# Final Technical Report for DOE Grant No. DE-FG02-00ER15036-A009

**Title of Project:** Electrophilic Metal Alkyl Chemistry in New Ligand Environments

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## A. Project Objectives

The goals of this project were to design new electrophilic metal alkyl complexes and to exploit these systems in fundamental studies of olefin polymerization and other important and new catalytic reactions. A key target reaction is insertion copolymerization of olefins and polar $CH_2$=CHX vinyl monomers such as vinyl halides and vinyl ethers. During the period covered by this report we (i) investigated the properties of ortho-alkoxy-arylphosphine ligands in Ni-based olefin polymerization catalysts, (ii) studied the synthesis of double-end-capped polyethylene using group 4 metal catalysts that contain tris-pyrazolylborate ligands, (iii) explored the ethylene insertion reactivity of group 4 metal tris-pyrazolyl-borate complexes, (iv) showed that (α-diimine)$PdMe^+$ species undergo multiple insertion of silyl vinyl ethers, (v) synthesized and explored the reactivity of base-free Ni benzyl complexes that contain ortho-phosphino-arene sulfonate ligands, (vi) established the mechanism of the reaction of vinyl chloride with (α-diimine)$PdMe^+$ catalysts, (vii) explored the role of cationic polymerization and insertion chemistry in the reactions of vinyl ethers with (α-diimine)$PdMe^+$ species, (viii) discovered a new class of self-assembled tetranuclear Pd catalysts that produce high molecular weight linear polyethylene and copolymerize ethylene and vinyl fluoride, and (ix) developed model systems that enabled investigation of cis-trans isomerization of {phosphine-sulfonate}Pd(II) complexes.

## B. Results

*(i) Synthesis, Structures, Dynamics and Ethylene Polymerization Activity of Nickel Complexes Containing an Ortho-methoxy-aryl Diphosphine Ligand.* The Ni coordination chemistry of $\{(2\text{-OMe-4-Me-Ph})_2P\}_2NMe$ (**2**, PNP) has been studied. The reaction of (dimethoxyethane)$NiBr_2$ with **2** yields {PNP}$NiBr_2$ (**3**, 75 %). The reaction of $Ni(cod)_2$ (cod = 1,5-cyclooctadiene) with two equiv of **2** affords $\{PNP\}_2Ni$ (**4**, 61%). The reaction of $Ni(cod)_2$ with one equiv of **2** yields {PNP}Ni(cod) (**5**, 90 %) via initial formation of **4** (50 %), followed by comproportionation with $Ni(cod)_2$. X-ray crystallographic analyses of **3** and **4** show that the methoxy groups do not coordinate to Ni but reveal the presence of weak CH---Ni interactions involving the ortho aryl hydrogens, and weak CH-π interactions involving the OMe hydrogens and the aryl rings. The reaction of **5** with $[H(OEt_2)_2][B(3,5\text{-}(CF_3)_2C_6H_3)_4]$ or $[H(OEt_2)_2][B(C_6F_5)_4]$ generates a cationic species formulated as $\{PNP\}Ni(codH)^+$ (**6**) based on ESI-MS data. Cation **6**, generated *in situ* from $Ni(cod)_2$/**2**/$[H(OEt_2)_2][B(3,5\text{-}(CF_3)_2C_6H_3)_4]$ or **5**/$[H(OEt_2)_2][B(C_6F_5)_4]$, catalyzes ethylene polymerization.

*(ii) Synthesis of Double-End-Capped Polyethylene by a Cationic Tris(pyrazolyl)borate Zirconium Benzyl Complex.* The cationic complexes $Tp^*Zr(CH_2Ph)_2^+$ (**I**, $B(C_6F_5)_4^-$ salt; Tp* =

$HB(3,5\text{-}Me_2\text{-pyrazolyl})_3$) and $\{(PhCH_2)(H)B(\mu\text{-}Me_2pz)_2\}Zr(\eta^2\text{-}Me_2pz)(CH_2Ph)^+$ (**II**; $Me_2pz$ = 3,5-$Me_2$-pyrazolyl) polymerize ethylene at –78 to –60 °C to linear polyethylene (PE) without significant chain transfer. For **I**, chain growth takes place at only one benzyl group. Quenching these polymerizations with MeOH yields benzyl-capped PE ($PhCH_2(CH_2CH_2)_nCH_2CH_3$). Quenching **I**-catalyzed ethylene polymerization with $Br_2$ yields double-end-capped PE containing benzyl and bromo chain ends ($PhCH_2(CH_2CH_2)_nCH_2CH_2Br$). DFT calculations on model catalysts show that ethylene insertion into a Zr-$\eta^2$-$CH_2Ph$ bond requires greater structural distortion than insertion into a Zr-$CH_2CH_2CH_2Ph$ bond. The calculations also show that the β-H transfer to monomer and β-H elimination chain transfer pathways are both strongly disfavored for **I**, but the β-H transfer to monomer path may be possible for **II**.

*(iii) Synthesis and Reactivity of a Sterically Crowded Tris(pyrazolyl)borate Hafnium Benzyl Complex.* The reaction of $Hf(CH_2Ph)_4$ and $Tl[Tp^{Ms*}]$ ($Tp^{Ms*}$ = HB(3-mesityl-pyrazolyl)$_2$(5-mesityl-pyrazolyl)$^-$) yields $Tp^{Ms*}Hf(CH_2Ph)_3$ (**1**), bibenzyl, and $Tl^0$ via ligand exchange followed by thermal decomposition of $Tl[CH_2Ph]$. **1** reacts with $[H(OEt_2)_2][B(C_6F_5)_4]$ to form $Tp^{Ms*}Hf(CH_2Ph)_2(OEt_2)^+$ (**2**, 100%) and with $[Ph_3C][B(C_6F_5)_4]$ or $B(C_6F_5)_3$ to form an unstable species characterized by NMR as $Tp^{Ms*}Hf(CH_2Ph)_2^+$. **1**/$[Ph_3C][B(C_6F_5)_4]$ behaves similarly to $Tp^{Ms*}HfCl_3$/MAO in olefin polymerization, producing high molecular weight, linear PE and ethylene/1-hexene copolymer with good hexene incorporation. These results are consistent with the proposal that similar cationic $Tp^{Ms*}Hf(X)R^+$ species (X = Cl or R) are active species in these catalysts. Ethylene polymerization by **1**/$[Ph_3C][B(C_6F_5)_4]$ at low temperature proceeds without significant chain transfer, enabling the synthesis of bromo benzyl double-end-capped linear PE ($PhCH_2(CH_2CH_2)_nBr$).

*(iv) Multiple Insertion of a Silyl Vinyl Ether by (α-diimine)PdMe+ Species.* We discovered that (α-diimine)$PdMe^+$ species (**1**) (α-diimine = $(2,6\text{-}{}^iPr_2\text{-}C_6H_3)N{=}CMeCMe{=}N(2,6\text{-}{}^iPr_2\text{-}C_6H_3)$) undergo multiple insertions of $CH_2{=}CHOSiPh_3$ (**2**), ultimately forming Pd allyl products. The reaction of (α-diimine)PdMeCl, $[Li(Et_2O)_{2.8}][B(C_6F_5)_4]$ (1 equiv), and **2** (8 equiv) in $CH_2Cl_2$ yields $[(\alpha\text{-diimine})Pd\{\eta^3\text{-}CH_2CHCHCH(OSiPh_3)CH_2CH(OSiPh_3)Me\}][B(C_6F_5)_4]$ (**7**-$B(C_6F_5)_4$) in 83% NMR yield. **7** is formed as a 95/5 mixture of isomers (**7a**/**b**), which converts to an equilibrium 40/60 mixture at 23 °C. X-ray diffraction analysis established that the configuration of the kinetically favored isomer **7a** is *S,S,S* (*ent-R,R,R),* where the descriptors refer to the configurations of the substituted allyl carbon and the side chain methine carbons, respectively. **7b** has an *R,S,S* (*ent-S,R,R)* configuration and differs from **7a** in that the Pd is coordinated to the opposite allyl enantioface. The reaction of (α-diimine)PdMeCl, $Ag[SbF_6]$ (**1** equiv), and **2** (8 equiv) under the same conditions yields $[(\alpha\text{-diimine})Pd\{(\eta^3\text{-}CH_2CHCHCH(OSiPh_3)Me)\}][SbF_6]$ (**8**-$SbF_6$) in 90-100% NMR yield. **8** is formed as a 90/10 mixture of isomers (**8a**/**b**) that differ in the configuration of the substituted allyl carbon and evolve to a 70/30 equilibrium mixture at 23 °C. These results are consistent with a mechanism involving generation of **1** and insertion of **2** to give $(\alpha\text{-diimine})PdCH_2CH(OSiPh_3)Me^+$ (**4**). In the absence of **2**, 4 undergoes β-$OSiPh_3$ elimination and allylic C-H activation to give $(\alpha\text{-diimine})Pd(\eta^3\text{-}CH_2CHCH_2)^+$ (**6**) and $Ph_3SiOH$. In the presence of excess **2**, **4** undergoes a second insertion of **2** to form $(\alpha\text{-diimine})Pd\{CH_2CH(OSiPh_3)CH_2CH(OSiPh_3)Me^+$ (**9**), which can undergo β-$OSiPh_3$ elimination/allylic C-H activation to form **8**, or insert a third equiv of 2 ultimately leading to **7**. Further chain growth is probably disfavored by steric crowding.

*(v) Base-Free Phosphine-Sulfonate Nickel Benzyl Complexes.* Base-free $[2\text{-}PR_2\text{-}4\text{-}Me\text{-benzenesulfonate})]Ni(\eta^3\text{-benzyl})$ complexes (R = 2-OMe-Ph (**4a**), Cy (**4b**)) were prepared and tested for ethylene polymerization. **4a** produces low molecular weight polyethylene ($M_n$ = 1300)

that contains 10 Me branches/$10^3$ C and terminal and internal olefin units. The polymer yield and structure are unaffected by ethylene pressure (60 to 300 psi). **4b** is less active than **4a** and produces polymer with higher $M_n$, fewer branches and a higher fraction of terminal olefin units.

*(vi) Mechanism of the Reaction of Vinyl Chloride with (α-diimine)PdMe*$^+$ *Species.* The reaction of vinyl chloride (VC) with (α-diimine)PdMe$^+$ species yields (α-diimine)PdCl(propene)$^+$. Isotope labeling experiments using the deuterium-labeled vinyl chlorides 1-VC-$d_1$ and *Z*-VC-$d_1$ combined with DFT computations establish that this reaction proceeds by 2,1-insertion of VC to produce β-H agostic (α-diimine)Pd(CHClCH$_2$Me)$^+$, chain-walking isomerization to generate β-Cl dative (α-diimine)Pd(CHMeCH$_2$Cl)$^+$, and syn β-Cl elimination. The labeling experiments rule out mechanisms involving initial 1,2 insertion or C-Cl oxidative addition. The computational results and the observation of small amounts of propene-$d_2$ argue against mechanisms involving 2,1 insertion followed by α-Cl elimination and a 1,2 H-shift.

*(vii) Cationic Polymerization and Insertion Chemistry in the Reactions of Vinyl Ethers with (α-diimine)PdMe*$^+$ *Species.* The reactions of (α-diimine)PdMe$^+$ species (1, α-diimine = (2,6-$^i$Pr$_2$−C$_6$H$_3$)N=CMeCMe=N(2,6-$^i$Pr$_2$−C$_6$H$_3$)) with vinyl ethers CH$_2$=CHOR (2a-g: R = $^t$Bu (a), Et (b), SiMe$_3$ (c), SiMe$_2$Ph (d), SiMePh$_2$ (e), SiPh$_3$ (f), Ph (g)) (2a-g: R = $^t$Bu (a), Et (b), SiMe$_3$ (c), SiMe$_2$Ph (d), SiMePh$_2$ (e), SiPh$_3$ (**f**), Ph (**g**)) were investigated. Two pathways were observed. First, **1** initiates the cationic polymerization of **2a**-**c** with concomitant decomposition of **1** to Pd$^0$. This reaction proceeds by formation of (α-diimine)PdR'(CH$_2$=CHOR)$^+$ π complexs (R' = Me or CH$_2$CHMeOR from insertion), in which the vinyl ether C=C bond is polarized with carbocation character at the substituted carbon (C$_{int}$). Electrophilic attack of C$_{int}$ on monomer initiates polymerization. Second, **1** reacts with stoichiometric quantities of **2a**-**g** by formation of (α-diimine)PdMe(CH$_2$=CHOR)$^+$ (**3a**-**g**), insertion to form (α-diimine)Pd(CH$_2$CHMeOR)$^+$ (**4a**-**g**), reversible isomerization to (α-diimine)Pd(CMe$_2$OR)$^+$ (**5a**-**g**), β-OR elimination of **4a**-**g** to generate (α-diimine)Pd(OR)(CH$_2$=CHMe)$^+$ (not observed), and allylic C−H activation to yield (α-diimine)Pd(η$^3$-C$_3$H$_5$)$^+$ (**6**) and ROH. Binding strengths vary in the order **2a** > **2b** ~ **2c** > **2d** ~ **2g** > **2e** > **2**. Strongly electron donating OR groups increase the binding strength while steric crowding has the opposite effect. The insertion rates vary in the order **3a** < **3b** < **3c** < **3d** < **3e** < **3f** < **3g**; this trend is determined primarily by the relative ground-state energies of **3a**-**g**. The β-OR elimination rates vary in the order O$^t$Bu < OSiR$_3$ < OPh. For **2d**-**g**, the insertion chemistry outcompetes cationic polymerization even at high vinyl ether concentrations. β-OR elimination of **4**/**5** mixtures is faster for SbF$_6^-$ salts than B(C$_6$F$_5$)$_4^-$ salts.

*(viii) Self-Assembled Tetranuclear Palladium Catalysts That Produce High Molecular Weight Linear Polyethylene.* The phosphine-bis-arenesulfonate ligand PPh(2-SO$_3$Li-4-Me-Ph)$_2$ (Li$_2$[OPO]) coordinates as a κ$^2$-P,O chelator in Li[(Li-OPO)PdMe(Cl)] (**2a**) and (Li-OPO)PdMe(L) (L = pyridine (**2b**); MeOH (**2d**); 4-(5-nonyl)pyridine) (py′, **3**)). **2a** reacts with AgPF$_6$ to form {(Li-OPO)PdMe}$_2$ (**2c**). Photolysis of **2d** yields {(OPO)Pd}$_2$ (**5**) in which the [OPO]$^{2-}$ ligand coordinates as a κ$^3$-O,P,O pincer. **3** self assembles into a tetramer in which four (Li-OPO)PdMe(py′) units are linked by Li-O bonds that form a central Li$_4$S$_4$O$_{12}$ cage. The Pd centers are equivalent but are spatially separated into two identical pairs. The Pd-Pd distance within each pair is 6.04 Å. IR data (υ(Ar$SO_3^-$) region) suggest that the solid state structures of **2a**-**c** are similar to that of **3**. **3** reacts with the cryptand Krypt211 to form [Li(Krypt211)][(OPO)PdMe(py′)] (**4**). **3** is in equilibrium with a monomeric (Li-OPO)PdMe(py′) species (**3′**) in solution. **2a**-**c** and **3** produce polyethylene (PE) with high molecular weight and a broad molecular weight distribution, characteristic of multi-site catalysis. Under conditions

where the tetrameric structure remains substantially intact, the PE contains a substantial high molecular weight fraction, while under conditions where fragmentation is more extensive, the PE contains a large low molecular weight fraction. These results suggest that the tetrameric assembly gives rise to the high molecular weight polymer. In contrast, the monomeric complex **4**, which contains a free pendant sulfonate group that can bind to Pd, oligomerizes ethylene to a Schultz-Flory distribution of $C_4$-$C_{18}$ oligomers. These multinuclear Pd catalysts also incorporate a high level of vinyl fluoride in ethylene/vinyl-fluoride copolymerization.

*(ix) Cis/Trans Isomerization of {Phosphine-sulfonate}Pd(II) Complexes.* The basic coordination chemistry and dynamic properties of {PO}Pd complexes that contain ortho-phosphine-sulfonate ligands ($\{PO\}^-$) are important in the context of the mechanism of the copolymerization of ethylene and polar monomers by $\{PO\}PdR^+$ catalysts. The pyridine exchange properties of $\{PO\}Pd(py)_2^+$ were first investigated. NMR and X-ray crystallographic studies established that the sulfonate arm of the {PO} ligand dissociates in the presence of excess pyridine to form the *tris*-pyridine $\{PO\}Pd(py)_3^+$ cation. Solution studies revealed that $\{PO\}Pd(py)_3^+$ is in equilibrium with $\{PO\}Pd(py)_2^+$ and free pyridine. NMR studies showed that intermolecular pyridine exchange follows an associative mechanism, and that the rate of exchange of free pyridine with the *trans*-P pyridine is much faster that of the *cis*-P pyridine. Direct intramolecular pyridine exchange was not observed in the absence of free pyridine. The cis/trans isomerization neutral {PO}Pd(X)(L) complexes was studied. We varied the *trans* influence of the anionic X ligand and the neutral L ligand to access a system in which the *cis-P,X* and the *trans-P,X* isomers have similar ground-state energy, so that both isomers could be observed in equilibrium. One strategy employed {PO}Pd(R)(L) complexes which contained alkyl groups with a weak *trans* influence, such as $C_6F_5$ and $^nC_3F_7$. Another approach involved the synthesis of $\{PO\}Pd(Cl)(PR_3)$ complexes that contain a phosphine or phosphite ligand. This work led to the discovery that $\{PO\text{-}^iPr\}PdCl\{PO\text{-}o\text{-}tolyl)_3\}$ ($\{PO\text{-}^iPr\}$ = $2\text{-}^iPr_2P$-toluenesulfonate) can be generated as a non-equilibrium mixture of *cis-P,P*-$\{PO\text{-}^iPr\}PdCl\{PO\text{-}o\text{-}tolyl)_3\}$ and *trans-P,P*-$\{PO\text{-}^iPr\}PdCl\{PO\text{-}o\text{-}tolyl)_3\}$ isomers, which converts to an equilibrium mixture. Kinetics studies showed that the *cis-P,P/trans-P,P* isomerization obeys first-order approach-to-equilibrium kinetics, and required the presence of free $P(O\text{-}o\text{-}tolyl)_3$, chloride, or other potential ligands to occur. These results established that the mechanism of of *cis-P,P/trans-P,P* isomerization is not unimolecular, but rather involves either ionic or 5-coordinate intermediates or transition states.

## C. Publications

(1) "Synthesis, Structures, Dynamics and Ethylene Polymerization Activity of Nickel Complexes Containing an *Ortho*-methoxy-aryl Diphosphine Ligand." Rodrigues, A.; Lavanant, L.; Kirillov, E.; Carpentier, J.; Jordan, R. F. *Organometallics* **2008**, 27, 2107-2117.

(2) "Synthesis of Double-End-Capped Polyethylene by a Cationic Tris(pyrazolyl)borate Zirconium Benzyl Complex." Nienkemper, K.; Lee, H.; Jordan, R. F.; Ariafard, A.; Dang, L.; Lin, Z. *Organometallics*, **2008**, *27,* 5867-5875.

(3) "Synthesis and Reactivity of a Sterically Crowded Tris(pyrazolyl)borate Hafnium Benzyl Complex." Lee, H.; Nienkemper, K.; Jordan, R. F. *Organometallics* **2008**, *27,* 5075-5081.

(4) "Multiple Insertion of a Silyl Vinyl Ether by (α-diimine)$PdMe^+$ Species." Chen, C.; Luo, S.; Jordan, R. F. *J. Am. Chem. Soc*. **2008**, *130*, 12892-12893.

(5) "Base-Free (Phosphine-Sulfonate) Nickel Benzyl Complexes." Zhou, X.; Bontemps, S.; Jordan, R. F. *Organometallics* **2008**, *27*, 4821-4824.

(6) "Comparison of Olefin Polymerization Behavior of Sterically Crowded Tris(Pyrazolyl)Borate Group 4 Metal Complexes." Michiue, K.; Jordan, R. F. *J. Molecular Catalysts A: Chemical* **2008**, *282*, 107-116.

(7) "Self-Assembled Tetranuclear Palladium Catalysts That Produce High Molecular Weight Linear Polyethylene." Shen, Z.; Jordan, R. F. *J. Am. Chem. Soc*. **2010**, *132*, 52-53.

(8) "Mechanism of the Reaction of Vinyl Chloride with (α-diimine)$PdMe^+$ Species." Kilyanek, S. M.; Stoebenau, E. J. III, Vinayavekhin, N.; Jordan, R. F. *Organometallics* **2010**, *29*, 1750-1760.

(9) "Cationic Polymerization and Insertion Chemistry in the Reactions of Vinyl Ethers with (α-diimine)$PdMe^+$ Species." Chen, C.; Luo, S.; Jordan, R. F. *J. Am. Chem. Soc*. **2010**, *132,* 5273-5284.

(10) "Copolymerization of Ethylene and Vinyl Fluoride by ((Phosphine-bis(arenesulfonate))PdMe(pyridine) Catalysts: Insights into Inhibition Mechanisms." Shen, Z.; Jordan, R. F. *J. Macromolecules* **2010**, *43*, 8706–8708.

(11) "Cis/Trans Isomerization of {Phosphine-sulfonate}Pd(II) Complexes." Conley, M. P.; Jordan, R. F. *Angew. Chem. Int. Ed.* **2011**, *50,* 3744-3746.