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# Addition of C−H Bonds to the Catalytically Active Complex (PCP)Ir (PCP = $\eta^3$-2,6-($^t$Bu$_2$PCH$_2$)$_2$C$_6$H$_3$)

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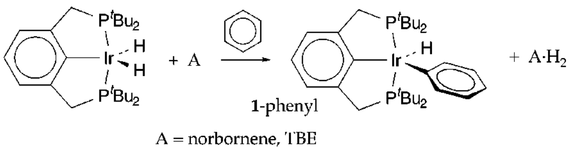
The development of catalysts for the selective functionalization of unactivated C−H bonds is presently one of the major goals of inorganic and organic chemistry. The oxidative addition of C−H bonds to transition metal centers is clearly of great interest in this context. Studies of systems that undergo observable C−H additions[1] have yielded deep insight into this reaction over the past two decades; however, there has existed for the most part a disparity between such systems and those that effect catalytic conversions. In the past several years, complexes containing the (PCP)Ir moiety (PCP = $\eta^3$-2,6-(R$_2$PCH$_2$)$_2$C$_6$H$_3$); typically R = $^t$Bu) have been reported to be efficient and, in some cases, selective catalysts for thermochemical alkane dehydrogenation.[2] Herein we report the observation of complexes resulting from the addition of vinyl and aryl C−H bonds to the Ir(PCP) unit, and characterization of their dynamic behavior. To our knowledge, these are the first observable examples of thermal C−H addition products in which the alkyl hydride analogues are presumed intermediates in a catalytic alkane functionalization cycle.

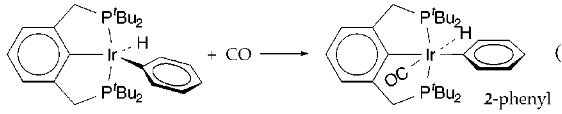
When (PCP)IrH$_2$ is reacted with either *tert*-butylethene (TBE) or norbornene, either in benzene solvent or in mesitylene with added benzene, disappearance of the dihydride is observed in the $^{31}$P NMR spectrum, accompanied by the appearance of a single peak at $\delta$ 67.2 ($\delta$ 67.5 in mesitylene). The $^1$H NMR spectrum at room temperature reveals signals characteristic of only a PCP ligand in a fully symmetrical ($C_{2v}$) environment. At lower temperatures (< ca. −10 °C), however, a hydride resonance at $\delta$ −45.56 (t, $J_{\text{P-H}} = 13.4$ Hz) is observed, strongly indicative of a five-coordinate d$^6$ species.[3] In addition, resonances attributable to an $\eta^1$-phenyl ligand appear,[4−6] the PCP *t*-butyl and benzylic protons are each resolved as two inequivalent sets, and P−H coupling appears in the selectively decoupled $^{31}$P NMR spectrum. These data are all consistent with characterization of the product as (PCP)Ir(Ph)H (**1**).



(1)

Analogous experiments with other arenes further support this characterization. With toluene, low-temperature $^1$H NMR reveals three addition products in a ratio of ca. 1:1:1.[4] Since the addition of arene C−H bonds ortho to a methyl group is generally much less favorable than meta and para addition,[5] we attribute the signals to two *m*-tolyl rotamers and the *p*-tolyl isomer.[6,7] Consistent with the lack of formation of an ortho-substituted tolyl complex, *m*-xylene and 2-chloro-*m*-xylene each give only one signal in the low-temperature $^{31}$P NMR and upfield $^1$H NMR spectra, while *p*-xylene and mesitylene give no observable C−H addition products.[4]

Addition of CO to **1**-phenyl in benzene at 6 °C results in the appearance of a single resonance in the $^{31}$P NMR spectrum at $\delta$ 52.3 (selectively decoupled: d, $J_{\text{P-H}} = 17.3$ Hz) and a hydride $^1$H NMR signal at $\delta$ −8.83 (t, $J_{\text{P-H}} = 17.8$ Hz). A full spectral characterization[4] indicates the formation of **2**-phenyl (and its $^{13}$CO isotopomer).



(2)

Unlike the five-coordinate precursor, **2** does not undergo arene exchange and is stereochemically rigid at ambient temperature. Addition of CO to the mixture of three isomers/rotamers of **1**-tolyl in toluene gives the three corresponding CO adducts, while each reaction with the *m*-xylene and 2-chloro-*m*-xylene adducts gives a single adduct.

Most reported products of C−H addition to late-metal centers lack a vacant coordination site necessary for $\beta$-H-elimination and therefore cannot directly serve as potential intermediates for alkane dehydrogenation, or as models thereof. An outstanding exception to this, closely related to **1**, was reported by Werner: Ir(P$^i$Pr$_3$)$_2$-Cl(Ph)H (**3**),[6] which was formed via benzene addition.[8] Complex **3** has a 16-valence-electron count and, more specifically, it has the five-coordinate, d$^6$, M(III) configuration which has been shown to be critical in olefin hydrogenation[9] as well as alkane dehydrogenation (though not directly observed in either case). Accordingly, complex **3** attracted our interest several years ago, and we have reported kinetic[10] and calorimetric[11] studies of it; both approaches illustrate very high stability. The kinetic barrier to elimination of benzene from **3** is found to be quite high (only slow arene exchange with concomitant decomposition at 120 °C); this is in agreement with the calorimetric studies which indicate that Ph−H addition is ca. 32 kcal/mol exothermic.[11] Complexes **1** and **3** are closely related, at least formally. We have previously calculated, however, that C−H addition to Ir(PMe$_3$)$_2$X is ca. 30 kcal/mol more favorable for X = Cl than for X = Ph (Ph held coplanar with P−Ir−P so as to model the PCP ligand).[12] In accordance with this prediction, we find that C−H elimination from **1** is far more facile than elimination from **3**.

Indeed, in contrast to the behavior of **3**, a broad range of observations demonstrate that intermolecular arene exchange with **1** occurs rapidly *even on the NMR time scale.* Addition of excess C$_6$D$_6$ to mesitylene solutions of **1**-(phenyl-$h_5$) results in disappearance of the phenyl and hydride resonances. As noted above, warming above ca. −10 °C results in reversible loss of phenyl

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(1) For an introduction to stoichiometric C−H activation by late-metal complexes, see, for example: (a) Arndtsen, B. A.; Bergman, R. G.; Mobley, T. A.; Peterson, T. H. *Acc. Chem. Res.* **1995**, *28*, 154−162. (b) Jones, W. D.; Feher, F. J. *Acc. Chem. Res.* **1989**, *22*, 91−100. (c) Harper, T. G. P.; Desrosiers, P. J.; Flood, T. C. *Organometallics* **1990**, *9*, 2523−2528.

(2) (a) Gupta, M.; Hagen, C.; Flesher, R. J.; Kaska, W. C.; Jensen, C. M. *Chem. Commun.* **1996**, 2083−2084. (b) Xu, W.; Rosini, G. P.; Gupta, M.; Jensen, C. M.; Kaska, W. C.; Krogh-Jespersen, K.; Goldman, A. S. *Chem. Commun.* **1997**, 2273−2274. (c) Liu, F.; Pak, E. B.; Singh, B.; Jensen, C. M.; Goldman, A. S. *J. Am. Chem. Soc.* **1999**, *121*, 4086−4087.

(3) For example, (PCP)IrHCl has a hydride NMR signal at $\delta$ −43.0 ($J_{\text{P-H}} = 12.0$ Hz): Moulton, C. J.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1976**, 1020−1024.

(4) See Supporting Information for details. All reactions were conducted under an argon atmosphere.

(5) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1984**, *106*, 1650−1663.

(6) Werner, H.; Höhn, A.; Dziallas, M. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1090−1092.

(7) Hindered rotation about M−phenyl bonds is well precedented; see, for example, ref 6.

(8) For other closely related examples, see: (a) Desrosiers, P. J.; Shimomoto, R. S.; Flood, T. C. *J. Am. Chem. Soc.* **1986**, *108*, 1346−1347. (b) Renkema, K. B.; Bosque, R.; Streib, W. E.; Maseras, F.; Eisenstein, O.; Caulton, K. G. *J. Am. Chem. Soc.* **1999**, *121*, 10895−10907 and references therein.

(9) Halpern, J. *Inorg. Chim. Acta* **1981**, *50*, 11−19 and references therein.

(10) Rosini, G. P.; Wang, K.; Patel, B.; Goldman, A. S. *Inorg. Chim. Acta* **1998**, *270*, 537−542.

(11) Rosini, G. P.; Liu, F.; Krogh-Jespersen, K.; Goldman, A. S.; Li, C.; Nolan, S. P. *J. Am. Chem. Soc.* **1998**, *120*, 9256−9266.

(12) Krogh-Jespersen, K.; Goldman, A. S. *Transition State Modeling for Catalysis*; ACS Symposium Series 721; American Chemical Society: Washington, DC, 1998; pp 151−162.

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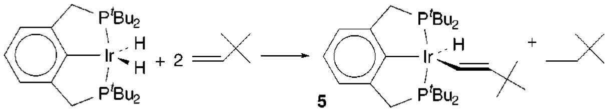
and hydride signals in the $^{1}$H NMR, loss of P−H coupling in the $^{31}$P NMR, and full symmetrization of the PCP ligand. Nondegenerate arene exchange is displayed by solutions of **1** in benzene/*m*-xylene. These show clearly resolvable (though overlapping) $^{31}$P NMR doublets attributable to both **1**-phenyl and **1**-*m*-xylyl at −38 °C, but at ambient temperature these signals coalesce to give $\delta$ values reflecting the equilibrium of eq 3, with $K_{eq} \approx 40$ (∼7:1 on a per C−H bond basis).

$$\mathbf{1}\text{-}(m\text{-xylyl}) + \text{benzene} \rightleftharpoons \mathbf{1}\text{-phenyl} + m\text{-xylene} \qquad (3)$$

The observation of rapid hydrocarbon exchange has important implications for the mechanism and selectivity of (PCP)Ir-catalyzed alkane dehydrogenation (including, but not limited to, the elimination of hydrogenated acceptor and the subsequent addition of alkane substrate). While other C−H addition systems have been reported to undergo rapid exchange, generally dissociatively,[1] in the case of a coordinatively unsaturated species, the limited precedent suggests that exchange may well be expected to proceed associatively.[13] We have thus begun to investigate in detail the dynamics of arene exchange in **1**. The rate of benzene exchange is found to be independent of the concentration of free benzene, indicative of a dissociative mechanism. This is manifest in the $^{1}$H NMR, where the broadening and coalescence behavior is independent of [benzene] over a range from 0.008 to 0.43 M, at temperatures ranging from −30 to 0 °C. The most quantitative data were obtained from the selectively decoupled $^{31}$P NMR spectra. Coalescence of the two branches of the hydride-coupled doublet occurred at −4 °C, independent of [benzene] over a range of 0.2−3.5 M. Treating this coalescence as the result of a simple exchange between two states of equal population ($\Delta\nu = 13.0$ Hz; $k = \pi\Delta\nu/\sqrt{2} = 29$ s$^{-1}$) yields $\Delta G^{\ddagger} = 13.9$ kcal/mol at −4 °C. Also consistent with a dissociative mechanism, the rate of H/D scrambling between *m*-xylene-$d_{10}$ and benzene-$h_6$ solvents in the presence of **1**-aryl is over 7 orders of magnitude slower than the arene exchange rate.

While a dissociative benzene-loss pathway is clearly indicated, the experimental results do not afford any further insight into the nature of the transition state or any possible intermediates. Assistance by agostic interactions or solvent must be considered. Ab initio electronic structure calculations (DFT/B3LYP; with phosphino methyl groups used in place of *tert*-butyl) indicate that a fully dissociative pathway is kinetically quite accessible ($\Delta H = 7.2$ kcal/mol; $\Delta H^{\ddagger} = 7.7$ kcal/mol) and much more favorable than any purely associative pathway (involving either Ir(V) species or Ir(III) $\sigma$-bond complexes).[14,15] However, the calculations cannot be used to rule out the possibility of agostic-assisted[16] or perhaps weakly solvent-assisted pathways.

In the absence of benzene, the reaction of (PCP)IrH$_2$ with TBE in either mesitylene or neat TBE results in the appearance of a single resonance in the $^{31}$P NMR spectrum at $\delta$ 70.3. The $^{1}$H NMR spectrum of this complex at ambient temperature (like that of **1**) reveals only a symmetrical PCP ligand, but at lower temperature the spectrum is easily assigned to the product of addition to the trans C−H bond of TBE. The temperature dependence of the $^{1}$H NMR spectra of **5** and the free TBE present reveals intermolecular exchange on the NMR time scale, in analogy with **1** and arene. The rate is independent of [TBE]; thus, the exchange mechanism, like that of **1**, is apparently dissociative. The time scale of exchange seems comparable to that of the arene exchange, and equilibrium studies indicate a ca. 1.6:1 preference for C$_6$H$_6$ versus TBE addition (on a per C−H bond basis). This preference is surprisingly small (0.28 kcal/mol) in light of a recent study by Wick and Jones, who have found that addition of TBE to Tp′Rh(CN-neopentyl) is 5.43 kcal/mol less favorable than addition of benzene;[17] this may reflect a greater tendency toward M−$\pi$* back-bonding in the case of (PCP)Ir.



(4)

Addition of cyclooctane to **1**-phenyl[18] results in alkane dehydrogenation to give (PCP)IrH$_2$ and cyclooctene with a half-life of ca. 30 min at 25 °C. The reaction (which is the reverse of eq 1, where A = cyclooctene) presumably proceeds via loss of benzene and addition of alkane; the resulting alkyl hydride, present in a very small steady-state or equilibrium concentration, then undergoes $\beta$-H elimination. Based upon other low-valent late-metal systems,[5,17,19] alkane addition is expected to be ca. 9−15 kcal/mol endothermic relative to benzene addition; such a barrier is consistent with the observed rate of reaction with cyclooctane. It bears note that benzylic C−H bonds (e.g., in mesitylene) show no indication of addition to (PCP)Ir; the addition of alkane C−H bonds is probably even less favorable[5,17] and very possibly even endergonic, but certainly not so much as to preclude alkyl hydride intermediates.

In conclusion, we have observed and characterized coordinatively unsaturated products of the addition of aryl and vinyl C−H bonds to (PCP)Ir. Exchange occurs rapidly via a dissociative mechanism. We can infer that the corresponding alkyl hydrides should be energetically accessible, though significantly less stable than **1** or **5**. Elimination and addition of C−H bonds are requisite steps for alkane transfer-dehydrogenation; we now have some insight into the mechanism and energetics of these steps, and we can deduce that they occur much more rapidly than the overall catalytic turnover rate of the (PCP)Ir-based dehydrogenation systems.[20]

**Acknowledgment.** Support by the National Science Foundation (Grant CHE-9704304) is gratefully acknowledged.

**Supporting Information Available:** $^{1}$H and $^{31}$P NMR data for complexes **1**, **2**, **5**, and the CO adduct of **5** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) Os(PMe$_3$)$_3$(neopentyl)H, which is isoelectronic to **1**, undergoes associative C−H exchange with benzene via Os(PMe$_3$)$_3$(neopentyl)(C$_6$H$_5$)H$_2$ (ref 8a). OsH(C$_6$H$_5$)(CO)(P$^t$Bu$_2$Me)$_2$ (also isoelectronic to **1**) was recently reported to undergo arene exchange via an unusual mechanism—associative with respect to arene but involving phosphine dissociation (ref 8b). Further precedent for a possible associative pathway includes recent work by Jones, who reported that even an 18-electron complex, Tp′Rh(L)(CH$_3$)H, undergoes associative hydrocarbon/hydrocarbon exchange (likely via an alkane complex intermediate). Tilley and Bergman have recently reported the first observation of C−H addition to give a M(V) adduct (iridium); this suggests that methyl/hydrocarbyl exchange by [Cp*Ir(PMe$_3$)(CH$_3$)]$^+$ proceeds via an Ir(V) intermediate (although in this case the alternative alkane elimination dissociative pathway is not possible). (a) Wick, D. D.; Reynolds, K. A.; Jones, W. D. *J. Am. Chem. Soc.* **1999**, *121*, 3974−3983. (b) Klei, S. R.; Tilley, T. D.; Bergman, R. G. *J. Am. Chem. Soc.* **2000**, *122*, 1816−1817.

(14) Krogh-Jespersen, K.; Czerw, M.; Goldman, A. S. Abstracts of Papers, 219th ACS National Meeting, San Francisco, 27 March 2000; American Chemical Society: Washington, DC, 2000; COMP 15.

(15) Li and Hall have also concluded that hydrocarbon (alkane) C−H exchange by (PCP)Ir proceeds dissociatively: Hall, M. B., personal communication.

(16) Belli, J.; Jensen, C. M. *Organometallics* **1996**, *15*, 1532−1534.

(17) Wick, D. D.; Jones, W. D. *Organometallics* **1999**, *18*, 495−505.

(18) Removal of solvent from benzene solutions of **1**-phenyl gives a stable solid, but redissolving in mesitylene reveals residual benzene. Attempts to remove all benzene lead to decomposition, probably due to bimolecular aryl C−H addition.

(19) Nolan, S. P.; Hoff, C. D.; Stoutland, P. O.; Newman, L. J.; Buchanan, J. M.; Bergman, R. G.; Yang, G. K.; Peters, K. G. *J. Am. Chem. Soc.* **1987**, *109*, 3143−3145.

(20) The fastest turnover rates observed at relatively low temperature for the [(2,6-($^t$Bu$_2$PCH$_2$)$_2$C$_6$H$_3$)Ir]-catalyzed dehydrogenation are $5.1 \times 10^{-4}$ turnovers·s$^{-1}$ at 55 °C; $\Delta G^{\ddagger} = 24.2$ kcal/mol (Renkema, K., to be published). This compares, for example with a C−H *elimination* rate of 29 s$^{-1}$ at −4 °C observed in the present work, which implies a C−H *addition* rate at least several orders of magnitude faster since the equilibrium lies far to the addition side. Although addition of alkane C−H bonds may well be slower than addition of vinyl or arene C−H bonds, there is no precedent for a difference so great (see ref 1) that we should believe that it might be slower than the catalytic rate noted above. DFT calculations indicate that $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for primary C−H addition (propane) to (PCP)Ir are 6.1 kcal/mol and −27 eu, respectively, corresponding to a rate of $6 \times 10^{3}$ s$^{-1}$ in neat alkane (ca. 8 M) at 55 °C.