Structural Characterization of $[\kappa^2\text{-}(t\text{-Bu})_2PCH_2C(O)C_6H_5]PdMe(\eta^2\text{-}C_2H_4)^+BAr'_4{}^-$: A Model for the Catalyst Resting State for Ethylene Polymerization

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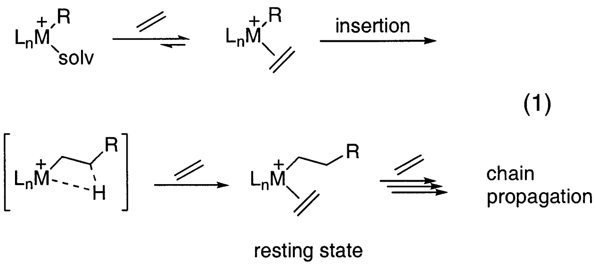
Summary: The Pd methyl−ethylene complex (P,O)PdMe(η^2-C_2H_4)$^+$BAr′$_4{}^-$ ((P,O) = phenacyldi-tert-butylphosphine; Ar′ = 3,5-(CF_3)$_2C_6H_3$) has been isolated and structurally characterized by X-ray crystallography. The ethylene ligand is oriented perpendicular to the square plane and is cis to the methyl ligand. This compound closely models the resting state(s) for ethylene oligomerization/polymerization by such complexes.

The development of single-site, homogeneous transition-metal catalysts for olefin polymerization has led to a greater understanding of the nature of the catalytic species and the mechanisms of monomer enchainment in these systems. Much of the work in this area has focused on early-metal d^0 catalysts, in particular metallocene complexes.[1−5] Recently, however, considerable efforts have been directed at developing cationic and neutral late-transition-metal catalysts for olefin polymerization.[6−9] The discovery that Ni(II) and Pd(II) complexes bearing bulky α-diimine ligands are highly active catalysts has led to a number of experimental and theoretical mechanistic investigations.[10−16] Central to these studies is the generation of a cationic catalyst precursor which, upon addition of an olefin such as ethylene, rapidly forms an alkyl−olefin species which models the resting state for catalytic olefin polymerization (eq 1). Metal alkyl−olefin complexes are typically thermally unstable, as migratory insertion of ethylene into the metal−alkyl bond is facile. These species are normally observed in situ via NMR experiments at low temperatures. Warming of these samples allows observation of migratory insertion rates as well as chain propagation and isomerization processes.



(1)

We recently reported a series of Ni(II) and Pd(II) complexes bearing the bulky P,O chelate phenacyldi-*tert*-butylphosphine that are active at elevated temperature and ethylene pressure for the production of linear polyethylene in the case of the Ni(II) catalyst and ethylene oligomers in the case of the Pd(II) complexes.[17,18] Complexes used for initiation of polymerization are shown in Figure 1. We report here the synthesis, isolation, and structural characterization of the Pd methyl−ethylene complex (P,O)PdMe(η^2-C_2H_4)$^+$BAr′$_4{}^-$ ((P,O) = phenacyldi-*tert*-butylphosphine; Ar′ = 3,5-(CF_3)C_6H_3), a model for the catalyst resting state in the (P,O)Pd^{II} system.

The previously reported ether adduct (P,O)PdMe(OEt_2)$^+$BAr′$_4{}^-$ (**1**) was prepared from the neutral complex (P,O)PdMeCl via chloride abstraction by NaBAr′$_4$ in diethyl ether solvent. Complex **1** is a powdery white solid that is stable for several days at ambient temperature under an inert atmosphere. Treatment of a solution of **1** in methylene chloride at −30 °C with a large excess of ethylene followed by precipitation into stirring pentane at −78 °C yields the white solid (P,O)PdMe(η^2-C_2H_4)$^+$BAr′$_4{}^-$ (**2**) (eq 2). Complex **2** is stable up to 0 °C in the solid state and can be stored for several days under argon at −35 °C. Above 0 °C the white powder quickly decomposes to an uncharacterizable

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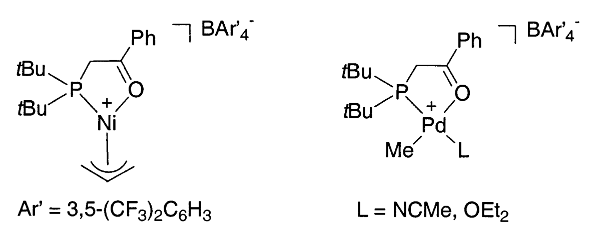


Figure 1. (P,O)Ni^{II} and (P,O)Pd^{II} precatalysts for ethylene polymerization.

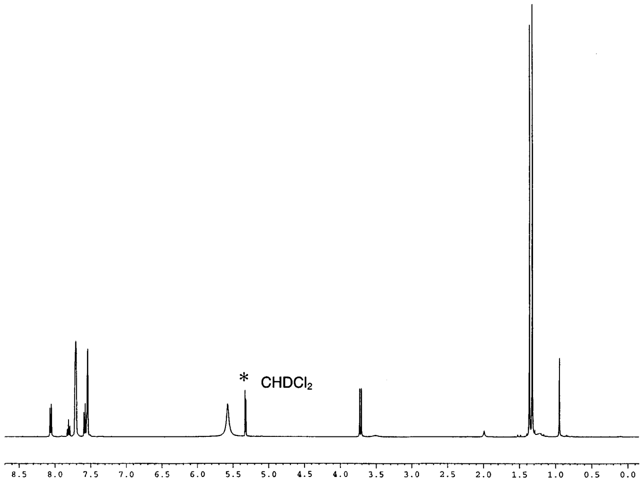
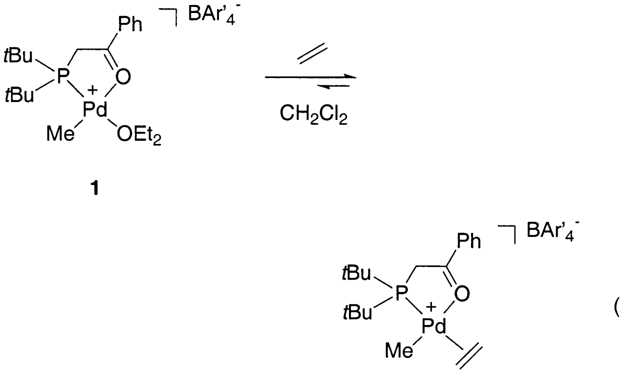


Figure 2. ^{1}H NMR spectrum of (P,O)PdMe(η^2-C$_2$H$_4$)$^+$-BAr′$_4$$^-$ (400 MHz, CD$_2$Cl$_2$, −20 °C).



(2)

2

dark oil. In CD$_2$Cl$_2$ solution **2** begins to decompose at −50 °C; however, its stability can be greatly enhanced by the addition of several equivalents of ethylene. Figure 2 shows a ^{1}H NMR spectrum of **2** in CD$_2$Cl$_2$ at −20 °C with 3 equiv of added ethylene. The Pd−methyl resonance is visible at δ 0.95 ($^3J_{\mathrm{HP}} = 2$ Hz), while the Pd−(η^2-C$_2$H$_4$) resonance appears at δ 5.57 as a broad singlet, indicating rapid exchange of bound and free ethylene on the NMR time scale. Even at −95 °C separate resonances for free and bound ethylene were not observed. The ^{31}P{^{1}H} spectrum of **2** at −40 °C shows one sharp singlet at δ 66.3 ppm, which is indicative of a single Pd species.

X-ray-quality crystals of **2** were grown from diethyl ether/pentane at −35 °C under argon. An ORTEP diagram of complex **2** is shown in Figure 3. The coordination geometry around Pd is square planar, with the methyl and ethylene ligands in a cis configuration (C(1)−Pd(1)−(C(2)−C(3) centroid) = 91.3(3)°). The ethylene unit binds trans to the phosphorus ligand in an η^2 fashion and is oriented nearly perpendicular to the square plane of the molecule (81.4(7)° relative to the plane defined by C(1)−Pd(1)−P(1)). Although there are no other reported crystal structures of Pd methyl−ethylene complexes, the near-orthogonal orientation of the bound ethylene is consistent with other examples of d^8 metal−ethylene complexes.[19−21] The carbon−carbon bond length for the bound ethylene is very similar to that in free ethylene, indicating little back-bonding from Pd into the antibonding π^* orbital.[22,23] The distance from Pd to the ethylene C(2)−C(3) centroid is 2.18 Å. As expected on electronic grounds, the strong donor methyl ligand lies trans to the carbonyl oxygen and ethylene is trans to the strong donor phosphine ligand. The phenyl ring of the P,O ligand is slightly twisted from coplanarity with C(6)−C(5)−O(4) (torsion angle C(6)−C(5)−C(7)−C(8) = 14.7(14)°), while the tetrahedral geometry of phosphorus results in projection

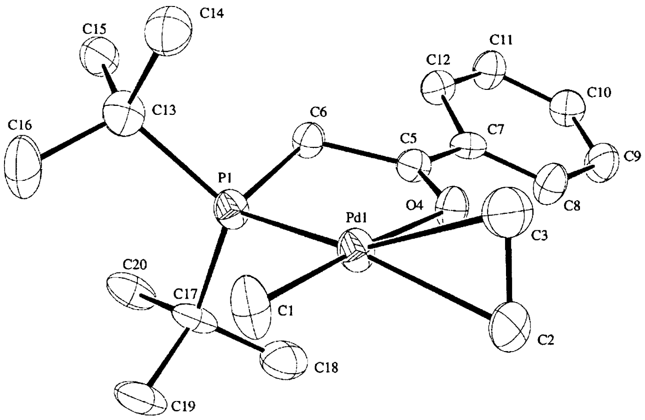


Figure 3. Thermal ellipsoid plot of **2**. The BAr′$_4$$^-$ counterion is omitted for clarity. Relevant bond distances (Å) and angles (deg): Pd(1)−C(1) = 2.029(8), Pd(1)−C(2) = 2.297(7), Pd(1)−C(3) = 2.274(8), Pd(1)−P(1) = 2.2782(18), Pd(1)−O(4) = 2.188(5), C(2)−C(3) = 1.346(12), Pd−(C(2)−C(3) centroid) = 2.18, C(5)−C(6) = 1.518(10), C(5)−O(4) = 1.245(8); C(1)−Pd(1)−C(2) = 88.9(3), C(1)−Pd(1)−C(3) = 93.7(3), P(1)−Pd(1)−O(4) = 82.83(18), C(6)−P(1)−C(13) = 102.6(4), C(6)−P(1)−C(17) = 104.6(3).

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of the bulky *tert*-butyl groups toward the axial sites above and below the square plane. To the best of our knowledge, this is the first example of a structurally characterized Pd(II) alkyl−ethylene complex, the catalyst resting state for ethylene polymerization.

The kinetics of insertion of ethylene into the Pd−Me bond in **2** were measured by ^{1}H NMR spectroscopy. At 0 °C the observed rate constant was $k_{obs} = 5.2 \times 10^{-5}$ s^{-1}, corresponding to a free energy barrier to insertion of $\Delta G^{\ddagger} = 21.3$ kcal/mol. Subsequent insertions resulted in polyethylene oligomers that were identical with those produced by complex **1**. The insertion barrier measured for **2** matches that previously measured using **1** as a precursor for the active systems.

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Supporting Information Available: Text detailing the synthesis and characterization of **2** as well as crystal structure data. This material is available free of charge via the Internet at http://pubs.acs.org.

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