Design and Preparation of a Novel Tetraphosphine Ligand for Use in the Hydroformylation of 1-Alkenes

Alexandre R. Monteil and George G. Stanley*
Department of Chemistry, Louisiana State University and Agricultural and Mechanical College, Baton Rouge, LA 70803-1804 (USA)
*gstanley@lsu.edu

Introduction

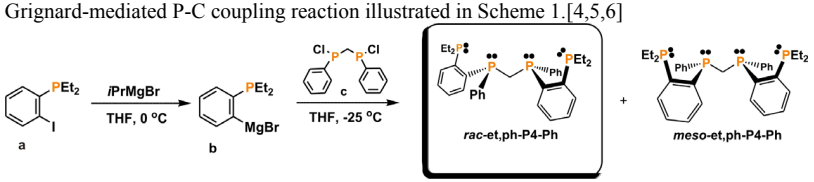
We have developed a bridging tetraphosphine ligand, *rac*-et,ph-P4 ($PEt_2(CH_2)_2P(Ph)CH_2(Ph)P(CH_2)_2PEt_2$) designed to tether two rhodium metal centers and generate a stereochemically favorable environment for bimetallic cooperativity to occur [1]. The reaction of *rac*-et,ph-P4 with 2 equiv. of $[Rh(nbd)_2]^{2+}$ (nbd = norbornadiene) generates the catalyst precursor $[rac\text{-}Rh_2(nbd)_2(et,ph\text{-}P4)]^{2+}$, and subsequent reaction with H_2/CO leads to the formation of the highly active and regioselective (initial TOF of 30 min^{-1}, l:b ratio of 33:1) key dihydrido catalyst species $[rac\text{-}Rh_2H_2(\mu\text{-}CO)_2(et,ph\text{-}P4)]$, **1r**, in the hydroformylation of 1-hexene [2]. *In situ* high-pressure NMR studies have strongly indicated that facile fragmentation occurs under the mild catalytic conditions (90 °C, 90 psig 1:1 H_2/CO) to generate very poor hydroformylation catalysts [3]. The fragmentation of the bimetallic catalyst **1r** was also shown to occur at 25 °C under H_2/CO, albeit at a much slower rate. This is a serious problem that we are attempting to address through the design of a more robust, sterically enforced and far more strongly chelating modified tetraphosphine ligand *rac*-et,ph-P4-Ph ($PEt_2(o\text{-}C_6H_4)P(Ph)CH_2$-$(Ph)P(o\text{-}C_6H_4)PEt_2$). This new ligand should generate a faster and possibly more regioselective catalyst with the rhodium metal centers as compared to our current tetraphosphine ligand.

Materials and Methods

All manipulations were carried out under inert atmosphere of nitrogen and in oven-dried glassware using a glovebox or by using standard Schlenk techniques. All solvents were obtained anhydrous and in high purity from commercial sources. The characterization of the products was performed by ^{31}P, ^{1}H, and ^{13}C NMR spectroscopies on a Bruker DPX-250 spectrometer. Catalytic experiments were performed in 150 mL stainless steel autoclaves from Parr operated by Parr 4870 process controllers. The progress of the reaction was monitored by gas uptake from the higher pressure gas storage reservoir connected to a two-stage regulator delivering synthesis gas at a constant pressure of 90 psig to the reaction vessel. Products were analyzed using an Agilent 6890N/5975B GC/MS system.

Results and Discussion

The successful preparation of *rac*-et,ph-P4-Ph has been efficiently achieved via the Grignard-mediated P-C coupling reaction illustrated in Scheme 1.[4,5,6]



Scheme 1. Preparation of *rac,meso*-et,ph-P4-Ph via Grignard-mediated P-C coupling reaction.

The novel tetraphosphine ligand *rac,meso*-et,ph-P4-Ph (Figure 1a) was characterized by single crystal X-ray crystallography as the dinickel complex *meso*-Ni_2Cl_4(et,ph-P4-Ph) (Figure 1b).

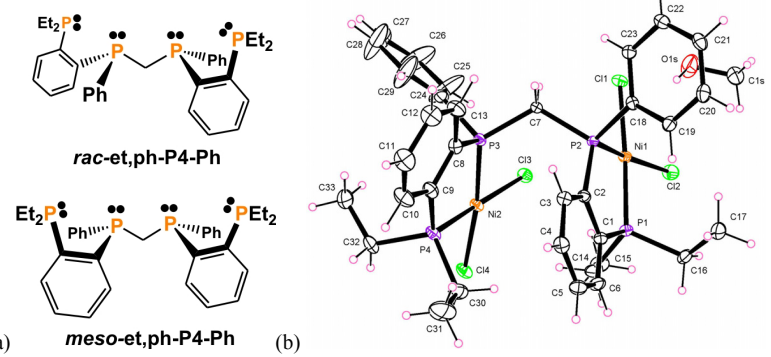


Figure 1. (a) Structure of the new tetraphosphine ligands *rac,meso*-et,ph-P4-Ph. **(b)** X-ray structure of the dinickel complex *meso*-Ni_2Cl_4(et,ph-P4-Ph).

Significance

The new tetraphosphine ligand is expected to generate a far more robust bimetallic catalyst system with rhodium and thus increase the reactivity of the catalyst with respect to the hydroformylation of 1-alkenes due to the lower propensity of this system to generate inactive fragments under catalytic conditions. This will be tested in the hydroformylation of 1-hexene, and the results will be compared to those obtained with the previously established system $[rac\text{-}Rh_2(nbd)_2(et,ph\text{-}P4)]^{2+}$ under identical catalytic conditions.

References

1. Laneman, S.A., Fronczek, F.R., and Stanley, G.G. *J. Am. Chem. Soc.* 110(16), 5585 (1988).
2. Aubry, D.A., Bridges, N.N., Ezell, K., and Stanley, G.G. *J. Am. Chem. Soc.* 125(37), 11180 (2003).
3. (a). Hunt, C., Jr., Nelson, B.D., Harmon, E.G., Fronczek, F.R., Watkins, S.F., Billodeaux, D.R., and Stanley, G.G. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* C56(5), 546 (2000). (b). Hunt, C. Jr., Fronczek, F. R., Billodeaux, D. R., and Stanley G. G. *Inorg. Chem.* 40(20), 5192 (2001).
4. (a). Boymond, L., Rottlander, M., Cahiez, G., and Knochel, P. *Angew. Chem. Int. Ed.*37(12), 1701 (1998). (b). Gommermann, N., Koradin, C., and Knochel, P. *Synthesis* 14, 2143 (2002).
5. Langhans, K.P., and Stelzer, O. *Chem. Ber.* 120(10), 1707 (1987).
6. Weferling, N.*Z. Anorg. Allg. Chem.* 548, 55 (1987).