

1. PRF# 57690-ND3
2. Project Title: Nickel and Cobalt Ethylene Polymerization Catalysts Supported by Novel Macrocyclic Phosphine Ligands
3. Christopher C. Cummins, Massachusetts Institute of Technology

The goal of this project is to develop an innovative phosphorus ligand framework for nickel and cobalt ethylene polymerization catalysts that addresses steric crowding of the axial metal coordination sites – a feature that prevents premature dissociation of the polymer chain. While previous diphosphine ligand designs, such as 1,2-bis(di-tert-butylphosphino)methane (dtbpm), increase steric bulk on phosphorus substituents in order to block the axial sites of the metal center, we proposed to use the ligand backbone as a blocking group. We aimed to synthesize a macrocyclic diphosphine group that would more effectively accomplish this goal by virtue of rigid aromatic groups situated in the axial positions.

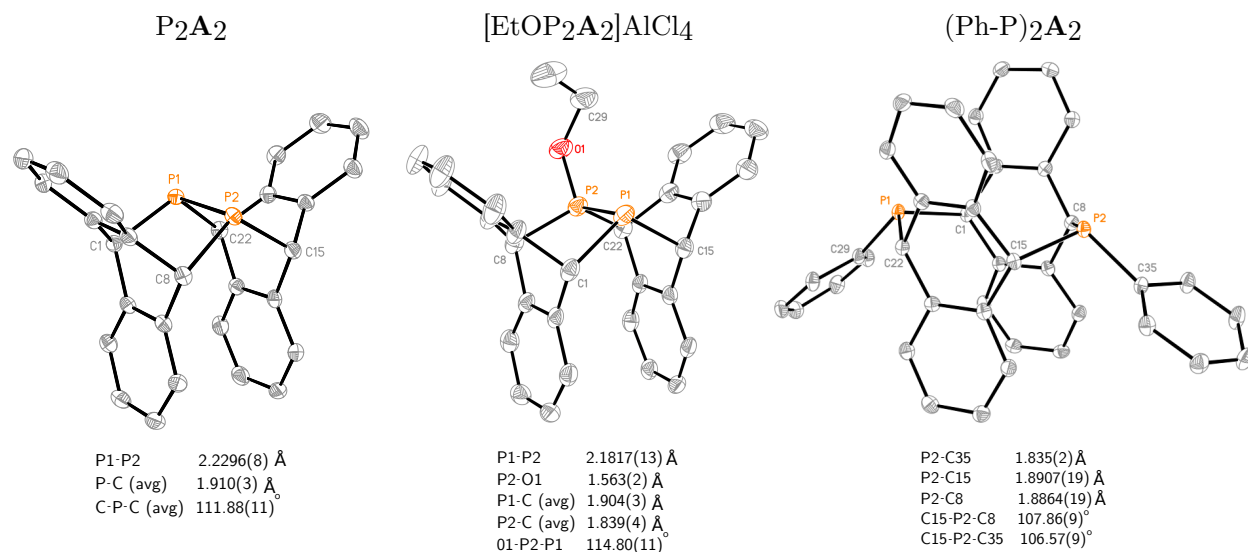


Figure 1: Molecular structure of  $P_2A_2$ ,  $[EtOP_2A_2]AlCl_4$ , and  $(Ph-P)_2A_2$  with hydrogen atoms omitted for clarity and thermal ellipsoids shown at 50% probability level.

When identifying potential ligand frameworks, we were drawn to the protruding anthracene rings of  $P_2A_2$  (Fig. 1,  $A = C_{14}H_{10}$  or anthracene), a diphosphane that harbors a  $P_2$  unit at the junction of fused dibenzodiphosphabicycloocta[2.2.2]-diene bicycles recently reported by our group.  $P_2A_2$  can be accessed by initially coupling two 7-phosphadibenzonorbornadiene groups, yielding  $[XP_2A_2]AlCl_4$  (Fig. 1,  $X = EtO-$  or  $Cl-$ ), followed by reduction using lithium aluminum hydride (LAH). We found that by substituting LAH for two equivalents of Grignard reagent, disubstitution, along with P–P bond cleavage, is observed (Fig. 2). Due to the availability of a variety of Grignard reagents, this synthetic method allows us elegantly tune steric bulk in the equatorial plane. The derivatives  $(R-P)_2A_2$  ( $R = Me, Ph, n-Bu,$  and  $Mes$ ), have been isolated and characterized by NMR spectroscopy. The molecular structure of  $(Ph-P)_2A_2$  was also determined (Fig. 1) by single-crystal X-ray diffraction.

Treatment of  $(Ph-P)_2A_2$  with  $NiCl_2 \cdot DME$  yields a pseudo-square-planar nickel complex (Fig. 3) with a ligand bite angle of  $88.43(3)^\circ$  and a notably large  $\%V_{bur}$ , a parameter often used to quantify ligand steric effects. While  $\%V_{bur}$  for  $(dtbpe)NiCl_2$  ( $dtbpe = 1,2$ -bis(di-tert-butylphosphino)ethane)

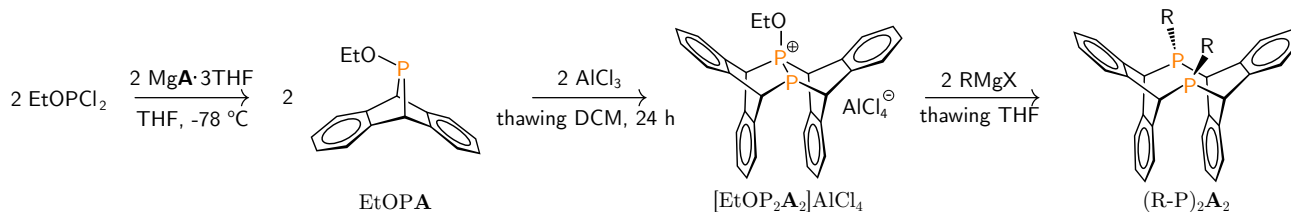


Figure 2: Synthesis of  $(R-P)_2A_2$  starting from  $EtOPCl_2$  and  $MgA \cdot 3THF$

and  $(dtbpm)NiCl_2$  ( $dtbpm = 1,2$ -bis(di-*tert*-butylphosphino)methane) are  $\%V_{bur} = 58.4\%$  and  $54.5\%$  respectively, that of  $(Ph-P)_2A_2NiCl_2$  is  $61.4\%$  (Fig. 3). Upon inspection of the steric map of  $[(Ph-P)_2A_2]NiCl_2$ , our anthracene-based diphosphine ligand is quite distinct from diphosphines that contain an alkyl backbone. As predicted, the substituents of  $(Ph-P)_2A_2$  are oriented in both the axial and equatorial planes of the square planar nickel center. In contrast, steric bulk in  $dtbpm$  lie between those planes (Fig. 3).

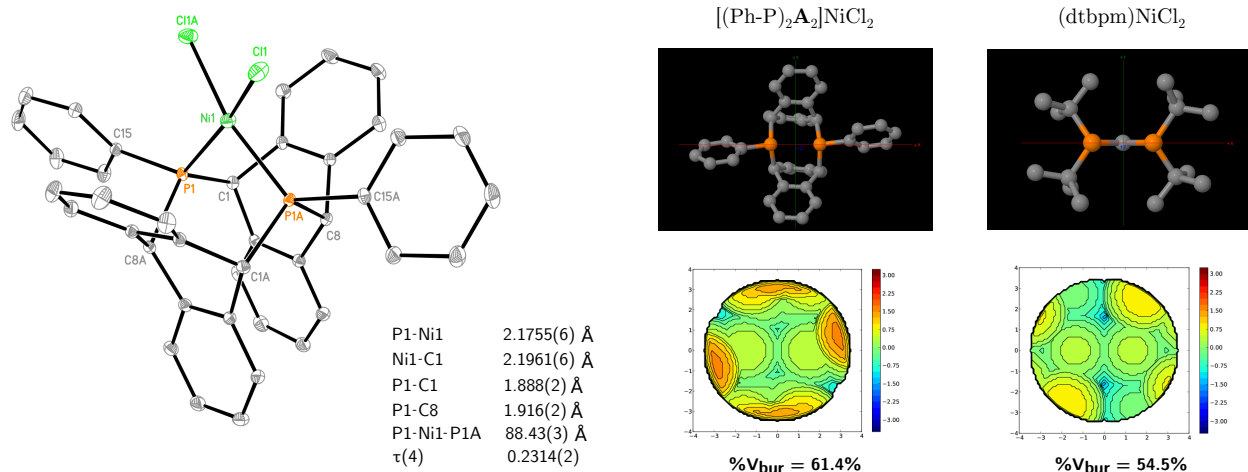


Figure 3: Molecular structure structure of  $[(Ph-P)_2A_2]NiCl_2$  with hydrogen atoms omitted for clarity and thermal ellipsoids shown at 50% probability level and a comparison of  $\%V_{bur}$  and steric maps for  $[(Ph-P)_2A_2]NiCl_2$  and  $(dtbpm)NiCl_2$ .

In addition, we found that treatment of this dichloride with  $K[B(C_6F_5)_4]$  results in chloride abstraction and formation of a cationic nickel complex (Fig 3). The structure of this deep red compound was determined by X-ray crystallography and contains a  $Ni_2(\mu-Cl)_2$  core. While we have been able to synthesize a variety of metal dichloride diphosphine complexes using this ligand, attempts to synthesize organometallic nickel complexes are ongoing in our lab.

**Impact on Student and Career:** This project has allowed my group to make significant progress in a new direction, seeding future lines of inquiry within my lab. For the student, Martin-Louis Riu, this represents a major milestone on the pathway to the Ph.D. His original research discoveries, made in carrying out the experiments described above, form the basis for several impactful publications and presentations at national/international conferences. It is fair to say that this PRF funding has kickstarted Martin's career as a scientist.