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# Ethylene hydrogenation by the hydride alkoxide species $Ir(H)_2(OCH_2CF_3)(P^tBu_2Ph)_2$. Ethylene-induced reductive elimination of alcohol from $Ir^{III}$

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**Abstract**

$Ir(H)_2(OR_f)P_2$ ($P = P^tBu_2Ph$, $R_f = CH_2CF_3$) reacts with ethylene at 25°C to give $R_fOH$, ethane and $Ir(P \sim C)P(C_2H_4)$ (**2**) then $Ir(P \sim C)(C_2H_4)_2$ (**1**) and $Ir(P \sim C)H(OR_f)P$ (**3**) ($P \sim C = \eta^2\text{-}C_6H_4P^tBu_2$). It is shown that **2** and **1** are in equilibrium by P and $C_2H_4$ addition/dissociation. Compound **3** is a product "late" in the reaction sequence, and results from $H\text{–}OR_f$ oxidative addition to **2**. Since **3** reacts with ethylene to give **2**, **2** and **3** are in thermal equilibrium. Compound **3** reacts readily with $H_2$ to give $IrH_5P_2$ and $R_fOH$. The reason why $OR_f$ and ethylene ligands seem to be mutually incompatible is discussed.

## 1. Introduction

We have reported earlier [1–3] on our proposal that apparent unsaturation (*i.e.*, 16-valence electron count) in a halide-, amide- or alkoxide-ligated compound may in fact involve masking, or temporary stabilization of such unsaturation by ligand-to-metal $\pi$-donation (eqn. (1)). We envisage that form **A** may represent the ground state bonding situation, but that **B** will either be in thermal equilibrium with **A** (* = heat) or that **B** will form during the approach of some nucleophile (* = nucleophile). For the case of $Ir(H)_2(OCH_2CF_3)(PCy_3)_2$ [4], we found [1] **A** to be the ground-state structure, yet it adds CO or $H_2$ under mild conditions (1 atm, < 25°C). We report here on the reactivity of $Ir(H)_2(OR_f)P_2$ towards a reducible substrate (ethylene), where hydrogen transfer becomes possible.

$$L_nM{=}X \overset{*}{\rightleftharpoons} L_nM\text{–}\bar{X} \qquad (1)$$

**A** **B**

In attempting to study the reactivity of $Ir(H)_2(OR_f)(PCy_3)_2$ ($R_f = CH_2CF_3$) towards olefins, it became clear that the cyclohexyl protons obscure a large and important region of the $^1H$ NMR spectral window, and we therefore sought another, more suitable phosphine. In order to preserve the "$\pi$-stabilization of unsaturation" implicit in eqn. (1), the phosphine must be sufficiently bulky to prohibit the dimerization reaction of eqn. (2) [5a*]. We therefore chose $P^tBu_2Ph$, since it also incorporates diastereotopic reporter centers in the t-butyl groups. We report here on the synthesis and olefin chemistry of $Ir(H)_2(OR_f)P_2$ where $P = P^tBu_2Ph$.

$$Ir(H)_2(OR_f)(PR_3)_2 \rightleftharpoons \tfrac{1}{2}\,[Ir(H)_2(OR_f)(PR_3)]_2 \qquad (2)$$

## 2. Results

It is possible to characterize three products of the reaction between $IrH_2(OR_f)(P^tBu_2Ph)_2$ and ethylene

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* Reference number with an asterisk indicates a note in the list of references.

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at 25°C and 1 atm. The spectroscopic identification of the products and the conditions for their preparation will be discussed in detail. First, however, a brief description of reactivity with solvent is required.

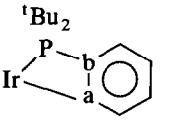
*2.1. Isotope exchange of $IrH_2(P^tBu_2Ph)_2(OCH_2CF_3)$ and $C_2H_4$ with $C_6D_6$*

The reaction of $IrH_2(OR_f)(P^tBu_2Ph)_2$ with one equivalent of ethylene in $C_6D_6$ was monitored for several hours. During this time, the bulk of the starting material remained unreacted. Only a small peak at 70 ppm in the $^{31}P\{^1H\}$ NMR spectrum was observed as a product. Over the course of eight hours, the signal at 5.2 ppm in the proton NMR spectrum due to free ethylene vanished, yet the solution still contained 95% $Ir(H)_2(OR_f)P_2$. This reagent compound still showed a hydride resonance [5b*]. Over the same time period, the signal due to the residual benzene was observed to gain intensity. Control experiments showed no reactivity between $Ir(H)_2(OR_f)P_2$ and $C_6D_6$. These data are consistent with the intermediacy of an iridium(I) species containing ethylene which can oxidatively add solvent C–D bonds at a rate significantly faster than $Ir(H)_2(OR_f)P_2$ is consumed by ethylene. In order to eliminate the complication of arene C–D activation, only cycloalkanes or protioarenes were employed as solvents in the reactions reported below.

*2.2. Synthesis and characterization of $Ir(C_6H_4P^tBu_2)(C_2H_4)_2$ (1)*

Reaction of $IrH_2(OCH_2CF_3)(P^tBu_2Ph)_2$ with more than three equivalents of ethylene proceeds (20 h, 25°C) through several intermediates to one organometallic product; with production of free $P^tBu_2Ph$. The $^{31}P\{^1H\}$ NMR signal for the product is a singlet at −61 ppm which translates into an upfield shift of 100 ppm from the free phosphine or 128 ppm from the alkoxide reagent. This is consistent with the inclusion of phophorus into a four-membered ring [6].

There are two possibilities for the formation of four-membered rings which include the phosphorus; alkyl C–H activation (metallation) or aryl C–H activation (*ortho*-metallation). Observation of only one doublet in the t-butyl region of the proton NMR spectrum definitively determines that *ortho*-metallation has occurred (C). The observation of two doublets (coupling to phosphorus of carbons a and b) in the $^{13}C\{^1H\}$ NMR spectrum (at chemical shifts downfield [6] of all phenyl carbons of the free phosphine) confirms that *ortho*-metallation has occurred. The lack of any $^1H$ NMR signals upfield at 0 ppm establishes that this compound is not a hydride. A singlet at 1.94 ppm is observed for the ethylene which integrates as 4 : 18 against the t-butyl doublet. A broad signal at 2.5 ppm is assigned to the second ethylene. Signals consistent with the production of trifluoroethanol and ethane are also observed.




(C)

Overall, these data are consistent with the following reaction (eqn. (3)). This is an extensive dehydrogenation of the reagent complex, with hydrogen transferred to both ethylene and alkoxide, and with further H "extracted" from the phosphine aryl group. Reductive elimination of alcohol leads to an $Ir^I$ product from an $Ir^{III}$ reagent.

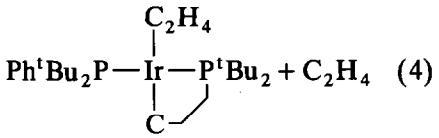
$$Ir(H)_2(OR_f)P_2 + 3C_2H_4 \longrightarrow \underset{\mathbf{1}}{C_2H_4(C_2H_4)Ir(P^tBu_2)(C_6H_4)} + C_2H_6 + R_fOH + P \quad (3)$$

*2.3. Synthesis and characterization of $Ir(C_6H_4P^tBu_2)(P^tBu_2Ph)(C_2H_4)$ (2)*

Upon vacuum removal of solvent from the above reaction mixture containing $Ir(C_6H_4P^tBu_2)(C_2H_4)_2$, a color change from yellow to deep red is observed. Di-tert-butyl phenyl phosphine has low volatility under these conditions (b.p. > 70°C at 100 millitorr), allowing it to coordinate to iridium as $C_2H_4$ is removed. The $^{31}P\{^1H\}$ NMR spectrum of the resulting solution shows two doublets, characteristic of an AX spin system. The large coupling constant (351 Hz) is indicative of a *trans* configuration. One of the doublets is shifted 77 ppm upfield of the free phosphine or 103 ppm upfield of the reagent alkoxide compound. This is consistent with the retention, in this new product, of the *ortho*-metallation found in **1**. Compound **2** is thus assigned the formula $Ir(C_6H_4P^tBu_2)(P^tBu_2Ph)(C_2H_4)$. This conclusion is supported by the observation of two signals in the $^{13}C\{^1H\}$ NMR spectrum, shifted downfield of the ring carbons of the free phosphine.

Further support for the identification of this complex is provided by the $^1H$ NMR spectrum which shows a complicated phenyl region, a broadened signal for coordinated ethylene, and two $^t$Bu signals. All of these data are consistent with the occurrence of reaction (4).

$$\underset{\mathbf{1}}{C_2H_4(C_2H_4)Ir(P^tBu_2)(C)} + P^tBu_2Ph \longrightarrow$$



$$Ph^tBu_2P-Ir(C_2H_4)(C)-P^tBu_2 + C_2H_4 \quad (4)$$

2

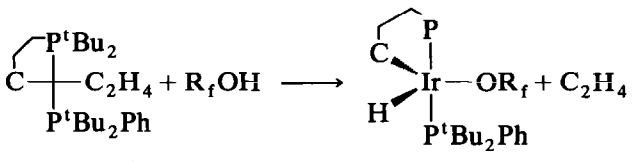
*2.4. Synthesis and characterization of $Ir(H)(OCH_2CF_3)(C_6H_4P^tBu_2)(P^tBu_2Ph)$ (3)*

The addition of one equivalent of trifluoroethanol to $Ir(C_6H_4P^tBu_2)(P^tBu_2Ph)(C_2H_4)$ results in the observation of a new AX system in the $^{31}P\{^1H\}$ NMR spectrum. The large coupling constant (343 Hz) is indicative of a *trans* configuration. One of the doublets is shifted 40 ppm upfield of the signal for free phosphine or 66 upfield of the alkoxide. This is consistent with the retention of *ortho*-metallation in the product, **3**.

The selectively hydride-coupled $^{31}P$ NMR spectrum shows two doublets of doublets (AMX pattern) with apparent $J$(H–Ir–P) coupling of 11 Hz for the downfield signal and 6 Hz for the upfield signal. This is indicative of the presence of a hydride *cis* to the mutually *trans* phosphines.

The proton NMR spectrum reveals an apparent triplet at −36.0 ppm for the hydride. Also evident are four doublets in the t-butyl region (indicating diastereotopic t-butyl groups), broadened signals at 4.72 and 4.50 ppm for the diastereotopic alkoxide protons, and a complicated phenyl region.

All of these data are consistent with oxidative addition of the H–$OR_f$ bond to $Ir^I$ in **2**, with retention of the *ortho*-metallated phenyl ring (eqn. (5)).



$$C(P^tBu_2)(C_2H_4)(P^tBu_2Ph) + R_fOH \longrightarrow H-Ir(C)(P)-OR_f + C_2H_4$$

2 3 (5)

The reaction of $R_fOH$ with $Ir(C_6H_4P^tBu_2)(P^tBu_2C_6H_5)(C_2H_4)$ to re-form the Ir–$OR_f$ bond is useful in that it begins to close a reaction cycle, moving in the general direction of regeneration of $Ir(H)_2(OR_f)(P^tBu_2Ph)_2$. It is noteworthy that ethylene is dissociated in this reaction, and that the alcohol proton does not attack the Ir–C (aryl) bond, but instead effects oxidative addition.

*2.5. Synthesis of $Ir(H)(OCH_2CF_3)(C_6H_4P^tBu_2)(P^tBu_2Ph)$ using propene*

The addition of one equivalent of propene to $Ir(H)_2(OCH_2CF_3)(P^tBu_2Ph)_2$ results (25°C, 4 days, $C_6D_{12}$ solvent) in the production of compound **3**. This product is characterized by $^{31}P\{^1H\}$, $^{13}C\{^1H\}$, and $^1H$ NMR spectra as $Ir(H)(OR_f)(C_6H_4P^tBu_2)(P^tBu_2Ph)$, thereby establishing that no alkene-derived fragments are retained in the product. Signals consistent with the production of propane are observed in both the $^{13}C\{^1H\}$ and the $^1H$ NMR spectra.

*2.6. Reaction mechanism*

With these three compounds identified, it is appropriate to address their reactivity, their interconversions, and the temporal sequence of their production.

*2.6.1. Reactions with a deficiency of ethylene*

Since the balanced eqn. 3 involves three moles of ethylene per mole of iridium, it was anticipated that intermediates might be detected in a 1:1 reaction at 25°C. After 5% conversion, one observes ($^{31}P$ NMR) compounds **1**, **2**, **3**, $P^tBu_2Ph$ and one new compound. The last compound shows only a $^{31}P\{^1H\}$ NMR singlet (70 ppm, *vide supra*), a value inconsistent with *ortho*-metallation. With the passage of time, the 70 ppm singlet and $Ir(C_6H_4P^tBu_2)(C_2H_4)_2$ disappear and $IrH(OR_f)(C_6H_4P^tBu_2)(P^tBu_2Ph)$ grows relative to $Ir(C_6H_4P^tBu_2)(P^tBu_2Ph)(C_2H_4)$. Finally, only unreacted $IrH_2(OR_f)P_2$ and $IrH(OR_f)(C_6H_4P^tBu_2)(P^tBu_2Ph)$ remain.

*2.6.2. Hydrogenolysis*

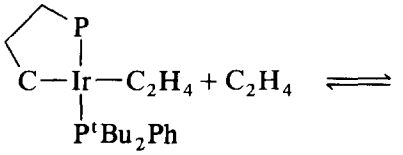
The final solution produced above reacts, within five min, with excess $H_2$ at one atm to convert both $Ir(H)_2(OR_f)P_2$ and $IrH(OR_f)(C_6H_4P^tBu_2)(P^tBu_2Ph)$ completely to $IrH_5P_2$ and $R_fOH$.

*2.6.3. Time of production of ortho-metallated products*

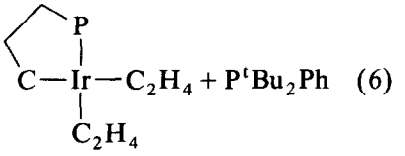
The relative time of appearance of $Ir(C_6H_4P^tBu_2)(P^tBu_2Ph)(C_2H_4)$, $Ir(C_6H_4P^tBu_2)(C_2H_4)_2$ and $IrH(OR_f)(C_6H_4P^tBu_2)(P^tBu_2Ph)$ are essential to knowing when alcohol is lost during the hydrogenation of ethylene. This was established by examining the evolving reaction mixture at times shorter than used in section 2.6.1. above. After 135 min, $Ir(C_6H_4P^tBu_2)(P^tBu_2Ph)(C_2H_4)$ was detected but $IrH(OR_f)(C_6H_4P^tBu_2)(P^tBu_2Ph)$ and $Ir(C_6H_4P^tBu_2)(C_2H_4)_2$ were present to negligible extents. Alcohol elimination is thus an early event in the mechanism and $IrH(OR_f)(C_6H_4P^tBu_2)(P^tBu_2Ph)$ is a later product and is a consequence of re-addition of $R_fO$–H. This reaction finally evolved to a steady state containing only $IrH_2(OR_f)P_2$ and $IrH(OR_f)(C_6H_4P^tBu_2)(P^tBu_2Ph)$. Adding excess ethylene to this solution slowly converted this mixture to ($^{31}P$ NMR assay) $Ir(C_6H_4P^tBu_2)(P^tBu_2Ph)(C_2H_4)$ and $Ir(C_6H_4P^tBu_2)(C_2H_4)_2$. Eqn. (5) is thus an equilibrium reaction.

*2.6.4. $P^tBu_2Ph$ and ethylene as competitor ligands*

Compounds **1** and **2** differ in their content of $P^tBu_2Ph$ and $C_2H_4$. It is thus natural to question whether these two compounds can be interconverted, and are thus participants in an equilibrium (eqn. (6)). It was established that this is in fact the case: the removal of $C_2H_4$ from **1** in the presence of $P^tBu_2Ph$ produces **2** (*vide supra*, eqn. (4)) and the addition of one equivalent of $C_2H_4$ to **2** produces **1** and free phosphine.



**2**



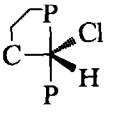
(6)

**1**

*2.7. Synthesis of the chloride analog of 3*

We hoped to develop an independent synthesis of a compound analogous to **3** using cyclooctene (COE) as the olefin (or leaving group). As will be seen below, this goal furnishes additional evidence of the great tendency of $Ir^I$ with this ligand set to undergo *ortho*-metallation.

Reaction of $[Ir(coe)_2Cl]_2$ with 4 equivalents of $P^tBu_2Ph$ (Ir:P ratio 1:2) at 25°C in methyl cyclohexane for 5 h gives, as the only metal-containing product, a compound with an AX $^{31}P$ NMR pattern. The large upfield shift of one $^{31}P$ resonance (−11 *vs.* 52 ppm), suggests *ortho*-metallation of one of the two phosphines [6]. The large P–P coupling constant (345 Hz) indicates *trans* stereochemistry of these two nuclei. The $^1H$ NMR spectrum shows a hydride resonance (−41.2 ppm) with coupling to two phosphorus nuclei (an apparent triplet with $J(H-P) = 11$ Hz). The $^1H$ NMR also shows four $^t$Bu methyl doublets, indicating that the P/(*ortho*-C)/P unit cannot lie on a molecular plane of symmetry. The $^{13}C\{^1H\}$ NMR spectrum shows two aryl carbons shifted downfield from the remaining ones, consistent with their inclusion in an *ortho*-metallated ring. The $^1H$ NMR spectrum in the aryl region shows four intensity-one triplets (actually doublets of doublets) in the 5.8–6.7 ppm regions; these are assigned to the *ortho*-metallated ring hydrogens. These data are consistent with structure **D**.



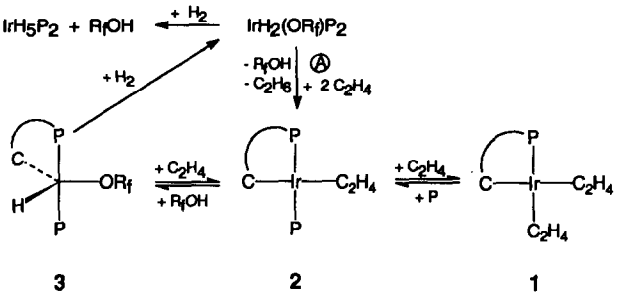
**(D)**

Compound **D** has an unusually broad resonance far downfield in the aryl region (7.9 ppm) at 25°C. This sharpens to a triplet at +70°C, but exhibits coalesence behavior and resolves into a double doublet (8.1 ppm) and a triplet (7.7 ppm) at −60°C, where each resonance has half the intensity it had at 25°C. Throughout this temperature range, the $^{31}P\{^1H\}$ NMR spectrum remains invariant. This behaviour we attribute to hindered rotation of an aryl ring of the $P^tBu_2Ph$ ligand in structure **D**. This makes clear that the species reported here are quite crowded [7].

Compound **D** demonstrates the high reactivity expected for a 16-electron complex of $Ir^{III}$. It reacts with $H_2$ (1 atm) within 15 min at 25°C in cyclohexane-$d_{12}$ to give $Ir(H)_2ClP_2$. Consistent with its crowded character, it binds neither cyclooctene nor $C_2H_4$ (1 atm, 25°C).

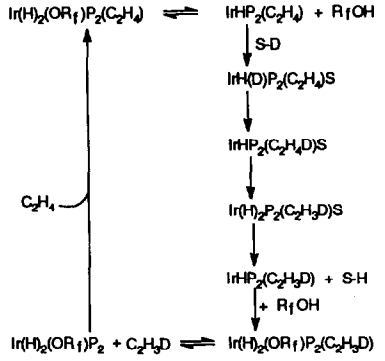
## 3. Discussion

The full set of observations reported above leads to the sequence of reactions shown in Scheme 1. It is noteworthy that none of the $Ir^I$ compounds is five-coordinate. This is consistent with the fact that we observe *no* exchange of free and coordinated $C_2H_4$ (in **1** and **2**) on the $^1H$ NMR time scale ($C_2H_4$ : Ir mole ratio 10:1). The part of the Scheme which remains lacking in detail is the multi-step transformation marked **A**. The $^{31}P\{^1H\}$ NMR singlet (70 ppm) is the only detectable species in this part of the reaction network. By its $^{31}P$ chemical shift, this species must be an intermediate prior to *ortho*-metallation. Concurrent with the transient production of this singlet, we have observed $^1H$ NMR signals at 2.09 ppm (singlet) and −3.42 ppm (triplet $J(P-H) = 27$ Hz) which integrate as 4:1, respectively. It is natural to propose that $IrH(C_2H_4)P_2$ (**E**) is the $Ir^I$ intermediate which oxidatively adds C–D



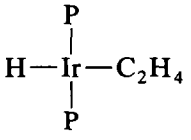
**3** **2** **1**

Scheme 1.




Scheme 2.

arene bonds (see beginning "Results") and forced us to perform all reactions in protio solvents or cyclohexane-$d_{12}$.



(E)

The path from E to Ir(P ~ C)P($C_2H_4$) involves loss of ethane, aryl *ortho*-metallation, and coordination of ethylene. We can say little about the timing of these addition, elimination, and intramolecular events. However, this formulation for the intermediate E offers a key to understanding both the isotopic exchange of ethylene protons with arene deuteriums and the further reactivity in the ethylene chemistry. The absence of $\pi$-acid ligands, together with the presence of the donor ligand $P^tBu_2Ph$ makes E highly susceptible (facile at 25°C) to C–H oxidative addition not only of the phosphine aryl group, but also of arene solvent. Thus, we propose the sequence in Scheme 2 (S = aryl) to effect the exchange of ethylene hydrogens with deuterated solvent.

## 4. Conclusions

The results reported here show that, in a hydrogen "lean" environment, $Ir(H)_2(OR_f)P_2$ shows a complex reactivity towards terminal olefins, including:

(a) olefin-induced reductive elimination of H and $OR_f$ groups as alcohol;

(b) ethyl formation and ethane elimination;

(c) scavenging of additional hydride ligands by P-aryl *ortho*-metallation;

(d) oxidative addition of $R_fO$–H to $Ir^I$ to produce an additionally $\pi$-stabilized five-coordinate $Ir^{III}$ complex;

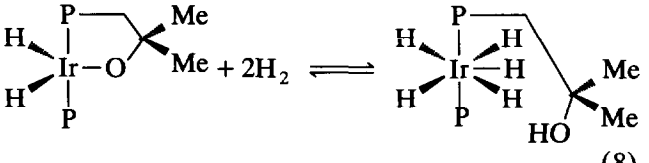
(e) displacement of bulky phosphine by ethylene.

It is noteworthy that this reaction system shows no evidence for insertion of ethylene in the *ortho*-metallated Ir–C bond. Such a reaction is observed for an *ortho*-metallated $Os^{II}$ complex of $PPh_3$ [8].

Points *c* and *e* clearly relate to properties of the phosphine which are less than optimal for a reagent intended to be of general utility for substrate hydrogenation. Both phosphine ligand loss and *ortho*-metallation are symptoms of phosphine steric bulk (*cf.* Thorpe–Ingold effect), and *ortho*-metallation is characteristic of running reactions under conditions starved of hydrogen. Irreversible ethane elimination can produce transients which effect attack on even relatively unreactive aryl C–H bonds at 25°C and without the photoactivation necessary in many C–H activation systems [9]. If these reactions were run under hydrogen-rich conditions, to avoid *ortho*-metallation, then another feature of late transition metal alkoxides comes into play: hydrogenolysis of the Ir–$OR_f$ bond (eqn. (7)). This loss of the very $\pi$-donor ligand which we consider an asset for substrate

$$IrH_2(OR_f)P_2 + 2H_2 \longrightarrow IrH_5P_2 + R_fOH \quad (7)$$

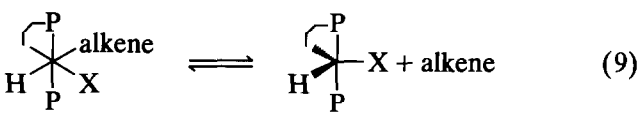
(*e.g.*, olefin) binding represents a fundamental danger, and suggests that such reagents are better utilized for reactions *not* involving $H_2$ thereby precluding it from many catalytic systems except as a precursor to the active catalyst. However a tethered alkoxide (eqn. (9)) may circumvent the irreversible loss of the $\pi$-donor in that intramolecular O–H oxidative addition would be facilitated. Such a tethered alcohol also serves as an intramolecular source of protons for protonation of substrate. The vulnerability of $P^tBu_2Ph$ to *ortho*-metallation is, on the other hand, a problem which can readily be solved by the use of $P^tBu_2Me$. We shall report independently on the consequences of making these changes in late transition metal alkoxide chemistry.



(8)

That alcohol-reductive elimination is promoted by binding of ethylene, is observed both in the initial reaction of $Ir(H)_2(OR_f)P_2$ and in the reaction of $Ir(H)(OR_f)(C_6H_4P^tBu_2)(P^tBu_2Ph)$ with $C_2H_4$. The phenomenon thus has some generality, and represents another way that the $\pi$-donor ligand can be lost. This is why a "simple" product like $Ir(C_2H_4)(OR_f)P_2$ (and ethane) is not formed in the chemistry reported here. It is, of course, true that nucleophiles often induce reductive elimination of $H_2$ from polyhydrides, but we

think the origin of this reaction is different for alcohol elimination: the ethylene adduct of each of these two five-coordinate compounds has a "pure-$\sigma$-donor" alkoxide ligand, which experiences a four-electron destabilization [2] (repulsion between $d_\pi$ electrons and the oxygen lone pairs). Such repulsion is, of course, removed by reductive elimination. The product (**D**) of the reaction of $[Ir(coe)_2Cl]_2$ with phosphine does not bind cyclooctene or ethylene. Thus (eqn. (9), X = $OR_f$ and Cl) $\pi$-stabilization exceeds the olefin binding energy, and both equilibria lie to the right. However, in both of these cases, ethylene binding should also be impeded by steric effects. The observation in **D** of hindered phenyl rotation at temperatures as high as +25°C emphasizes the crowded character of this class of molecules.




(9)

## 5. Experimental section

### 5.1. General

All manipulations were carried out under an inert atmosphere ($N_2$ or argon) using standard Schlenk techniques. Solid transfers were accomplished in a Vacuum Atmosphere Corp. glove box. THF and hexanes were distilled under nitrogen from potassium/benzophenone. Toluene and methyl cyclohexane were distilled under nitrogen from sodium. $C_6D_6$, toluene-$d_8$ and $C_6D_{12}$ were dried over NaK prior to use and stored in a glove box.

$^1H$ (360 MHz) and $^{31}P$ (146 MHz) NMR spectra were obtained on a Nicolet NT-360 instrument. $^{13}C$ (125 MHz) NMR spectra were obtained on a Bruker AM-500 spectrometer. Where noted, precise quantities of gases were added using a standard calibrated gas manifold. The gases $C_2H_4$ (Air Products) and $H_2$ (Air Products) and $C_3H_6$ (Matheson) were used as received. $IrH_2Cl(P^tBu_2Ph)_2$ has been synthesized previously [10]. Trifluoroethanol (PCR Industries) was dried over activated 3 Å sieves. $Na(OCH_2CF_3)$ was prepared from NaH and excess $R_fOH$ in benzene.

### 5.2. Synthesis and characterization of $IrH_2(OCH_2CF_3)(P^tBu_2Ph)_2$

Metathesis of $IrH_2(P^tBu_2Ph)_2Cl$ (0.200 g, 0.296 mmol) against $NaOCH_2CF_3$ (0.050 g, 0.410 mmol) in THF (40 ml) gives the product in good yield. The THF is removed *in vacuo* and the product is extracted into hexanes. The solution is filtered and the solvent removed *in vacuo*. $^{31}P\{^1H\}$ NMR in $C_6D_6$: 65.4 (s). $^{13}C\{^1H\}$ NMR in $C_6D_{12}$: 30.0 (s) $CCH_3$, 35.9 (vt, $CCH_3$, $^1J(PC)$ = 11 Hz), 17.5 (q, $OCH_2CF_3$, $^2J(CF)$ = 29 Hz), 126.3 (q, $OCH_2CF_3$, $^1J(CF)$ = 282 Hz), 126.5 (s, phenyl carbon), 128.8 (s, phenyl carbon), 133.0 (vt, $C_{ipso}$, $^1J(PC)$ = 15 Hz), 136.5 (s, phenyl carbon). $^1H$ NMR in $C_6D_6$: 8.15 (m, *ortho* protons), 7.2–7.0 (m, *meta* and *para* protons), 4.02 (q, $J(H-F)$ = 10 Hz), 1.40 (vt, $P^tBu$, 13 Hz), −30.3 (t, $J(PH)$ = 14 Hz).

### 5.3. Spectroscopic data for $Ir(C_6H_4P^tBu_2)(C_2H_4)_2$ (1)

$^{31}P\{^1H\}$ NMR in $C_6D_{12}$: −60.5 (s). $^{13}C\{^1H\}$ NMR in $C_6D_{12}$: 150.6 (d, *ipso* ring, $^1J(PC)$ = 41 Hz), 143.7 (d, *ortho* ring, $^2J(PC)$ = 13 Hz), 131.3 (m, phenyl carbon), 130.4 (m, phenyl carbon), 128.7 (m, phenyl carbon), 126.5 (s, phenyl carbon), 124.2 (s, phenyl carbon), 122.0 (m, phenyl carbon), 56.4 (ethylene carbon), 38.8 (d, $^1J(PC)$ = 4 Hz), 32.2 (d, $^2J(PC)$ = 3 Hz). $^1H$ NMR in $C_6D_{12}$: 7.6–6.7 (m, phenyl protons), 2.5 (broad singlet, ethylene protons), 1.9 (s, ethylene protons), 1.5 (d, $P^tBu$, $^3J(PH)$ = 13 Hz).

### 5.4. Spectroscopic data for $Ir(C_6H_4P^tBu_2)(P^tBu_2Ph)(C_2H_4)$ (2)

$^{31}P\{^1H\}$ NMR in $C_6D_{12}$: 45.5 (d, $^2J(PP')$ = 351 Hz), −39.1 (d, $^2J(PP')$ = 351 Hz). $^{13}C\{^1H\}$ NMR in $C_6D_{12}$: 160.9 (apparent triplet, *ortho* ring, 15 Hz), 155.4 (d, *ipso* ring, $^1J(PC)$ = 41 Hz), 138.8 (d, *ipso* carbon, $^1J(PC)$ = 32 Hz), 136.8 (d, *ortho* carbon $^2J(PC)$ = 14 Hz), 129.0 (s, phenyl carbon), 126.5 (s, phenyl carbon), 124.2 (s, phenyl carbon), 34.7 (broad singlet, $CCH_3$), 33.1 (s, $CCH_3$), 31.6 (broad singlet, $CCH_3$). $^1H$ NMR in $C_6D_{12}$: 7.6–6.0 (m, phenyl protons), 3.0 (broad singlet, ethylene), 1.4 (apparent triplet, $P^tBu$, 13 Hz).

### 5.5. Spectroscopic data for $Ir(H)(OCH_2CF_3)(C_6H_4P^tBu_2Ph)(P^tBu_2Ph)$ (3)

$^{31}P\{^1H\}$ NMR in $C_6D_{12}$: 49.7 (dd, $^2J(PP')$ = 343 Hz, $^2J(PH)$ = 11 Hz), −0.7 (dd, $^2J(PP')$ = 343 Hz, $^2J(P'H)$ = 6 Hz). $^{13}C\{^1H\}$ NMR in $C_6D_{12}$: 149.5 (d, *ipso* metallated, $^1J(PC)$ = 44 Hz), 142.4 (s, phenyl carbon), 138.0 (d, *ortho* metallated, $^2J(PC)$ = 16 Hz), 133.2 (d, *ipso*, $^1J(PC)$ = 35 Hz), 129–127 (m, phenyl carbons), 123.0 (s, phenyl carbon), 120.2 (s, phenyl carbons), 82.9 (m, $OCH_2CF_3$), 38.1 (s, $CCH_3$), 37.9 (s, $CCH_3$), 37.4 (s, $CCH_3$), 37.3 (s, $CCH_3$), 32.6 (s, $CCH_3$), 30.9 (s, $CCH_3$), 30.8 (s, $CCH_3$), 29.9 (s, $CCH_3$). $^1H$ NMR in $C_6D_{12}$: 8.0–5.8 (m, phenyl protons), 4.72 (m, $OCH_2CF_3$), 4.50 (m, $OCH_2CF_3$), 1.63 (d, $^3J(PH)$ = 13 Hz), 1.49 (d, $^3J(PH)$ = 13 Hz), 1.40 (d, $^3J(PH)$ = 13 Hz), 1.34 (d, $^3J(PH)$ = 13 Hz), −36.0 (apparent triplet, IrH, 21 Hz).

### 5.6. Isotopic exchange: treatment of $IrH_2(OCH_2CF_3)(P^tBu_2Ph)_2$ + 1 $C_2H_4$ in $C_6D_6$

A solution of 28.6 mg (0.039 mmol) of $IrH_2(OCH_2CF_3)(P^tBu_2Ph)_2$ in $C_6D_6$ was freeze/pump/

thaw degassed three times. One equivalent of ethylene was condensed into the tube, which was then sealed. $^{31}P\{^1H\}$ NMR at one-half, two, and eight hours all showed both unreacted starting material and a peak at 70 ppm. After eight hours, the $^{31}P\{^1H\}$ NMR showed the solution to be comprised of *ca.* 95% starting material. $^1H$ NMR over this period of time showed the gradual disappearance of free ethylene signal at 5.2 ppm while the peak at 7.15 ppm for residual benzene gradually increased. At eight hours, a hydride resonance was still observed.

*5.7. Time evolution of the ethylene hydrogenation*

Thirty-eight mg (0.0514 mmol) of $IrH_2(OCH_2CF_3)(P^tBu_2Ph)_2$ was weighed into an NMR tube and dissolved in 1/2 ml of $C_6D_{12}$. The resulting orange solution was freeze/pump/thaw degassed three times and 0.0515 mmol of ethylene gas was then condensed into the tube.

After 20.5 h, the $^{31}P\{^1H\}$ NMR spectrum revealed several new products as well as 50% of unreacted starting material. The new products were characterized as follows: $Ir(H)(OCH_2CF_3)(C_6H_4P^tBu_2)(P^tBu_2Ph)$, $Ir(C_6H_4P^tBu_2)(P^tBu_2Ph)(C_2H_4)$, $Ir(C_6H_4P^tBu_2)(C_2H_4)_2$, free $P^tBu_2Ph$, and a singlet at 70 ppm.

At 32 h, the $^{31}P\{^1H\}$ NMR spectrum is essentially unchanged except that the amount of $Ir(H)(OCH_2CF_3)(C_6H_4P^tBu_2)(P^tBu_2Ph)$ increased relative to the amount of $Ir(C_6H_4P^tBu_2)(P^tBu_2Ph)(C_2H_4)$.

At 72 h, the $^{31}P\{^1H\}$ NMR spectrum revealed that the singlet at 70 ppm and $Ir(C_6H_4P^tBu_2)(C_2H_4)_2$ were no longer present. However, the amount of $Ir(H)(OCH_2CF_3)(C_6H_4P^tBu_2)(P^tBu_2Ph)$ continued to increase relative to the amount of $Ir(C_6H_4P^tBu_2)(P^tBu_2Ph)(C_2H_4)$.

This trend continued until, after 20 days, only unreacted starting material and $Ir(H)(OCH_2CF_3)(C_6H_4P^tBu_2)(P^tBu_2Ph)$ remained in solution.

At this time, 1 atm of $H_2$ gas was introduced into the NMR tube and the tube was resealed. A single peak was observed in the $^{31}P\{^1H\}$ NMR spectrum for $IrH_5(P^tBu_2Ph)_2$.

*5.8. $Ir(C_6H_4P^tBu_2)(P^tBu_2Ph)(C_2H_4)$ precedes production of $Ir(H)(OCH_2CF_3)(C_6H_4P^tBu_2)(P^tBu_2Ph)$ and $Ir(C_6H_4P^tBu_2)(C_2H_4)_2$*

Twenty-six mg (0.0351 mmol) of $IrH_2(OCH_2CF_3)(P^tBu_2Ph)_2$ was weighed into an NMR tube and dissolved in 1/2 ml $C_6H_{12}$. The resulting solution was freeze-pump-thaw degassed three times and 0.0351 mmol of ethylene gas was condensed into the NMR tube.

At 135 min, the $^{31}P\{^1H\}$ NMR spectrum revealed mainly starting material. However, perceptible amounts of $Ir(C_6H_4P^tBu_2)(P^tBu_2Ph)(C_2H_4)$ were observed, thereby establishing that it precedes the production of $Ir(H)(OCH_2CF_3)(C_6H_4P^tBu_2)(P^tBu_2Ph)$ and $Ir(C_6H_4P^tBu_2)(C_2H_4)_2$. After several days, only unreacted starting material and $Ir(H)(OCH_2CF_3)(C_6H_4P^tBu_2)(P^tBu_2Ph)$ remained in solution by $^{31}P\{^1H\}$ NMR.

At this time, the solvent was removed *in vacuo* and replaced by $C_6H_6$. The $^{31}P\{^1H\}$ NMR spectrum was unchanged. The head space of the NMR tube was then filled with 1 atm of ethylene.

After several days, predominantly $P^tBu_2Ph$ and $Ir(C_6H_4P^tBu_2)(C_2H_4)_2$ remained.

*5.9 $Ir(C_6H_4P^tBu_2)(P^tBu_2Ph)(C_2H_4)$ and $Ir(C_6H_4P^tBu_2)(C_2H_4)_2$ are in equilibrium*

Twenty-two mg (0.0298 mmol) of $IrH_2(OCH_2CF_3)(P^tBu_2Ph)_2$ were weighed into an NMR tube and dissolved in 1/2 ml $C_6H_{12}$. The resulting orange solution was freeze/pump/thaw degassed three times and 0.142 mmol (4.8 equiv) of ethylene was condensed into the NMR tube, which was then sealed. After four days, the $^{31}P\{^1H\}$ NMR spectrum showed predominantly two species in solution, free $P^tBu_2Ph$ and $Ir(C_6H_4P^tBu_2)(C_2H_4)_2$. The solvent was removed *in vacuo*. The resulting solid was pumped on for 30 min and was then redissolved in $C_6H_{12}$. The $^{31}P\{^1H\}$ NMR spectrum showed free $P^tBu_2Ph$, $Ir(C_6H_4P^tBu_2)(P^tBu_2Ph)(C_2H_4)$, and a trace of $Ir(C_6H_4P^tBu_2)(C_2H_4)_2$.

The solution was freeze/pump/thaw degassed three times and 0.0284 mmol (0.96 equiv) of ethylene was condensed into the NMR tube, which was then sealed. Periodic monitoring of the $^{31}P\{^1H\}$ NMR spectrum of the solution over a 24 h period established the gradual disappearance of $Ir(C_6H_4P^tBu_2)(P^tBu_2Ph)(C_2H_4)$ and the gradual appearance of free phosphine and $Ir(C_6H_4P^tBu_2)(C_2H_4)_2$. In the final spectrum, only a trace of $Ir(C_6H_4P^tBu_2)(P^tBu_2Ph)(C_2H_4)$ remained.

*5.10. $Ir(C_6H_4P^tBu_2)(P^tBu_2Ph)(C_2H_4) + 1\ CF_3CH_2OH \rightarrow Ir(H)(OCH_2CF_3)(C_6H_4P^tBu_2)(P^tBu_2Ph)$*

Thirty-five mg (0.0473 mmol) of $IrH_2(OCH_2CF_3)(P^tBu_2Ph)_2$ was weighed into an NMR tube and dissolved in 1/2 ml of $C_6H_{12}$. The resulting orange solution was freeze/pump/thaw degassed three times and 0.188 mmol (4.0 equiv) of ethylene was condensed into the tube which was then sealed. After three days, the $^{31}P\{^1H\}$ NMR spectrum showed quantitative production of $P^tBu_2Ph$ and $Ir(C_6H_4P^tBu_2)(C_2H_4)_2$. The solvent was removed *in vacuo* and the resulting solid was pumped on for 30 min.

The solid was dissolved in approximately 1 ml of $C_6H_{12}$ and 3.5 $\mu$l (4.7 mg, 1 equiv) of $CF_3CH_2OH$

(dried and degassed) was added. The $^{31}P\{^1H\}$ NMR spectrum immediately after the introduction of the alcohol showed a 50 : 50 mixture of $Ir(C_6H_4P^tBu_2)(P^tBu_2Ph)(C_2H_4)$ and $Ir(H)(OCH_2CF_3)(C_6H_4P^tBu_2)(P^tBu_2Ph)$. After 24 h, $Ir(H)(OCH_2CF_3)(C_6H_4P^tBu_2)(P^tBu_2Ph)$ was the predominant species in solution, but 30% of $Ir(C_6H_4P^tBu_2)(P^tBu_2Ph)(C_2H_4)$ remained. The head space was evacuated briefly. $^{31}P\{^1H\}$ NMR spectrum showed nearly quantitative production of $Ir(H)(OCH_2CF_3)(C_6H_4P^tBu_2)(P^tBu_2Ph)$.

*5.11. Independent synthesis of $Ir(H)(OCH_2CF_3)(C_6H_4P^tBu_2)(P^tBu_2Ph)$*

Twenty-eight mg (0.0378 mmol) of $IrH_2(OCH_2CF_3)(P^tBu_2Ph)_2$ was weighed into an NMR tube and dissolved in 1/2 ml of $C_6D_{12}$. The NMR tube was fitted with a gas adapter. The resulting orange solution was freeze/pump/thaw degassed three times and 0.0379 mmol of propene was condensed into the tube which was then flame sealed. After five days, an appreciable amount of $Ir(H)(OCH_2CF_3)(C_6H_4P^tBu_2)(P^tBu_2Ph)$ was observed by $^{31}P\{^1H\}$ NMR. The $^1H$ and $^{13}C\{^1H\}$ data were consistent with this formulation. Propane was observed in the $^1H$ NMR spectrum.

*5.12. Reaction of $Ir(H)(OCH_2CF_3)(C_6H_4P^tBu_2)(P^tBu_2Ph)$ with $C_2H_4$*

An NMR tube containing a $C_6D_{12}$ solution of $Ir(H)(OCH_2CF_3)(C_6H_4P^tBu_2)(P^tBu_2Ph)$ was freeze/pump/thaw degassed three times. The head space was then filled with one atmosphere of ethylene. After 24 h, signals due to $Ir(H)(OCH_2CF_3)(C_6H_4P^tBu_2)(P^tBu_2Ph)$, $Ir(C_6H_4P^tBu_2)(P^tBu_2Ph)(C_2H_4)$ and $Ir(C_6H_4P^tBu_2)(C_2H_4)_2$ were observed in the $^{31}P\{^1H\}$ NMR spectrum.

*5.13. Low-temperature reaction with ethylene*

Thirty-seven mg (0.050 mmol) of $IrH_2(OCH_2CF_3)(P^tBu_2Ph)_2$ was weighed into an NMR tube and dissolved in methyl cyclohexane. The solution was freeze/pump/thaw degassed three times and 0.051 mmol of ethylene was condensed into the tube. The tube was then allowed to stand in a dry ice/isopropanol bath at −80°C and was introduced into an NMR probe which had been precooled to −80°C. No reaction was observed up to −20°C. Between −20°C and 0°C, a very small singlet was observed in the $^{31}P\{^1H\}$ NMR spectrum at 70 ppm. After 1 h at 10°C, signals due to $Ir(C_6H_4P^tBu_2)(P^tBu_2Ph)(C_2H_4)$ were observed.

*5.14. Synthesis and characterization of $Ir(H)(Cl)(C_6H_4P^tBu_2)(P^tBu_2Ph)$*

$[Ir(coe)_2Cl]_2$ (200 mg, 0.221 mmol) and $P^tBu_2Ph$ (200 mg, 0.896 mmol, 4.05 equiv) were stirred in methyl cyclohexane overnight. The resulting red solution was pumped dry to yield a red oil. The oil was extracted with pentane to yield a red solution and an orange solid. The solid was discarded and the solution was pumped dry to yield a red oil. The oil was redissolved in methyl cyclohexane and washed onto a column of activated silica. Eluent polarity was increased from methyl cyclohexane to toluene. The toluene fraction was observed to be slightly yellow in color. The column was then washed with THF yielding a deep red solution. The red solution was pumped dry and triturated with pentane to yield the product as a red powder. $^{31}P\{^1H\}$ NMR in $C_6D_6$: 51.6 (dd, $^2J(PP) = 345$ Hz, $^2J(PH) = 10$ Hz), −11.4 (dd, $^2J(PP') = 345$ Hz, $^2J(P'H) = 8$ Hz). $^{13}C\{^1H\}$ NMR in $C_6D_6$: 150.8 (d; $^1J(P'C) = 40$ Hz), 137.4 (m), 132.7 (dd, $^1J(PC) = 34$ Hz, $^3J(P'C) = 2$ Hz), 129.6 (s), 125.8 (m), 121.7 (d, $J(PC) = 8$ Hz), 38.0 (dd, $CCH_3$, $^1J(PC) = 18$ Hz, $^3J(P'C) = 3$ Hz), 37.2 (dd, $CCH_3$, $^1J(PC) = 16$ Hz, $^3J(PC) = 1$ Hz), 35.5 (dd, $CCH_3$, $^1J(PC) = 14$ Hz, $^3J(PC) = 4$ Hz), 33.2 (dd, $CCH_3$, $^1J(PC) = 14$ Hz, $^3J(PC) = 4$ Hz), 32.6 (d, $CCH_3$, $^2J(PC) = 4$ Hz), 30.6 (s, $CCH_3$), 30.2 (s, $CCH_3$), 29.6 (s, $CCH_3$). $^1H$ NMR in $C_6D_6$ at 298 K: 7.9 (broad signal, phenyl protons), 7.0 (broad signal), 6.7 (singlet), 6.2 (singlet), 1.6 (d, $^3J(PH) = 13$ Hz), 1.5 (d, $^3J(PH) = 13$ Hz), 1.5 (d, $^3J(PH) = 14$ Hz), 1.4 (d, $^3J(PH) = 14$ Hz), −41.2 (apparent triplet, IrH, 22 Hz). $^1H$ NMR in $C_7D_8$ at 213 K: 8.1 (dd, $J(HH) = 8$ Hz, $J(HH) = 8$ Hz), 7.7 (t), 6.7 (t, $J(HH) = 7$ Hz), 6.6 (t, $J(HH) = 7$ Hz), 6.5 (t, $J(HH) = 8$ Hz), 6.2 (m), 1.6 (d, $^3J(PH) = 13$ Hz), 1.4 (d, $^3J(PH) = 14$ Hz), 1.3 (d, $^3J(PH) = 14$ Hz), −41.2 (apparent triplet, IrH, 22 Hz). $^1H$ NMR in $C_6D_6$ at 343 K: 8.0 (t), 7.0 (m), 6.7 (m), 6.1 (m), 1.59 (d, $^3J(PH) = 13$ Hz), 1.48 (d, $^3J(PH) = 14$ Hz), 1.47 (d, $^3J(PH) = 13$ Hz), 1.38 (d, $^3J(PH) = 14$ Hz), −41.0 (apparent triplet, IrH, 22 Hz).

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## References and notes

1 D. M. Lunder, E. B. Lobkovsky, W. E. Streib and K. G. Caulton, *J. Am. Chem. Soc., 113* (1991) 1837.
2 T. J. Johnson, J. C. Huffman and K. G. Caulton, *J. Am. Chem. Soc., 114* (1992) 2725.
3 J. T. Poulton, K. Folting, W. E. Streib and K. G. Caulton, *Inorg. Chem., 31* (1992) 3190.
4 A. S. Goldman and J. Halpern, *J. Organomet. Chem., 382* (1990) 237.
5 (a) A bulky phosphine is also necessary in order to prevent

formation of $Ir(H)_2(OR)P_3$. (b) That is, not all metal-bound hydrogen has become deuterium.
6 P. Garrou, *Chem. Rev., 81* (1981) 229.
7 Compounds containing two $P^tBu_2Ph$ ligands are reported to show interconversion among conformers at subambient temperature. See L. A. Luck, W. L. Elcesser, J. L. Hubbard and C. H. Bushweller, *Magn. Res. Chem., 27* (1989) 488 and references therein.
8 P. J. Desrosiers, L. Cai and J. Halpern, *J. Am. Chem. Soc., 111* (1989) 8513.
9 R. G. Bergman, *J. Organomet. Chem., 400* (1990) 273.
10 H. D. Empsall, E. M. Hyde, E. Mentzer, B. L. Shaw and M. F. Uttley, *J. Chem. Soc., Dalton Trans., 20* (1976) 2069.