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# A POCO type pincer complex of iridium: Synthesis, characterization, and catalysis

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ABSTRACT

A convenient synthesis of a new POCO-type pincer ligand, "$^{tBu}$POCOH", (3-(di-*tert*-butylphosphinito)acetophenone is reported. Metallation using $[Ir(COD)Cl]_2$ provides the dimeric species (μ-Cl-[$^{tBu}$POCOIrHCl]$_2$) (**1a**) as a major product, along with isomer **1b**. Though not fully characterized, **1b** is shown to be chemically equivalent to **1a** by a series of experiments with AgOTf and CO which lead to formation of a single product, $^{tBu}$POCOIr(CO)HOTf (**3**). The **1a/b** mixture gives inferior results to $^{iPr}$PCPIr when used as pre-catalyst in the dehydrogenative coupling of vinyl arenes, though olefin isomerization activity is enhanced. This system was also evaluated in the Geurbet conversion of ethanol to *n*-butanol and higher alcohols. The CO adducts of **1a/b**, ***cis/trans*-2**, were found to give the best results as pre-catalyst, achieving a 33% yield of *n*-butanol and an overall 47% yield of *n*-alcohols with a catalyst loading of 0.5% when heated at 150 °C for 4 hours. This represents the first example of a pincer ligated iridium complex as catalyst in the Geurbet reaction of ethanol.



## 1. Introduction

The use of pincer ligated transition metal complexes has become widespread in the realm of organometallic transformations [1–7]. Earlier work focused mainly on second and third row metal complexes and helped to elucidate many of the fundamental aspects of pincer complex reactivity. Notable findings include the addition of strong C—H and C—C bonds to $^{tBu}$PCP rhodium complexes [8,9], a stable ruthenium agostic C—H complex [10], and efficient palladium catalysts for Heck and Suzuki coupling reactions using POCOP type pincer ligands [11–13]. More recently, pincer chemistry has ventured to the first row transition metals and now includes impressive examples such as the cobalt catalyzed stereospecific hydrogenation of alkynes to *Z* and *E*-alkenes [14], the reversible iron catalyzed acceptorless dehydrogenation/hydrogenation of alcohols and ketones [15], and the manganese catalyzed hydrogenation of amides to the corresponding alcohols and amines [16].

With respect to iridium a rich body of pincer chemistry exists, primarily exploiting the facile addition and elimination of element-hydrogen bonds to iridium centers in these complexes [17–19]. Accordingly, a number of important discoveries have been facilitated by iridium pincer complexes including the efficient transfer dehydrogenation of cycloalkanes [20,21], the acceptorless dehydrogenation of cyclic and *n*-alkanes by a homogenous catalyst [22,23], and the catalytic dehydrogenation of ammonia borane [24], an important candidate in hydrogen storage technology. While these examples utilized symmetric pincer ligands, an increasing number of reported pincer complexes are asymmetric which vastly increases the variability/tunability of steric and electronic factors in these systems, sometimes providing advantages over related symmetric species [5]. For example, $^{iPr}$POCOPIr has been reported to achieve 13 turn-overs min$^{-1}$ (by inference ~780 turn-over hour$^{-1}$) in the transfer dehydrogenation of cyclooctane using *tert*-butylethylene as acceptor [25], but the analogous $^{iPr}$PSCOPIr complex with one phosphinite and one phosphinothious group is reported to give 2649 turn-overs hour$^{-1}$ under nearly identical conditions, correlating to a more than three times increase in activity [26].

As part of an ongoing program to explore and expand the scope of iridium pincer chemistry, a new asymmetric POCO type pincer ligand, "$^{tBu}$POCOH" (3-(di-*tert*-butylphosphinito)acetophenone), has been synthesized and metallated using $[Ir(COD)Cl]_2$ (Scheme 1). The product formed, $^{tBu}$POCOIrHCl, is obtained as a mixture of two species, **1a** and **1b** in a 1–0.35 ratio. Herein, the reactivity of these compounds with AgOtf and carbon monoxide is reported, as well

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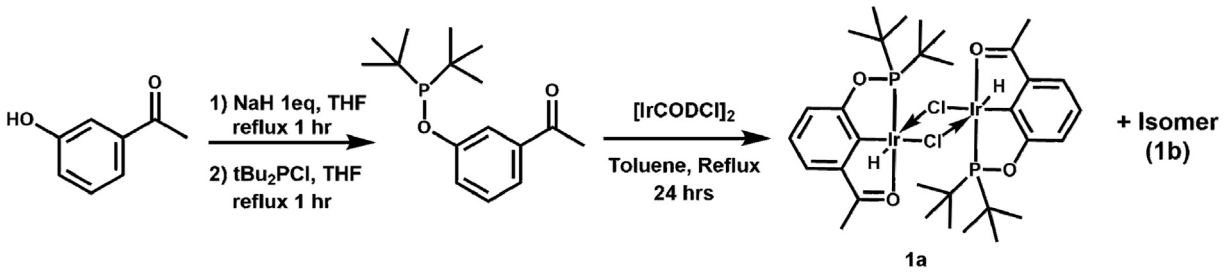



**Scheme 1.** Synthesis of $^{tBu}$POCOH ligand and metallation using $[Ir(COD)Cl]_2$.

as their use as pre-catalysts in the dehydrogenative coupling of styrene, and Geurbet conversion of ethanol to *n*-butanol.

## 2. Results and discussion

The $^{tBu}$POCOH ligand is readily prepared by refluxing 1 equiv. of sodium hydride with 3-hydroxyacetophenone in THF followed by addition of 1.1 equiv. di-*tert*-butylchlorophosphine, briefly refluxing, and then allowing to stir overnight at room temperature. Removal of volatiles from this mixture and extraction of the resultant residue with THF, followed by concentration under vacuum provides the ligand in 96% yield as a slightly yellow oil. The product appears as a singlet in the $^{31}P\{^1H\}$ NMR spectrum at $\delta$ 155.0 in $C_6D_6$. Over several weeks after synthesizing, a number of large crystals of $^{tBu}$POCOH were found to have spontaneously formed from the oil allowing for structure analysis by X-ray diffraction (Fig. 1).

Refluxing $^{tBu}$POCOH and $[Ir(COD)Cl]_2$ in toluene for 24 h followed by concentration to dryness, and washing of the solids obtained with pentane, provides an orange solid material in 84% yield formulated as $^{tBu}$POCOIrHCl. Indeed, the elemental analysis results are consistent with this formulation. However, inspection of the $^{31}P\{^1H\}$ NMR spectrum revealed two species (**1a**, **1b**) as singlets at $\delta$ 156.5 and 154.7 in a 1–0.35 ratio, respectively. The hydride region of the $^1$H NMR displays two doublets at $\delta$ −27.3 (major) and −27.6 (minor) in the same ratio observed by $^{31}$P NMR spectroscopy. These species do not appear to be in equilibrium as the ratio of **1a** and **1b** does not change with variable temperature (0–70 °C), or solvent (benzene, toluene, chloroform, THF). Recrystallization from toluene provided crystals suitable for X-ray diffraction which showed the major species **1a** to be the μ-Cl dimer of $^{tBu}$POCOIrHCl (Fig. 2). Surprisingly, dissolution of these crystals revealed identical $^{31}$P and $^1$H NMR spectra to that obtained before recrystallization. However, close inspection of the crystals under a microscope showed that while the bulk of the material was hexagonal platelets of **1a**, all of the crystals had a coating of fine polycrystalline material, likely **1b**. NMR analysis of the supernatant also revealed identical spectra. Apparently, **1a** and **1b** crystallize separately, but concomitantly. The identity of **1b** is not completely defined, but it is almost certainly an isomer or monomeric form of **1a**, which is corroborated by reaction studies with AgOTf and CO (vide infra).

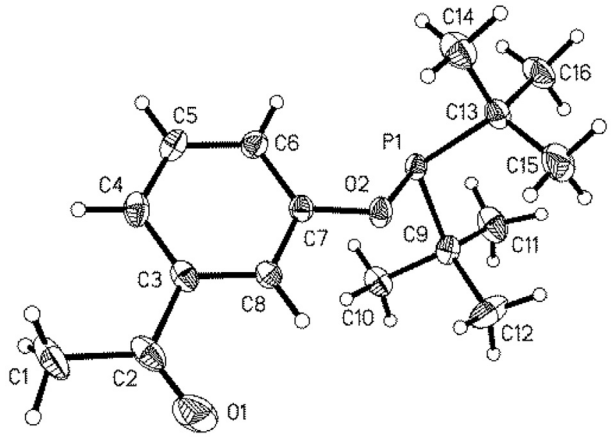



**Fig. 1.** ORTEP diagram of the $^{tBu}$POCOH ligand with thermal ellipsoids at 50% probability level.

As in the solid state, **1a** most likely remains in dimeric form in solution as well. While $^{tBu}$POCOIrHCl may exist as two enantiomers, this cannot account for the two species observed, because if all $^{tBu}$POCOIrHCl assumed monomeric form in solution only one species would be detected by NMR. One possibility for the identity of **1b** is the μ-H analog of **1a** which would be consistent with the somewhat more upfield resonance of the **1b** hydride, however, this would likely present a triplet hydride resonance in the $^1$H NMR spectrum which is not observed. Since dimer **1a** is formed from enantiomeric pairs of $^{tBu}$POCOIrHCl, and formation of a racemate from the reaction of $^{tBu}$POCOIrH and $[Ir(COD)Cl]_2$ would likely lead solely to **1a**, the remaining possibilities are that one enantiomer forms in excess and may either remain in monomeric form, or form a sterically strained μ-Cl dimer with phosphinite groups facing each other. Of these species, the μ-Cl dimer seems the most likely candidate in view of the very similar chemical shifts of the hydride signals for **1a** and **1b**. Related monomeric PCPIrHCl and POCOPIrHCl species with a hydride *trans* to a vacant site display exceptionally upfield hydride resonances, as far as $\delta$ −45 [27,21]. While the possibility that **1b** is actually monomeric with a solvent molecule occupying the "vacant" site cannot be completely ruled out, it seems quite unlikely in light of the fact that $^1$H NMR resonances for coordinated solvent could not be located upon addition of excess toluene, $CHCl_3$, or THF to solutions of **1a/b** in $CDCl_3$. Furthermore, since a significant difference in molecular weight (~500 amu), and likely solution diffusion rate, would exist between monomeric and dimeric forms, a DOSY-NMR experiment was conducted on a sample of **1a/b** in $CDCl_3$ (see SI). Based on the hydride region of the $^1$H NMR spectrum, diffusion rates for **1a** and **1b** were found to be nearly identical (0.7% difference based on longest rate), whereas under identical conditions ferrocene and acetonitrile (~145 amu difference) were found to have a an approximately 50% difference in diffusion rate. These findings indicate that **1a** and **1b** are both either monomeric or dimeric, of which dimeric seems more likely. In order to ascertain the chemical equivalency of **1a** and **1b**, a series of experiments reacting the as synthesized **1a/b** mixture with AgOTf and CO were conducted, which led to convergence to a single product, confirming the overall formulation of **1a/b** as $^{tBu}$POCOIrHCl.

In the solid state, **1a/b** is found to be quite air stable. Samples left open to air for one month were found to provide the same

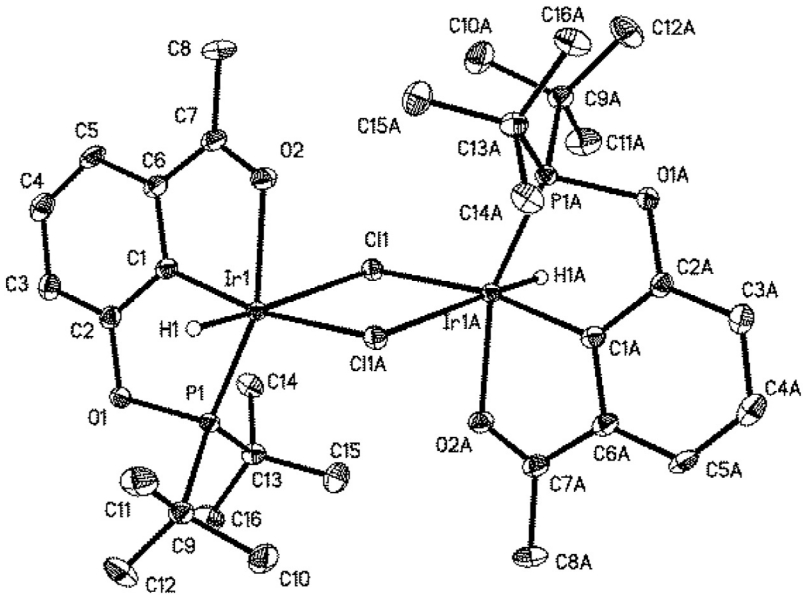


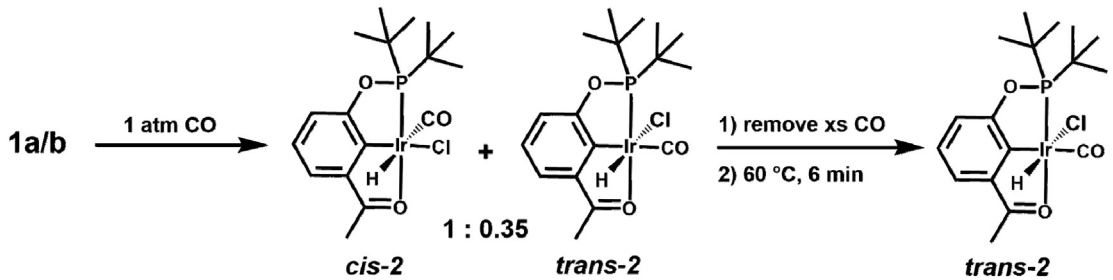

**Fig. 2.** ORTEP diagram of $[^{tBu}POCOIrHCl]_2$, **1a**, with thermal ellipsoids at 50% probability.

$^{31}P$ and $^{1}H$ NMR spectra as freshly synthesized material. Furthermore, although all solvents were dried prior to use for the sake of consistency, no water sensitivity has been found with this complex, and removing oxygen by freeze–pumpthaw cycles or purging with argon is the only pretreatment necessary for solvents in practical use. In solution, **1a/b** decomposes slowly over 16 h to several days in solvents which have not been degassed, dependent on the solvent used.

Assuming that **1a** and **1b** are dimeric isomers of each with the molecular formula $[^{tBu}POCOIrHCl]_2$, it was expected that addition of carbon monoxide would generate a single species by cleavage of these dimers into their coordinatively saturated monomeric form. However, when a saturated solution of **1a/b** in toluene is exposed to 1 atm CO, accompanied by a color change from orange to pale yellow, two new species are generated, again in a 1–0.35 ratio as detected by $^{31}P\{^{1}H\}$ NMR spectroscopy as singlets at $\delta$ 164.0, and 162.3, respectively. Informatively, the hydride resonances of these compounds appear as doublets at $\delta$ −9.4 (minor) and −19.8 (major). These chemical shifts are consistent with assignment as the *cis* (***cis*-2**) and *trans* (***trans*-2**) H-Cl isomers of $^{tBu}$POCOIr(CO)HCl (Scheme 2), and are in good agreement with reported data for related species [28,29]. The analogous $^{tBu}$-POCOPIr(CO)HCl complex is reported to exist as both the *cis* and *trans* forms in equilibrium, favoring the *trans* form, as determined by thermolysis studies [29]. When the as prepared mixture of ***cis*-2** and ***trans*-2** is heated at 60 °C for 6 min (after removal of excess CO) complete, irreversible, conversion to ***trans*-2** is observed. These results indicate that the formation of ***cis*-2** and ***trans*-2** from **1a/b** results for kinetic reasons due to steric/structural differences in these isomers, and that the thermodynamic product is ***trans*-2**, which is not in equilibrium with ***cis*-2**.

When solutions of ***trans*-2**, or mixed ***cis*-2** and ***trans*-2**, in aromatic solvent or $CH_2Cl_2$ are treated with a stoichiometric amount of AgOTf, quantitative conversion to a single new product with a resonance at $\delta$ 162.7 in the $^{31}P\{^{1}H\}$ NMR spectrum is observed after stirring overnight. A single hydride resonance (doublet, $J_{PH}$ = 21.2 Hz) is found in the $^{1}H$ NMR spectrum at $\delta$ −26.0, consistent with a hydride in an apical position *trans* to OTf. Removal of AgCl by filtration, concentration, and recrystallization by vapor diffusion of pentane into a concentrated benzene solution of this product and storing at −17 °C provided crystals suitable for X-ray diffraction. The structure determined confirmed formation of the expected product, $^{tBu}$POCOIr(CO)(H)OTf (**3**) (Fig. 3, Scheme 3), though the crystals obtained contained ½ co-crystallized benzene per iridium complex.

This series of reactions may also be conducted in the opposite order, first reacting **1a/b** with AgOTf, ostensibly forming $^{tBu}$POCOIrHOTf (**4**), followed by addition of CO to form **3**. The triflate ligand in **4** appears to be highly labile, and exceptionally broad resonances are observed in the $^{31}P\{^{1}H\}$ NMR spectra of **4** in arene solvents. However, upon addition of ≥1 equiv. AgOTf to toluene or benzene solutions of **4**, a single sharp resonance is observed, accompanied by an accordingly well resolved $^{1}H$ NMR spectrum displaying a single hydride signal (see SI). NaOTf may also be used, though due to poorer solubility it was found




**Scheme 2.** Reactivity of **1a** and **1b** with carbon monoxide to form ***cis*-2** and ***trans*-2**, and thermal conversion of ***cis*-2** to ***trans*-2**.

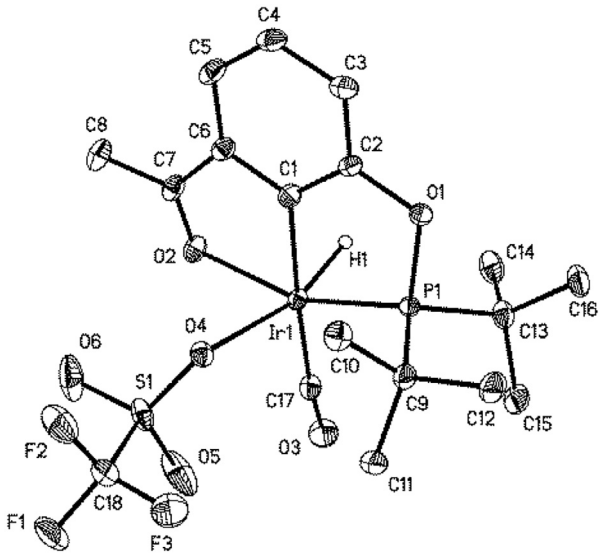


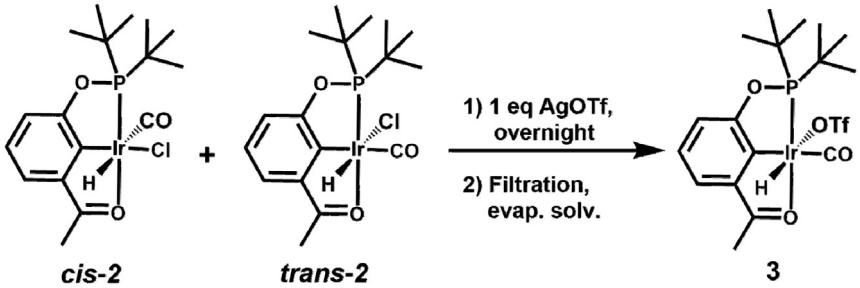

**Fig. 3.** ORTEP diagram of $^{tBu}$POCOIr(CO)(H)OTf (**3**) with thermal ellipsoids at 50% probability.

necessary to generate a saturated solution of NaOTf by sonication/heating before adding to **4**. Likewise, when a 30% v/v solution of THF in benzene is used, a single defined product is observed by $^{31}P\{^{1}H\}$ NMR spectroscopy, likely due to formation of [$^{tBu}$POCOIr(THF)H][OTf]. These proposed equilibria are shown in Scheme 4.

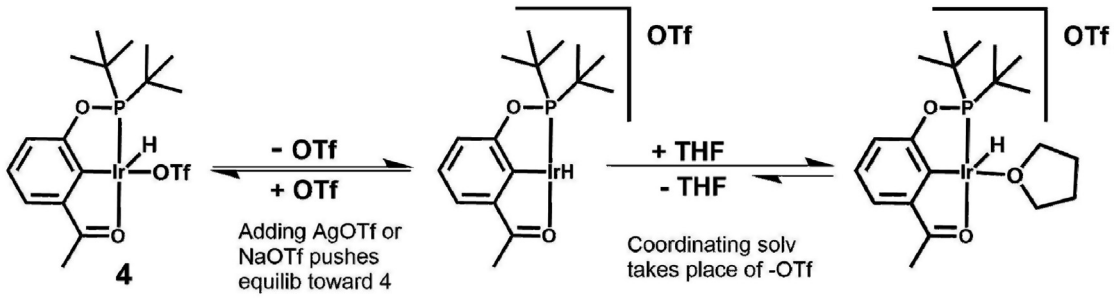
Immediately after addition of 1 atm CO to a freshly prepared toluene solution of **4**, formation of **3** is observed by $^{31}P\{^{1}H\}$ NMR spectroscopy, representing 68% of total products. Another resonance at $\delta$ 166.8, representing 27% of total products, is also observed with an associated hydride doublet at $\delta$ −8.66 in the $^{1}H$ NMR spectrum. The remaining 5% of products is accounted for by another unidentified species with a $^{31}P\{^{1}H\}$ NMR resonance at $\delta$ 164.4, which also presents a hydride signal at $\delta$ −10.4. Concentration of this solution to dryness in vacuo, followed by addition of fresh solvent, effects quantitative conversion to **3**. These results are consistent with the formation of **3** and the *cis* isomer of **3** as the major products of addition of CO to $^{tBu}$POCOIrHOTf.

The dehydrogenative coupling of vinyl-arenes to form (*E,E*)-1,4-diaryl-1,3-butadienes has recently been reported using $^{iPr}$PCPIrHCl and $^{iPr}$PCPIr($C_2H_4$) as pre-catalysts (Scheme 5) [30]. Under identical conditions to those reported for $^{iPr}$PCPIrHCl, **1a/b** was evaluated as pre-catalyst in this reaction. It was anticipated that the reduced steric congestion around the active site in the $^{tBu}$POCOIr fragment, in comparison to $^{iPr}$PCPIr, might correlate with increased activity. However, using 5 mole% **1a/b**, 2 equiv. of KOtBu (based on Ir), and 654 mM styrene in toluene heated at 150 °C for 24 h in a sealed ampoule under argon, only 40% conversion of styrene and a 20% yield of (*E,E*)-1,4-diphenyl-1,3-butadiene were observed by GCMS based on the stoichiometry in Scheme 5. Unlike the $^{iPr}$PCPIr catalyzed reaction, no evidence of (*E,Z*)-1,4-diphenyl-1,3-butadiene was found, likely due to the greater isomerization activity of $^{tBu}$POCOIr (vide infra). However, substantial amounts of two products with *m/z* 208, presumably (*E*) and (*Z*) 1,4-diphenyl-1-butene, were detected, representing a further ~13% yield of coupled products. When the reaction was run for 48 hours, no improvement in yield of (*E,E*)-1,4-diphenyl-1,3-butadiene was observed, though the amount of product with *m/z* 208 increased somewhat to ~18%. Despite the reduced activity of **1a/b** with respect to $^{iPr}$PCPIr, it was considered that the reduced steric bulk of the $^{tBu}$POCOIr fragment might provide some advantage in the coupling of sterically demanding substrates such as α-methylstyrene. However, only 6% conversion was observed, compared to 9% reported for $^{iPr}$PCPIrHCl.

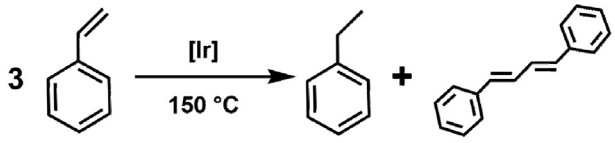
Allylbenzene was also tested as a substrate and >99% conversion was observed. However, 97% of the products resulted from isomerization to *cis* and *trans*-1-phenylpropene in a 1:30 ratio, respectively. This is similar to $^{iPr}$PCPIr, although in this case $^{tBu}$POCOIr is more reactive (82% conversion with $^{iPr}$PCPIr). Propylbenzene and 2 peaks with masses consistent with coupled allylbenzene isomers account for the remaining 3% of products. It would seem that the less encumbered sterics of $^{tBu}$POCOIr leads to improved performance in olefin isomerization, while providing no beneficial effects in dehydrogenative coupling, likely largely influenced by electronic differences between the POCO and PCP systems. These results also suggest that $^{tBu}$POCOIr operates by the same mechanism as $^{iPr}$PCPIr in dehydrogenative coupling. This requires a vinyl arene substrate which forms a metalloindene intermediate, and addition of a second vinyl arene, which must undergo C—H oxidative addition of a terminal vinylic proton forming a congested transition state complex, before hydride insertion and ultimately C—C reductive elimination. In this mechanism the addition of the second vinyl arene molecule is highly inhibited, or prevented, by α and β substitutions on the incoming vinyl arene (Scheme 6). Also, instead of invoking loosely defined "electronic differences", it is possible that reduced activity of $^{tBu}$POCOIr results from deactivation by cyclometalation of a *tert*-butyl group through C—H addition to iridium, which has been reported to occur in related $^{tBu}$POCOPIrHCl species in the presence of protic acids [31]. Another deactivation pathway, perhaps more likely, results from the dehydrogenative coupling of a phosphine *tert*-butyl methyl group to a cyclometallated styrene molecule (iridaindene moiety). Formation of such a complex was found to prevent any turnovers for butadiene formation in attempts at dehydrogenative coupling of vinyl arenes using $^{tBu}$PCPIr, while $^{iPr}$PCPIr efficiently catalyzed the process [30]. Additionally, although the metal center of $^{iPr}$PCPIr is sterically congested in comparison to $^{tBu}$POCOIr, this may actually hold the initial cyclometallated vinyl arene molecule in an optimal geometry for addition of a second molecule, which may be deviated from in $^{tBu}$POCOIr.



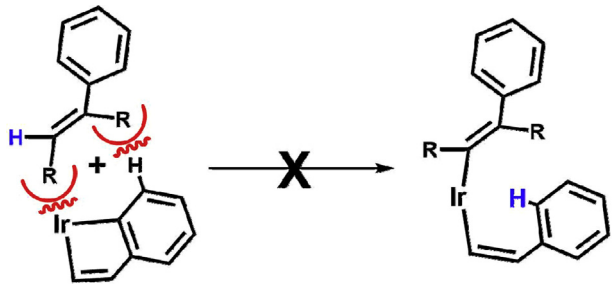

**Scheme 3.** Reaction of AgOTf with ***cis*-2** and ***trans*-2** to form **3**.




**Scheme 4.** Proposed equilibria of fluxional species **4** in solution.

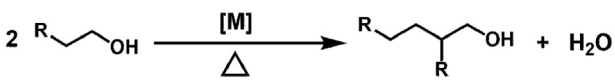



**Scheme 5.** Iridium catalyzed dehydrogenative coupling of vinyl arenes.



**Scheme 6.** Proposed metalloindene intermediate showing steric interactions of α and β substitutions preventing iridium catalyzed dehydrogenative coupling of vinyl arenes.

An iridium complex has also recently been reported as catalyst in the Geurbet conversion of ethanol to *n*-butanol with remarkable selectivity (>99%) utilizing bulky transition-metal hydroxides as bases [32]. This reaction involves the dehydrogenation of a primary alcohol to the corresponding aldehyde, base catalyzed aldol condensation to form an α,β-unsaturated aldehyde, and subsequent hydrogenation using the hydrogen removed in the dehydrogenation step. Ideally, the overall reaction provides the coupling of two alcohols into a larger chain alcohol with water as the sole byproduct (Scheme 7). This reaction has garnered substantial attention in recent years due to the enhanced fuel characteristics of *n*-butanol and higher alcohols in comparison to ethanol [33–35], and a number of advances have been made in the homogenous catalysis of this process, mainly based on ruthenium complexes [36–39], as well as two examples employing manganese PNP pincer complexes [40,41]. However, to the knowledge of the authors, no iridium pincer complexes have been reported as catalysts for the Geurbet reaction of ethanol to form longer chain alcohols. To begin filling this gap, $^{tBu}$POCOIr based pre-catalysts have been evaluated in this process for formation of primary linear alcohols, and found to give comparable yields to some of the best reported systems in terms of *n*-butanol produced.




**Scheme 7.** Overall stoichiometry in the Geurbet reaction of primary alcohols.

Catalysis was first attempted in neat ethanol using a loading of 1% **1a/b**, and 50 equiv. KOtBu (based on Ir), at 150 °C for 4 hours. Under these conditions, 64% conversion was observed with a 27% yield of *n*-butanol in 68% selectivity along with 8% and 2% yield of *n*-hexanol and *n*-octanol, respectively (Table 1, entry 1). The remaining conversion not accounted for by >$C_4$ *n*-alcohols may be mainly attributed to branched $C_6$ and $C_8$ alcohols, formation of MOEt species by protonation of base (in this case protonation gives *tert*-butanol), and somewhat surprisingly, only traces of ethyl acetate (<1%). Selectivity for *n*-butanol is calculated as the percent of *n*-butanol out of conversion products not resultant from base protonation. Lowering of the catalyst loading was investigated next. Using 0.1% **1a/b** provided a 16% yield of *n*-butanol in 73% selectivity, as well as 4% and 1% yields of *n*-hexanol and *n*-octanol (Table 1, entry 2). Unlike many of the reported systems to date, this catalyst does not present particularly high selectivity for *n*-butanol at low conversions. Increasing the loading to 0.2% gave only 22% yield of *n*-butanol, and conducting the reaction for 24 h gave negligible improvement (Table 1, entries 3 and 4). At 0.5% loading the best yield of *n*-butanol using **1a/b** was achieved, giving 31% yield in 64% selectivity (Table 1, entry 5). The yield of *n*-butanol actually decreased to 26% when the reaction was conducted for 72 h, though the yield of *n*-hexanol and *n*-octanol remained essentially constant (Table 1, entry 6). This may be the result of competitive dehydrogenation of $C_6$ and $C_8$ alcohols at higher conversions leading to even higher chain alcohols, or possibly insoluble oligo/polymeric side products not detected by GC analysis. Using lower loadings of base proved ineffective (Table 1, entries 7 and 8), and using more than 50 equiv. at 0.5% loading of **1a/b** tended to give heterogeneous reaction mixtures, and made post reaction analysis especially difficult due to slurry or gel-like mixtures obtained upon cooling.

Pre-catalyst **1a/b** was next assessed using other bases. Unexpectedly, sodium ethoxide, which is commonly used as a base in the Geurbet process, gave nearly negligible conversion and no detectable amounts of higher alcohols (Table 1, entry 9). Potassium hydroxide performed better than sodium ethoxide, but gave a lower yield of *n*-butanol compared to using KOtBu under otherwise identical conditions, as well as producing a larger amount of unidentified side-products (Table 1, entry 10). In light of the unmatched selectivity for *n*-butanol reported using Cp*Ir[(2-OH-6-phenyl)pyridine]Cl and bulky Ni or Cu transition metal hydroxide bases [32], [Tp′Ni(μ – OH)]$_2$ was also tested as a base in the $^{tBu}$POCOIr catalyzed Geurbet system. However, using **1a/b** as pre-catalyst no formation of *n*-butanol, or conversion of ethanol, was observed and a coating of Ni metal was seen to form on the inner surface of the reaction vessel (Table 1, entry 11). The relatively bulky organic bases sodium triphenylmethoxide and sodium tricyclohexylmethoxide were also tested, providing diminished or negligible yields, respectively (Table 1, entries 12 and 13). To date, the most active homogenous catalyst reported for the Geurbet process of ethanol is a Ru PNP pincer complex which is believed to

**Table 1**
Catalytic conversion of ethanol to higher alcohols using $^{tBu}$POCOIr based catalysts.

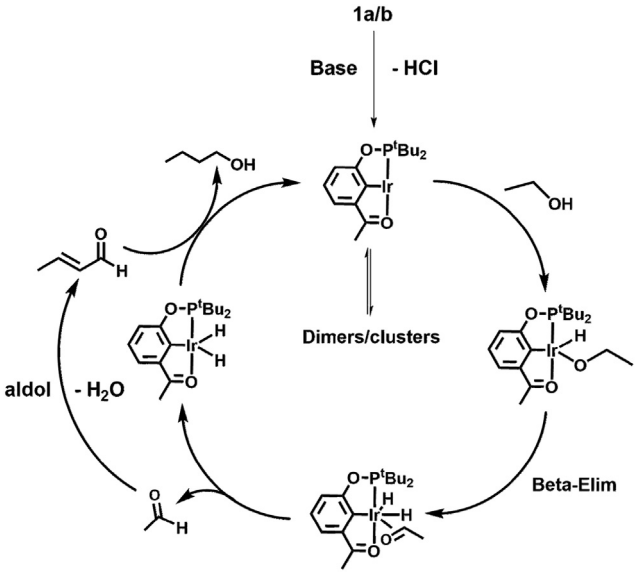
| Entry | Catalyst loading (%) | Base (equiv. based on Ir) | Time (h) | Conversion (%)[a] | Yield *n*-BuOH (%)[b]/Selectivity (%)[c] | Yield *n*-HexOH (%) | Yield *n*-OctOH (%) |
|---|---|---|---|---|---|---|---|
| **1** | 1 | KOtBu (50) | 4 | 64 | 27/68 | 8 | 2 |
| **2** | 0.1 | KOtBu (50) | 4 | 23 | 16/73 | 4 | 1 |
| **3** | 0.2 | KOtBu (50) | 4 | 38 | 22/79 | 6 | 1 |
| **4** | 0.2 | KOtBu (50) | 24 | 35 | 23/71 | 6 | 1 |
| **5** | 0.5 | KOtBu (50) | 4 | 62 | 31/64 | 9 | 2 |
| **6** | 0.5 | KOtBu (50) | 72 | 75 | 26/52 | 9 | 2 |
| **7** | 0.5 | KOtBu (1) | 4 | <1 | n/a | n/a | n/a |
| **8** | 0.5 | KOtBu (10) | 4 | 20 | 14/75 | 3 | <1 |
| **9** | 0.5 | NaOEt (50) | 4 | 3 | n/a | n/a | n/a |
| **10** | 0.2 | KOH (50) | 4 | 41 | 14/60 | 4 | 1 |
| **11** | 0.2 | $[TpNiOH]_2$ (50) | 4 | 0 | n/a | n/a | n/a |
| **12** | 0.5 | $Ph_3CONa$ | 4 | 63 | 17/46 | 4 | <1 |
| **13** | 0.5 | $(C_6H_{11})_3CONa$ (50) | 4 | 23 | <1/n/a | n/a | n/a |
| **14** | 0.5 (Ir(CO)HCl) | KOtBu (50) | 4 | 69 | 33/62 | 11 | 3 |
| **15** | 0.5 (1 atm $H_2$) | KOtBu (50) | 4 | 64 | 26/65 | 8 | 2 |

Conditions: **1a/b** used as pre-catalyst unless otherwise noted, 150 °C, neat ethanol, argon atmosphere.
[a] Disappearance of ethanol.
[b] Determined by GC, tridecane used as standard.
[c] Percent out of conversion not accounted for by base protonation.

retain a CO ligand during catalysis [38]. To see what effect the presence of a CO ligand might have on the $^{tBu}$POCOIr catalyzed reaction, a mixture of ***cis/trans*-2** was generated in situ by the addition of 1 atm CO to **1a/b** in toluene, removal of volatiles, and then addition of base and ethanol. Indeed, the highest yield of *n*-butanol was obtained using ***cis/trans*-2** as pre-catalyst (33%), as well as the highest overall yield of *n*-alcohols (47%) (Table 1, entry 14). The highest reported yield of *n*-butanol by a homogenous catalyst in this process is 38.4% [38]. Lastly, the reaction was conducted under 1 atm of hydrogen in the hopes that selectivity might be increased due to re-hydrogenation of $C_4$ and greater aldehydes as they are formed, and the statistically greater probability of ethanol dehydrogenation at moderate conversion levels would be predominant (Table 1, entry 15). Unfortunately, the yield of $>C_4$ alcohols was barely effected, while the yield of *n*-butanol was reduced 16% compared to identical conditions without $H_2$ added. However, this modest inhibition in the presence of a significant amount of $H_2$ would seem to indicate that the $^{tBu}$POCOIr catalyst may be a candidate for the acceptorless dehydrogenation of alcohols given an efficient means of expelling hydrogen from the reaction system.

In light of these findings, the mechanism of this reaction came in to question, and in this interest the stoichiometric reactivity of $^{tBu}$POCOIr with ethanol was investigated. Upon dehydrohalogenation of **1a/b** by KOtBu in $C_6D_6$ a mixture of products with broad resonances is observed by $^{31}$P NMR spectroscopy. The associated $^1$H NMR spectrum presents extensively overlapped and broadened peaks quite unaccommodating to characterization, likely due to reversible dimerization and solvent coordination. Formation of dinuclear clusters, and difficult to characterize mixtures, have been reported for variants of $^{tBu}$PCPIr where the steric congestion around iridium is reduced by replacing only two phosphine *tert*-butyl groups with methyl substituents [42]. Only very slight traces of 2 hydride resonances were observed. Addition of ethanol only slightly improves matters and addition of 1 equiv. to this mixture in $C_6D_6$ gives rise to two definite major products (out of >10 seen) in an approximately 1:6 ratio as observed by $^{31}$P NMR spectroscopy ($\delta$ 190.6, 167.9). What appears to be a quartet signal for the $CH_2$ protons of coordinated, or O—H activated, ethanol ($\delta$ 3.83, $J_{HH}$ = 7.1 Hz) is also observed in the $^1$H NMR spectrum. The iridium alkoxide $Cp^*IrPPh_3H(OEt)$ is reported to display a $OCH_2CH_3$ resonance at $\delta$ 3.79 ($J_{HH}$ = 6 Hz) [43]. Furthermore, the signal for the OH proton of ethanol, which was observed at $\delta$ 4.00 in the $^1$H NMR spectrum of a sample of pure ethanol in $C_6D_6$, is completely absent. These data are consistent with formation of an Ir-ethoxide complex. However, it is difficult to determine conclusively if this species is resultant from κ-O coordination, or O—H addition as suspected, because of the inability to reliably assign a hydride signal to the species responsible for the quartet observed due to the myriad hydride resonances found in the $^1$H NMR spectrum, as well as extensive signal overlap preventing location of the putative Ir-$OCH_2CH_3$ protons. After addition of 10 equiv. EtOH, and heating for ~10 min at 150 °C, a quartet consistent with the C($sp^2$)-H proton of acetaldehyde is also noted at $\delta$ 9.05 ($J_{HH}$ = 2.8 Hz). Attempts to crystallize potential intermediates from these mixtures were unsuccessful.

Given these results, a plausible, though certainly highly simplified, mechanism for ethanol dehydrogenation by $^{tBu}$POCOIr may be proposed which follows a "classic" pathway of oxidative addition, $\beta$-hydride elimination, dissociation of product, and reductive elimination of hydrogen or, most likely in this case, hydrogenation of another substrate molecule such as the crotonaldehyde formed by aldol condensation of acetaldehyde (Scheme 8). While extensive




**Scheme 8.** A plausible, though simplified, catalytic cycle for the Geurbet reaction of ethanol using $^{tBu}$POCOIr.

speciation though dimeric/oligomeric cluster formation, as well as facile reversible coordination/activation of solvent or substrate, is readily apparent in this system, it is possible that these equilibria represent unproductive pathways outside of the catalytic cycle, and present a potential means for catalytic improvement by prevention of their formation by steric or electronic modifications. For example, the good performance of $^{tBu}$POCOIr(CO) (generated from ***cis*/*trans*-2** and base) indicates that the presence of an L-type ligand may help to stabilize the active catalytic species with respect to non-productive side equilibria or deactivation pathways, and careful selection of the appropriate ligand might further improve efficiency.

## 3. Conclusions

In conclusion, a new POCO-type pincer ligand has been synthesized, characterized, and metallated using $[Ir(COD)Cl]_2$ to form **1a** (μ-Cl-[$^{tBu}$POCOIrHCl]$_2$) and isomer **1b**. The chemical equivalency of **1a** and **1b** has been demonstrated by reaction of **1a/b** with AgOTf and CO, irrespective of order of addition, resulting in convergence to **3** as the sole product. The performance of **1a/b** as a pre-catalyst for the dehydrogenative coupling of vinyl arenes has been investigated, giving poor yields in comparison to $^{iPr}$PCPIr, demonstrating that reduced steric hindrance does not inherently correlate with increased activity in this process, though performance in olefin isomerization was enhanced with respect to $^{iPr}$PCPIr. Both **1a/b** and ***cis*/*trans*-2** were evaluated in the Geurbet conversion of ethanol to linear alcohols, and optimal results were obtained using a 0.5% catalyst loading of ***cis*/*trans*-2** in conjunction with 50 equiv. KOtBu as base, giving 33% yield of *n*-butanol and an overall 47% yield of *n*-alcohols. Further investigation is currently underway in terms of mechanistic understanding of the $^{tBu}$POCOIr catalyzed Geurbet reaction, reaction condition and ligand modifications aimed at increased Geurbet performance, and other catalytic processes involving H-element bond manipulation.

## 4. Experimental

All manipulations were carried out under argon atmosphere either in a Vacuum Atmospheres glove box, or by modified Schlenk techniques. All NMR spectra were collected on a Bruker AMX 400 MHz, or JEOL JNM-ECZS 400 MHz spectrometer. All $^{31}$P NMR spectra were referenced to external $H_3PO_4$. Proton NMR spectra were referenced to residual deuterated solvent signal. DOSY-NMR were collected using a 16 point linear array starting at a gradient of 3.0 mT/m, final gradient of 0.27 T/m, and with a diffusion time of 0.125 s. All aromatic, alkane, and ether solvents were dried over sodium/benzophenone, distilled from the resultant purple solution prior to use, and stored over 3 Å molecular sieves. $CDCl_3$, $CHCl_3$, $CH_2Cl_2$, and EtOH were dried/stored with 3 Å molecular sieves activated by heating at 250 °C under vacuum until a constant pressure of ~10 mTorr was reached. All other reagents were used as received from commercial sources without further purification. X-ray structure collection was conducted on a Bruker SMART APEX II CCD platform diffractometer. GC was carried out on a Shimadzu GC-2010 with a DB-WAXetr column (30 m × 0.25 mm ID, 0.50 μm film) at 50–250 °C, 4.76 mL/min flow. All GCMS utilized a Thermo Fisher Scientific Focus-GC and DSQ-II MS with a TR-5MS column (30 m × 0.25 mm ID × 0.1 μm film) at 40–260 °C, 3 mL/min flow.

### 4.1. Synthesis of $^{tBu}$POCOH (3-(di-tert-butylphosphinito) acetophenone)

To a 100 mL round-bottom Schlenk flask, 0.675 g (4.96 mmol) 3-hydroxyacetophenone, 120 mg (5.00 mmol) NaH, and a stir bar are added followed by 50 mL THF. Rapid bubbling is noted and the mixture stirred at room temperature for 30 min. The flask is then fit with a septum sealed condenser and refluxed for 1 h under argon. After this period the reaction mixture is allowed to cool to room temperature and 1.00 g (5.54 mmol) di-*tert*-butylchlorophosphine dissolved in 20 mL THF is then added by syringe. The mixture is then refluxed an additional 1 h, before stirring overnight at room temperature. All volatiles are then removed under reduced pressure and the residue extracted with THF (3 × 15 mL), which is filtered and then concentrated in vacuo to provide 1.342 g (97% yield) of a viscous slightly yellow oil. Complete removal of excess di-*tert*-butylchlorophosphine was found to require repeated dissolution in THF followed by concentration in vacuo. Crystals suitable for X-ray diffraction were found to spontaneously form from this oil after several weeks of storage. $^{31}P\{^1H\}$ NMR ($C_6D_6$): $\delta$ 155.0 (s). $^1$H NMR ($C_6D_6$): $\delta$ 8.03 (vq, 1H, aryl), 7.36 (d, $J_{HH}$ = 8.4 Hz, 2H, *meta*-aryl), 7.02 (t, $J_{HH}$ = 7.9 Hz, 1H, *para*-aryl), 2.11 (s, 3H, $CH_3$), 1.09 (d, $J_{PH}$ = 12 Hz, 18H, $^t$Bu-H). *Anal.* Calc. for $C_{16}H_{25}O_2P$: C, 68.55; H, 8.99. Found: C, 68.37; H, 8.94%.

### 4.2. Synthesis of *1a/b*

To a 50 mL round-bottom Schlenk flask, 0.25 g (0.37 mmol) of $[Ir(COD)Cl]_2$ is added along with 20 mL toluene providing a clear orange solution. To this, 0.208 g (0.74 mmol) $^{tBu}$POCOH dissolved in 5 mL toluene is added, accompanied by a color change to deep reddish brown. The flask is then fit with a septum sealed condenser and the reaction solution is refluxed for 24 h under argon atmosphere. After this period the reaction mixture is allowed to cool to room temperature, and an orange-red supernatant is seen over a large amount of orange solid. Concentration of this mixture to dryness in vacuo, and washing of the obtained solids with pentane (3 × 5 mL), provides 0.315 g (84% yield) of an orange solid after drying under reduced pressure. Dissolving in hot toluene followed by slow cooling provided single crystals suitable for X-ray diffraction which proved to be **1a**, though they were coated in a fine polycrystalline material. The solubility of this product is rather poor, and a large number of scans were required for acceptable NMR spectra. Best results were obtained in $CDCl_3$. $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta$ 156.5 (s, **1a**), 154.7 (s, **1b**). $^1$H NMR ($CDCl_3$) All downfield peaks are found to overlap, ranges reported: $\delta$ 7.28–7.1 (m, aryl H's), 6.81–6.61 (m, aryl H's), 2.71 (2 overlapping bs, $CH_3$), 1.61 (m, $^t$Bu-H), 1.26 (m, $^t$Bu-H), −27.3 (d, $J_{PH}$ = 24.4 Hz, Ir-H **1a**), −27.5 (d, $J_{PH}$ = 26.8 Hz, Ir-H, **1b**). *Anal.* Calc. for $[C_{16}H_{25}ClIrO_2P]_2$: C, 37.83; H, 4.96. Found: C, 38.42; H, 4.92%.

### 4.3. Formation of *cis/trans-2* and isomerization to solely *trans-2*

A saturated solution of **1a/b** is generated in arene solvent or chloroform by heating ~15 mg **1a/b** in 1 mL of solvent at 80–130 °C in a sealed ampoule under argon followed by filtration. Then, 0.5 mL of this solution is added to a *J*-Young NMR tube which is degassed by 3 freeze–pumpthaw cycles prior to addition of 1 atm CO. A color change from orange to pale yellow is observed within <1 min after mixing. $^{31}$P NMR spectroscopy of this solution revealed formation of ***cis*/*trans*-2** in a 1–0.35 ratio. Subsequent removal of CO by concentration in vacuo, addition of fresh solvent, and heating at 60 °C for 6 min provides ***trans*-2** in quantitative yield. Removal of solvent gives a yellow solid. Analytical data reported for ***trans*-2**. $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta$ 163.9 (s). $^1$H NMR ($CDCl_3$): $\delta$ 7.30 (d, $J_{HH}$ = 7.2 Hz, 1H, aryl), 6.95 (m, 2H, aryl), 2.70 (s, 3H, $CH_3$), 1.39 (d, $J_{PH}$ = 16.0 Hz, 9H, $^t$Bu-H), 1.22 (d, $J_{PH}$ = 15.6 Hz, 9H, $^t$Bu-H), −19.81 (d, $J_{PH}$ = 20.4 Hz, 1H, Ir-H). *Anal.* Calc. for $C_{17}H_{25}ClIrO_3P$: C, 38.09; H, 4.70. Found: C, 37.65; H, 4.63%.

### 4.4. Synthesis of **3**

To a 25 mL round-bottom ampoule, a stir bar, 25 mg (0.0492 mmol by monomer) **1a/b**, and 20 mL $CH_2Cl_2$ are added. The sealed vessel is sonicated for 1 hr to dissolve all solids. The solution is then degassed by 3 freeze–pumpthaw cycles and 1 atm CO applied, providing a light yellow solution after briefly mixing. The solution is then subject to an additional freeze–pumpthaw cycle before adding 13 mg (0.0506 mmol) AgOTf and stirring overnight. After this time, the mixture is filtered to remove AgCl and any excess AgOTf and then concentrated to dryness in vacuo. Pentane is then added and the resultant mixture re-filtered to further ensure removal of AgOTf. After evaporation of solvent 30.7 mg of an orange-yellowish solid is obtained (96% yield). Vapor diffusion of pentane into a concentrated benzene solution of this product over 2 days, followed by storing at −17 °C afforded crystals suitable for X-ray diffraction which contained ½ equivalent co-crystallized benzene per Ir. $^{31}P\{^1H\}$ NMR (THF-$d_8$): $\delta$ 162.9 (s). $^1H$ NMR (THF-$d_8$): $\delta$ 7.59 (m, 1H, aryl), 7.19 (m, 2H, aryl), 2.8 (s, 3H, $CH_3$), 1.41 (d, $J_{PH}$ = 16 Hz, 9H, $^t$Bu-H), 1.34 (d, $J_{PH}$ = 16 Hz, 9H, $^t$Bu-H), −26.0 (d, $J_{PH}$ = 21.2 Hz, 1H, Ir-H). $^{19}F$ NMR ($C_6D_6$): $\delta$ −77.2 (s). *Anal.* Calc. for $C_{18}H_{25}F_3IrO_6PS{\cdot}0.5\ C_6H_6$: C, 36.62; H, 4.10. Found: C, 35.95; H, 3.93%.

### 4.5. Synthesis of **4**

To a small Erlenmeyer flask, 25.0 mg (0.0492 mmol) **1a/b**, a stir bar, and 10 mL toluene are added. This mixture is stirred, creating a suspension, and 12.6 mg (1 equiv.) AgOTf is then added followed by stirring overnight. After this period the mixture is filtered with a fine frit to remove AgCl, and concentrated in vacuo. Once "dry" a hot tap water bath was applied for ~45 min while still under vacuum. This provided 30.0 mg of an orange-yellow solid (98% yield). Due to the highly fluxional nature of this complex spectral data are reported for **4** in the presence of 1.2 equiv. AgOTf. $^{31}P\{^1H\}$ NMR ($C_6D_6$): $\delta$ 154.7 (s). $^1H$ NMR ($C_6D_6$): 6.8 (d, $J_{HH}$ = 7.6, 1H, aryl), 6.65 (d, $J_{HH}$ = 7.6 Hz, 1H, aryl), 6.51 (t, $J_{HH}$ = 7.8 Hz, 1H, aryl), 2.3 (s, 1H, $CH_3$), 1.36 (d, $J_{PH}$ = 14.8 Hz, 9H, $^t$Bu-H), 1.19 (d, $J_{PH}$ = 15.2 Hz, 9H, $^t$Bu-H), −31.30 (vd, $J_{PH}$ = 23.6 Hz, 1H, Ir-H). $^{19}F$ NMR ($C_6D_6$): $\delta$ −77.09 (bs), ligated and free OTf are in exchange and likely overlap.

### 4.6. General procedure for dehydrogenative coupling

To a 4 mL glass ampoule with Teflon closure, 9.0 mg (0.0177 mmol) **1a/b**, 4 mg (0.0356 mmol) potassium *tert*-butoxide, a stir bar, and 0.5 mL toluene are added. This is followed by addition of 0.354 mmol substrate. The sealed vessel is then heated, with stirring, at 150 °C for a given amount of time in an aluminum heating block. After this period the reaction is cooled to room temperature, and then 80 μL dodecane is added and mixed. From this mixture 1.5 μL is withdrawn and diluted with THF to 2 mL in a volumetric flask for GCMS analysis.

### 4.7. General procedure for Geurbet reaction of ethanol

To a 4 mL glass ampoule with Teflon closure, a given amount of catalyst and base are added along with a stir bar. Then, 0.3 mL dry, argon purged, ethanol is added by syringe under positive argon pressure and the vessel is quickly sealed. This is then heated at 150 °C, with stirring, for a prescribed amount of time. After the reaction time is complete and reaction cooled to room temperature, 1–3 mL THF is added and mixed, followed by filtration through a short plug of celite. Then, 120 μL of the filtrate is added to 6 mL THF, along with 40 μL tridecane, for GC analysis.

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## Appendix A. Supplementary data

CCDC 1859925–1859927 contains the supplementary crystallographic data for $^{tBu}$POCOH, and complexes **1a** and **3**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data to this article can be found online at https://doi.org/10.1016/j.poly.2018.12.001.

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