Appendix 1

Investigation of PXP Ligand Architecture in the Selective Trimerization of Ethylene

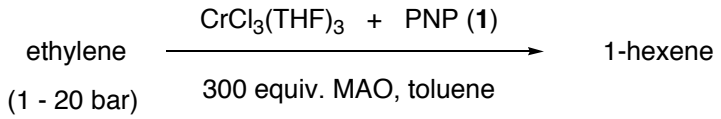
Abstract

Models of a chromium diphosphine catalyst for selective ethylene trimerization were prepared and investigated to gain molecular-level insight into the importance of the ligand backbone for successful catalysis. *Bis*(diarylphosphino)methane ligand $CH_2(P(C_6H_4(o\text{-}OCH_3))_2)_2$ (**9**), also called PCP, was originally demonstrated as being an inactive system for ethylene trimerization when associated with a chromium(III) source and an aluminoxane activator under ethylene. Chromium complex (PCP-d_{12})$CrPh_3$ (**10**) was synthesized and structurally characterized. When activated with a stoichiometric amount of $H[(OEt_2)_2B(C_6H_3(CF_3)_2)_4]$, complex **10** generates an active species for ethylene trimerization, albeit with low activity. Structural characterization established a highly distorted octahedral geometry around the chromium center leading to poor ligand biding. Equilibrium studies with analog (PNP-d_{12})$CrPh_3$ (**11**) (PNP-d_{12} = $N(CH_3)(P(C_6H_4(o\text{-}OCH_3))_2)_2$) show that chromium(III) preferentially binds the PNP ligand over PCP. Furthermore, IR spectra of chromium(0) complex (PCP-d_{12})$Cr(CO)_4$ (**12**) suggest that electronic effects are not a significant factor in the reduced activity when compared with the PNP analog.

Introduction

Linear α-olefins, such as 1-hexene and 1-octene, are used, among other applications, as comonomers in the production of linear low-density polyethylene (LLDPE). The conventional method of producing 1-hexene and 1-octene is by non-selective ethylene oligomerization, which leads to a Schulz-Flory distribution of linear α-olefins.[1,2] Over the last decade however, several reports have described catalytic systems that generate 1-hexene selectively (see Chapter 1, references 6-28). While some of these systems involve titanium (refs 17-19) and tantalum-based (ref 22) catalysts, the most common and successful systems involve chromium-based catalysts.

Wass and coworkers at BP Chemicals recently reported a highly active chromium diphosphine system that produces 1-hexene with unprecedented selectivity, particularly in the purity of the 1-hexene within its C_6 fraction (> 99.9% purity, Eq. 1).[3] Initial ligand screening suggested that two features were critical for catalytic activity (Figure 1). Firstly, a nitrogen atom was required in the ligand backbone, such that ligands **6** and **7** did not lead to an active catalyst system. The second requirement was the presence of ether functionalities at the *ortho* position of the phenyl groups on the phosphines. The presumed role of the ether groups was to act as hemilabile donors to the metal center and help stabilize the active species and other transition states involved during catalysis.



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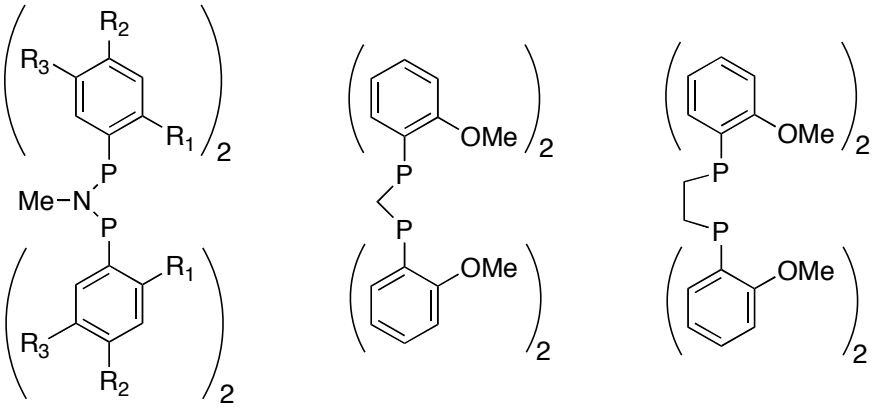


6 **7**

* **1**: R^1 = OMe, R^2 = R^3 = H
2: R^1 = Et, R^2 = R^3 = H
3: R^1 = R^3 = H, R^2 = OMe
* **4**: R^1 = R^3 = OMe, R^2 = H
* **5**: R^1 = OMe, R^2 = H, R^3 = F

* = active for trimerization

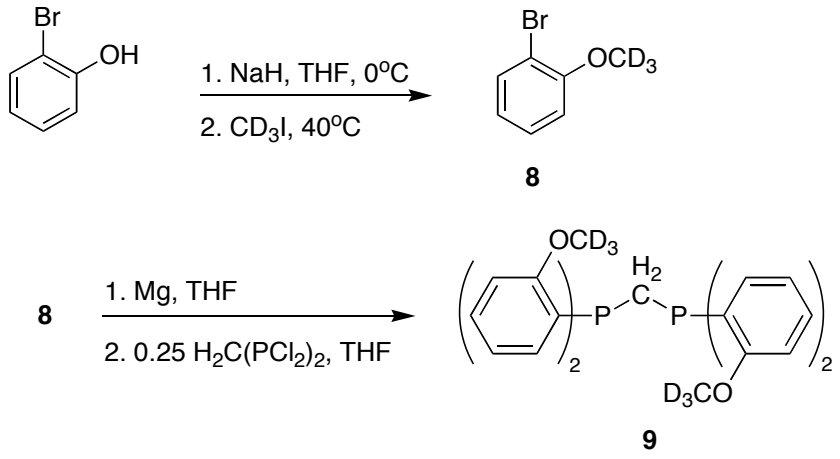
Figure 1. Ligands studied in the catalytic chromium system of ethylene trimerization.

In this report, we have investigated the requirements of a nitrogen atom in the ligand backbone for catalyst activity. By preparing chromium(III) and chromium(0) complexes supported by a ligand analogous to **6**, steric and electronic effects were evaluated as possible reasons for the differences in activity when a catalyst is supported by a PNP ligand compared to the PCP analog.

Results and Discussion

Due to the paramagnetic nature of the investigated chromium(III) complexes, appropriate deuteration of the diphosphine ligand was carried out as a strategic tool to obtain a handle on NMR studies. Incorporation of a deuterated methoxy group on the

ligand was accomplished by initial methylation of the appropriate bromophenolate salt with CD_3I (Scheme 2). The generated bromoanisole **(8)** was then reacted with Mg, after which the resulting Grignard reagent was added to a solution of $H_2C(PCl_2)_2$ to afford the desired PCP-d_{12} ligand **(9)**.

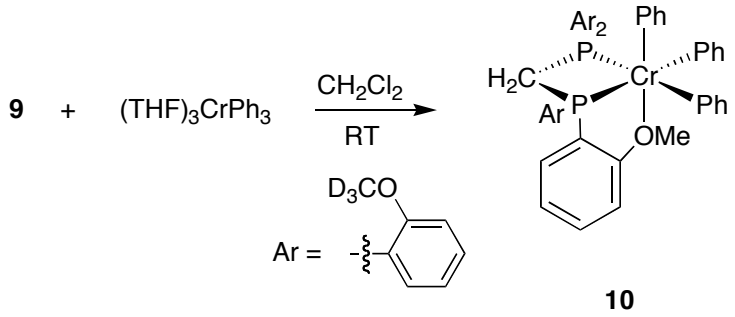


Scheme 1. Synthesis of ligand **9**.

The synthesis was rendered difficult due to facile phosphine oxidation as well as coordination of magnesium salts. However, careful handling under an argon atmosphere and work up in the glovebox, followed by treatment with dioxane in order to separate salt byproducts afforded the desired compound in pure form and moderate yield (52%).

Metalation on a chromium(III) species was obtained by the reaction of $(THF)_3CrPh_3$ with a CH_2Cl_2 solution of **9** (Eq. 2). The resulting complex, (PCP-d_{12})$CrPh_3$ **(10)**, was isolated as a reddish-brown powder in low to moderate yield (40%). A single-crystal X-ray diffraction study confirmed the coordination of the chromium complex as a

(P,P,O)-κ^3 coordination mode (Figure 2), which had already been established for the (PNP-d_{12})$CrPh_3$ (**11**) analog reported previously.[4]



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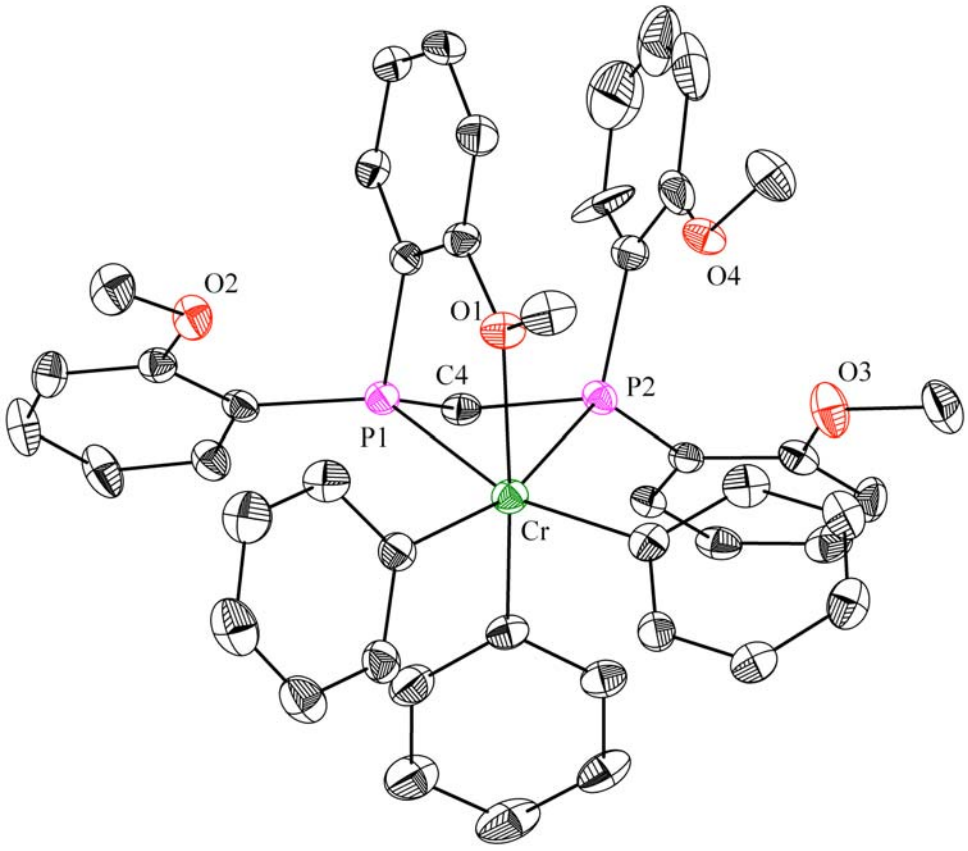


Figure 2. Structural drawing of **10** with displacement ellipsoids at the 50% probability level. Selected bind lengths (Å) and angles (°): Cr-P1, 2.4888(7); Cr-P2, 2.8828(7); Cr-O1, 2.2101(15); P1-Cr-P2, 62.51(1); P1-C4-P2, 100.14(1).

Structurally, complexes **10** and **11** display interesting differences: while in both cases the Cr-P bond involving the methoxy-bound aryl group is shorter than the other Cr-P bond, this difference in length is almost twice as large in the case of **10**. The Cr-P2 bond distance in **10** (2.8828(7) Å) is the longest ever reported and may even stand close to the limit of an actual bond, even though the value lies within the van der Waals radii. An additional feature contrasting the two complexes is the P-X-P angle (100.14^{o}), which in the case of **10** is almost 6^{o} smaller than in **11**. This sharp angle leads to a more accentuated distortion of the octahedral geometry around the metal center. The ligand is thus not tightly bound to the chromium center, which was supported by an equilibrium experiment, whereby a CH_2Cl_2 solution containing a 1:1 mixture of **10** and free ligand PNP-d_{12} was allowed to reach equilibrium (Eq. 3). A ^{31}P NMR spectrum was acquired, which revealed that $K_{eq}(RT) = [\mathbf{11}]/[\mathbf{10}] = 2.36 \pm 0.08$, further highlighting the lability of ligand **9** on the chromium center. Variable temperature ^{2}H NMR was used to study the solution behavior of complex **10**. As described previously, studies on analogous complexes suggest the presence of a dynamic process involving exchange of the ether groups for coordination to the chromium center.[5] At room temperature, complex **10** displays one peak at 11.65 ppm in the ^{2}H NMR spectrum. Upon cooling, decoalescence processes are observed (Figure 3). At –70˚C, one broad paramagnetically-downshifted peak corresponding to the coordinated methoxy group and another peak in the diamagnetic region corresponding to the other three unbound methoxy groups in a 1:3 ratio are observed.

$$(\text{PCP-}d_{12})\text{CrPh}_3 \;+\; \text{PNP-}d_{12} \;\underset{}{\overset{K_{eq}(RT)}{\rightleftharpoons}}\; (\text{PNP-}d_{12})\text{CrPh}_3 \;+\; \text{PCP-}d_{12} \qquad (3)$$

10 **11** **9**

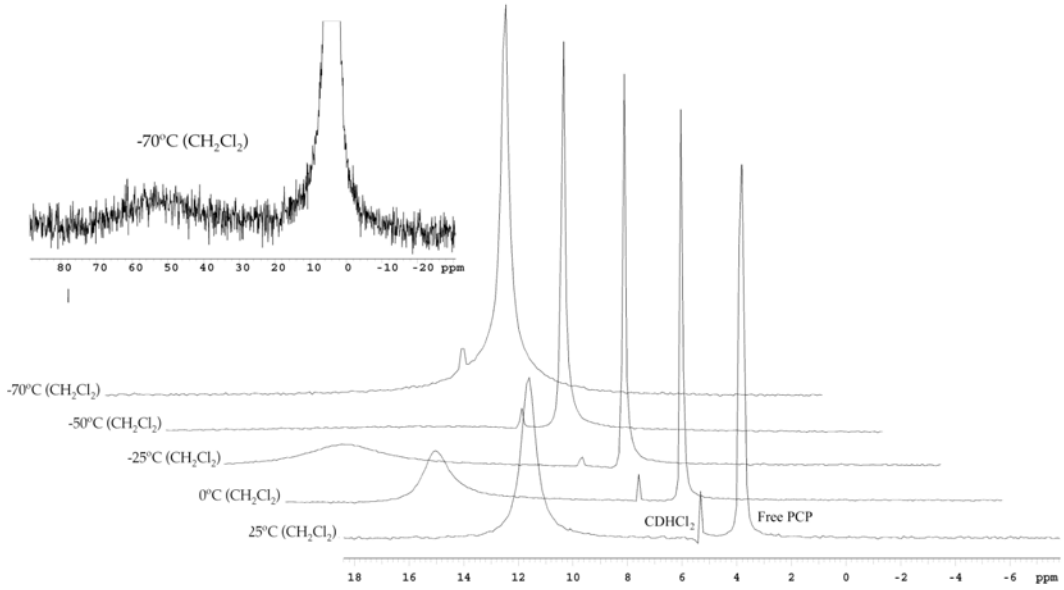


Figure 3. Variable temperature ^{2}H NMR of **10**.

In order to compare the electronic effects from the ligand in complexes **10** and **11**, a chromium(0) species bearing **9** was prepared (Eq. 4). Reaction of **9** with $Cr(CO)_6$ in toluene at 110˚C for 36 hours affords in good yield (70%) the desired complex (PCP-d_{12})$Cr(CO)_4$ (**12**) as a yellow crystalline solid, for which an X-ray structure determination was obtained (Figure 4). Spectroscopic data is consistent with a (P,P)-κ^2 coordination mode, without involvement of the ether groups. The average CO stretching frequency for the four CO normal modes is 1913 cm^{-1} (CD_2Cl_2), which is only three wavenumbers lower than the corresponding (PNP-d_{12})$Cr(CO)_4$ analog **13** prepared previously (Table

1).[5] These results suggest that electronic effects do not play a significant role in altering the reactivity of complex **10** in the ethylene trimerization reaction.

Table 1. CO stretching frequencies of **12** and related carbonyl complexes (in CD_2Cl_2).

Complex	ν(CO) (cm^{-1})	$\nu(CO)_{avg}$ (cm^{-1})
$Cr(CO)_4[CH_2(P(o\text{-}MeOC_6H_4)_2)_2]$ (**12**)	2000, 1908, 1883, 1859	1913
$Cr(CO)_4[MeN(P(o\text{-}MeOC_6H_4)_2)_2]$ (**13**)	2003, 1906, 1886, 1867	1916
$Cr(CO)_4[CH_2(PPh_2)_2]$	2011, 1918, 1903, 1878	1927
$Cr(CO)_4[MeN(PPh_2)_2]$	2008, 1917, 1895, ~1881	1925

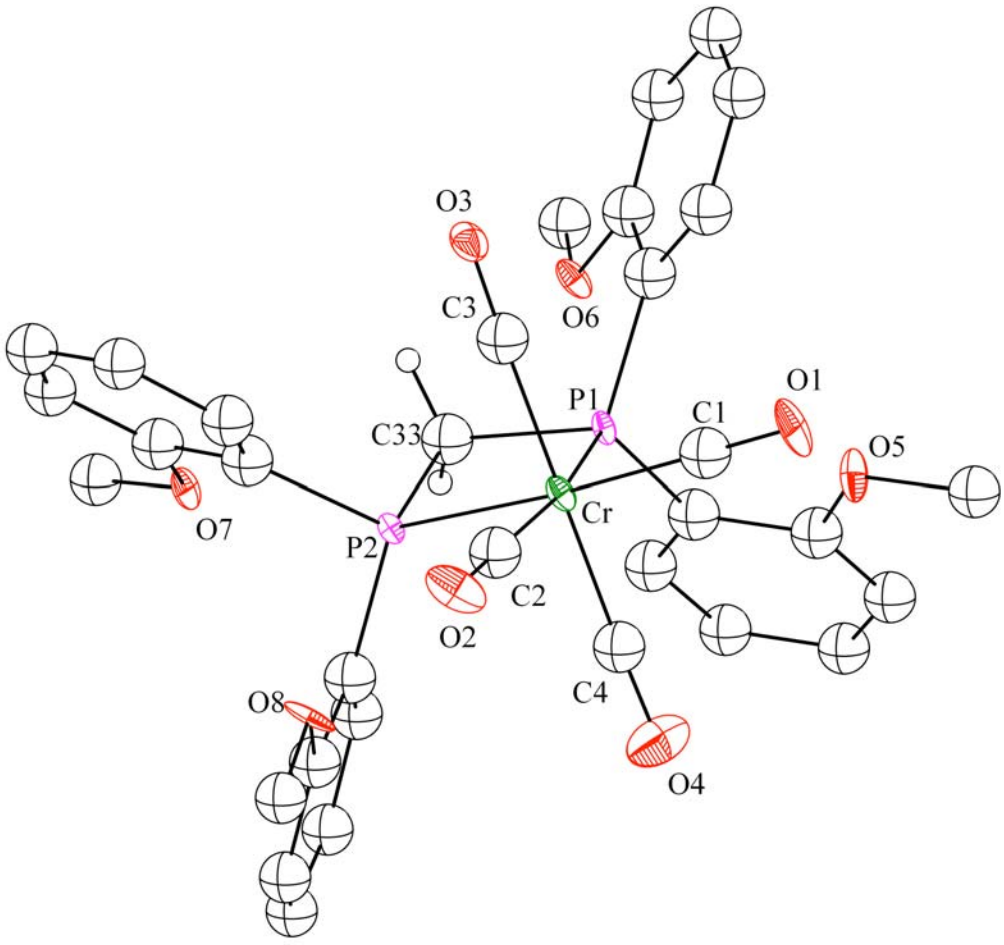
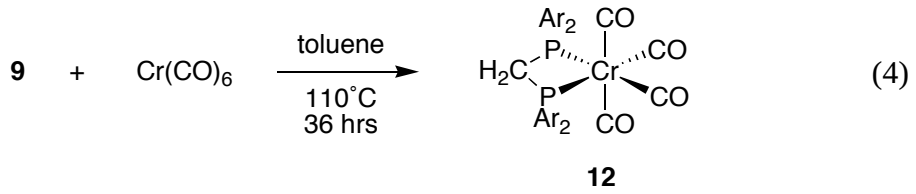
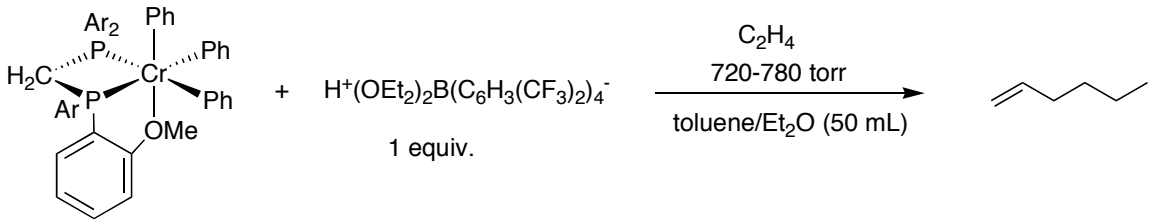


Figure 3. Structural drawing of **12** with displacement ellipsoids at the 50% probability level. Selected bond lengths (Å) and angles (°): Cr-P1, 2.3619(14); Cr-P2, 2.3519(14); P1-C33, 1.8282(40); P2-C33, 1.8299(41); P1-Cr-P2, 71.56(4); P1-C33-P2, 97.78(20).



(4)

Complex **10** was also tested for activity in the selective trimerization of ethylene. In about 50 mL of toluene were added 0.02 mmol of **10** and one equivalent of $H[(OEt_2)_2B(C_6H_3(CF_3)_2)_4]$ as a stoichiometric activator. Various amounts of diethyl ether were also added to increase solubility and concentration of coordinating donor to the vacant site on chromium (Scheme 3). On the high vacuum line, the reaction flask was subjected to an atmosphere of ethylene. After the system had reached saturation, the valve to the ethylene tank was closed and its consumption recorded on a mercury manometer in a similar manner as described in Chapter 1. Various conditions, such as amounts of Et_2O added and temperature, were investigated, as is depicted in Table 2. High turnover numbers were never obtained, however, contrary to initial claims, this system does exhibit catalytic activity towards selective trimerization of ethylene. Turnovers of up to 45 $mol_{1\text{-}hex}/mol_{Cr}$ were obtained in about 18 hours of reaction (entry 1), while 19 turnovers were achieved in less than two hours when more Et_2O was added (entry 3).



10
0.02 mmol

Scheme 2. Selective trimerization of ethylene using **10** as the precatalyst.

Table 2. Trimerization reactions using precatalyst **10**.

Entry	Solvent Toluene/Et_2O (mL)	Solvent Dried over Na/Ph_2CO	Temperature (˚C)	Reaction Time (min)	Total Turnover (mol 1-hex / mol Cr)
1	48/2	No	25	1099	44.6
2	48/2	Yes	-78	156	0
3	45/5	Yes	25	106	18.6
4	30/20	No	25	90	9.8
5	40/10	Yes	25	90	8.9

Conclusions

From the catalytic runs performed using precatalyst **10**, it is now reasonable to believe that the nature of the heteroatom in PXP is not required to be nitrogen as previously claimed by Wass and coworkers. However, while the system investigated herein does exhibit catalytic activity for the selective trimerization of ethylene, activity remains significantly lower than similar reactions using analogous **11**. IR spectra of chromium(0) complexes bearing ligands **9** and PNP-d_{12} have suggested that electronic effects do not play an important role in the difference in catalytic activity between the

two systems. On the other hand, the crystal structure of **10** as well as equilibrium studies involving **10** and **11** suggest that geometric effects are at least partly responsible for the drastic change in ethylene trimerization activity. The small P-C-P angle, compared to the analogous P-N-P, presumably causes an overly distorted octahedral geometry of the chromium(III) complex, which consequently leads to poor ligand binding.

Experimental Section

General Considerations. All air- and moisture-sensitive compounds were manipulated using standard vacuum line, Schlenk, or cannula techniques or in a glovebox under a nitrogen atmosphere. All gases were purified by passage over MnO on vermiculite and activated molecular sieves. Ethereal solvents were stored over sodium benzophenone ketyl, and halogenated solvents were dried over calcium hydride. Dichloromethane-d_2, toluene-d_8, and chloroform-*d* were purchased from Cambridge Isotopes and dried over sodium benzophenone ketyl. Other materials were used as received. $CH_2(PCl_2)_2$ and $(THF)_3CrCl_3$ were obtained from Aldrich.

Instrumentation. ^1H and ^{31}P NMR spectra were recorded on a Varian Mercury 300 spectrometer at 299.868 MHz and 121.389 MHz respectively, at room temperature. ^2H NMR spectra were recorded on a Varian INOVA 500 spectrometer at 499.852 MHz at indicated temperatures. All ^1H NMR chemical shifts are reported relative to TMS, and ^1H (residual) chemical shifts of the solvent are used as secondary standard. ^{31}P NMR chemical shifts are reported relative to an external H_3PO_4 standard. ^2H NMR chemical shifts are reported with respect to $CDHCl_2$ (natural abundance, 5.32 ppm) from the

CH_2Cl_2 solvent. GC measurements were taken on an Agilent 6890 Series GC using an Agilent HP-5 column. X-ray crystallography was carried out by Dr. Michael W. Day and Lawrence M. Henling using an Enraf-Nonius CAD-4 diffractometer. IR spectra were recorded on a Nicolet 6700 FT-IR spectrometer.

Synthesis of 2-Bromoanisole-*d_3* (8). In the glovebox, dry NaH (4.139 g, 172 mmol, 1.2 equiv.) was placed in a 500 mL bomb. On the vacuum line approximately 250 mL of THF was added to the bomb *via* vacuum transfer. The bomb was placed on the Schlenk line, and 2-bromophenol (16.6 mL, 143 mmol, 1 equiv.) was added *via* syringe at 0˚C. Dihydrogen evolution was observed. After this reaction was allowed to warm to room temperature and stir for 2-3 hours, CD_3I (10.6 mL, 166 mmol, 1.2 equiv.) was added *via* syringe. The bomb was sealed and protected from light, and the reaction was heated to 40˚C for 36 hours. The product was quenched with aqueous NH_4Cl and isolated by a basic aqueous workup to give 23.923 g of 2-bromoanisole-*d_3* in 88% yield. The compound was dried over CaH_2 overnight and distilled under full vacuum.

Synthesis of PCP-*d_{12}* (9). In the glovebox, a Schlenk flask was charged with magnesium turnings (1.412 g, 58 mmol, 1.1 equiv.) and equipped with a reflux condenser. Dry THF (125 mL) was added to the flask via vacuum transfer. Neat 2-bromoanisole-*d_3* (10.038 g, 53 mmol, 1 equiv.) was added slowly via syringe. A crystal of I_2 was added to initiate the Grignard reaction. The reaction was heated to 40˚C overnight. The Grignard solution was added dropwise via cannula to a solution of $(Cl_2P)_2CH_2$ (2.300 g, 10.6 mmol, 0.2 equiv.) in dry THF (~50 mL). A white precipitate crashed out of solution within minutes of reaction. The mixture was allowed to react overnight under stirring, after which all

volatiles were pumped off. In the glovebox, CH_2Cl_2 was added with a large excess of dioxane to crash out all magnesium salts. The mixture was filtered through celite and the filtrate pumped on. The resulting mixture was recrystallized from CH_2Cl_2/MeOH (~1:10) in the absence of air to give 2.815 g of a fine white powder, PCP-d_{12} in 52% yield. ^{1}H NMR (RT, 300 MHz, C_6D_6): δ = 3.20 (2H, t, J_{HP} = 3.8 Hz, C*H*$_2$), 6.44 – 6.50 (4H, m, Ar*H*), 6.85 – 6.93 (4H, m, Ar*H*), 7.08 – 7.19 (4H, m, Ar*H*), 7.67 – 7.75 (4H, m, Ar*H)*. ^{31}P NMR (RT, 121 MHz, $CDCl_3$): δ= -40.78 ppm (s). ^{2}H NMR (RT, 500 Mhz, CH_2Cl_2): δ = 3.85 ppm (s). MS (FAB+): 517 (M+H).

Synthesis of (PCP-d_{12})$CrPh_3$ (10). In the glovebox, compound **9** (0.456 g, 0.88 mmol, 1 equiv.) was dissolved in 10 mL of dichloromethane. Portions of $(THF)_3CrPh_3$ (0.771 g, 1.55 mmol, 1.75 equiv) were added as a slurry in THF to the stirring solution of **9** over 5 minutes. The color of the mixture turned deep red instantaneously. Volatile materials were removed *in vacuo* and the residue triturated in CH_2Cl_2 twice to remove any trace of tetrahydrofuran. The resulting solid was recrystallized twice from CH_2Cl_2/petroleum ether to give 0.273 g of a reddish-brown powder in 39% yield. ^{2}H NMR (RT, 500 Mhz, CH_2Cl_2): δ = 11.65 ppm (s, OC*D*$_3$). X-ray quality crystals of **10** were obtained from slow diffusion of petroleum ether into a concentrated CH_2Cl_2 solution of the complex at – 35˚C.

Synthesis of (PCP-d_{12})$Cr(CO)_4$ (12). In a bomb were placed compound **9** (0.100 g, 0.194 mmol) and $Cr(CO)_6$ (0.043 g, 0.194 mmol) in toluene (20 mL). The reaction mixture was allowed to stir at 110^{o}C for 36 hours. The resulting yellow solution was stripped off any volatiles and the yellow residue recrystallized from CH_2Cl_2/THF to

afford 0.092 g of the complex in 70% yield. ^{1}H NMR (RT, 300 MHz, toluene-d_8): δ = 4.58 (2H, t, J_{HP} = 9.7 Hz, CH_2), 6.75 – 6.88 (4H, m, ArH), 6.91 – 7.06 (4H, m, ArH), 7.28 – 7.41 (4H, m, ArH), 7.62 – 7.74 (4H, m, ArH). ^{31}P NMR (RT, 121 MHz, toluene-d_8): δ = 16.98 ppm (s). IR (CD_2Cl_2): ν_{CO} (cm^{-1}) = 2000, 1908, 1883, 1859. X-ray quality crystals of **12** were obtained from slow diffusion of tetrahydrofuran into a concentrated CH_2Cl_2 solution of the complex at –35˚C.

Equilibrium studies of 10 and 11. Two experiments were run; in a first experiment, a J-Young tube was charged with **10** (7.5 mg, 0.0094 mmol) and PNP-d_{12} (5.0 mg, 0.0094 mmol) and dissolved in CH_2Cl_2. The mixture was was shaken for 1.5 hrs until equilibrium was reached. A ^{31}P NMR spectrum was obtained, which showed 2 peaks corresponding to **9** and PNP-d_{12} in a ratio of 2.441:1. In a second experiment, a J-Young tube was charged with **11** (10.3 mg, 0.0126 mmol) and **9** (6.5 mg, 0.0126 mmol) and dissolved in CH_2Cl_2. After 1.5 hrs, a ^{31}P NMR spectrum was obtained which showed two peaks as **9** and PNP-d_{12} in a ratio of 2.273:1. The $K_{eq,avg}$(RT) was calculated as the average between the two values obtained: $K_{eq,avg}$(RT) = 2.36 ± 0.08.

References

1) Vogt, D. *Applied Homogeneous Catalysis with Organometallic Compounds*; Cornils, B., Herrmann, W. A., Eds.; VCH: Weinheim, Germany, **1996**, Vol. 1, 245.

2) Skupinska, J. *Chem. Rev.* **1991**, *91*, 613.

3) Carter, A.; Cohen, S. A.; Cooley, N. A.; Murphy, A.; Scutt, J.; Wass, D. F. *Chem. Commun*. **2002**, 858.

4) Schofer, S. J.; Day, M. W.; Henling, L. M.; Labinger, J. A.; Bercaw, J. E. *Organometallics* **2006**, *25*, 2743.

5) Agapie, T.; Day, M. W.; Henling, L. M.; Labinger, J. A.; Bercaw, J. E. *Organometallics* **2006**, *25*, 2733.