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Synthesis and Coordination Chemistry of New Asymmetric Donor/Acceptor Pincer Ligands, 1,3-$C_6H_4(CH_2P^tBu(R_f))_2$ ($R_f = CF_3$, C_2F_5)

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Abstract

Syntheses of new asymmetric pincer precursors 1,3-$C_6H_4\{CH_2P(^tBu,X)\}_2$ (^{tBu,X}PCPH; X = Cl, $SiMe_3$, OPh) and a new class of hybrid donor/acceptor pincer ligands 1,3-$C_6H_4\{CH_2P$-$(^tBu,R_f)\}_2$ (^{tBu,Rf}PCPH; $R_f = CF_3$, C_2F_5) are reported. All ^{tBu,X}PCPH compounds are obtained as mixtures of *meso* and *rac* diastereomers in varying ratios (*meso*:*rac* ~ 4:1 to 3:2) which were used without separation. Treatment of Ru(cot)(cod) with ^{tBu,CF_3}PCPH under 1 atm H_2 in acetone at 20 °C produced the hydride solvate (^{tBu,CF_3}PCP)Ru(acetone)$_x$H which was not isolated, but could be trapped as stable diene complexes (^{tBu,CF_3}PCP)Ru(L)$_2$H (L_2 = cod (**1**), nbd (**2**)). Catalytic cyclooctane dehydrogenation studies demonstrate that **2** has ~50% the activity of (^{CF_3}PCP)Ru(cod)(H), but significantly higher catalyst stability and is able to operate at higher catalyst loading concentrations without deactivation via bimolecular decomposition.

†*Submitted in honor of Richard A. Andersen, on the occasion of his 75th birthday*

Introduction.

Since the original 1976 report by Moulton and Shaw,[1] the chemistry of pincer-ligated transition-metal complexes has experienced substantial development and expanded applications.[2] This class of ligands is generally regarded as promoting a stable meridional tridentate coordination environment with exceptional thermal stability.[3] The "PCP" subclass of ligands, 1,3-$C_6H_4(CH_2PR_2)_2$ (unmetallated) and 2,6-$C_6H_3(CH_2PR_2)_2$ (metallated; generally abbreviated as ^{R}PCP ligands) gained prominence with Jensen's 1996 report of thermally stable alkane dehydrogenation catalysis using [$^{t\text{Bu}}$PCP]IrH_x precatalysts.[4] This initial work was subsequently expanded upon by the Goldman and Brookhart research groups, which largely employed both [^{R}PCP]IrH_x and [^{R}POCOP]IrH_x precursors with sterically-demanding donor phosphine pendant alkyl groups R = ^{t}Bu or ^{i}Pr.[5,6] Some significant limitations of alkylphosphine-based pincer alkane dehydrogenation systems are catalyst sensitivity to nitrogen and air,l as well as strong product alkene inhibition.[4,7,8]

In 2007 our research group introduced perfluoroalkyl-substituted PCP pincer ligands[9] and subsequently demonstrated their applicability to alkane dehydrogenation chemistry. Group 8 dehydrogenation catalysts employing the CF_3-substituted pincer, (^{CF_3}PCP)M(cod)H (M = Ru, Os),[10] along with the corresponding iridium catalyst (^{CF_3}PCP)Ir(cod)[11] are all stable to air and moisture and relatively insensitive to alkene product inhibition. While the initial cyclooctane (coa) dehydrogenation activity of (^{CF_3}PCP)Ir(cod) was modest (40 TO hr^{-1}) in 1:1 coa/tbe (tbe = ^{t}butylethylene) mixtures at 200 °C, high total TON's (~3000) and complete conversion of coa to cyclooctene (coe) was observed in more dilute 5:1 coa/tbe solutions. (^{CF_3}PCP)Ir(cod) is moreover quite insensitive to product inhibition: in the presence of 800 equiv. coe, the initial dehydrogenation activity is only reduced by 33%. Group 8 ^{CF_3}PCP-based catalysts are much

more reactive, yet significantly less stable: thermolysis of (^{CF_3}PCP)Ru(cod)H in 1:1 coa/tbe at 200 °C gave an initial activity of 1,000 turnovers hr^{-1} for the formation of coe. The hydrogen transfer activity of the corresponding osmium catalyst was slightly less (75%), but activity was maintained ~6 times longer.

A decrease in catalyst activity over time for (^{CF_3}PCP)Ru(cod)H is due to thermal catalyst decomposition as well as the reversible formation of an unusual [μ-η^1,η^6,κ^3-(^{CF_3}PCP)]-bridged ruthenium dimer under higher catalyst loadings;[10a] a similar bimetallic product, the unusual aryl-bridged [(μ-1κ^2(P,C),2κ^2(P′,C)-^{CF_3}PCP)Ir(H)$_2$]$_2$(μ-^{CF_3}PCPH)(μ-H) complex, was also observed in (^{CF_3}PCP)Ir(cod) chemistry (**Figure 1**).[11] The tendency of (^{CF_3}PCP)M systems to participate in bimolecular chemistry reflects the tendency of the less sterically-encumbered ^{CF_3}PCP ligand to form non-meridional pincer complexes.[12,13]

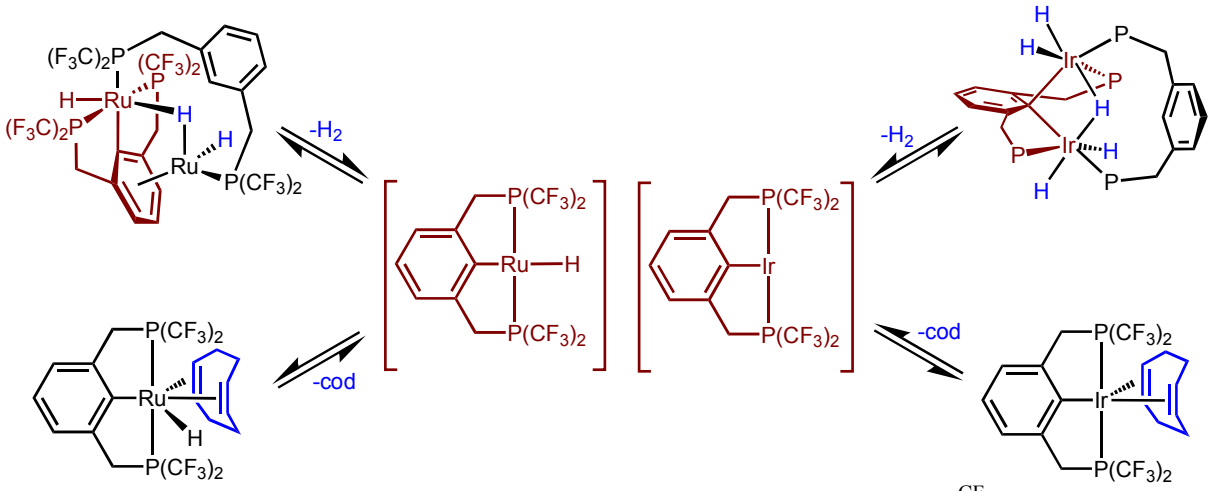


Figure 1. Reversible formation of catalytically inactive dimers from (^{CF_3}PCP)Ru(cod)H and (^{CF_3}PCP)Ir(cod) pincer systems

The role of pincer sterics for donor PCP pincer cyclooctane dehydrogenation systems has been investigated by Goldman *et al.*[14] Replacing one of the four ^{t}Bu groups on ($^{t\text{Bu}}$PCP)IrH_4 with a methyl group to form ($^{t\text{Bu}_3\text{Me}}$PCP)IrH_4 resulted in a modest increase (~5 fold) in catalytic activity; calculations indicated that this increase resulted from lowered steric congestion for

rate-limiting β-H elimination from (^{R4}PCP)Ir(*n*-alkyl)(H). Replacement of a second ^{t}Bu group on the opposite pincer phosphine arm had a negative effect on catalytic rates: (^{tBu_2Me_2}PCP)IrH$_4$ was less active and decomposed to a bimetallic product with a bridging metallated P-Me group. It is evident that steric tuning of pincer catalyst activity requires a delicate balance between catalyst metal site protection, substrate/product binding, and bimolecular decomposition pathways.

Noting the above considerations, we have developed new hybrid perfluoroalkyl/^{t}butyl functionalized PCP ligands ^{tBu,Rf}PCPH (R_f = CF_3, C_2F_5) which might combine the desirable N_2/air/moisture stability and lower alkene inhibition properties of electron-poor ^{CF_3}PCP systems with the steric protection and stability of established ^{tBu}PCP-based iridium catalysts. ^{tBu,Rf}PCP pincers with two asymmetric phosphine centers lead to diastereomeric metal coordination with either a bisecting mirror plane ("*meso*") or a C_2 axis along the metal-aryl bond ("*rac*"):

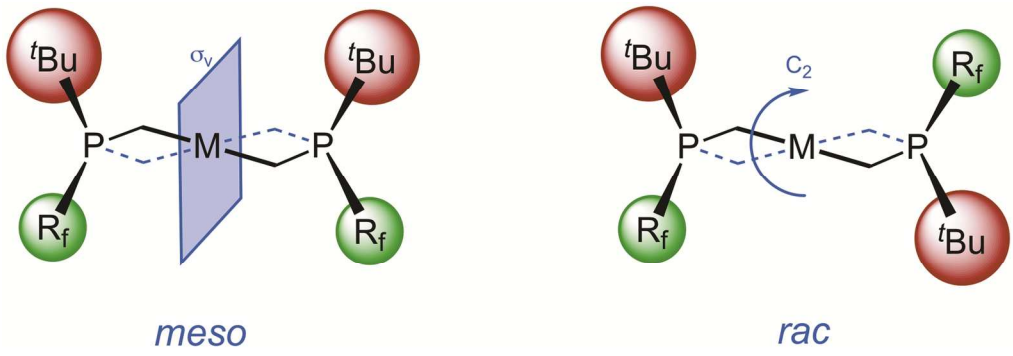


Figure 2. Possible stereoisomers for pincer ligands with P(^{t}Bu)(R_f) substitution. The solid and dashed lines to the metal center depict alternate conformations of the central aryl group and benzylic CH_2 arms.

These stereoisomers should have very similar net phosphine donor properties but distinctly different pincer "quadrant" steric properties. In particular, the *meso* stereoisomer has an intrinsically unfavorable *syn* ^{t}Bu-^{t}Bu interaction that hinders bending toward this side of the

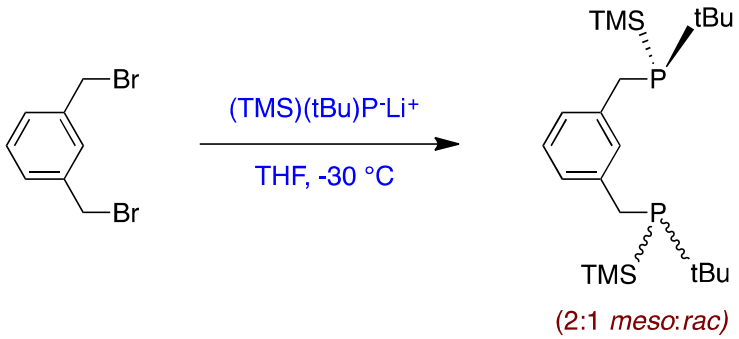
pincer plane while the *rac* stereoisomer, with less hindered *syn* ^{t}Bu-R_f interactions, allows for non-meridional pincer bending. Differing "quadrant" sterics can potentially alter the chemistry and corresponding catalytic chemistry of *meso* and *rac* stereoisomers. The results presented in this paper sought to test this hypothesis.

Results and Discussion

There are relatively few reports of asymmetrical PCP pincer compounds in the literature. Introduction of chirality in pincer ligands was first achieved by installation of chiral substituents at the benzylic positions.[15,16] PCP pincer ligands with cyclic[17] and acyclic[18,19] stereogenic P-centers were subsequently developed and applied to enantioselective catalysis. Of particular note is Jensen's report of the mixed phenyl/*t*-butyl ligand R,R-{C_6H_4-2,6-(CH_2P*PhBu^{t})$_2$}, which was shown to be a transfer dehydrogenation catalyst with turnover numbers similar to those observed for ($^{t\mathrm{Bu}}$PCP)IrH_2.[18b]

Synthesis of 1,3-C_6H_4{CH_2P(^{t}Bu,R_f)}$_2$ ($^{t\mathrm{Bu,Rf}}$PCPH) (R_f = CF_3, C_2F_5). We initially examined asymmetric silylated pincers $^{t\mathrm{Bu,TMS}}$PCPH as precursors to the desired $^{t\mathrm{Bu,Rf}}$PCPH systems, since P-$SiMe_3$ groups may be readily converted to P-H and P-Cl precursors, or directly to P-R_f groups. Racemic P^{t}Bu(TMS)H was prepared by the reaction of 1 equiv. of methanol with P^{t}Bu(TMS)$_2$ in THF; a small amount (*ca* 10%) of ^{t}BuPH_2 side product was also formed. Reaction of P^{t}Bu(TMS)H with α,α′-dibromo-*m*-xylene gave a mixture of products. The major product (*ca.* 30-35%) was assigned as $^{t\mathrm{Bu,TMS}}$PCPH. The sensitivity of the product P-TMS bonds toward the released HBr side product likely accounts for the poor selectivity and low observed yield. Use of the corresponding phosphide proved more effective: deprotonation of P^{t}Bu(TMS)H with *n*-BuLi in THF at −30 °C followed by warming to ambient temperature and addition of α,α′-dibromo-*m*-xylene afforded the desired asymmetric pincer $^{t\mathrm{Bu,TMS}}$PCPH (**Equation 1**). A single ^{31}P

resonance for $^{t\text{Bu,TMS}}$PCPH appears as a broad singlet at −41.7 ppm; however, a ~2:1 mixture of *meso*- and *rac*-diastereomers is evident in ^{1}H NMR spectra, which show clearly separated *t*-Bu and TMS resonances associated with each diastereomer. The assignment of the major stereoisomer as *meso* is supported by X-Ray diffraction data for the related borane adduct $^{t\text{Bu,Cl}}$PCPH$(BH_3)_2$ (see Supplementary Material).

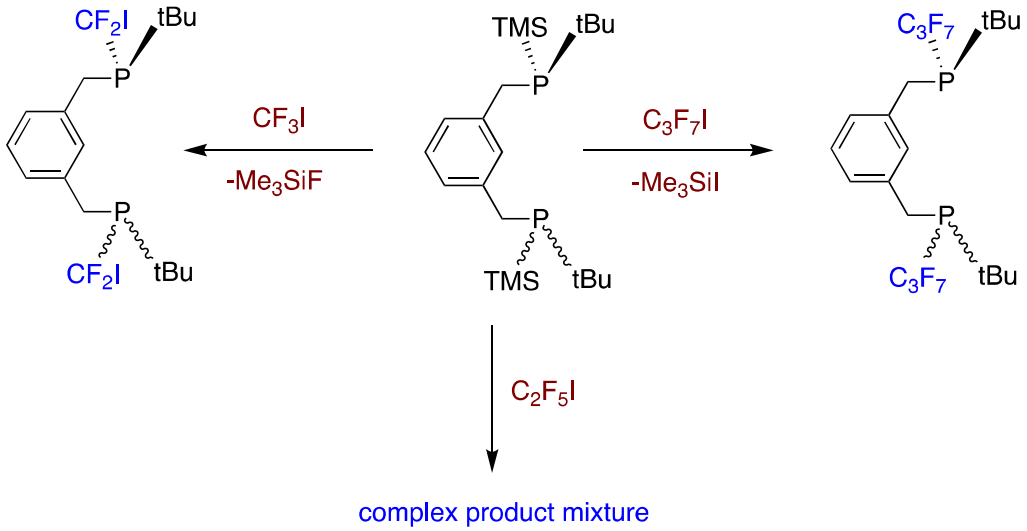


(1)

Brisdon has reported perfluoroalkyl-containing phosphines are obtained by treatment of the trimethylsilyl-substituted phosphines with perfluoroalkyl iodides (R_fI).[20] Accordingly, NMR-scale reactions with $^{t\text{Bu,TMS}}$PCPH and R_fI (R_f = CF_3, C_2F_5, *i*-C_3F_7) were examined (**Scheme 1**). Treatment of $^{t\text{Bu,TMS}}$PCPH with 4 equiv. CF_3I resulted in clean conversion (~95%) to a single product, as indicated by the appearance of a single ^{31}P NMR resonance at 61.0 ppm. ^{19}F spectra exhibit two doublets of doublets at −32.6 ($^2J_{FF}$ = 186 Hz, $^2J_{PF}$ = 60 Hz) and −35.7 ppm ($^2J_{FF}$ = 186 Hz, $^2J_{PF}$ = 71 Hz), characteristic of a ABX splitting pattern for diastereotopic Y-CF_2-X fluorines, along with characteristic ^{1}H and ^{19}F resonances due to trimethylsilyl fluoride. An additional set of ABX resonances were observed for the minor *rac* stereoisomer (***meso*:*rac*** ~ 3:1). Based on the ^{19}F data and the unexpected formation of Me_3SiF rather than Me_3SiI, we tentatively assign this complex as the unusual P(CF_2I)-substituted compound $^{t\text{Bu,CF}_2\text{I}}$PCPH. In contrast, treatment of $^{t\text{Bu,TMS}}$PCPH with *i*-C_3F_7I in benzene-d_6 at ambient temperature produced $^{t\text{Bu},i\text{C}_3\text{F}_7}$PCPH as the major product (*ca* 65%) after 2 hours with the accompanying release of

trimethylsilyl iodide. In addition to a single broad ^{31}P NMR resonance at 41.5 ppm, ^{19}F NMR spectra of ^{tBu,iC_3F_7}PCPH show a perfluoroisopropyl CF_3 doublet resonance −72.9 ppm with an accompanying doublet of septet C-F resonance appearing at −179.8 ppm. The benzylic CH_2 groups appear as a complex multiplet at δ 3.26 in the ^{1}H NMR spectrum. The observation of two resolved *tert*-butyl doublets at δ 1.08 and 1.05 in 3:2 ratio confirm the presence of *meso* and *rac* stereoisomers. In contrast to the reactions of ^{tBu,TMS}PCPH with CF_3I and $(CF_3)_2CFI$, the reaction of ^{tBu,TMS}PCPH with C_2F_5I failed to produce a major identifiable product. The formation of a P-CF_2I substituted pincer rather than the expected P-CF_3 product indicates surprisingly different regioselectivities for the reactions of CF_3I and *i*-C_3F_7I with ^{tBu,TMS}PCPH. Both steric and electronic factors can influence four-center transition states involved in C-F versus C-I addition across P-TMS bonds, and the non-specific nature of C_2F_5I addition appears to reflect a crossover in the underlying bond metathesis preferences.

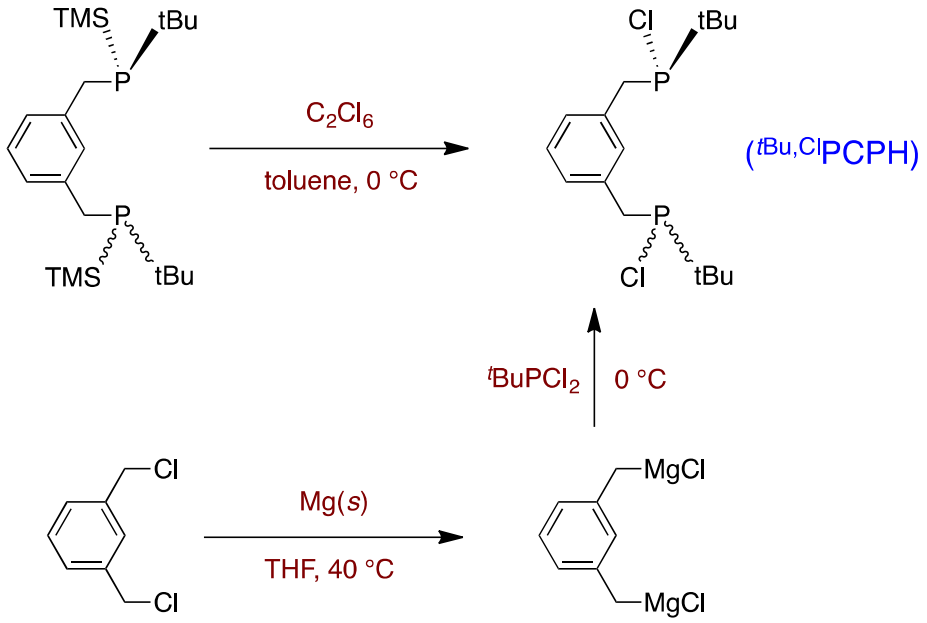
Scheme 1



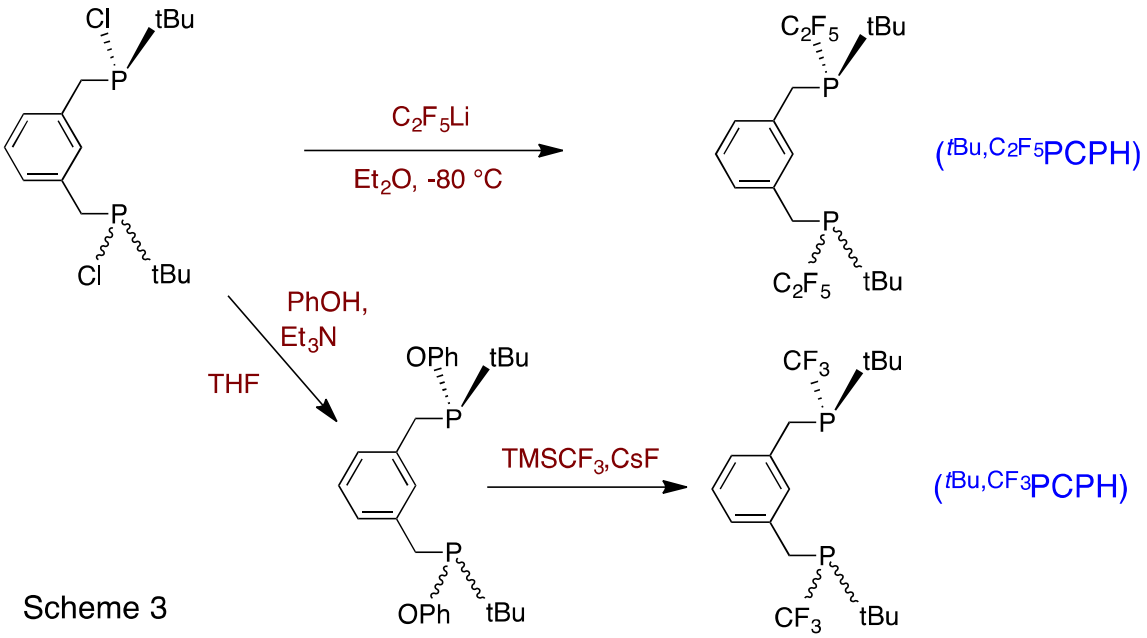
The chlorophosphine derivative, 1,3-$C_6H_4\{CH_2P(^tBu,Cl)\}_2$ (^{tBu,Cl}PCPH), serves as a versatile precursor to asymmetric ^{tBu,R}PCPH pincer ligands (**Scheme 2**). Treatment of ^{tBu,TMS}PCPH with hexachloroethane afforded ^{tBu,Cl}PCPH in high yield. An alternate, more

efficient $^{t\text{Bu,Cl}}$PCPH synthesis was also developed based on Hayes' procedure:[21] Reaction of α,α′-dichloro-*m*-xylene with 3 equiv. of magnesium followed by 2 equiv. of ^{t}BuPCl$_2$ directly produced $^{t\text{Bu,Cl}}$PCPH in moderate yield.

Scheme 2



The perfluoroalkyl-substituted ligand $^{t\text{Bu,C}_2\text{F}_5}$PCPH was prepared from $^{t\text{Bu,Cl}}$PCPH in a manner analogous to other perfluoroethyl-substituted phosphines in our laboratory (**Scheme 3**):[22] addition of $^{t\text{Bu,Cl}}$PCPH to *in situ* prepared C_2F_5Li at −80 °C gave $^{t\text{Bu,C}_2\text{F}_5}$PCPH as a viscous oil. The CF_3-substituted pincer derivative was obtained following Caffyn's procedure:[23] Addition of Me_3SiCF_3 to an ether suspension of $^{t\text{Bu,OPh}}$PCPH (prepared by metathesis of $^{t\text{Bu,Cl}}$PCPH with phenol) and excess CsF produced a dark brown solution. Distillation under reduced pressure afforded 1,3-$C_6H_4(CH_2P\{^{t}Bu,CF_3\})_2$ ($^{t\text{Bu,CF}_3}$PCPH) as a viscous brown oil.

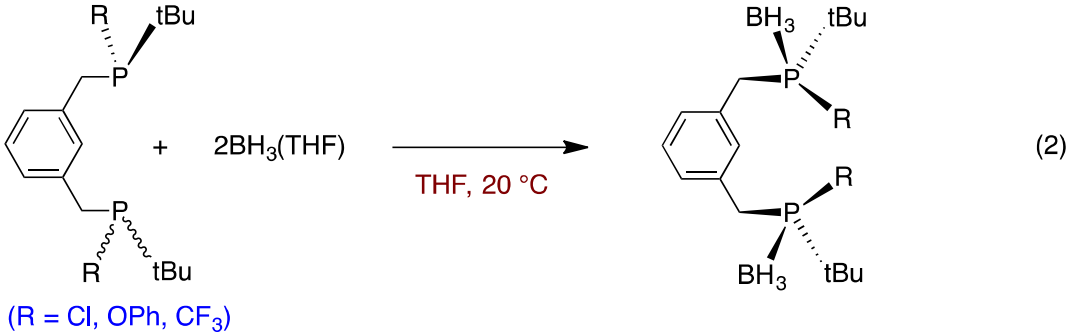


Scheme 3

Direct monotrifluoromethylation of secondary and primary aryl- and alkylphosphines using hypervalent iodine (III)-CF_3 reagents was reported by Togni in 2008.[24] The required secondary phosphine ^{tBu,H}PCPH was readily prepared from ^{tBu,TMS}PCPH by treatment with methanol. Reaction of ^{tBu,H}PCPH with either stoichiometric or excess 1-trifluoromethyl-1,2-benziodoxol-3(1H)-one (Togni Reagent II), however, led to the formation of only ~20% of expected ^{tBu,CF_3}PCPH ligand along with other uncharacterized products. Alternatively, reaction of Togni reagent II directly with the TMS pincer precursor ^{tBu,TMS}PCPH at room temperature for 4 hours resulted in 50-55% formation of ^{tBu,CF_3}PCPH, however attempts to isolate pure ^{tBu,CF_3}PCPH ligand from this reaction mixture were unsuccessful.

NMR data for all compounds obtained in **Scheme 3** indicated *ca.* 2:1 mixtures of *meso* and *rac* diastereomers. Attempts to separate diastereomers by fractional distillation or recrystallization were unsuccessful. Reaction of ^{tBu,Cl}PCPH with two equiv. of BH_3·THF resulted in the clean formation of the diborane adduct in moderate yield (**Equation 2**). X-ray diffraction

data for [$^{t\text{Bu,Cl}}$PCPH](BH$_3$)$_2$ was obtained for the preferentially crystallized the *meso* isomer (see ESI).



(2)

Imamoto has reported an efficient method for phosphine-borane deprotection with an excess of various types of amines to form the free phosphine ligand;[25] however, our attempts to isolate pure *meso*-$^{t\text{Bu,Cl}}$PCPH following this approach were unsuccessful. Accordingly, distereomeric ($^{t\text{Bu,Rf}}$PCPH) mixtures were used for all our metallation studies.

Metallation Studies with $^{t\text{Bu,CF}_3}$PCPH and $^{t\text{Bu,C}_2\text{F}_5}$PCPH. Since Ru(cod)($\eta^3$-2-methylallyl)$_2$ has been employed as a ruthenium pincer complex precursor in previous studies,[10a,26] metallation experiments were performed using similar conditions to those employed for the reactions of $^{\text{CF}_3}$PCPH with Ru(cod)(η^3-2-methylallyl)$_2$. Thermolysis of 1:1 mixtures of $^{t\text{Bu,CF}_3}$PCPH and Ru(cod)(η^3-2-methylallyl)$_2$ in toluene at 130 °C in the presence of 3-10 equiv. of 1,5-cyclooctadiene under an H_2 atmosphere gave only 10% conversion to the expected metallated product after 1 hr, and $^{t\text{Bu,C}_2\text{F}_5}$PCPH was found to be completely unreactive with Ru(cod)(η^3-2-methylallyl)$_2$ under analogous metallation conditions.

In view of these limited results, we next examined Ru(0) complex (η^4-1,5-cyclooctadiene)(η^6-1,3,5-cyclooctatriene)ruthenium(0) (Ru(cod)(cot)) as a potential metallation precursor. Forcing conditions used in previous metallation studies were first examined: Warming equimolar mixtures of Ru(cod)(cot) and $^{t\text{Bu,CF}_3}$PCPH in benzene to 100 °C under 3 atm of H_2 gas

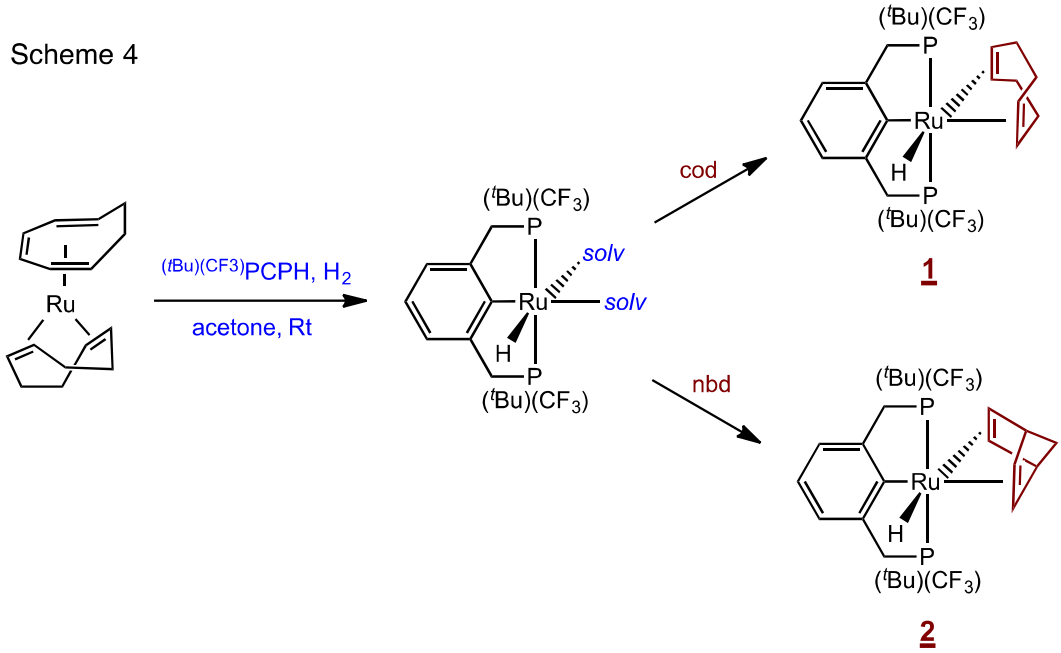
in the presence of 3 equiv. of cod gave an uncharacterized mixture of products. Repeating this metallation reaction at room temperature for 24 hrs, however, gave a major product with a hydride triplet at δ −14.42 as well as a 106.8 ppm ^{31}P resonance that was previously observed in Ru(cod)(η^3-2-methylallyl)$_2$ metallation attempts. Integration of unreacted $^{t\text{Bu,CF}_3}$PCPH versus the product peak showed that product conversion was ~50%. No further spectroscopic changes were observed after 24 hours. After warming to 100 °C for 2 hours, the 106.8 ppm product had disappeared and no pincer product was observed; from these observations we conclude that the asymmetric pincer product ($^{t\text{Bu,CF}_3}$PCP)Ru(cod)H is much less thermally stable under metallation conditions relative to ($^{\text{CF}_3}$PCP)Ru(cod)(H).

We have optimized conditions to afford ($^{t\text{Bu,CF}_3}$PCP)Ru(cod)H and related ($^{t\text{Bu,CF}_3}$PCP)Ru(L)$_2$H derivatives more selectively and in higher yield (**Scheme 4**). A 1.1:1 mixture of $^{t\text{Bu,CF}_3}$PCPH and Ru(cod)(cot) stirred in acetone for 20 hours under 1 atm hydrogen resulted in ^{31}P product resonances at 99.4 and 93.9 ppm in a 2:1 ratio. A single hydride triplet was observed at δ −19.57 which was significantly downfield from the hydride triplet reported for ($^{\text{CF}_3}$PCP)Ru(cod)H (−11.94 ppm). This suggests the initial formation of a solvated pincer hydride adduct ($^{t\text{Bu,CF}_3}$PCP)Ru(acetone)$_x$H. This solvated hydride complex has limited stability: removal of the solvent before the addition of a trapping diene ligand resulted in decomposition and ^{31}P NMR spectra showed significant amounts of free $^{t\text{Bu,CF}_3}$PCPH. Subsequent reaction of *in situ*-formed ($^{t\text{Bu,CF}_3}$PCP)Ru(acetone)$_2$H solutions with 1,5-cyclooctadiene and norbornadiene resulted in the formation of stable ($^{t\text{Bu,CF}_3}$PCP)Ru(diene)H products: addition of cod (10 equiv.) gave ($^{t\text{Bu,CF}_3}$PCP)Ru(cod)H, a brown oil, as the major product (~80%), which could be only partially purified by extraction and cold precipitation from petroleum ether. Two triplet hydride resonances appear at −14.96 ($^2J_{\text{HP}}$ = 24.5 Hz) and −14.74 ppm ($^2J_{\text{HP}}$ = 24.3 Hz) in a 55:45 ratio

which are assigned to *meso* and *rac*-($^{t\text{Bu,CF}_3}$PCP)Ru(cod)H (**1**) diastereomers. In all obtained ($^{t\text{Bu,CF}_3}$PCP)Ru(L)H products we have observed additional unresolved hydride fine structure for the downfield *rac* resonance due to pincer asymmetry and the chemical inequivalence of the pincer P centers. The cod adduct is moderately stable: no decomposition is observed after repeated addition/removal of solvent at ambient temperatures.

Using an analogous procedure to **1**, the norbornadiene adduct ($^{t\text{Bu,CF}_3}$PCP)Ru(cod)H (**2**) is readily prepared; cold filtration from petroleum ether resulted in the isolation of an analytically-pure solidified oil that also liquefied upon warming to room temperature. ^{1}H NMR spectra for **2** exhibit two hydride resonances, at δ –13.82 (*meso*) and –12.68 (*rac*) in a 57:43 ratio. Unlike the single unresolved resonance found for **1**, ^{31}P NMR spectra for **2** show three clearly distinguishable ^{31}P resonances: a broad singlet at 116.0 ppm, assigned as the *meso* isomer, and two doublets corresponding to a *rac* AB phosphorus system at 119.8 and 114.1 ppm with a large trans coupling $^{2}J_{PP}$ = 175 Hz. Repeated recrystallization attempts to isolate pure *meso*-**2** and/or *rac*-**2** were unsuccessful.

Scheme 4



In contrast to the moderately clean chemistry observed for $^{t\text{Bu,CF}_3}$PCPH, $^{t\text{Bu,C}_2\text{F}_5}$PCPH under identical reaction conditions with Ru(cod)(cot) showed only ~50% conversion to the expected ($^{t\text{Bu,C}_2\text{F}_5}$PCP)Ru(acetone)$_2$H product, as judged by ^{31}P NMR. Addition of excess cod or nbd to the acetone solvate solution gave a complex mixture of products which were not further characterized.

Alkane Dehydrogenation Catalysis by ($^{t\text{Bu,CF}_3}$PCP)Ru(nbd)H. We have previously reported that ($^{\text{CF}_3}$PCP)Ru(cod)H exhibits strong catalytic activity for dehydrogenation of cycloalkanes at low catalyst loading and concentration (0.033 mol %, 1.25 mM); however, at higher catalyst loadings (0.33 mol%, 12.5 mM) conversion to (μ-$^{\text{CF}_3}$PCPH)Ru(H)(μ-H)(μ-η^6,κ^3-$^{\text{CF}_3}$PCP)Ru(H) dominates and minimal turnovers were observed.[10a] In light of these previous results, catalyst studies were initially carried out using low **2** catalyst loading in order to obtain useful comparisons to the original ($^{\text{CF}_3}$PCP)Ru(cod)H system. Thermolysis of 0.033 mol % of **2** in (1:1) mixtures of cyclooctane (coa) and *tert*-butylethylene (tbe) at 150 °C and 200 °C were monitored by ^{1}H NMR (**Figure 3**).

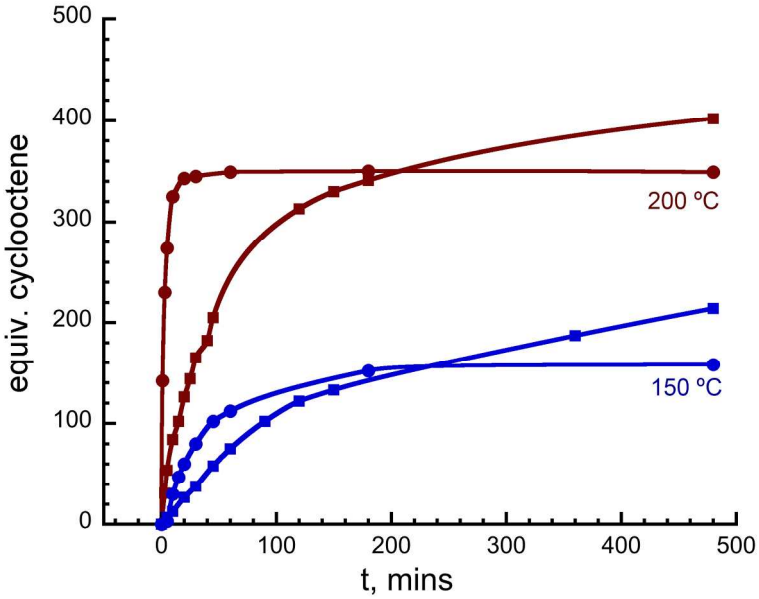


Figure 3. Comparative catalyst activity plot for (^{tBu,CF_3}PCP)Ru(nbd)H (■) and (^{CF_3}PCP)Ru(cod)H (●) in 1:1 cyclooctane/*t*-butylethylene at 150 °C and 200 °C (0.033 mol % catalyst loading, 1.25 mmol catalyst).

Initial rates of coe production using **2** were taken from ^{1}H NMR integrations after 10 minutes and estimated to be 78 turnovers hr^{-1} at 150 °C, compared to 180 turnovers hr^{-1} initial activity found for (^{CF_3}PCP)Ru(cod)H. Catalyst lifetime was, however, significantly improved: after 480 min., 214 TO's were observed for **2** and a TON of 312 was achieved after 4 days. In contrast, the catalytic activity of the (^{CF_3}PCP)Ru(cod)H system ceased due to catalyst decomposition after 3 h with a TON of 152. ^{19}F NMR spectra of catalyst solution **2** after 4 days at 150 °C show that some catalyst was still present in solution (~20%), but no further cyclooctene production was observed.

At 200 °C, **2** produced 460 TO's after 24 hrs with an initial rate of 504 turnovers hr^{-1}, approximately 50% that of (^{CF_3}PCP)Ru(cod)H, which shows a TON 350 and is completely deactivated after only 30 min. ^{19}F NMR spectra of (^{tBu,CF_3}PCP)Ru(nbd)(H) catalyst solutions after 24 h at 200 °C show only the presence of unligated ^{tBu,CF_3}PCPH; the major decomposition product for the (^{CF_3}PCP)Ru(cod)H system has not been identified. The initial turnover rate and total turnovers for the hybrid system **2** are considerably less than those reported for iridium phosphinite complexes such as (*p*-Ar^{F}PCP^{tBu})IrH$_2$ (8715 turnovers hr^{-1}, 2200 TON at 200 °C)[27,28] and the ferrocene-bridged pincers (^{tBu}PCP^{Fe})IrH$_2$ (3,300 TON at 180 °C).[29] The TON for **2** is, however, higher than reported for (^{tBu}PCP)IrH$_2$ (230 TON at 200 °C),[28] and comparable to the 5d analogue acceptor system (^{CF_3}PCP)Os(cod)H (510 TON at 200 °C).[10b]

Strong catalytic rate inhibition by alkene product build up is observed for all reported alkane dehydrogenation catalyst systems. Inhibition for the (^{tBu,CF_3}PCP)Ru(nbd)(H) system was examined in the presence of 0-800 equiv. added coe (**Figure 4**). Initial activities in the presence

of 400 and 800 equiv. coe, were 52% and 32% of the initial activity, respectively, half the inhibition effect found for (^{CF_3}PCP)Ru(cod)H under identical conditions (400 equiv: 29%, 800 equiv: 16%).[10a]

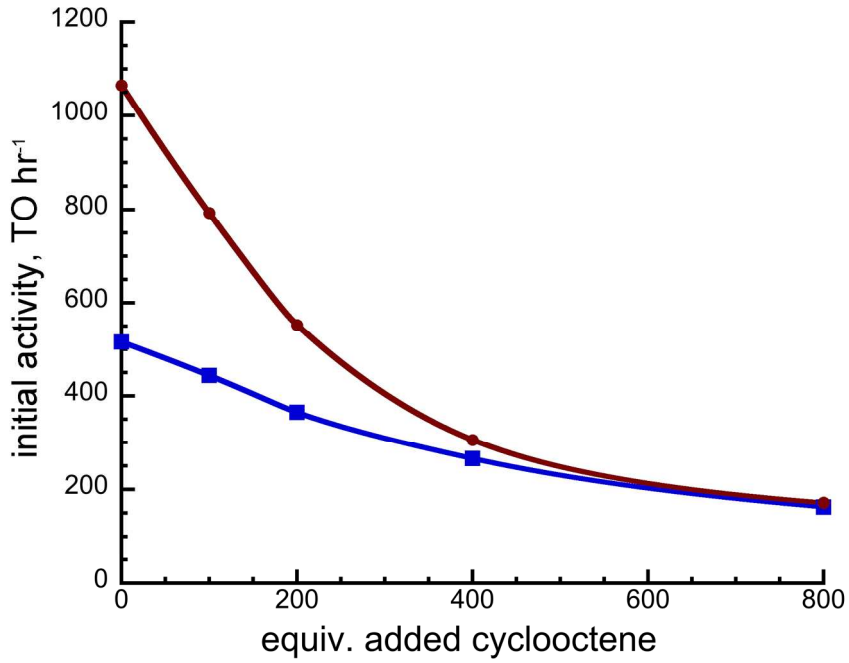


Figure 4. Product inhibition study: Initial catalyst activity plots for ($^{t\text{Bu},CF_3}$PCP)Ru(nbd Ru(nbd)H (■) and (^{CF_3}PCP)Ru(cod)H (●) in 1:1 coa/tbe at 200 °C (0.033 mol % catalyst loading) as a function of equivalents added cyclooctene.

To further test catalyst stability, thermolysis of **2** in 1:1 coa:tbe was carried out for 3 hrs at 200 °C (**Figure 5**). At this point the catalysis rate had slowed to 20 turnovers hr^{-1}. From inhibition data in **Figure 4**, we would estimate that the rate would be slowed to ~290 turnovers hr^{-1} in the presence of 339 equiv. coe. if only product inhibition was occurring. All volatiles were removed, the residue was taken up in a fresh 1:1 coa/tbe mixture, and the thermolysis was reinitiated. A renewed dehydrogenation activity of 174 turnovers hr^{-1} was observed, which indicates the inhibition by coe was contributing significantly to the diminished activity. The

restart activity is 35% of the initial rate, suggesting that 65% of the activity loss after 180 min. is due to decomposition of the catalyst at 200 °C.

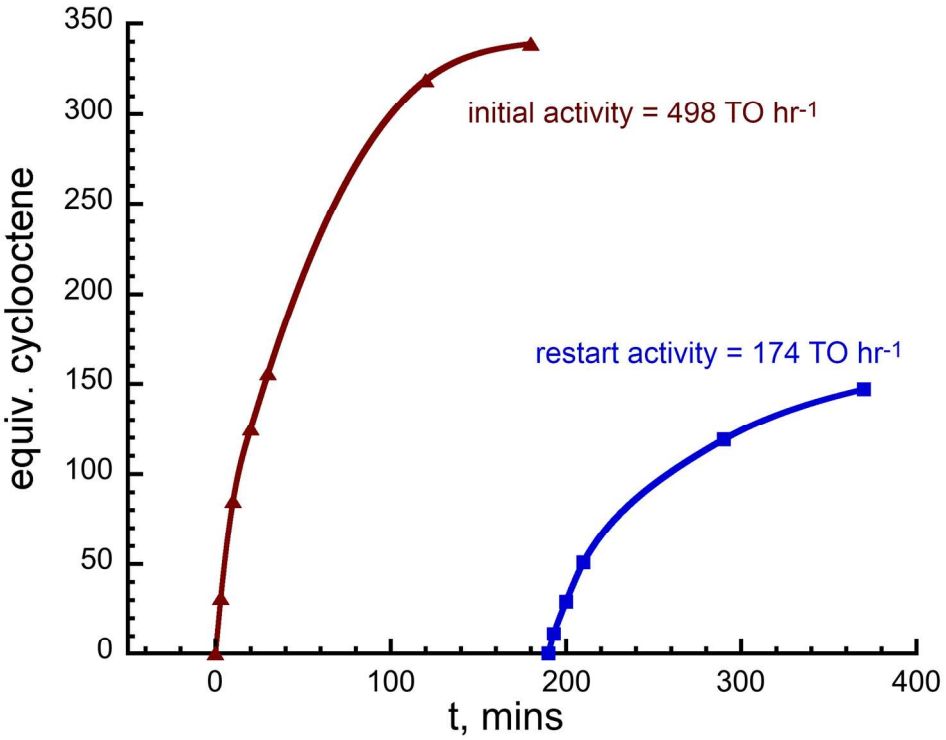


Figure 5. Catalyst activity plots for fresh (▲, t = 0 min.) and restarted (■, t = 180 min.) ($^{t\text{Bu,CF}_3}$PCP)Ru(nbd)H in 1:1 coa/tbe at 200 °C (0.033 mol % catalyst loading).

Acceptorless dehydrogenation by **2** was also examined. Refluxing 2.5 mM catalyst in cyclooctane (~150 °C at 590 Torr ambient pressure) for 24 hr produced 30 turnovers of cyclooctene (**Figure 6**) with an initial rate of 18 turnovers hr^{-1}. Interestingly, while **2** was still the major species (~60% of total pincer species observed by ^{31}P NMR) after 24 h, no further catalytic activity was observed. Under analogous reflux conditions, (^{CF_3}PCP)Ru(cod)H produced 10 turnovers of cyclooctene after 2 hr with an initial rate of 14 turnovers hr^{-1}, and ^{19}F showed complete conversion to the catalytically inactive dimer (μ-^{CF_3}PCPH)Ru(H)(μ-H)(μ-η^6,κ^3-

^{CF_3}PCP)Ru(H).[10a] For comparison, 2 mM ($^{t\text{Bu}}$PCP)IrH_2 is reported to produce 190 turnovers after 120 h, with an initial rate of 11 turnovers hr^{-1}.[30]

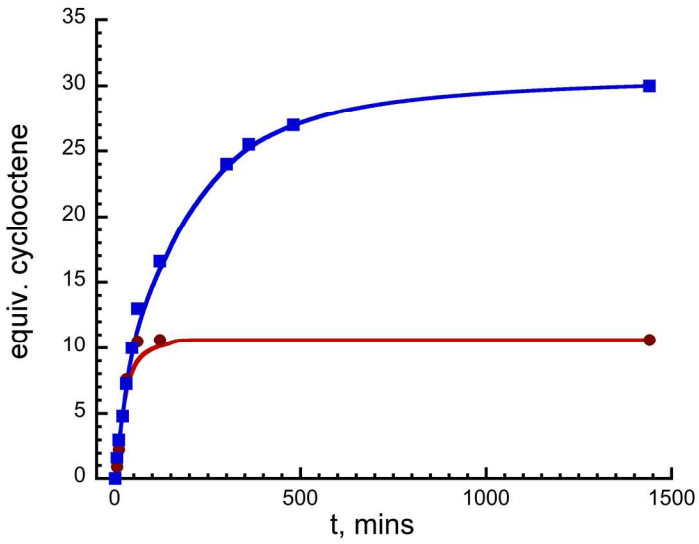


Figure 6. Acceptorless dehydrogenation catalyst activity for ($^{t\text{Bu,CF}_3}$PCP)Ru(nbd)H (■) and (^{CF_3}PCP)Ru(cod)H (●) (2.5 mmol catalyst loading) in cyclooctane under reflux conditions (~150 °C, 590 Torr N_2).

Previous alkane dehydrogenation studies of (PCP)Ir systems have been carried out under argon due to strong inhibition by nitrogen owing to the formation of stable bridged $Ir_2(\mu\text{-}N_2)$ products.[4,7] A key result of the previous work on alkane dehydrogenation by (^{CF_3}PCP)Ru(cod)H was the ability for the catalyst to function in a variety of environments.[10a] No change in initial rate or total turnovers was found when catalyst runs with (^{CF_3}PCP)Ru(cod)H were performed under N_2, vacuum, air, or in the presence of excess H_2O. A series of controls with ($^{t\text{Bu,CF}_3}$PCP)Ru(nbd)H over 24 h at 200 °C under vacuum, N_2, or in the presence of 100 equiv. H_2O also showed no notable change in initial rate, total turnovers, or decomposition products. Dehydrogenation activity in the presence of oxygen was not evaluated.

We have also examined the cyclooctane (coa) dehydrogenation activity of **2** at higher catalyst loading. As reported previously,[10a] thermolysis of 12.5 mM (0.33 mol %) (^{CF_3}PCP)Ru(cod)H in a 1:1 mixture of coa and *tert*-butylethylene at 200 °C showed minimal dehydrogenation activity. After the mixture was cooled to 20 °C, a red brown precipitate was observed and complete conversion to (μ-^{CF_3}PCPH)Ru(H)(μ-H)(μ-η^6,κ^3-^{CF_3}PCP)Ru(H) was indicated by ^{31}P and ^{19}F NMR. In contrast, thermolysis of 12.5 mM (0.33 mol%) of the asymmetric hybrid pincer catalyst ($^{t\text{Bu},CF_3}$PCP)Ru(nbd)H at 200 °C in 1:1 coa and *tert*-butylethylene produced 51 turnovers of cyclooctene after 6 h with an initial rate of 120 turnovers h^{-1} (**Figure 7**). ^{19}F NMR spectra of catalyst solution at this point show significant amount (~90%) of free $^{t\text{Bu},CF_3}$PCPH, but no significant resonances attributable to deactivation by dimer formation.

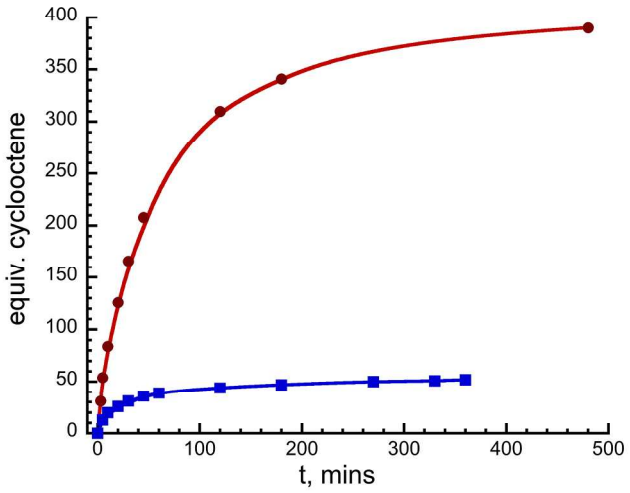


Figure 7. Catalyst activity of ($^{t\text{Bu},CF_3}$PCP)Ru(nbd)H, at 1.25 mM (●) and 12.5 mM (■) in 1:1 cyclooctane/tert-butylethylene at 200 °C.

Summary. New hybrid alkyl/perfluoroalkyl phosphine pincer ligands have been prepared and their ruthenium coordination chemistry has been examined. Unstable ($^{t\text{Bu,CF}_3}$PCP)Ru(*solv*)$_2$(H) is obtained by reacting $^{t\text{Bu,CF}_3}$PCPH with the labile Ru(0) precursor Ru(cod)(cot) in acetone at ambient temperatures under H_2. Subsequent addition of excess cod or nbd afforded ($^{t\text{Bu,CF}_3}$PCP)Ru(cod)(H) or ($^{t\text{Bu,CF}_3}$PCP)Ru(nbd)(H) in reasonable yield as the major products; these oily diastereomeric mixtures have proven difficult to purify further. ($^{t\text{Bu,CF}_3}$PCP)Ru(nbd)(H) (**2**) shows an initial cyclooctane dehydrogenation activity only ~50% that of ($^{\text{CF}_3}$PCP)Ru(cod)(H), however the catalytic lifetime is significantly increased, coe product inhibition is reduced, and catalytic activity under acceptorless conditions is slightly improved. The desirable N_2 and moisture stability of the parent acceptor system was effectively conferred to the donor/acceptor hybrid pincer catalysts. **2** shows reduced yet significant catalytic activity at higher catalyst loadings (0.33 mol%, 51 turnovers after 6 hours) whereas ($^{\text{CF}_3}$PCP)Ru(cod)(H) is inactive at this catalyst concentration. This suggests that the more sterically-hindered asymmetric catalyst **2** may prevent the formation of arene-bridged dimer which is responsible for the activity loss in ($^{\text{CF}_3}$PCP)Ru(cod)(H) system, but demetallation and loss of free $^{t\text{Bu,CF}_3}$PCPH at later stages of catalysis is observed and may be a limiting feature of this asymmetric hybrid system.

It is unfortunate that we were not able to address the initial guiding concept of preparing electronically yet stereochemically distinct *meso* and *rac* pincer complexes, since the stereoisomers could not be separated and compared in their pure forms. Nevertheless, while the stereochemical complexity introduced by the new hybrid pincer ligands in this work was not specifically exploited, these types of ligands may prove to be advantageous in future enantioselective chemistry.

Experimental Section.

General Procedures. All manipulations were conducted under N_2 or vacuum using high-vacuum-line and glovebox techniques unless otherwise noted. All ambient-pressure chemistry was carried out at approximately 590 Torr (elevation ~2195 m). Dry, oxygen free solvents were prepared using standard procedures and stored under vacuum. Aprotic deuterated solvents used in NMR experiments were dried over activated 3 Å molecular sieves. NMR spectra were obtained with a Bruker DRX-400 instrument using 5 mm NMR tubes fitted with Teflon valves (Chemglass, CG-512 or New Era CAV-VBP). ^{31}P spectra were referenced to an 85% H_3PO_4 external standard. ^{19}F spectra were referenced to a CF_3CO_2Et (δ −75.32) external standard. Elemental Analyses were performed using a Perkin Elmer Series II CHNS/O 2400 Analyzer. The compounds ^{t}BuPCl$_2$,[31] (^{t}Bu)(TMS)$_2$P,[32] 1-Trifluoromethyl-1,2-benziodoxol-3(1H)-one (Togni Reagent II),[33] Ru(cod)(η^3-2-methylallyl)$_2$,[34] and Ru(cod)(cot)[35] were prepared following published procedures. Me_3SiCF_3 and C_2F_5Cl were purchased from Synquest Labs, Inc., and $RuCl_3(H_2O)_3$ from Pressure Chemical Co.; all other reagents were purchased from Aldrich and were used without further purification.

(*t*-butyl)(trimethylsilyl)phosphine. To (^{t}Bu)(TMS)$_2$P (24.7 g, 0.105 mol) dissolved in 100 mL THF at 0 °C was added 4.2 mL (3.2 g, 0.11 mol) of methanol dissolved in 100 mL of THF via cannula over the course of 1h. After an additional 8 h at ambient temperature the THF, methoxytrimethylsilane, and a small amount (*ca* 10%) of side product ^{t}BuPH$_2$ were removed *in vacuo* and the crude product was purified by distillation (bp 40 - 45 °C, ~ 0.01 torr) to give a colorless liquid (9.24 g, 54.2 % yield). (^{t}Bu)(TMS)PH has been prepared previously by an alternate route.[36] ^{1}H NMR (C_6D_6, 400.13 MHz, 25 °C): δ 2.45 (br. d, J_{PH} = 192 Hz, 1H; PH), 1.22 (dd, $^3J_{HP}$ = 12.0 Hz, $^4J_{HP}$ = 2.1 Hz, 9H; C(CH$_3$)$_3$), 0.21 (dd, $^3J_{HP}$ = 4.3 Hz, $^4J_{HP}$ = 2.5 Hz 9H;

$Si(CH_3)_3$). ^{31}P NMR (C_6D_6, 161.97 MHz, 25 °C): δ −85.5 (d, J_{PH} = 192 Hz). *Caution*: (^{t}Bu)(TMS)PH is pyrophoric.

1,3-C_6H_4{$CH_2P(^tBu)(TMS)$}$_2$ (^{tBu,TMS}PCPH). To a solution of (^{t}Bu)(TMS)PH (7.14 g, 43.8 mmol) in 60 mL of THF was added 17.52 mL of a 2.5 M solution of *n*-BuLi (44 mmol) in hexanes at −30 °C. The reaction mixture was allowed to warm to ambient temperature and was stirred for 2 h. and then 5.50 g (20.8 mmol) of α, α′-dibromo-*m*-xylene dissolved in 40 mL of THF was added and the reaction mixture was stirred for 12 h at room temperature. The solvent and volatiles were removed and replaced by 30 mL of petroleum ether. The resulting precipitate was removed by filtration and removal of the filtrate solvent afforded $^{t\text{Bu,TMS}}$PCPH as an oily colorless liquid (6.68 g, 75.2% yield), which was judged by NMR to be a 3:2 mixture of *meso* and *rac* diastereomers, respectively. The crude mixture (> 95% pure, by ^{31}P NMR) was not purified further. ^1H NMR (C_6D_6, 400.13 MHz, 25 °C), ***meso* isomer:** δ 7.7 – 7.0 (m, 4H; ArH), 3.05 (d, $^2J_{AB}$ = 14 Hz, 2H; C$\underline{H}_A$H$_B$P), 2.92 (d, $^2J_{AB}$ = 14 Hz, 2H; CH$_A\underline{H}_B$P), 1.14 (d, $^3J_{PH}$ = 11.6 Hz, 18H; $C(CH_3)_3$), 0.14 (d, $^3J_{PH}$ = 3.9 Hz, 18H; $Si(CH_3)_3$); ***rac* isomer:** δ 7.7 – 7.0 (m, 4H; ArH), 3.04 (d, $^2J_{AB}$ = 14 Hz, 2H; C$\underline{H}_A$H$_B$P), 2.91 (d, $^2J_{AB}$ = 14 Hz, 2H; CH$_A\underline{H}_B$P), 1.14 (d, $^3J_{PH}$ = 11.6 Hz, 18H; $C(CH_3)_3$), 0.12 (d, $^3J_{PH}$ = 3.8 Hz, 18H; $Si(CH_3)_3$). ^{31}P NMR (C_6D_6, 161.97 MHz, 25 °C): δ −41.8 (br. s ($\nu_{½}$ = 80 Hz)); unresolved *meso* and *rac* resonances).

Reactions of $^{t\text{Bu,TMS}}$PCPH with CF_3I, *i*-C_3F_7I, and C_2F_5I. To solutions of $^{t\text{Bu,TMS}}$**PCPH**, prepared as described above, in 0.5 mL benzene-d_6 were added excess (4 equiv.) CF_3I and C_2F_5I by vacuum transfer and 4 equiv. *i*C_3F_7I by microliter syringe. NMR spectra after warming to ambient temperature for 2 h showed complete reaction; a complex product mixture was observed with C_2F_5I, but CF_3I and C_3F_7I afforded the major products 1,3-C_6H_4{$CH_2P(^tBu)(CF_2I)$}$_2$ ($^{t\text{Bu,CF}_2\text{I}}$PCPH, ~90%; ~3:1 ***meso*:*rac***) and 1,3-C_6H_4{$CH_2P(^tBu)(i C_3F_7)$}$_2$ ($^{t\text{Bu},i\text{C}_3\text{F}_7}$PCPH, ~70%;

~3:2 ***meso***:***rac***), respectively. The formation of Me_3SiF and Me_3SiI metathesis products was confirmed by ^1H and ^{19}F NMR. Isolation of these products on a preparative scale was not attempted. **^{tBu,CF_2I}PCPH data:** ^1H NMR (C_6D_6, 400.13 MHz, 25 °C), δ 7.4 – 6.8 (m, 4H; ArH), 3.23 (m, 2H; $C\underline{H}_AH_BP$; ***meso***), 2.85 (m, 2H; $CH_A\underline{H}_BP$; ***meso***), 3.4 – 2.7(m, 2H; CH_2P; ***rac***), 0.98 (d, $^3J_{PH}$ = 12 Hz, 18H; $C(CH_3)_3$; ***rac***), 0.96 (d, $^3J_{PH}$ = 12 Hz, 18H; $C(CH_3)_3$; ***meso***); ^{31}P NMR (C_6D_6, 161.97 MHz, 25 °C): δ 61.0 (m ($\nu_{½}$ = 135 Hz)); unresolved *meso* and *rac* resonances). ^{19}F NMR (C_6D_6, 376.50 MHz, 25 °C): δ -32.6 (dd, $^2J_{FF}$ = 186 Hz , $^2J_{PF}$ = 60 Hz, 2F; $P(C\underline{F}_aF_b)$; ***meso***), -32.6 (dd, $^2J_{FF}$ = 186 Hz, $^2J_{PF}$ = 19 Hz, 2F; $P(C\underline{F}_aF_b)$; ***rac***), -35.7 (dd, $^2J_{FF}$ = 186 Hz , $^2J_{PF}$ = 71 Hz, 2F; $P(CF_a\underline{F}_b)$; ***meso***), -35.8 (dd, $^2J_{FF}$ = 186 Hz, , $^2J_{PF}$ = 70 Hz, 2F; $P(CF_a\underline{F}_b)$; ***rac***). **^{tBu,iC_3F_7}PCPH data:** ^1H NMR (C_6D_6, 400.13 MHz, 25 °C), δ 7.3 – 6.8 (m, 4H; ArH), 3.34 (m, 2H; $C\underline{H}_AH_BP$; overlapping ***meso*** and ***rac***), 3.20 (m, 2H; $CH_A\underline{H}_BP$; overlapping ***meso*** and ***rac***), 1.09 (d, $^3J_{PH}$ = 12 Hz, 18H; $C(CH_3)_3$; ***rac***), 1.07 (d, $^3J_{PH}$ = 12 Hz, 18H; $C(CH_3)_3$; ***meso***); ^{31}P NMR (C_6D_6, 161.97 MHz, 25 °C): δ 41.6 (m ($\nu_{½}$ = 290 Hz)); unresolved *meso* and *rac* resonances). ^{19}F NMR (C_6D_6, 376.50 MHz, 25 °C): δ -72.8 (m, 6F; $PCF(C\underline{F}_3)_a(CF_3)_b$); ***meso*** and ***rac***), -73.2 (m, 6F; $PCF(CF_3)_a(C\underline{F}_3)_b$); ***meso*** and ***rac***), -179.9 (overlapping heptets, $^3J_{FF}$ = 12 Hz , 2F; $PC\underline{F}(CF_3)_a(CF_3)_b$); ***meso*** and ***rac***).

1,3-C_6H_4{$CH_2P(^tBu)(Cl)$}$_2$ (^{tBu,Cl}PCPH). To a solution of ^{tBu,TMS}PCPH (3.48 g, 8.15 mmol) in 30 mL of toluene was added 4.63 g (19.56 mmol) of C_2Cl_6 dissolved in 30 mL of toluene at 0 °C. The reaction mixture was stirred for an hour and then warmed up to room temperature and stirred for additional 1h. The volatiles were removed and the resulting white solid residue was extracted with petroleum ether and filtered. Removal of volatiles from the filtrate gave ^{tBu,Cl}PCPH as an oily white solid (1.70 g, 59.2 %), which was judged by NMR to be a 2:1 mixture of *meso* and *rac* diastereomers, respectively. The crude isomeric mixture (> 95% pure, by ^{31}P NMR) was not

purified further. ^{1}H NMR (C_6D_6, 400.13 MHz, 25 °C), ***meso* isomer:** δ 7.3 – 7.0 (m, 4H; ArH), 3.1 – 2.7 (m, 4H; overlapping *meso* and *rac* C$\underline{H}_A$H$_B$P multiplets), 0.97 (d, $^{3}J_{PH}$ = 12.8 Hz, 18H; C(CH$_3$)$_3$); ***rac* isomer:** δ 7.3 – 7.0 (m, 4H; ArH), 3.1 – 2.7 (m, 4H; overlapping *meso* and *rac* C$\underline{H}_A$H$_B$P multiplets), 0.99 (d, $^{3}J_{PH}$ = 12.5 Hz, 18H; C(CH$_3$)$_3$). ^{31}P NMR (C_6D_6, 161.97 MHz, 25 °C): δ 126.3 (br. s ($\nu_{½}$ = 70 Hz)); unresolved *meso* and *rac* resonances).

Alternative synthesis of $^{t\mathrm{Bu,Cl}}$PCPH. Following a modified literature procedure,[21] THF (100 mL) was added to a flask containing α,α'-dichloro-*m*-xylene (10.0 g, 57.2 mmol) and magnesium turnings (4.16 g, 172 mmol). The resulting mixture was stirred at room temperature for 5 h, then at 40 °C for an additional 17 h. The dark yellow-green solution was cooled to room temperature and then added dropwise to a solution of *tert*-butyldichlorophosphine (18.42 g, 115.8 mmol) in THF (100 mL) at −78 °C. The reaction mixture was allowed to warm to room temperature and then stirred for an additional 1 h. Volatiles were removed, 50 mL of petroleum ether was added and the resulting slurry was stirred for an hour. The slurry was allowed to stand undisturbed, and the separated liquid layer was transferred into a 100 mL round-bottom flask via cannula. Removal of petroleum ether from the filtrate gave an oily white solid (10.46 g, 52.4%) which was judged to be > 95% pure by NMR.

1,3-C$_6$H$_4${CH$_2$P(^{t}Bu)(OPh)}$_2$ ($^{t\mathrm{Bu,OPh}}$PCPH). To dry phenol (4.50 g, 47.9 mmol) dissolved in 100 mL of THF was added 6.66 mL of Et$_3$N (4.84 g, 47.9 mmol) via syringe, and the solution was cooled to 0 °C. $^{t\mathrm{Bu,Cl}}$PCPH (8.02 g, 22.8 mmol) dissolved in 100 mL of THF was added to the phenol/Et$_3$N/THF solution via syringe and precipitation of Et$_3$NHCl was observed. The reaction mixture was warmed to room temperature and stirred for additional 4 h. The resulting ammonium salt was removed by filtration and washed several times with THF. Removal of volatiles from the filtrate resulted in an oily colorless liquid (7.54 g, 71.4%), which was judged

by ^{31}P NMR to be a 3:1 mixture of *meso* and *rac* diastereomers, respectively. The crude isomeric mixture (~95% pure, by ^{31}P NMR, contaminated with ~ 0.12 equiv. THF) was not purified further. ^{1}H NMR (C_6D_6, 400.13 MHz, 25 °C), ***meso* isomer:** δ 7.4 – 6.7 (m, 14H; overlapping OPh and ArH), 3.08 (br. d, $^{2}J_{HH}$ = 14 Hz, 2H; *meso* C$\underline{H}_A$H$_B$P), 2.65 (m, 2H; overlapping CH$_A\underline{H}_B$P multiplets), 1.03 (dd, $^{3}J_{HP}$ = 12 Hz, J_{HH} = 1 Hz, 18H; C(CH$_3$)$_3$, *meso* isomer); ***rac* isomer:** δ 7.4 – 6.7 (m, 14H; overlapping OPh and ArH), 3.16 (dm, $^{2}J_{HH}$ = 14 Hz, 2H; *rac* C$\underline{H}_A$H$_B$P), , 2.65 (m, 2H; overlapping CH$_A\underline{H}_B$P multiplets), 1.08 (d, $^{3}J_{HP}$ = 12 Hz, 18H; C(CH$_3$)$_3$, *rac* isomer). ^{31}P NMR (C_6D_6, 161.97 MHz, 25 °C): δ 145.4 (s; *meso* isomer), 144.8 (s; *rac* isomer).

1,3-C$_6$H$_4${CH$_2$P(^{t}Bu)(CF$_3$)}$_2$ ($^{t\text{Bu,CF}_3}$PCPH). 3.54 mL CF_3SiMe_3 (3.40 g, 24.0 mmol) was added via syringe over the course of 15 min to a mixture of $^{t\text{Bu,OPh}}$PCPH (3.72 g, 7.97 mmol) and CsF (3.63 g, 23.9 mmol) in 30 mL diethyl ether at 0 °C. The reaction mixture was allowed to warm up to room temperature and stirred for 24 h, during which time the slurry turned from clear to dark brown with a white CsF suspension. The volatiles were removed and the resulting brown slurry was extracted with petroleum ether. Removal of volatiles and vacuum distillation to remove the silyl ether side product (80-83 °C, 25 Torr) gave >95% pure $^{t\text{Bu,CF}_3}$PCPH as a brown viscous oil (2.48 g, 74.1%), which was judged by integration of ^{t}Bu proton resonances to be a 4:1 mixture of *meso* and *rac* diastereomers, respectively. Anal. Calcd for $C_{18}H_{26}F_6P_2$: C, 51.68; H, 6.26. Found: C, 51.17; H, 6.04. ^{1}H NMR (C_6D_6, 400.13 MHz, 25 °C) ***meso* isomer:** δ 7.3 – 6.9 (m, 4H; overlapping ArH), 3.03 (dd, $^{2}J_{AB}$ = 14.5 Hz, $^{2}J_{HP}$ = 2.8 Hz, 2H; C$\underline{H}_A$H$_B$P), 2.73 (d, $^{2}J_{AB}$ = 14.5 Hz, 2H; CH$_A\underline{H}_B$P), 0.96 (d, $^{3}J_{HP}$ = 12.4 Hz, 18H; C(CH$_3$)$_3$). ***rac* isomer:** δ 7.3 – 6.9 (m, 4H; overlapping ArH), 3.08 (dm, $^{2}J_{AB}$ = 14.5 Hz, 2H; C$\underline{H}_A$H$_B$P), 2.76 (m, 2H; CH$_A\underline{H}_B$P), 0.98 (d, $^{3}J_{HP}$ = 12.2 Hz, 18H; C(CH$_3$)$_3$). ^{31}P NMR (C_6D_6, 161.97 MHz, 25 °C): δ 21.8 (m; *meso* and

rac isomers). ^{19}F NMR (C_6D_6, 376.50 MHz, 25 °C): δ -51.5 (d, $^{2}J_{PF}$ = 54 Hz; *meso* and *rac* $P(CF_3)$).

1,3-C_6H_4{$CH_2P(^tBu)(C_2F_5)$}$_2$ (^{tBu,C_2F_5}PCPH). 18.56 mL 2.5 M *n*-BuLi in hexanes (46.4 mmol) was transferred into a 500 mL three-neck flask fitted with a vacuum adapter and a digital thermometer probe. Hexanes were removed, the *n*-BuLi was redissolved in 125 mL of diethyl ether, and the solution was cooled to −90 °C. A 6.85 mL aliquot of C_2F_5Cl (bp −39 °C, density 1.568 g/mL, 69.6 mmol) was measured out in a calibrated volume at −80 °C and was slowly added to the *n*-BuLi solution by vacuum transfer so as to maintain the reaction temperature below −80 °C. After 30 min the addition was complete and the solution was stirred for an additional 1h. A solution of ^{tBu,Cl}PCPH (4.08 g, 11.6 mmol) dissolved in 30 mL of diethyl ether and 15 mL of THF was added by syringe under nitrogen over a period of *ca* 30 min to maintain the temperature below −80 °C. The solution turned brown during this time. After the addition was complete the mixture was maintained at −80 °C for an additional 1 h and then allowed to warm to room temperature. After 12 h at room temperature the solution was separated from the solids via cannula filtration. The solids were washed with diethyl ether (2×50 mL) and combined with the initial filtrate. Removal of volatiles afforded the crude product. The crude product was extracted with petroleum ether to give a yellow filtrate. Removal of petroleum ether yielded >95% pure product as a viscous yellow oil (3.92 g, 65.4%). ^{1}H and ^{19}F NMR indicate a 3:1 mixture of *meso* and *rac* diastereomers, respectively, as judged by the $C(CH_3)_3$ and CF_3 resonances. Anal. Calcd for $C_{20}H_{26}F_{10}P_2$: C, 46.34; H, 5.06. Found: C, 46.67; H, 4.74. ^{1}H NMR (acetone-d_6, 400.13 MHz, 25 °C): δ 7.4 – 6.9 (m, 4H; overlapping ArH; ***meso*** and ***rac***), 3.28 (overlapping AB patterns, 4H; CH_2P; ***meso*** and ***rac***), 1.32 (d, $^{3}J_{HP}$ = 12.8 Hz, 18H; $C(CH_3)_3$; ***meso***), 1.31 (d, $^{3}J_{HP}$ = 12.7 Hz, 18H; $C(CH_3)_3$; ***rac***). ^{31}P NMR (acetone-d_6, 161.97 MHz, 25 °C):

δ 19.7 (br. s; unresolved ***meso*** and ***rac***). ^{19}F NMR (acetone-d_6, 376.50 MHz, 25 °C): δ −82.3 (d, $^2J_{PF}$ = 16 Hz, 6F; C$\underline{F}_3$CF$_2$P; ***rac***), −82.4 (d, $^2J_{PF}$ = 16 Hz, 6F; C$\underline{F}_3$CF$_2$P; ***meso***), −114.6 (overlapping ABX multiplets, $^2J_{PF}$ = 294 Hz, 4F; CF$_3$C$\underline{F}_2$P).

(^{tBu,CF3}PCP)Ru(cod)(H). Ru(cod)(cot) (0.227 g, 0.721 mmol), ^{tBu,CF3}PCPH (0.302 g, 0.721 mmol) and 10 ml acetone were added to a 25 ml round bottom flask and placed under 1 atm of H_2. Stirring for 20 h at room temperature resulted in a deep brown solution. After removal of H_2 pressure, 440 μL of cyclooctadiene (0.389 g, 3.60 mmol) was added to the solution and the mixture was stirred for an additional 24 h under 1 atm of N_2. The solvent was removed and the brown residue was triturated with petroleum ether and stirred for an additional hour. A small amount of precipitate formed which was filtered off, and the brown filtrate volume was reduced to 5 mL in volume, cooled to −78 °C, and cold filtered to give initially a brown powder which melted to become a brown liquid at room temperature. The product purity was ~80%, along with ~10% free ^{tBu,CF3}PCPH and small amount of other unidentified side products, as judged by ^{31}P NMR. A second precipitation/cold filtration step gave ~90% pure product. Integration of ^{1}H NMR hydride resonances indicated 55:45 mixture of *meso* and *rac* stereoisomers. ^{1}H NMR (C_6D_6, 400.13 MHz, 25 °C): δ 7.1 – 6.7 (m, 3H; overlapping *meso* and *rac* ArH), 5.85 (br. s, 2H; vinylic cod), 5.83 (br. s, 2H; vinylic cod), 3.72 (dm, $^2J_{HP}$ = 16 Hz, 2H; C$\underline{H}_A$H$_B$P; ***meso***), 3.46 (dm, $^2J_{HP}$ = 16 Hz, 2H; CH$_A$$\underline{H}_B$P; ***meso***), 3.8 – 3.4 (m, 4H; CH$_2$P; ***rac***), 2.09 (m, 8H; aliphatic cod; overlapping ***meso*** and ***rac***), 1.41 (m, 18H; C(CH$_3$)$_3$; overlapping ***meso*** and ***rac***), −14.75 (tm, ^{2}J$_{HPa}$ ~ ^{2}J$_{HPb}$ = 24 Hz, 1H; RuH; ***rac***), −14.97 (t, $^2J_{HP}$ = 25 Hz, 1H; RuH; ***meso***). ^{31}P {H} NMR (C_6D_6, 161.97 MHz, 25 °C): δ 106.3 (br. s ($\nu_{½}$ = 70 Hz) unresolved ***meso*** and ***rac*** resonances).

^{19}F NMR (C_6D_6, 376.50 MHz, 25 °C): δ −51.1 (m, 6F; CF_3; ***meso***), −51.7 (d, $^2J_{PF}$ = 50 Hz, 3F; CF_3; ***rac***), −55.3 (d, $^2J_{PF}$ = 43 Hz, 3F; CF_3; ***rac***).

(*t*^{Bu,CF_3}PCP)Ru(nbd)(H) (2). Ru(cod)(cot) (0.300 g, 0.950 mmol), *t*^{Bu,CF_3}PCPH (0.397 g, 0.950 mmol) and 15 ml acetone were added to a 25 mL round bottom flask and placed under 1 atm of H_2. Stirring for 20 h at room temperature resulted in a deep brown solution. After removal of H_2 pressure, 488 μL of norbornadiene (0.442 g, 4.80 mmol) was added to the solution and the mixture was stirred for an additional 6 h under a N_2 atmosphere. The solvent was removed and the remaining brown residue was triturated with benzene and the resulting precipitate was removed by filtration and removal of benzene gave ~95% pure crude product along with ~5% free *t*^{Bu,CF_3}PCPH. The crude product was dissolved in 5 mL of petroleum ether and cooled to −78 °C; cold filtration and warming of the isolated solid gave (*t*^{Bu,CF_3}PCP)Ru(nbd)(H) as a brown highly viscous oil in > 95% purity, as judged by NMR. (0.220 g, 38.6%). ^{1}H, ^{31}P and ^{19}F NMR data indicate a 57:43 mixture of *meso* and *rac* stereoisomers. Anal. Calcd for $C_{25}H_{34}F_6P_2Ru$: C, 49.10; H, 5.60. Found: C, 49.59; H, 5.31. ^{1}H NMR (C_6D_6, 400.13 MHz, 25 °C): δ 7.1 – 6.7 (m, 3H; ArH, overlapping ***meso*** and ***rac***), 4.07 (br. s, 2H; ***meso***), 5.62 (m, 2H; ***rac***), 4.04 (br. s, 2H; ***meso***), 3.70 (br. s, 2H; ***meso***), 3.66 (br. s, 2H; ***meso***), 4.0 – 3.0 (m, 10H; overlapping nbd and ***rac*** CH_2P), 1.39 (d, $^2J_{HP}$ = 13 Hz, 9H; $PC(CH_3)_3$; ***rac***), 1.14 (d, $^2J_{HP}$ = 15 Hz, 9H; $PC(CH_3)_3$; ***rac***), 1.05 (pseudo t, J_{HP} = 15 Hz, 18H; $PC(CH_3)_3$; ***meso***), 0.96 (m, 2H; nbd CH_aH_b), −12.68 (tm, $^2J_{HPa}$ ~ $^2J_{HPb}$ = 29 Hz, 1H; RuH; ***rac***), −13.82 (t, $^2J_{HP}$ = 31 Hz, 1H; RuH; ***meso***). ^{31}P{^{1}H} NMR (C_6D_6, 161.97 MHz, 25 °C): δ 119.9 (d, $^2J_{PP}$ = 175 Hz, 1P; ***rac***), 116.0 (s; ***meso***), 114.1 (d, $^2J_{PP}$ = 175 Hz, 1P; ***rac***). ^{19}F NMR (C_6D_6, 376.50 MHz, 25 °C): δ −51.4 (d, $^2J_{FP}$ = 35 Hz, 3F; CF_3; ***rac***), −51.5 (pseudo t, J_{PF} = 19 Hz, 6F; CF_3; ***meso***), −55.9 (d, $^2J_{FP}$ = 35 Hz, 3F; CF_3; ***rac***).

Transfer Dehydrogenation Studies. A stock catalyst solution was prepared from 4.7 mg of the 57:43 ($^{t\text{Bu,CF}_3}$PCP)Ru(nbd)(H) isomeric mixture (7.7 μmol) and 3.14 mL of cyclooctane (3,030 equiv.). 250 μL of stock solution and 240 μL of *tert*-butylethylene (3,030 equiv.) were added via microliter syringe to a 5 mm medium wall NMR tube containing an acetone-d_6 capillary and sealed under vacuum. Thermolyses were carried out in an isothermal oven. NMR tubes were periodically removed from the oven and allowed to cool for at least 10 min and mixed thoroughly before taking NMR spectra. The equivalents of cyclooctene produced were calculated by integration of the product vinylic coe resonance at 4.96 ppm against the *tert*-butylethylene resonance at 5.18 ppm.

Acceptorless Dehydrogenation Studies. Mesitylene (7.0 μL, 6.5 equiv.) was added as an internal standard to the catalyst stock solution prepared as described above. The solution was refluxed under a N_2 atmosphere for the desired time before cooling to room temperature and withdrawing an aliquot for NMR analysis. The equivalents of cyclooctene produced were calculated by integration of the vinylic resonance at 4.96 ppm against the mesitylene CH_3 resonance at 1.44 ppm.

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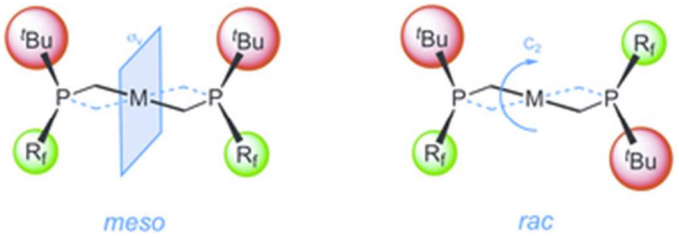

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