

Final Report for Award DE-SC0021403 "Catalytic Conversion of Ethylene to Value-added Materials"

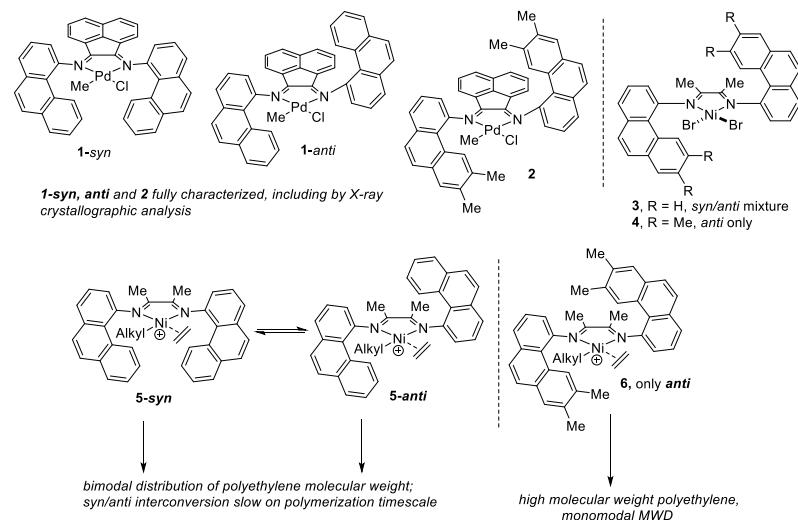
Olafs Daugulis (PI), Maurice Brookhart (Co-PI)

Department of Chemistry, University of Houston, Houston, TX 77204-5003

In accordance with project objectives, we have designed and synthesized a variety of new bidentate ligand platforms and their associated Ni(II) and Pd(II) catalyst systems. New catalysts include systems bearing unusual "capping" ligands and zwitterionic ligands whose complexes are particularly stable and ultimately may allow copolymerizations of ethylene with polar vinyl monomers. Mechanistic features of the new catalyst systems have been probed. Furthermore, we have polymerized norbornene in a living fashion, producing polymers which are end-capped with -OH or -CHO groups. The research has been published in four peer-reviewed publications.

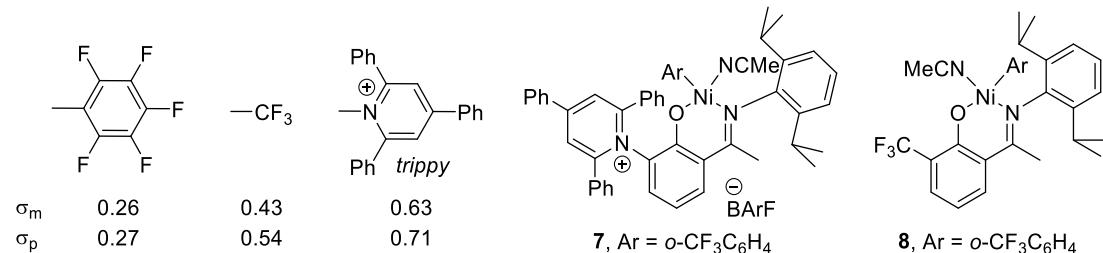
1. "Cationic α -Diimine Nickel and Palladium Complexes Incorporating Phenanthrene Substituents: Highly Active Ethylene Polymerization Catalysts and Mechanistic Studies of Syn/Anti Isomerization" Tran, Q. H.; Wang, X.; Brookhart, M.; Daugulis, O. *Organometallics* **2020**, *39*, 4704-4716.

α -Diimine palladium and nickel complexes incorporating phenanthryl substituents have been synthesized and tested in polymerization of ethylene. The (α -diimine)PdMeCl complex **1** bearing the unsubstituted phenanthrylimino groups exist as a mixture *syn* and *anti* isomers in a ca. 1:1 ratio. Separation and X-ray diffraction analysis of **1-syn** and **1-anti** isomers confirms the assignments. The barrier to interconversion of **1-syn** and **1-anti** via ligand rotation, ΔG^\ddagger , was found to be 25.5 kcal/mol. The corresponding (diimine)PdMeCl complex incorporating the more bulky 6,7-dimethylphenanthrylimino group exists solely as the *anti* isomer **2**, due to steric crowding which destabilizes the *syn* isomer. Analogous (diimine)NiBr₂ complexes incorporating the phenanthrylimino group, **3**, and the 6,7-dimethylphenanthrylimino group, **4** were also prepared. Nickel-catalyzed polymerizations of ethylene were carried out by activation of the dibromide complexes **3** and **4** using aluminum alkyl activators. Complex **3** yields a bimodal distribution polymer, the low molecular weight fraction originating from the *syn*-**5** active species and the high molecular weight fraction arising from the *anti*-**5** isomer. Polymerizations carried out by **4** yield only high molecular weight polymers with monomodal distributions due to the existence of a single *anti*-**6** isomer as the active catalyst. Catalysts derived from **4** are exceptionally active and exhibit turnover frequencies up to 5×10^6 per hour (40 °C, 27.2 atm ethylene, 15 min).



2. "2,4,6-Triphenylpyridinium: A Bulky, Highly Electron-Withdrawing Substituent Which Enhances Properties of Nickel(II) Ethylene Polymerization Catalysts" Janeta, M.; Heidlas, J. X.; Daugulis, O.; Brookhart, M. *Angew. Chem., Int. Ed.* **2021**, *60*, 4566–4569.

This work reports the first use of the 2,4,6-triphenylpyridinium substituent, which we designate “trippy”, for electronic and steric modification of late transition metal complexes. This unique substituent possesses both strong electron-withdrawing power and exceptional steric bulk. The electron-withdrawing power as judged by the Hammett σ -meta and -para substituent constants is substantially greater than that for either the trifluoromethyl or the perfluorophenyl groups which are routinely used to enhance reactivity in late transition metal olefin polymerization catalysts. The high steric bulk of trippy compared to these fluorinated substituents is used to advantage in the Ni system to shield axial sites and retard chain transfer as well as to diminish catalyst decomposition pathways. Specifically, due to the stronger electron-withdrawing nature of trippy the turnover frequency of catalyst **7** is 8-fold greater than that of **8** incorporating the common trifluoromethyl substituent in short runs. Chain transfer is effectively retarded resulting in a four-fold increase in polymer molecular weight relative to **2**. Furthermore, the trippy group lengthens catalyst lifetime, presumably due to increasing the barrier to second-order catalyst decay. We believe trippy group will find extensive use in polymerization catalyst design.

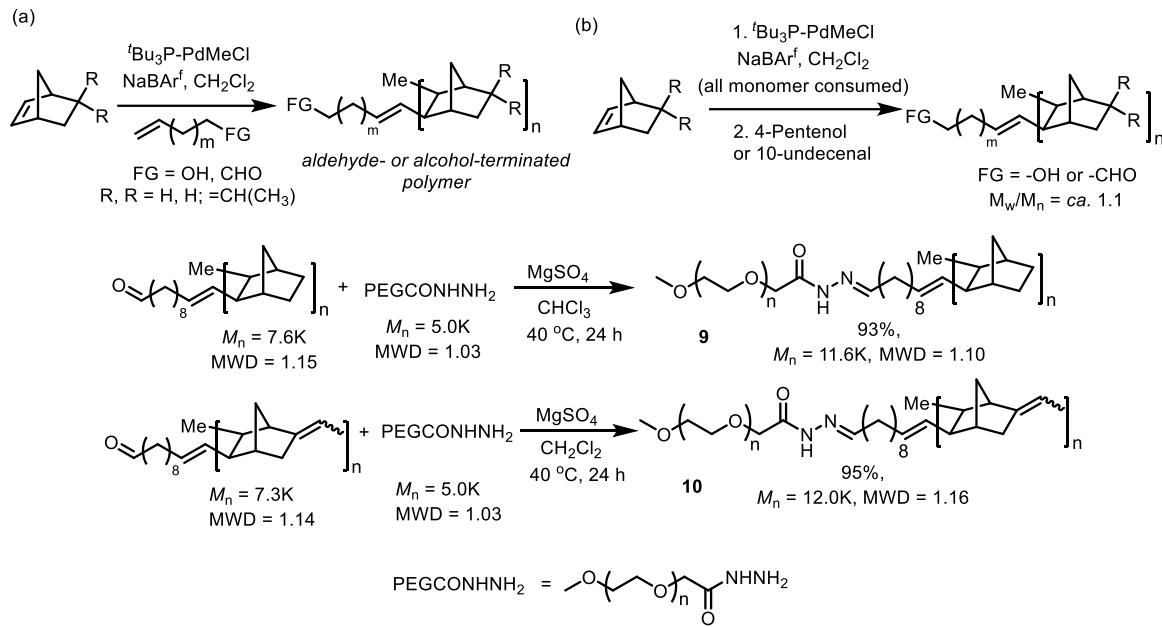


Polymerization results: 13.6 atm ethylene, 19 °C, 25 eq B(C₆F₅), 10 μmol catalyst, 4 hours.

Catalyst **7**: TOF (h⁻¹) = 13,000; M_n (g/mol) = 14,000;
 Catalyst **8**: TOF (h⁻¹) = 980; M_n (g/mol) = 3,500.

3. “Synthesis of End-Functionalized Poly(norbornenes) and Poly(ethylidene norbornenes) Using a Pd(II) Catalyst in Combination with Chain Transfer Agents” Han, X-W.; Daugulis, O.; Brookhart, M. *Organometallics* **2021**, *40*, 2709–2715.

Building on our earlier work for installing aldehyde end groups in polyolefins we investigated routes to synthesize end-functionalized poly(norbornenes). We found that using palladium catalyst t-Bu₃PPdMeCl/NaBAR_f (Ar_f = (3,5-(CF₃)₂C₆H₃)₄) in combination with 4-penten-1-ol and 10-undecenal produces poly(norbornenes) end-capped with -OH or -CHO groups with high efficiency. Norbornene is polymerized in a living fashion with the palladium catalyst and, when the chain transfer olefin inserts, β -elimination occurs to yield the end-functionalized polynorbornene and the palladium hydride which initiates a new chain. No unfunctionalized homopolymer is formed. The average molecular weight of the end-capped polymers can be controlled by the ratio of the chain transfer agent to the norbornene monomer. The aldehyde-terminated poly(norbornene) (PNB) and poly(ethylidene norbornene) (PENB) were efficiently coupled to poly(ethylene glycol) (PEG) to yield interesting ambiphilic diblock copolymers, PNB-b-PEG **9** and PENB-b-PEG **10**, consisting of a hydrophilic, low T_g PEG block and a hydrophobic very high T_g (ca. 250–300 °C) PNB (or PENB) block. Clearly these easily prepared end-functionalized poly(norbornenes) provide a convenient route to numerous interesting block copolymer structures which have potential uses as compatibilizers for blending polar and nonpolar polymers.



4. “Copper Iodide-Mediated Synthesis of α -Diimine Ligands from Bis(imidoyl Chlorides) and Arylstannanes” Lieu, T.; Daugulis, O. *Organometallics* **2022**, *41*, 3249–3256.

We have often encountered difficulties in polyfluoroaryl-substituted α -diimine preparation. Recently, we reported a method for aryl-substituted α -diimine synthesis by means of an operationally simple copper iodide-mediated Stille-type coupling between polyfluoro(chloro)aryl tributylstannanes and bis(imidoyl chlorides). Reaction conditions are simple and robust, proceeding in commercial grade *N*, *N*-dimethylformamide at 70 °C and requiring no additives or bases. Couplings are successful for aryl stannanes possessing two or more fluoro or chloro substituents on the aromatic ring. This methodology allows for a simple synthesis of α -diimine ligands potentially useful in olefin polymerization.

