediates. The substituent dependent electronic properties of their parent 14e$^-$ fragments **Aa**−**f** have been probed by measuring the ν_{CO} values of their respective (CO) complexes **8a**−**f**. Additional information has been obtained from the $^1J_{HD}$ values of isotopically labeled complexes (*p*-XPCP)IrHD (**6a**−**f**-d_1). Except for the F substituent both methods provide the same order of increasing electron deficiency ($Ar^F \approx C_6F_5$ > F > H > Me > MeO based on ν_{CO}, Ar^F > C_6F_5 > H > F ≈ Me > MeO based on $^1J_{HD}$). The initial TOFs in the transfer dehydrogenation of COA with TBE catalyzed by **6a**−**f** as well as the rates of reductive arene elimination in complexes **10a**−**f** correlate with the electronic properties of the ligand, with the more electron-deficient systems being more active.

Experimental Section

General Considerations. All manipulations were carried out using standard Schlenk, high-vacuum, and glovebox

(25) Gordon, A. J.; Ford, R. A. *The Chemist's Companion*; John Wiley & Sons: New York, 1972; p 107.

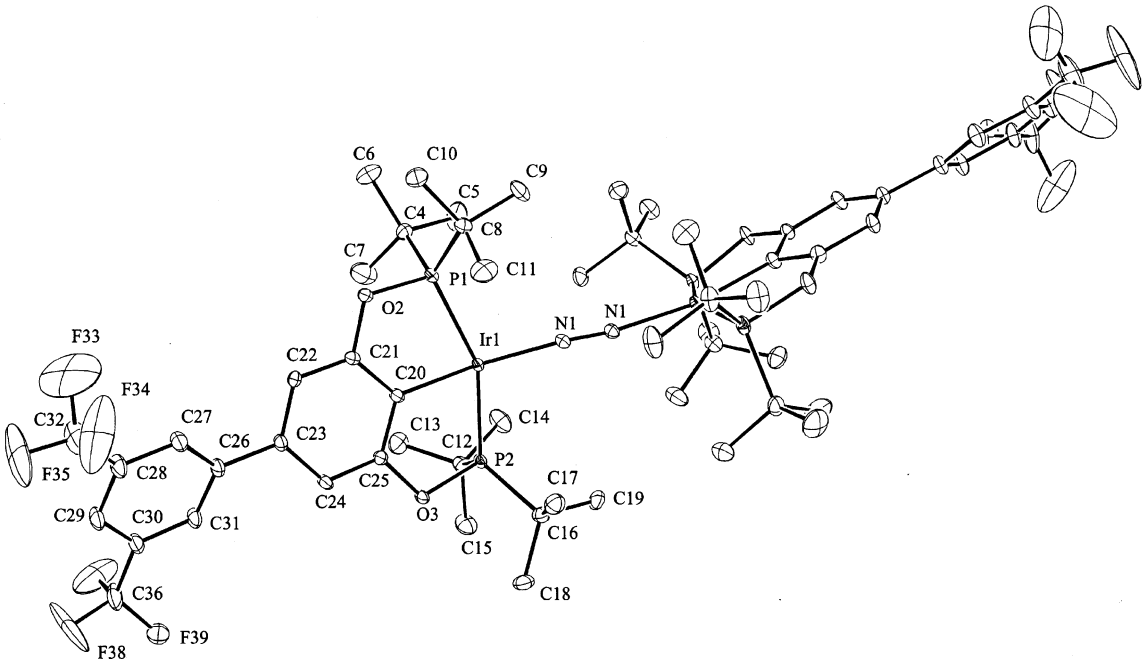


Figure 1. ORTEP plot of {(*p*-Ar^{F}PCP)Ir}$_2${μ-N$_2$}·2toluene (**11f**) with thermal ellipsoids at the 50% probability level (toluene omitted for clarity). Selected bond distances (Å) and angles (deg): Ir1−P1 2.2859(11), Ir1−P2 2.2724(10), Ir1−N1 1.982(3), N1−N1a 1.119(6), Ir1−C20 2.001(4), C21−O2 1.388(5), O2−P1 1.665(3), C25−O3 1.389(5), O3−P2 1.6607(25), P1−Ir1−P2 154.86(3), N1−Ir1−C20 169.84(15), Ir1−N1−N1a 172.9(3).

Table 2. Catalytic Activity of in Situ-Generated Species Compared to Catalysts 6a−f and 11f in the Transfer Dehydrogenation of COA with TBE

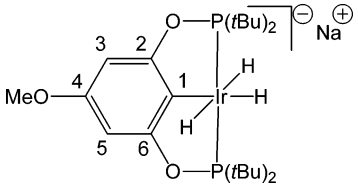
entry	complex	X	headspace	TON per Ir (40 h, 200 °C)[a]	initial TOF per Ir [s^{-1}][b]	COE:COD (40 h, 200 °C)[c]
1	**4/6a**	MeO	argon	1904[d]/1886	1.68[d]/1.69	81:19[d]/81:19
2	**4/6b**	Me	argon	1484[d]/1532	1.69[d]/1.68	86:14[d]/85:15
3	**4/6c**	H	argon	1583[d]/1601	1.92[d]/1.88	84:16[d]/84:16
4	**4/6d**	F	argon	1530[d]/1519	1.75[d]/1.71	84:16[d]/84:16
5	**4/6e**	C_6F_5	argon	2041[d]/2056	2.40[d]/2.39	78:22[d]/77:23
6	**4/6f**	Ar^F	argon	2070[d]/2051	2.42[d]/2.47	76:24[d]/75:25
7	**11f**	Ar^F	argon	2026	2.17	76:24
8	**11f**	Ar^F	N_2	227	0.33	100:0

[a] TONs of TBE in reaction mixtures containing 30.3 mmol of COA, 30.3 mmol of TBE, and 10 μmol of iridum, determined by ^{1}H NMR experiments. [b] Average value over the first 8 min of the reaction. [c] Determined by ^{1}H NMR experiments. [d] Values obtained by in situ generation of catalytically active species from hydridochloro precatalysts **4a**−**f** and NaO*t*Bu according to ref 16.

techniques. Argon and nitrogen were purified by passage through columns of BASF R3-11 (Chemaolg) and 4 Å molecular sieves. THF was distilled from sodium benzophenone ketyl under nitrogen. 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 by several freeze−pump−thaw cycles and stored in an argon atmosphere glovebox if not stated otherwise. Toluene-d_8, benzene-d_6, mesitylene-d_{12}, and THF-d_8 were dried over sodium, degassed, vacuum transferred, and stored in a glovebox. CD_2Cl_2 was dried over P_2O_5, degassed, and vacuum transferred prior to use. Cyclooctane (COA) was stirred with concentrated H_2SO_4 for several hours until it was olefin and arene free and then distilled under vacuum prior to use. Hydrogen and carbon monoxide were used as received from National Speciality Gases of Durham, NC. Hydrogen deuteride (HD) was generated by adding a solution of deuterium oxide in THF to a suspension of sodium hydride in THF. 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. Samples in neat protio solvent were shimmed by optimizing the intensity of the FID and referenced to the solvent chemical shift in $CDCl_3$ or by external standard capillaries (benzene-d_6). ^{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.

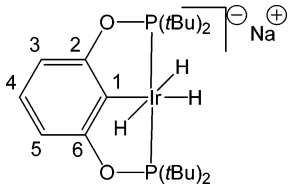
General Procedure for in Situ Generation of Anionic Trihydrides 5a,c,f. THF-d_8 (0.25 mL) was added to 30 μmol of the respective precursor **4a**,**c**,**f** and 2 mg of NaH (84 μmol) in a thick walled J. Young tube in a glovebox. One small crystal of phenol was added, and the tube was closed and shaken while hydrogen evolution was observed. The tube was transferred out of the box and treated for 30 min in an ultrasound bath. ^{1}H and ^{31}P NMR analysis indicated quantitative generation of iridium trihydrides **5**.

(*p*-MeOPCP)IrH$_3$Na (5a). ^{1}H NMR (300 MHz, 23 °C, THF-



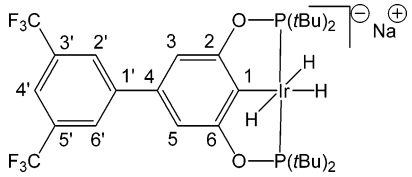
d_8): δ 5.91 (s, 2H, 4- and 6-H), 3.58 (s, 3H, OCH_3), 1.32 (vt, J_{P-H} = 6.5 Hz, 36H, 4 × *t*Bu), −13.35 (m, 1H, IrH), −13.65 [dt, $^2J_{P-H}$ = 15.9 Hz, $^2J_{cisH-H}$ = 4.8 Hz, 2H, *trans*-IrH$_2$]. ^{31}P-{^{1}H} NMR (121.5 MHz, 23 °C, THF-d_8): δ 187.4.

(*p*-HPCP)IrH$_3$Na (5c). ^{1}H NMR (400 MHz, 23 °C, THF-



d_8): δ 6.30 (t, $^3J_{H-H}$ = 7.6 Hz, 1H, 4-H), 6.13 (d, $^3J_{H-H}$ = 7.6 Hz, 2H, 3- and 5-H), 1.32 (vt, J_{P-H} = 4.8 Hz, 36H, 4 × *t*Bu), −13.33 (m, 1H, IrH), −13.55 [dt, $^2J_{P-H}$ = 16.0 Hz, $^2J_{cisH-H}$ = 4.8 Hz, 2H, *trans*-IrH$_2$]. ^{1}H{^{31}P} NMR, hydridic region (400 MHz, 23 °C, THF-d_8): δ −13.33 (t, $^2J_{H-H}$ = 4.8 Hz, IrH), −13.55 [d, $^2J_{cisH-H}$ = 4.8 Hz, *trans*-IrH$_2$]. ^{31}P{^{1}H} NMR (162 MHz, 23 °C, THF-d_8): δ 185.9. ^{13}C{^{1}H} NMR (100.6 MHz, 23 °C, THF-d_8): δ 164.4 (C$_q$, vt, J_{P-C}, = 7.0 Hz, C2 and C6), 133.6 (C$_q$, t, $^2J_{P-C}$ = 6.9 Hz, C1), 119.7 (CH, C4), 101.8 (CH, vt, J_{P-C} = 5.7 Hz, C3 and C5), 39.2 [C$_q$, vt, J_{P-C} = 12.3 Hz, 2 × P(*t*Bu)$_2$], 29.7 [CH$_3$, vt, J_{P-C} = 3.6 Hz, 2 × P(*t*Bu)$_2$].

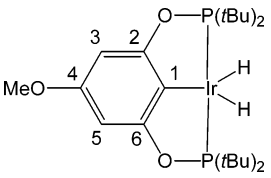
(*p*-Ar^{F}PCP)IrH$_3$Na (5f). ^{1}H NMR (400 MHz, 23 °C, THF-



d_8): δ 8.10 (s, 2H, 2′- and 6′-H), 7.67 (s, 1H, 4′-H), 6.63 (s, 2H, 4- and 6-H), 1.36 (vt, J_{P-H} = 6.6 Hz, 36H, 4 × *t*Bu), −13.12 (m, 1H, IrH), −13.32 (dt, $^3J_{P-H}$ = 16.0 Hz, $^2J_{cisH-H}$ = 4.9 Hz, *trans*-IrH$_2$). ^{31}P{^{1}H} NMR (162 MHz, 23 °C, THF-d_8): δ 190.3. ^{13}C{^{1}H} NMR (100.6 MHz, 23 °C, THF-d_8): δ 165.8 (C$_q$, vt, J_{P-C}, = 7.1 Hz, C2 and C6), 147.0 (C$_q$, s, C4), 141.9 (C$_q$ t, $^2J_{P-C}$ = 7.0 Hz, C1), 132.2 (C$_q$, q, $^2J_{F-C}$ = 32.4 Hz, C3′ and C5′), 129.8 (C$_q$, s, C1′), 126.4 (CH, s, C2′ and C6′), 125.0 (C$_q$, q, $^1J_{C-F}$ = 272 Hz, 2 × CF$_3$), 118.1 (CH, m, C4′), 100.5 (CH, vt, J_{P-C} = 5.5 Hz, C3 and C5), 39.5 (C$_q$, vt, J_{P-C} = 12.2 Hz, 4 × *t*Bu), 29.7 (CH$_3$, vt, J_{P-C} = 3.6 Hz, 4 × *t*Bu).

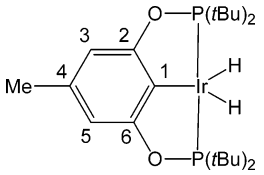
General Procedure for the Synthesis of Complexes (*p*-XPCP)IrH$_2$ (6a−f). One equivalent of the respective (*p*-XPCP)IrHCl complex **4a**−**f** and 1.1 equiv of NaO*t*Bu were dissolved in nitrogen-free benzene in an rubber septum capped Schlenk flask while the flask was purged with hydrogen. The solution was stirred for 0.5−1.5 h at 23 °C under a slow flow of hydrogen while becoming nearly colorless. The reaction mixture was then cooled to 0 °C, and the (frozen) solvent was removed in vacuo (10^{-3} mbar, 3 h). The Schlenk flask was transferred to the glovebox, argon and nitrogen-free pentane were added, and the solution was filtered through a 0.2 μm pore size syringe filter (Nalgene 199-2020) into another rubber septum capped Schlenk flask. The solvent was removed in vacuo (10^{-3} mbar), the residue dissolved in 3 mL of nitrogen-free benzene, and the benzene sublimed at 0 °C for 2 h to yield the (*p*-XPCP)IrH$_2$ complexes as brown-red to red fine powders. The respective (*p*-XPCP)IrH$_4$ (**7**) complexes cannot be isolated in pure form since they lose hydrogen even in the solid state when not stored over a hydrogen atmosphere. Spectroscopic data are exemplified for complex **7f**.

(*p*-MeOPCP)IrH$_2$ (6a). Following the general procedure 113 mg (0.18 mmol, 91%) of compound **6a** was obtained from 131 mg (0.2 mmol) of precursor **4a**, 19.3 mg (0.20 mmol) of NaO*t*Bu, and H$_2$ as a red-brown amorphous solid. ^{1}H NMR (400 MHz, 23 °C, C$_6$D$_6$): δ 6.62 (s, 2H, 3- and 5-H), 3.31 (s, 3H, OCH$_3$), 1.32 [vt, J_{P-H} = 7.1 Hz, 36H, 2 × P(*t*Bu)$_2$], −17.55 (t, $^2J_{P-H}$ = 8.1 Hz, 2H, IrH$_2$). ^{31}P{^{1}H} NMR (162 MHz, 23 °C, C$_6$D$_6$): δ 207.6. ^{13}C{^{1}H} NMR (100.6 MHz, 23 °C, C$_6$D$_6$): δ 171.9 (C$_q$, vt, J_{P-C} = 7.4 Hz, C2 and C6), 165.5 (C$_q$, s, C4), 149.4 (C$_q$, t, $^2J_{P-C}$ = 7.0 Hz, C1), 90.9 (CH, vt, J_{P-C} = 6.0 Hz,



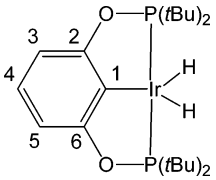
C3 and C5), 55.0 (CH$_3$, s, OCH$_3$), 40.0 (C$_q$, vt, J_{P-C} = 11.6 Hz, 4 × *t*Bu), 29.0 (CH$_3$, vt, J_{P-C} = 3.7 Hz, 4 × *t*Bu). IR (pentane, cm^{-1}): 2105, 2086, 2003, 1997, 1946 (ν_{Ir-H}). IR (CH$_2$Cl$_2$, cm^{-1}): 2105, 2086, 2003, 1997, 1946 (ν_{Ir-H}). Anal Calcd for C$_{23}$H$_{43}$O$_3$P$_2$Ir (621.76): C, 44.43; H, 6.97. Found: C, 44.68; H, 7.28.

(*p*-MePCP)IrH$_2$ (6b). Following the general procedure 52 mg (86 μmol, 86%) of compound **6b** was obtained from 64 mg (0.1 mmol) of precursor **4b**, 11.0 mg (0.11 mmol) of NaO*t*Bu, and H$_2$ as a red-brown amorphous solid. ^{1}H NMR (400 MHz,



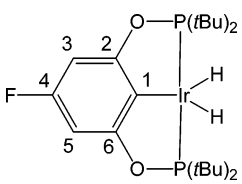
23 °C, C$_6$D$_6$): δ 6.75 (s, 2H, 3- and 5-H), 2.15 (s, 3H, *p*-Me), 1.30 [vt, J_{P-H} = 7.1 Hz, 36H, 2 × P(*t*Bu)$_2$], −17.19 (t, $^2J_{P-H}$ = 8.1 Hz, 2H, IrH$_2$). ^{31}P{^{1}H} NMR (121.5 MHz, 23 °C, C$_6$D$_6$): δ 205.3. ^{13}C{^{1}H} NMR (100.6 MHz, 23 °C, C$_6$D$_6$): δ 170.8 (C$_q$, vt, J_{P-C} = 7.3 Hz, C2 and C6), 152.8 (C$_q$, t, $^2J_{P-C}$ = 6.9 Hz, C1), 142.7 (C$_q$, s, C4), 104.9 (CH, vt, J_{P-C} = 5.8 Hz, C3 and C5), 40.1 (C$_q$, vt, J_{P-C} = 11.8 Hz, 4 × *t*Bu), 28.9 (CH$_3$, vt, J_{P-C} = 3.7 Hz, 4 × *t*Bu). IR (pentane, cm^{-1}): 2087, 2004, 1955, 1948 (ν_{Ir-H}). IR (CH$_2$Cl$_2$, cm^{-1}): 2098, 2076, 1999, 1937 (ν_{Ir-H}). Anal. Calcd for C$_{23}$H$_{43}$O$_2$P$_2$Ir (605.76): C, 45.60; H, 7.16. Found: C, 46.23; H, 7.73.

(*p*-HPCP)IrH$_2$ (6c). Following the general procedure 113 mg (191 μmol, 95%) of compound **6c** was obtained from 125 mg (0.2 mmol) of precursor **4c**, 21.0 mg (0.22 mmol) of NaO*t*Bu, and H$_2$ as a red amorphous solid. ^{1}H NMR (400.1 MHz, 23 °C,



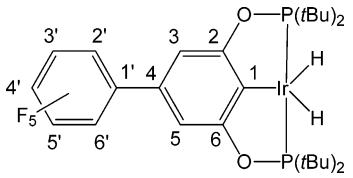
C$_6$D$_6$): δ 7.06 (m, 1H, 4-H), 6.95 (m, 2H, 3- and 5-H), 1.25 [vt, J_{P-H} = 7.1 Hz, 36H, 2 × P(*t*Bu)$_2$], −17.04 (t, $^2J_{P-H}$ = 8.2 Hz, 2H, IrH$_2$). ^{31}P{^{1}H} NMR (162 MHz, 23 °C, C$_6$D$_6$): δ 204.9. ^{13}C-{^{1}H} NMR (100.6 MHz, 23 °C, Tol-d_8): δ 170.5 (C$_q$, vt, J_{P-C} = 7.3 Hz, C2 and C6), 155.0 (C$_q$, t, $^2J_{P-C}$ = 6.6 Hz, C1), 131.6 (CH, s, C4), 103.9 (CH, vt, J_{P-C} = 5.7 Hz, C3 and C5), 40.1 (C$_q$, vt, J_{P-C} = 11.7 Hz, 4 × *t*Bu), 28.8 (CH$_3$, vt, J_{P-C} = 3.7 Hz, 4 × *t*Bu). IR (pentane, cm^{-1}): 2111, 2101, 2005, 1950 (ν_{Ir-H}). IR (CH$_2$Cl$_2$, cm^{-1}): 2111, 2000, 1934, 1899 (ν_{Ir-H}). Anal. Calcd for C$_{22}$H$_{41}$O$_2$P$_2$Ir (591.74): C, 44.65; H, 6.98. Found: C, 45.01; H, 6.58.

(*p*-FPCP)IrH$_2$ (6d). Following the general procedure 53 mg (0.87 μmol, 87%) of compound **6d** was obtained from 64 mg (0.1 mmol) of precursor **4d**, 11.0 mg (0.11 mmol) of NaO*t*Bu, and H$_2$ as a red-brown amorphous solid. ^{1}H NMR (400.1 MHz,



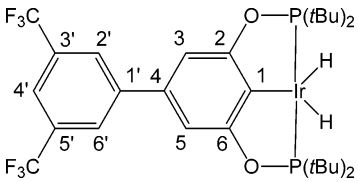
23 °C, Tol-d_8): δ 6.57 (d, $^3J_{F-H}$ = 10.3 Hz, 2H, 3- and 5-H), 1.23 [vt, J_{P-H} = 7.1 Hz, 36H, 2 × P(tBu)$_2$], −17.13 (t, $^2J_{P-H}$ = 8.1 Hz, 2H, IrH$_2$). ^{31}P{^{1}H} NMR (162 MHz, 23 °C, Tol-d_8): δ 208.4. ^{19}F NMR (376.5 MHz, 23 °C, Tol-d_8): δ −109.7. ^{13}C{^{1}H} NMR (100.6 MHz, 23 °C, Tol-d_8): δ 170.9 (C$_q$, dvt, $^3J_{F-C}$ = 15.4 Hz, J_{P-C} = 7.3 Hz, C2 and C6), 166.9 (C$_q$, d, $^1J_{F-C}$ = 242.9 Hz, C4), 150.9 (C$_q$, dt, $^4J_{F-C}$ = 26.4 Hz, $^2J_{P-C}$ = 7.0 Hz, C1), 92.4 (CH, dvt, $^2J_{F-C}$ = 25.8 Hz, J_{P-C} = 6.1 Hz, C3 and C5), 40.2 (C$_q$, vt, J_{P-C} = 11.5 Hz, 4 × tBu), 28.7 (CH$_3$, vt, J_{P-C} = 3.6 Hz). IR (pentane, cm^{-1}): 2112, 2094, 2006, 2001, 1952 (ν_{Ir-H}). IR (CH$_2$Cl$_2$, cm^{-1}): 2093, 2001, 1933, 1908 (ν_{Ir-H}). Anal. Calcd for $C_{22}H_{40}O_2P_2FIr$ (609.73): C. 43.33; H. 6.61. Found: C. 44.12; H, 7.23.

(*p*-C$_6$F$_5$PCP)IrH$_2$ (6e). Following the general procedure 68 mg (90 μmol, 90%) of compound **6e** was obtained from 79 mg (0.1 mmol) of precursor **4e**, 11.0 mg (0.11 mmol) of NaOtBu, and H$_2$ as a orange-red amorphous solid. ^{1}H NMR (400.1 MHz,



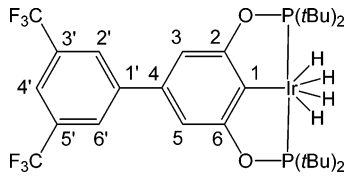
23 °C, C$_6$D$_6$): δ 6.99 (t br, $^5J_{F-H}$ = 1.4 Hz, 2H, 3- and 5-H), 1.24 [vt, J_{P-H} = 7.2 Hz, 36H, 2 × P(tBu)$_2$], −16.46 (t, $^2J_{P-H}$ = 8.5 Hz, 2H, IrH$_2$). ^{31}P{^{1}H} NMR (162 MHz, 23 °C, C$_6$D$_6$): δ 206.3. ^{13}C{^{1}H} NMR (100.6 MHz, 23 °C, Tol-d_8): δ 170.0 (C$_q$, vt, J_{P-C} = 7.2 Hz, C2 and C6), 155.7 (C$_q$, t, $^2J_{P-C}$ = 6.3 Hz, C1), 144.4 (C$_q$, dm, $^1J_{C-F}$ = 246 Hz, C2′ and C6′), 140.1 (C$_q$, dm, $^1J_{C-F}$ = 252 Hz, C4′), 138.0 (C$_q$, dm, $^1J_{C-F}$ = 252 Hz, C3′ and C5′), 128.4 and 116.9 (C$_q$ each, m each, C1′ and C4), 105.9 (CH, m, C3 and C5), 40.3 (C$_q$, vt, J_{P-C} = 11.9 Hz, 4 × tBu), 28.6 (CH$_3$, mb, 4 × tBu). ^{19}F{^{1}H} NMR (376.5 MHz, 23 °C, C$_6$D$_6$): δ −143.18 (m, 2 F, 2′- and 6′-F), −157.27 (t, $^3J_{F-F}$ = 21.7 Hz, 1 F, 4′-F), −163.51 (m, 2 F, 3′- and 5′-F). IR (pentane, cm^{-1}): 2120, 2009, 2003, 1954 (ν_{Ir-H}). IR (CH$_2$Cl$_2$, cm^{-1}): 2117, 2003, 1943, 1905 (ν_{IrH}). Anal. Calcd for $C_{28}H_{40}O_2P_2F_6Ir$ (757.78): C, 44.38; H, 5.32. Found: C, 44.62; H, 5.61.

(*p*-Ar^{F}PCP)IrH$_2$ (6f). Following the general procedure 151 mg (187 μmol, 93%) of compound **6f** was obtained from 168 mg (0.2 mmol) of precursor **4f**, 21.0 mg (0.22 mmol) of NaOtBu, and H$_2$ as a red amorphous solid. ^{1}H NMR (400.1 MHz, 23 °C,



C$_6$D$_6$): δ 7.80 (s, 2H, 2′- and 6′-H), 7.65 (s, 1H, 4′-H), 7.00 (s, 2H, 3- and 5-H), 1.30 [vt, J_{P-H} = 7.2 Hz, 36H, 2 × P(tBu)$_2$], −16.13 (t, $^2J_{P-H}$ = 8.1 Hz, 2H, IrH$_2$). ^{31}P{^{1}H} NMR (162 MHz, 23 °C, C$_6$D$_6$): δ 206.9. ^{13}C{^{1}H} NMR (100.6 MHz, 23 °C, Tol-d_8): δ 170.9 (C$_q$, vt, J_{P-C} = 7.3 Hz, C2 and C6), 155.2 (C$_q$, t, $^2J_{P-C}$ = 6.6 Hz, C1), 144.7 and 141.1 (C$_q$ each, s each, C4 and C1′), 132.2 (C$_q$, q, $^2J_{F-C}$ = 32.9 Hz, C3′ and C5′), 127.5 (CH, m, C2′ and C6′), 124.1 (C$_q$, q, $^1J_{F-C}$ = 273.0 Hz, 2 × CF$_3$), 120.6 (CH, m, C4′), 103.4 (CH, vt, J_{P-C} = 5.6 Hz, C3 and C5), 40.4 (C$_q$, vt, J_{P-C} = 11.8 Hz, 4 × tBu), 28.7 (CH$_3$, vt, J_{P-C} = 3.2 Hz, 4 × tBu). ^{19}F{^{1}H} NMR (376.5 MHz, 23 °C, C$_6$D$_6$): δ −62.83. IR (pentane, cm^{-1}): 2119 (ν_{Ir-H}), 1590, 1546, 1279, 1179, 1144. IR (CH$_2$Cl$_2$, cm^{-1}): 2118, 2010, 1954 (ν_{Ir-H}). Anal. Calcd for $C_{30}H_{43}O_2P_2F_6Ir$ (803.83): C, 44.82; H, 5.39. Found: C, 45.03; H, 5.03.

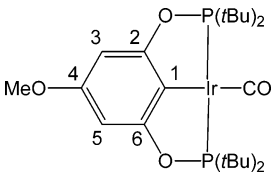
(*p*-Ar^{F}PCP)IrH$_4$ (7f). Complex **7f** was obtained upon treating a benzene-d_6 or toluene-d_8 solution of **6f** with 1.2 atm of hydrogen at 23 °C in a J. Young tube. Heating of the toluene-d_8 sample to 100 °C resulted in reversible loss of hydrogen to form **6f** even under 1.2 atm of hydrogen. ^{1}H NMR (400.1 MHz,



23 °C, C$_6$D$_6$): δ 7.76 (s, 2H, 2′- and 6′-H), 7.64 (s, 1H, 4′-H), 6.84 (s, 2H, 3- and 5-H), 1.30 [vt, J_{P-H} = 7.2 Hz, 36H, 2 × P(tBu)$_2$], −8.22 (s br, 4H, IrH$_4$). ^{31}P{^{1}H} NMR (162 MHz, 23 °C, C$_6$D$_6$): δ 186.0. ^{19}F{^{1}H} NMR (376.5 MHz, 23 °C, C$_6$D$_6$): δ −62.8. ^{13}C{^{1}H} NMR (100.6 MHz, 23 °C, C$_6$D$_6$): δ 164.5 (C$_q$, m br, C2 and C6), 144.6 (C$_q$, s, C1′), 136.5 and 124.3 (C$_q$ each, m br each, C1 and C4), 131.9 (C$_q$, q, $^2J_{F-C}$ = 32.9 Hz, C3′ and C5′), 127.3 (CH, m, C2′ and C6′), 124.1 (C$_q$, q, $^1J_{F-C}$ = 273.0 Hz, 2 × CF$_3$), 119.9 (CH, m br, C4′), 103.8 (CH, m br, C3 and C5), 38.4 (C$_q$, m br, 4 × tBu), 28.4 (CH$_3$, m br, 4 × tBu).

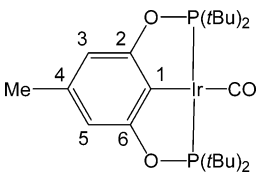
General Procedure for the Synthesis of Complexes (*p*-XPCP)Ir(CO) (8a−f). One equivalent of the respective complex (*p*-XPCP)IrHCl (**4a**−**f**) and 1.1 equiv of NaOtBu were dissolved in nitrogen-free benzene in a rubber septum capped Schlenk flask while purging the flask with hydrogen. The solution was stirred for 0.5−1.5 h at 23 °C with hydrogen flowing while the solutions become pale orange. Then the hydrogen flow was replaced by a CO flow. The solution changed color to yellow within a few seconds. The CO flow was maintained for 2 min, the solvent was then removed under vacuum (10^{-3} mbar, 23 °C), and the residue was extracted with methanol/water (1:1), washed with small amounts of cold pentane (−20 °C), and dried under vacuum to yield analytically pure samples. The complexes (*p*-XPCP)Ir(CO) **8a**−**f** are sensitive to air and need to be handled under argon.

(*p*-MeOPCP)Ir(CO) (8a). By using the general procedure 61 mg (94 μmol, 94%) of (*p*-MeOPCP)Ir(CO) (**8a**) was obtained from 66 mg (101 μmol) of (*p*-MeOPCP)IrHCl (**4a**) and 10.6 mg of NaOtBu as a fine powdered yellow solid. ^{1}H NMR (300 MHz,



23 °C, C$_6$D$_6$): δ 6.55 (s, 2H, 3- and 5-H), 3.30 (s, 3H, OCH$_3$), 1.33 [vt, J_{P-H} = 7.7 Hz, 36H, 2 × P(tBu)$_2$]. ^{31}P{^{1}H} NMR (121.5 MHz, 23 °C, C$_6$D$_6$): δ 200.9. ^{13}C{^{1}H} NMR (75.5 MHz, 23 °C, C$_6$D$_6$): δ 199.6 (C$_q$, t, $^2J_{P-C}$ = 5.0 Hz, C≡O), 170.7 (C$_q$, vt, J_{P-C} = 8.2 Hz, C2 and C6), 162.8 (C$_q$, s, C4), 141.2 (C$_q$, t, $^2J_{P-C}$ = 8.9 Hz, C1), 91.5 (CH, vt, J_{P-C} = 6.3 Hz, C3 and C5), 54.9 (CH$_3$, OCH$_3$), 40.9 (C$_q$, vt, J_{P-C} = 12.4 Hz, 4 × tBu), 28.4 (CH$_3$, vt, J_{P-C} = 3.2 Hz, 4 × tBu). IR (pentane, cm^{-1}): 1947 (ν_{CO}), 1901, 1594, 1561. Anal. Calcd for $C_{24}H_{41}O_4P_2Ir$ (647.76): C, 44.50; H, 6.38. Found: C, 44.96; H, 6.45.

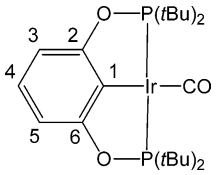
(*p*-MePCP)Ir(CO) (8b). By using the general procedure 58 mg (91 μmol, 91%) of (*p*-MePCP)Ir(CO) (**8b**) was obtained from 64 mg (100 μmol) of (*p*-MePCP)IrHCl (**4b**) and 10.6 mg (110 μmol) of NaOtBu as a fine powdered yellow solid. ^{1}H NMR



(300 MHz, 23 °C, C$_6$D$_6$): δ 6.65 (s, 2H, 3- and 5-H), 2.13 (s, 3H, *p*-Me), 1.32 [s br, 36H, 2 × P(tBu)$_2$]. ^{31}P{^{1}H} NMR (121.5

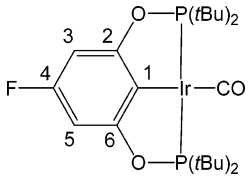
MHz, 23 °C, C_6D_6): δ 199.2. $^{13}C\{^1H\}$ NMR (75.5 MHz, 23 °C, C_6D_6): δ 199.8 (C_q, t, $^2J_{P-C}$ = 5.0 Hz, C≡O), 170.2 (C_q, vt, J_{P-C} = 8.2 Hz, C2 and C6), 145.9 (C_q, vt, J_{P-C} = 8.8 Hz, C1), 139.7 (C_q, s, C4), 105.3 (CH, vt, J_{P-C} = 5.7 Hz, C3 and C5), 40.9 (C_q, vt, J_{P-C} = 14.4 Hz, 4 × *t*Bu), 28.4 (CH_3, vt, J_{P-C} = 3.0 Hz, 4 × *t*Bu). IR (pentane, cm^{-1}): 1947 (ν_{CO}), 1903, 1598. Anal. Calcd for $C_{24}H_{41}O_3P_2Ir$ (631.76): C, 45.62; H, 6.54. Found: C, 45.59; H, 6.66.

(*p*-HPCP)Ir(CO) (8c). By using the general procedure 58 mg (95 μmol, 95%) of (*p*-HPCP)Ir(CO) (**8c**) was obtained from 62 mg (99 μmol) of (*p*-HPCP)IrHCl (**4c**) and 10.6 mg (110 μmol) of NaO*t*Bu as a fine powdered yellow solid. An alternative in situ generation of complexes **8c** was accomplished reacting a solution of 6.5 mg (0.01 mmol) of (*p*-HPCP)IrHCl (**4c**) in benzene-d_6 under 1 atm of CO [immediate change of color to colorless to form (*p*-HPCP)IrHCl(CO)] and heating of this solution after addition of 1 mg (0.011 mmol) of NaO*t*Bu for 2 h, 80 °C. ^1H NMR (300 MHz, 23 °C, C_6D_6): δ 6.86 (m, 3H,



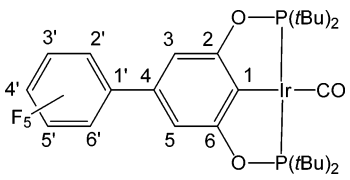
3−5-H), 1.30 [vt, J_{P-H} = 7.2 Hz, 36H, 2 × P(*t*Bu)$_2$]. $^{31}P\{^1H\}$ NMR (121.5 MHz, 23 °C, C_6D_6): δ 199.0. $^{13}C\{^1H\}$ NMR (75.5 MHz, 23 °C, C_6D_6): δ 199.7 (C_q, t, $^2J_{P-C}$ = 5.1 Hz, CO), 170.2 (C_q, vt, J_{P-C} = 8.2 Hz, C2 and C6), 149.0 (C_q, t, $^2J_{P-C}$ = 10.0 Hz, C1), 129.4 (CH, s, C4), 104.3 (CH, vt, J_{P-C} = 6.0 Hz, C3 and C5), 41.0 (C_q, vt, J_{P-C} = 12.4 Hz, 4 × *t*Bu), 28.4 (CH_3, vt, J_{P-C} = 3.4 Hz, 4 × *t*Bu). IR (pentane, cm^{-1}): 1949 (ν_{CO}), 1904. Anal. Calcd for $C_{23}H_{39}O_3P_2Ir$ (617.73): C, 44.72; H, 6.36. Found: C, 45.02; H, 6.36.

(*p*-FPCP)Ir(CO) (8d). By using the general procedure 61 mg (96 μmol, 96%) of (*p*-FPCP)Ir(CO) (**8d**) was obtained from 64 mg (99 μmol) of (*p*-FPCP)IrHCl (**4d**) and 10.6 mg (110 μmol) of NaO*t*Bu as a fine powdered yellow solid. ^1H NMR (300 MHz,



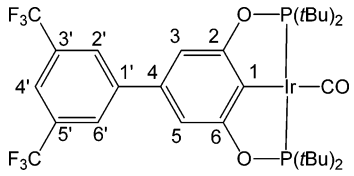
23 °C, C_6D_6): δ 6.57 (d, $^3J_{F-H}$ = 10.2 Hz, 2H, 3-H and 5-H), 1.25 [vt, J_{P-H} = 7.3 Hz, 36H, 2 × P(*t*Bu)$_2$]. $^{31}P\{^1H\}$ NMR (121.5 MHz, 23 °C, C_6D_6): δ 202.3. $^{19}F\{^1H\}$ NMR (376.5 MHz, 23 °C, C_6D_6): δ −113.2. $^{13}C\{^1H\}$ NMR (75.5 MHz, 23 °C, C_6D_6): δ 199.1 (C_q, t, $^2J_{P-C}$ = 5.1 Hz, C≡O), 170.0 (C_q, dvt, $^3J_{F-C}$ = 15.0 Hz and J_{P-C} = 8.1 Hz, C2 and C6), 165.0 (C_q, d, $^1J_{F-C}$ = 241.0 Hz, C4), 144.0 (C_q, dt, $^4J_{F-C}$ = 2.2 Hz and $^2J_{P-C}$ = 8.6 Hz, C1), 92.9 (CH, dvt, $^2J_{F-C}$ = 25.6 Hz, C3 and C5), 41.0 (C_q, vt, J_{P-C} = 12.2 Hz, 4 × *t*Bu), 28.3 (CH_3, vt, J_{P-C} = 3.4 Hz, 4 × *t*Bu). IR (pentane, cm^{-1}): 1953 (ν_{CO}), 1906, 1596, 1582. Anal. Calcd for $C_{23}H_{38}O_3P_2FIr$ (635.72): C, 43.45; H, 6.03. Found: C, 43.40; H, 6.03.

(*p*-C_6F_5PCP)Ir(CO) (8e). By using the general procedure 33 mg (42 μmol, 84%) of (*p*-C_6F_5PCP)Ir(CO) (**8e**) was obtained from 40 mg (50 μmol) of (*p*-C_6F_5PCP)IrHCl (**4e**) and 5.8 mg (60 μmol) of NaO*t*Bu as a fine powdered orange solid. ^1H NMR



(300 MHz, 23 °C, C_6D_6): δ 6.91 (s, 2H, 3- and 5-H), 1.30 [vt, J_{P-H} = 7.3 Hz, 36H, 2 × P(*t*Bu)$_2$]. $^{31}P\{^1H\}$ NMR (121.5 MHz, 23 °C, C_6D_6): δ 201.1. $^{19}F\{^1H\}$ NMR (376.5 MHz, 23 °C, C_6D_6): δ −143.35 (m, 2 F, 2′-and 6′-F), −157.15 (t, $^3J_{F-F}$ = 43.3 Hz, 1 F, 4′-F), −163.46 (m, 2 F, 3′- and 5′-F). $^{13}C\{^1H\}$ NMR (75.5 MHz, 23 °C, C_6D_6): δ 199.4 (C_q, $^2J_{P-C}$ = 5.0 Hz, C≡O), 170.0 (C_q, vt, J_{P-C} = 8.2 Hz, C2 and C6), 150.7 (C_q, $^2J_{P-C}$ = 8.4 Hz, C1); 144.4, 140.2, and 137.9 (dm each, $^1J_{F-C}$ = 247, 248, and 250 Hz, C2′−C6′), 126.7 (C_q, s, C4), 116.6 (C_q, m, C1′), 106.1 (CH, m, C3 and C5), 41.1 (C_q, vt, J_{P-C} = 12.3 Hz, 4 × *t*Bu), 28.3 (CH_3, vt, J_{P-C} = 3.4 Hz, 4 × *t*Bu). IR (pentane, cm^{-1}): 1955 (ν_{CO}), 1908, 1547, 1522. Anal. Calcd for $C_{29}H_{38}O_3P_2F_5Ir$ (783.78): C, 44.44; H, 4.89. Found: C, 45.10; H, 5.07.

(*p*-Ar^{F}PCP)Ir(CO) (8f). By using the general procedure 38 mg (46 μmol, 92%) of (*p*-HPCP)Ir(CO) (**8f**) was obtained from 42 mg (50 μmol) of (*p*-HPCP)IrHCl (**4f**) and 5.5 mg (57 μmol) of NaO*t*Bu as a fine powdered orange solid. ^1H NMR (300 MHz,



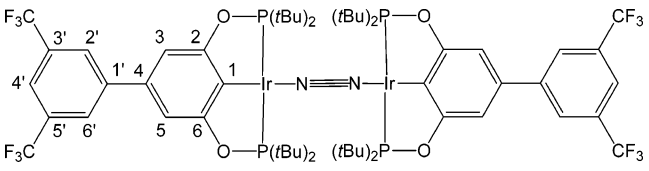
23 °C, C_6D_6): δ 7.75 (s, 2H, 2′- and 6′-H) 7.64 (s, 1H, 4′-H), 6.89 (s, 2H, 3- and 5-H), 1.34 [vt, J_{P-H} = 7.3 Hz, 36H, 2 × P(*t*Bu)$_2$]. $^{31}P\{^1H\}$ NMR (121.5 MHz, 23 °C, C_6D_6): δ 201.2. $^{19}F\{^1H\}$ NMR (376.5 MHz, 23 °C, C_6D_6): δ −62.82. $^{13}C\{^1H\}$ NMR (75.5 MHz, 23 °C, C_6D_6): δ 199.5 (C_q, $^2J_{P-C}$ = 5.1 Hz, C≡O), 170.7 (C_q, vt, J_{P-C} = 8.1 Hz, C2 and C6), 150.0 (C_q, t, $^2J_{P-C}$ = 8.5 Hz, C1), 144.2 and 139.5 (C_q each, s each, C4 and C1′), 131.5 (C_q, q, $^2J_{F-C}$ = 33.0 Hz, C3′ and C5′), 127.4 (CH, s br, C2′ and C6′), 123.9 (C_q, q, $^1J_{F-C}$ = 273.0 Hz, 3′-CF_3 and 5′-CF_3), 120.5 (CH, s br, C4′), 103.6 (CH, vt, J_{P-C} = 5.8 Hz, C3 and C5), 41.1 (C_q, vt, J_{P-C} = 12.3 Hz, 4 × *t*Bu), 28.3 (CH_3, vt, J_{P-C} = 3.3 Hz, 4 × *t*Bu). IR (pentane, cm^{-1}): 1955 (ν_{CO}), 1908, 1546, 1279, 1179, 1144. Anal. Calcd for $C_{31}H_{41}O_3P_2F_6Ir$ (829.82): C, 44.87; H, 4.98. Found: C, 44.96; H, 4.96.

General Procedure for the in Situ Generation of Hydrido Aryl Complexes (*p*-XPCP)Ir(aryl)(H) (9,10). To a mixture of 10 μmol of the respective hydrido chloro complex **4a**−**f** and 1.1 mg of NaO*t*Bu in a thick walled J.Young NMR tube was added ca. 350 mg of the respective nitrogen-free protio arene. After 30−60 min at 23 °C the starting complex had disappeared and one new signal was observed by $^{31}P\{^1H\}$ NMR. Cooling of the sample to −30−10 °C results in the appearance of hydridic resonances in the ^1H NMR with strongly temperature-dependent line widths $\Delta\nu_{1/2}$.

Exemplified NMR data are given for (*p*-XPCP)Ir(*m*-xylyl)(H) complexes **10a**−**f**. ^1H NMR data were obtained in both mesitylene-d_{12} and neat protio *m*-xylene by following the described procedure. However, mesitylene-d_{12} as purchased form Aldrich contains impurities, which gave rise to generation of trace amounts of both complexes **6a**−**f** and one other unidentified product. In neat protio *m*-xylene only one product was formed in each case on the basis of the ^{31}P NMR spectra. For most complexes **10a**−**f** all ^1H NMR resonances could be observed in neat protio *m*-xylene at −30 °C with intensities comparable to the solvent satellites. $^1H\{^{31}P\}$ NMR experiments were conducted between −40 and 23 °C either in neat *m*-xylene or in mesitylene-d_{12} solution containing variable amounts of *m*-xylene with respect to complexes **10a**−**f**. *m*-Xylene concentration-dependent line width determinations were conducted between −40 and 0 °C. The minimum line width $\Delta\nu_{1/2}$(min) for all compounds **10a**−**f** was observed at −30 °C, while appropriate differences $\Delta\nu_{1/2}$ for complexes **10a**−**f** were observed at 0 °C. **10a**: ^1H NMR (400.1 MHz, mesitylene-d_{12}, −30 °C): δ 7.32 (s br, 2H, 2- and 6-H of xylyl), 6.44 (s, 2H, 3- and 5-H), 6.42 (s br, 1H, 4-H of xylyl), 3.20 (s, 3H, *p*-MeO), 2.37 (s, 6H, 2 × CH_3 of xylyl), 1.08 [s br, 36H, 2 × P(*t*Bu)$_2$], −43.08 (t,

$^2J_{P-H}$ = 14.2 Hz, 1H, IrH). $^{31}P\{^1H\}$ NMR (162 MHz, mesitylene-d_{12}, −30 °C): δ 181.6. **10b**: ^1H NMR (400.1 MHz, mesitylene-d_{12}, −30 °C): δ 7.31 (s br, 2H, 2- and 6-H of xylyl), 6.59 (s, 2H, 3- and 5-H), 6.41 (s br, 1H, 4-H of xylyl), 2.38 (s, 6H, 2 × CH_3 of xylyl), 2.10 (s, 3H, *p*-CH_3), 1.07 [s br, 36H, 2 × P(*t*Bu)$_2$], −43.35 (t, $^2J_{P-H}$ = 14.4 Hz, 1H, IrH). $^{31}P\{^1H\}$ NMR (162 MHz, mesitylene-d_{12}, −30 °C): δ 179.7. **10c** (sample contained some solid material): ^1H NMR (400.1 MHz, mesitylene-d_{12}, −30 °C): δ 7.28 (s br, 2H, 2- and 6-H of xylyl), 6.82 (m, 3H, 3−6-H), 2.36 (s, 6H, 2 × CH_3 of xylyl), 1.07 [s br, 36H, 2 × P(*t*Bu$_2$)$_2$], −43.34 (t, $^2J_{P-H}$ = 14.2 Hz, 1H, IrH). $^{31}P\{^1H\}$ NMR (162 MHz, mesitylene-d_{12}, −30 °C): δ 179.0. **10d** (sample contained some solid material): ^1H NMR (400.1 MHz, mesitylene-d_{12}, −30 °C): δ 7.25 (s br, 2H, 2- and 6-H of xylyl), 6.51 (d, $^3J_{F-H}$ = 10.2 Hz, 3- and 5-H), 6.40 (s br, 1H, 4-H of xylyl), 2.35 (s, 6H, 2 × CH_3 of xylyl), 1.00 [s br, 36H, 2 × P(*t*Bu)$_2$], −43.33 (t, $^2J_{P-H}$ = 14.2 Hz, 1H, IrH). $^{31}P\{^1H\}$ NMR (162 MHz, mesitylene-d_{12}, −30 °C): δ 179.5. **10e**: ^1H NMR (400.1 MHz, mesitylene-d_{12}, −30 °C): δ 7.25 (s br, 2H, 2- and 6-H of xylyl), 6.89 (m, 2H, 3- and 5-H), 6.41 (s br 1H, 4-H of xylyl), 2.37 (s, 6H, 2 × CH_3 of xylyl), 1.04 [m br, 36H, 2 × P(*t*Bu)$_2$], −43.09 (t, $^2J_{P-H}$ = 14.2 Hz, 1H, IrH). $^{31}P\{^1H\}$ NMR (162 MHz, mesitylene-d_{12}, −30 °C): δ 181.2. **10f**: ^1H NMR(400.1 MHz, mesitylene-d_{12}, −30 °C): d 7.77 (s, 2H, 2′- and 6′-H), 7.61 (s, 1H, 4′-H), 7.27 (s br, 2H, 2- and 6-H of xylyl), 7.02 (s, 2H, 3- and 5-H), 6.42 (s br, 1H, 4-H of xylyl), 2.39 (s, 6H, 2 × CH_3 of xylyl), 1.06 [s, br., 36H, 2 × P(*t*Bu)$_2$], −43.03 (t, $^2J_{P-H}$ = 14.2 Hz, 1H, IrH). $^{31}P\{^1H\}$ NMR (162 MHz, mesitylene-d_{12}, −30 °C): δ 181.6.

{(*p*-Ar^{F}PCP)Ir}$_2${μ-N$_2$}*(2-x)Tol (11f). A solution of 168 mg (0.2 mmol) of precursor **4f** and 21.0 mg (0.22 mmol) of NaO*t*Bu in 3 mL of toluene under an nitrogen atmosphere was stirred for 60 min at 23 °C, while a red crystalline material precipitated. The solvent was removed in high vacuum (10^{-3} mbar), the residue extracted with 20 mL of pentane, and the pentane extract evaporated. The resulting residue was recrystallized from refluxing toluene (3 mL) under an atmosphere of nitrogen to yield 138 mg (76 μmol, 76%) of compound **11f** after drying under high vacuum. While X-ray crystallographic analysis of compound **11f** reveals exactly two molecules of toluene in the unit cell, the integration of the ^1H NMR spectra in THF-d_8 or benzene-d_6 gives less than 1 equiv of toluene per iridium depending on the vacuum applied on the samples. It was not possible, however, to totally remove toluene from either crystalline or amorphous **11f**. While monitoring the formation of **11f** in toluene-d_8, we have observed the formation of a minor side product, which did not crystallize and was not isolated. Acquisition of ^{13}C NMR spectra of compound **11f** requires the use of THF-d_8 due to low solubility in the commonly used solvents or instability in chlorinated solvents.



^1H NMR (300 MHz, 23 °C, THF-d_8): δ 8.19 ("s", 2H, 4′- and 6′-H), 7.87 (s, 1H, 2′-H), 7.16 (m, 5H, Tol), 6.87 (s, 2H, 3- and 5-H), 2.30 (s, 3H, Tol), 1.44 (vt, J_{P-H} = 7.0 Hz, 4 × *t*Bu). $^{31}P\{^1H\}$ NMR (121.5 MHz, 23 °C, Tol-d_8): δ 185.5. $^{19}F\{^1H\}$ NMR (376.5 MHz, 23 °C, C_6D_6): δ −63.9. $^{13}C\{^1H\}$ NMR (75.5 MHz, 23 °C, Tol-d_8): δ 170.8 (C_q, vt, J_{P-C} = 8.3 Hz, C2 and C6), 145.2 and 136.0 (C_q each, C4 and C1′), 138.6 (C_q, *i*-C Tol), 136.9 (C_q, t, $^2J_{P-C}$ = 7.6 Hz, C1), 132.7 (C_q, q, $^2J_{F-C}$ = 32.9 Hz, C3′ and C5′); 129.8, 129.1 and 126.2 (CH each, Tol), 127.6 (CH, m br, C2′ and C6′), 124.9 (C_q, q, $^1J_{F-C}$ = 272.5 Hz, 2 × CF_3), 120.6 (CH, m br, C4′), 103.0 (CH, vt, J_{P-C} = 5.7 Hz, C2 and C4), 41.8 (C_q, vt, $^2J_{P-C}$ = 11.6 Hz, 4 × *t*Bu), 29.5 (CH_3, vt, J_{P-C} = 3.6 Hz, 4 × *t*Bu), 21.7 (CH_3 Tol). IR (pentane, cm^{-1}): 2118 (ν_{N2}), 1475, 1467, 1461, 1381. Anal. Calcd for $C_{74}H_{98}N_2O_4P_4F_{12}Ir_2$ (1815.92): C, 48.94; H, 5.44. Found: C, 45.75; H, 5.29.[26] Crystals suitable for X-ray structure analysis precipitated shortly after reacting **4f** and NaO*t*Bu under an atmosphere of nitrogen in toluene-d_8 solution at 23 °C. X-ray crystal structure analysis of compound **11f** (−100 °C): space group and cell dimensions: monoclinic, *C*2/*c*, a = 21.1998(13) Å, b = 19.1070(12) Å, c = 21.0493(13) Å, β = 110.927(1)°, volume = 7963.9(9) Å^3, empirical formula $IrP_2C_{37}H_{49}F_6O_2N$, cell dimensions were obtained from 6048 reflections with 2θ angle in the range 5.00−56.00°. Crystal dimensions: 0.10 × 0.10 × 0.05 mm, fw = 907.95, Z = 8, F(000) = 3635.47, ρ_{calc} = 1.515 Mg/m^3, μ = 3.50 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 $h_{min,max}$ −28, 26; $k_{min,max}$ 0, 25; $l_{min,max}$ 0, 27; no. of reflections measured 30 602, no. of unique reflections 9618, no. of reflections with $I_{net} > 2.5\sigma(I_{net})$ = 7504, merging R-value on intensities 0.034. Correction was made for absorption using SADABS. Details of the last least squares cycle: 98 atoms, 442 parameters full-matrix on F_o counter wts (k 0.000150). The residuals are as follows: Significant reflections: 7503, R_F 0.032, R_w 0.035. All reflections: 9618, R_F 0.046, R_w 0.037. Included reflections: 7503, R_F 0.032, R_w 0.035, GoF 1.4825, 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 = $[\sum(w(F_o - F_c)^2)/$(no. of reflns − no. of params)$]^{-1/2}$. The maximum shift/σ ratio was 0.000. Last D-map: minimum density −1.070 e/Å^3, maximum density 1.400 e/Å^3.

General Procedure for the Transfer Dehydrogenation of COA with TBE. A 1.5 mL portion of 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), and 10 μmol of the respective (*p*-XPCP)IrH_2 (**6a**−**f**) was 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 (8 min and 40 h) the Kontes reactors were removed from the aluminum block and cooled by a stream of air. Aliquots of the reaction mixtures were then taken in the glovebox and analyzed by ^1H NMR. An average of two runs (from the same stock solution) were taken in order to determine the TONs after 8 min and 40 h. 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 ca. 5% impurity in the commercially available TBE (which was proven to be unreactive by use of a mesitylene-h_{12} standard capillary and 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.

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

Supporting Information Available: Crystallographic data of compound **11f**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(26) The elemental analysis probably reflects the partial loss of toluene from compound **11f**.