Inorg. Chem. **2003**, *42*, 6915–6922

Synthesis and Structures of Nickel and Palladium Salicylaldiminato 1,3,5-Triaza-7-phosphaadamantane (PTA) Complexes

Donald J. Darensbourg,* Cesar G. Ortiz, and Jason C. Yarbrough

Department of Chemistry, Texas A&M University, P.O. Box 30012, College Station, Texas 77843

Received February 5, 2003

The synthesis of nickel(II) and palladium(II) salicylaldiminato complexes incorporating the water-soluble phosphine 1,3,5-triaza-7-phosphaadamantane(PTA) has been achieved employing two preparative routes. Reaction of the original ethylene polymerization catalyst developed by Grubbs and co-workers (*Organometallics* **1998**, *17*, 3149), (salicylaldiminato)Ni(Ph)PPh_3, with PTA using a homogeneous methanol/toluene solvent system resulted in the formation of the PTA analogues in good yields. Alternatively, complexes of this type may be synthesized via a direct approach utilizing (tmeda)M$(CH_3)_2$ (M = Ni, Pd), the corresponding salicylaldimine, and PTA. Yields by this method were generally near quantitative. The complexes were characterized in solution by $^1H/^{13}C/^{31}P$ NMR spectroscopy and in the solid-state by X-ray crystallography. All derivatives exhibited square-planar geometry with the bulky isopropyl groups on the aniline being perpendicular to the plane formed by the metal center and its four ligands. Such orientation of these sterically encumbering groups is responsible for polymer chain growth during olefin polymerization in favor of chain termination via β-hydride elimination. Polymerization reactions were attempted using the nickel–PTA complexes in a biphasic toluene/water mixture in an effort to initiate ethylene polymerization by trapping the dissociated phosphine ligand in the water layer, thereby eliminating the need for a phosphine scavenger. Unfortunately, because of the strong binding ability of the small, donating phosphine(PTA) as compared to PPh_3, phosphine dissociation did not occur at a temperature where the complexes are thermally stable.

Introduction

Presently, most α-olefins are polymerized through the use of heterogeneous Ziegler−Natta catalysts or metallocene catalysts to achieve high molecular weight polymers.[1] Both of these systems are based on early transition metals, and although these catalysts are very active, they are highly oxophilic and vulnerable to decomposition. Therefore, extra purification costs must be added to the industrial polymerization process to ensure high conversions and high molecular weight polymers. Consequently, attention has been turned to late transition metals which are less oxophilic and therefore able to tolerate functional-containing monomers.[2] The copolymerization of functionalized monomers with ethylene has led to new polymeric materials with enhanced adhesive properties. In addition, catalytic activities and polymer molecular weights obtained by employing these catalysts rival those achieved by Ziegler−Natta and metallocene catalytic systems. A drawback of these systems involves competing β-elimination which leads to low molecular weight polymers. This is the premise of the SHOP (Shell higher olefin polymerization) process using the [(OCH(R_1)CH$(R_2)PPh_2$)Ni(L)(R)] catalyst developed in the late 1960s by Keim and co-workers.[3] This latter process is currently used to produce higher molecular weight α-olefins which may be later converted to other useful products (e.g. detergents).[3]

One of the most notable and well-understood ethylene polymerization systems utilizes Brookhart's cationic β-diimine catalysts [(ArN═C(R)C(R′)═NAr)M(L)(CH_3)]$^+$ (M =

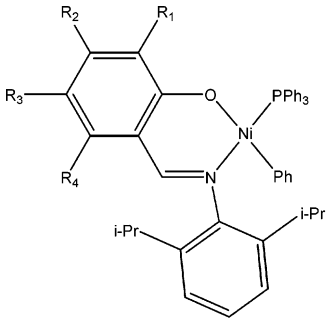
* To whom correspondence should be addressed. E-mail: djdarens@mail.chem.tamu.edu.

(1) For a comprehensive review, see: (a) Kuran, W. *Principles of Coordination Polymerization*; Wiley-VCH: New York, 2001; pp 53−215. (b) Coville, N. J.; Möhring, P. C. *J. Organomet. Chem.* **1994**, *479*, 1. (c) Hlatky, G. *Coord. Chem. Rev.* **2000**, *199*, 235. (c) Alt, H. G.; Köppl, A. *Chem. Rev.* **2000**, *100*, 1205. (d) Bendikt, G. M., Ed. *Metallocene Technology in Commercial Application*; Plastics Design Library: Norwich, NY, 1999.

(2) For a comprehensive review, see: (a) Brookhart, M.; Ittel, S. D.; Johnson, L. K. *Chem. Rev.* **2000**, *100*, 1169. (b) Mecking, S. *Coord. Chem. Rev.* **2000**, *203*, 325. (c) Gibson, V. C.; Britovsek, G. J.; Wass, D. F. *Angew. Chem., Int. Ed.* **1999**, *38*, 428.

(3) (a) Keim, W.; et al. (Shell Dev.). U.S. Patents 3635937, 3647914, 3686159, 3644563, 3647914, 1974. (b) Keim, W. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 235. (c) Keim, W.; Peuckert, M. *Organometallics*. **1983**, *2*, 594. (d) Skupinska, J. *Chem. Rev.* **1991**, *91*, 613.

10.1021/ic0341284 CCC: $25.00
Published on Web 09/17/2003



1a-f

a. $R_3 = NO_2$, $R_1 = R_2 = R_4 = H$
b. $R_1 = OMe$, $R_2 = R_3 = R_4 = H$
c. $R_3 = CH(CH)_2CH = R_4$, $R_1 = R_2 = H$
d. $R_1 = R_3 = Cl$, $R_2 = R_4 = H$
e. $R_1 = C_6H_5$, $R_2 = R_3 = R_4 = H$
f. $R_1 = 9$-anthra, $R_2 = R_3 = R_4 = H$

Figure 1. Nickel(II) salicylaldimine catalyst.

Ni, Pd).[2a,4] Optimization of the catalyst's activity over the years by ligand modification has led to the industrial implementation of the catalyst for the polymerization of ethylene.[5] Of primary interest to this study is the catalyst developed by Grubbs and co-workers which is based on the salicylaldimine ligand framework (Figure 1).[6] Similar to the SHOP catalyst, the ligand is monoanionic, rendering a neutral catalyst which is void of bulky counterions. However, unlike the SHOP catalyst, the incorporation of sterically demanding groups on the ligand effectively shields the axial sites of the metal center thereby allowing enchainment to predominate over β-hydride elimination processes. As with most olefin polymerization catalysts, a cocatalyst is usually needed to initiate polymerization. In the case of metallocene[1d] or Brookhart's[4a] catalysts, an excess of an aluminum cocatalyst such as MAO must be used. For **1**, a phosphine scavenger such as $Ni(COD)_2$ (COD = 1,5-cyclooctadiene) is needed to remove the phosphine from the metal center and allow alkene coordination.[6] An obvious drawback to this latter process is that this cocatalyst is highly air-sensitive and prone to autocatalytic decomposition.

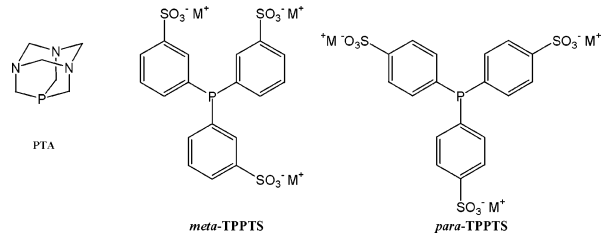


Figure 2. PTA, *meta*-TPPTS, and *para*-TPPTS water-soluble phosphines.

The purpose of this study is to explore the effect of incorporating a water-soluble phosphine (WSP) into **1** and using a biphasic toluene/water solvent mixture to allow irreversible phosphine dissociation, thereby eliminating the need for a phosphine scavenger. Although it has been shown in Grubb's system that initiation can take place without the need of a cocatalyst by using a more sterically demanding group in the R_1 position of the ligand, many of the active derivatives require cocatalysts.[6a] The polymerization of various olefins has been achieved in water; however, to our knowledge, this is the first attempt to use a biphasic solvent system to generate the active catalyst in the organic phase while allowing the WSP to enter and *remain* in the aqueous phase.[7]

The use of WSP in catalysis was first commercialized by Ruhrchemie in 1984 for the hydroformylation of higher molecular weight α-olefins to predominantly form terminal aldehydes.[8] The system uses the trisulfonated triphenylphosphine ligand *meta*-TPPTS (Figure 2),[9] coordinated to rhodium to form the active $RhH(CO)(TPPTS)_3$ catalyst. Another WSP, which is of main interest to this study, is the heterocyclic, aliphatic 1,3,5-triaza-7-phosphaadamantane (PTA).[10] Many complexes incorporating this ligand have been prepared, and the ruthenium and rhodium derivatives have been found to be effective catalysts in the hydrogenation of various unsaturated hydrocarbons.[11] Herein, we wish to report the synthesis of various PTA derivatives of **1** by two routes, (a) ligand exchange reaction and (b) direct synthesis, as well as the solid-state characterization of many of these derivatives.

(4) (a) Brookhart, M.; Johnson, L. K.; Killian, C. M. *J. Am. Chem. Soc.* **1995**, *117*, 6414. (b) Brookhart, M.; Johnson, L. K.; Mecking, S. *J. Am. Chem. Soc.* **1996**, *118*, 267. (c) Brookhart, M.; Killian, C. M.; Tempel, D. J.; Johnson, L. K. *J. Am. Chem. Soc.* **1996**, *118*, 11664. (d) Brookhart, M.; Killian, C. M.; Johnson, L. K. *Organometallics.* **1997**, *16*, 2005. (e) Brookhart, M.; Svejda, S. A.; Johnson, L. K. *J. Am. Chem. Soc.* **1999**, *121*, 10634. (f) Brookhart, M.; Tempel, D. J.; Johnson, L. K.; Huff, R. L.; White, P. S. *J. Am. Chem. Soc.* **2000**, *122*, 6686.

(5) (a) Arthur, S. D.; Bennett, A. M. A.; Brookhart, M. S.; Coughlin, E. B.; Feldman, J.; Ittel, S. D.; Johnson, L. K.; Killian, C. M.; Kreutzer, K. A. [DuPont (Polymerizations)]. U.S. Patent 5866663, Feb 2, 1999. (b) Brookhart, M. S.; Ittel, S. D.; Johnson, L. K.; Killian, C. M.; Kreutzer, K. A.; McCord, E. F.; McLain, S. J.; Tempel, D. J. [DuPont (Polymer Compositions)]. U.S. Patent 5880241, May 3, 1999. (c) Brookhart, M. S.; Johnson, L. K.; Killian, C. M.; Wang, L.; Yang, Z. Y. [DuPont (α-Olefins)]. U.S. Patent 5880323, March 9, 1999. (d) Arthur, S. D.; Bennett, A. M. A.; Brookhart, M. S.; Coughlin, E. B.; Feldman, J.; Ittel, S. D.; Johnson, L. K.; Killian, C. M.; Kreutzer, K. A.; Parthasarathy, A.; Temple, D. J. [DuPont (Ligand Compositions)]. U.S. Patent 5886224, March 23, 1999. (e) Arthur, S. D.; Brookhart, M. S.; Hohnson, L. K.; Killian, C. M.; McCord, El F.; McLain, S. J. [DuPont (Copolymers)]. U.S. Patent 5891963, April 6, 1999.

(6) (a) Grubbs, R. H.; Wang, C.; Friedrich, S.; Younkin, T. R.; Li, R. T.; Bansleben, D. A.; Day, M. W. *Organometallics* **1998**, *17*, 3149. (b) Grubbs, R. H.; Younkin, T. R.; Connor, E. F.; Henderson, J. I.; Friedrich, S.; Bansleben, D. A. *Science* **2000**, *287*, 460.

(7) Mecking, S.; Held, A.; Bauers, F. *Angew. Chem., Int. Ed.* **2002**, *41*, 545.

(8) (a) Cornils, B.; Wiebus, E. *CHEMTEC* **1995**, *25*, 33. (b) Cornils, B. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1575. (c) Cornils, B.; Kuntz, E. G. *J. Organomet. Chem.* **1995**, *502*, 177. For a comprehensive review, see: (d) Joó, F.; Kathó, Á. *J. Mol. Catal., A: Chem.* **1997**, *116*, 3. (e) Cornils, B.; Herrmann, W. A.; Eckl, R. W. *J. Mol. Catal., A: Chem.* **1997**, *116*, 27.

(9) (a) Herrmann, W. A.; Kohlpaintner, C. W. *Inorg. Synth.* **1998**, *32*, 8. For a comprehensive review on the use of TPPTS, see: (b) Joó, F. *Aqueous Organometallic Catalysis*; Kluwer Academic: Boston, MA, 2001. (c) Cornils, B., Herrmann, W. A., Eds. *Aqueous-Phase Organometallic Catalysis*; Wiley-VCH: Weinheim, Germany, 1998.

(10) (a) Daigle, D. J.; Peppermann, A. B.; Vail, S. L. *J. Heterocycl. Chem.* **1974**, *11*, 407. (b) Daigle, D. J. *Inorg. Synth.* **1998**, *32*, 40.

(11) (a) Darensbourg, D. J.; Joó, F.; Daigle, D. J.; Kannisto, M.; Kathó, A.; Reibenspies, J. H. *Inorg. Chem.* **1994**, *33*, 200. (b) Darensbourg, D. J.; Joó, F.; Kannisto, M.; Kathó, Á.; Riebenspies, J. H. *Organometallics.* **1992**, *11*, 1990. (c) Darensbourg, D. J.; Stafford, N. W.; Joó, F.; Reibenspies, J. H. *J. Organomet. Chem.* **1995**, *488*, 99. (d) Joó, F.; Nádasdi, L.; Bényei, A. C.; Darensbourg, D. J. *J. Organomet. Chem.* **1996**, *512*, 45. (e) Akbayeva, D. N.; Gonsalvi, L.; Oberhauser, W.; Peruzzini, M.; Vizza, F.; Brüggeller, P.; Romerosa, A.; Sava, G.; Bergamo, A. *Chem. Commun.* **2003**, 264.

Experimental Section

Materials and Methods. Unless otherwise indicated, all reactions were carried out under an inert argon atmosphere using standard Schlenk and drybox techniques. Prior to their use, all solvents were distilled using standard techniques. 2-Hydroxy-3-phenylbenzaldehyde was prepared from the corresponding phenol,[12] and all other benzaldehydes were purchased from Aldrich Chemicals. Ligands **a**−**g** were prepared by the condensation reaction of the corresponding aldehyde with commercially available 2,6-diisopropylaniline. PTA,[10] (TMEDA)Ni$(CH_3)_2$,[13a] (TMEDA)Pd$(CH_3)_2$,[13b] and **1a**[6a] were prepared according to literature procedures.

^{1}H, ^{13}C, and ^{31}P NMR data were obtained using a Varian Unity+ 300 MHz NMR instrument. ^{1}H and ^{13}C chemical shifts were referenced according to the deuterated solvent used. The ^{31}P chemical shifts were referenced using an external 85% H_3PO_4 sample. Elemental analysis was conducted by Canadian Microanalytical Inc.

Preparation of Nickel Salicylaldiminato PTA Complexes by Ligand Exchange with 1 (2a). To a 50 mL Schlenk flask containing **1a** (100 mg, 0.138 mmol) in 3 mL of toluene was added a concentrated methanol solution of PTA (23.7 mg, 0.152 mmol, in 5 mL of MeOH). A yellow precipitate immediately formed, and the reaction was stirred overnight. After filtration and washing with pentane, the solid was redissolved in CH_2Cl_2 and the solution was filtered. After removal of the solvent under vacuum, **2a** was obtained.

2a ($R_3 = NO_2$, $R_1 = R_2 = R_4 = H$): ^{1}H NMR (300 MHz, CD_2Cl_2, δ) 1.00 (d, $^3J_{HH} = 6.60$ Hz, 6H, CH$(CH_3)_2$), 1.29 (d, $^3J_{HH} = 6.90$ Hz, 6H, CH$(CH_3)_2$), 3.52 (sept, $^3J_{HH} = 6.90$ Hz, 2H, C$H$$(CH_3)_2$), 3.91 (s, 6 H, NCH_2N), 4.313 (dd, $^2J_{HP} = 19.79$ Hz, $^2J_{HH} = 12.90$ Hz, 6H, PCH_2N), 6.50−6.59 (m, 3H, Ar), 6.79−6.85 (m, 3H, Ar), 6.89−6.94 (m, 3H, Ar), 7.17−7.25 (m, 1H, Ar), 8.00 (d, $^4J_{HP} = 8.10$ Hz, 1H, HC═N), 8.11−8.17 (m, 2H, Ar); ^{13}C NMR (75 MHz, CD_2Cl_2, δ) 22.23, 25.61, 28.74, 50.46 (d, $^1J_{CP} = 14.86$ Hz, P−C−N), 73.20 (d, $^3J_{CP} = 6.26$ Hz, N−C−N), 118.03, 122.68, 122.74, 126.10, 126.19, 128.67, 132.33, 136.02, 137.18, 137.23, 139.97, 142.49, 143.23, 148.73, 165.82, 171.03; ^{31}P NMR (121 MHz, CD_2Cl_2, δ) −57.76; yield 58.3%. Anal. Calcd for $C_{31}H_{38}N_5O_3PNi$: C, 60.22; H, 6.19; N, 11.33. Found: C, 61.32; H, 6.07; N, 10.70.

Direct Synthetic Approach for the Preparation of Nickel and Palladium Salicylaldiminato PTA Complexes (3a−f and 4a−f). To a 50 mL Schlenk flask containing (TMEDA)Ni$(CH_3)_2$ (200 mg, 0.976 mmol) in 10 mL of toluene at −30 °C was introduced PTA (170 mg, 1.07 mmol) in 5 mL of methanol via cannula. To this mixture, H**a** (318 mg, 0.976 mmol) in 10 mL of toluene at −30 °C was slowly cannulated into the flask, and the solution was stirred for 30 min. Subsequently, the temperature was raised to room temperature, and the light red solution was further stirred overnight. After the solution was stirred overnight, the solvent was removed in vacuo until approximately 5 mL remained, and 20 mL of cold (−78 °C) pentane was added, resulting in the formation of a yellow precipitate. The solid was collected by cold cannula filtration and washed (3 × 5 mL) with cold (−78 °C) pentane, affording **3a** in 60% yield (350 mg). The other (salicylaldiminato)nickel and -palladium ((TMEDA)Pd$(CH_3)_2$ was used as the palladium source) PTA complexes were prepared in an analogous fashion. Complexes **3a**−**e** and **4a**−**e** were all obtained as yellow solids in good yields.

3a ($R_3 = NO_2$, $R_1 = R_2 = R_4 = H$): ^{1}H NMR (300 MHz, C_6D_6, δ) −1.33 (s, 3H, Ni−CH_3), 0.98 (d, $^3J_{HH} = 6.60$ Hz, 6H, CH$(CH_3)_2$), 1.35 (d, $^3J_{HH} = 6.90$ Hz, 6H, CH$(CH_3)_2$), 3.58 (sept, $^3J_{HH} = 6.90$ Hz, 2H, C$H$$(CH_3)_2$), 3.73 (s, 6H, NCH_2N), 4.09 (dd, $^2J_{HP} = 32.69$ Hz, $^2J_{HH} = 12.90$ Hz, 6H, PCH_2N), 6.41 (t, $^3J_{HH} = 9.60$ Hz, 1H, Ar), 7.05−7.13 (m, 3H, Ar), 7.46 (s, 1H, HN═C), 7.98 (d, $^3J_{HH} = 2.94$, 1H, Ar), 8.11 (dd, $^3J_{HH} = 2.94$ Hz, $^3J_{HH} = 9.60$ Hz, 1H, Ar); ^{13}C NMR (75 MHz, C_6D_6, δ) −15.84 (d, $^2J_{CP} = 4.25$ Hz, Ni−CH_3), 23.47, 25.09, 29.00, 50.85 (d, $^1J_{CP} = 5.93$ Hz, P−C−N), 73.93 (d, $^3J_{CP} = 4.85$ Hz, N−C−N), 122.93, 124.14, 127.36, 129.18, 132.84, 141.01, 165.92; ^{31}P NMR (121 MHz, C_6D_6, δ) −47.10.

3b ($R_1 = OMe$, $R_2 = R_3 = R_4 = H$): ^{1}H NMR (300 MHz, C_6D_6, δ) −1.26 (s, 3H, Ni−CH_3), 1.04 (d, $^3J_{HH} = 6.30$ Hz, 6H, CH$(CH_3)_2$), 1.40 (d, $^3J_{HH} = 6.60$ Hz, 6H, CH$(CH_3)_2$), 3.42 (s, 3H, OCH_3), 3.82 (sept, $^3J_{HH} = 6.60$ Hz, 2H, C$H$$(CH_3)_2$), 4.00 (s, 6H, NCH_2N), 4.08 (dd, $^2J_{HP} = 22.79$ Hz, $^2J_{HH} = 13.20$ Hz, 6H, PCH_2N), 6.46 (t, $^3J_{HH} = 7.80$ Hz, 1H, Ar), 6.59 (d, $^3J_{HH} = 7.50$ Hz, 1H, Ar), 6.67 (d, $^3J_{HH} = 7.20$ Hz, 1H, Ar), 6.94−7.48 (m, 3H, Ar), 7.90 (s, 1H, HC═N); ^{13}C NMR (75 MHz, C_6D_6, δ) −19.71 (d, $^2J_{CP} = 4.36$ Hz, Ni−CH_3), 21.10, 22.82, 26.50, 48.38 (d, $^1J_{CP} = 6.03$ Hz, P−C−N), 53.46 (d, $^3J_{CP} = 4.90$ Hz, N−C−N), 71.29 (OCH_3), 111.10, 116.88, 121.58, 123.80, 124.48, 128.34, 132.51, 139.29, 147.16, 151.42, 156.86, 163.32; ^{31}P NMR (121 MHz, C_6D_6, δ) −54.56; yield 51.1%. Anal. Calcd for $C_{27}H_{39}N_4OPNi$: C, 59.91; H, 7.26; N, 10.35. Found: C, 59.86; H, 7.10; N, 10.55.

3c ($R_3 = CH(CH)_2CH = R_4$, $R_1 = R_2 = H$): ^{1}H NMR (300 MHz, C_6D_6, δ) −1.26 (s, 3H, Ni−CH_3), 1.06 (d, $^3J_{HH} = 6.60$ Hz, 6H, CH$(CH_3)_2$), 1.39 (d, $^3J_{HH} = 6.60$ Hz, 6H, CH$(CH_3)_2$), 3.83 (s, 6H, NCH_2N), 3.90 (sept, $^3J_{HH} = 6.90$ Hz, 2H, C$H$$(CH_3)_2$), 4.02 (dd, $^2J_{HP} = 34.19$ Hz, $^2J_{HH} = 13.20$ Hz, 6H, PCH_2N), 6.96−7.14 (m, 6H, Ar), 7.46−7.52 (m, 3H, Ar), 8.87 (s, 1H, HC═N); ^{13}C NMR (75 MHz, C_6D_6, δ) −18.68 (d, $^2J_{CP} = 4.30$ Hz, Ni−CH_3), 21.14, 23.03, 26.51, 48.33 (P−C−N), 71.39 (N−C−N), 107.33, 116.44, 120.09, 121.67, 123.70, 124.52, 125.05, 127.41, 132.99, 133.52, 139.67, 148.00, 157.31, 165.72; ^{31}P NMR (121 MHz, C_6D_6, δ) −60.88; yield 55.0%. Anal. Calcd for $C_{30}H_{39}N_4OPNi$: C, 62.41; H, 6.81; N, 9.70. Found: C, 62.83; H, 6.74; N, 10.48.

3d ($R_1 = R_3 = Cl$, $R_2 = R_4 = H$): ^{1}H NMR (300 MHz, C_6D_6, δ) −1.29 (s, 3H, Ni−CH_3), 0.99 (d, $^3J_{HH} = 6.60$ Hz, 6H, CH$(CH_3)_2$), 1.38 (d, $^3J_{HH} = 6.60$ Hz, 6H, CH$(CH_3)_2$), 3.66 (sept, $^3J_{HH} = 6.60$ Hz, 2H, C$H$$(CH_3)_2$), 3.93 (s, 6H, NCH_2N), 4.04 (dd, $^2J_{HP} = 22.79$ Hz, $^2J_{HH} = 13.20$ Hz, 6H, PCH_2N), 6.71 (d, $^3J_{HH} = 2.70$ Hz, 1H, Ar), 7.07−7.13 (m, 3H, Ar), 7.38 (d, $^3J_{HH} = 2.70$ Hz, 1H, Ar), 7.54 (s, 1H, HC═N); ^{13}C NMR (75 MHz, C_6D_6, δ) −18.65 (d, $^2J_{CP} = 3.62$ Hz, Ni−CH_3), 21.06, 22.77, 26.56, 48.61 (d, $^1J_{CP} = 8.90$ Hz, P−C−N), 71.40 (d, $^3J_{CP} = 5.50$ Hz, N−C−N), 115.47, 117.90, 121.69, 124.87, 126.47, 129.58, 131.53, 138.81, 146.38, 158.35, 162.81; ^{31}P NMR (121 MHz, C_6D_6, δ) −59.36; yield 72.4%.

3e ($R_1 = C_6H_5$, $R_2 = R_3 = R_4 = H$): ^{1}H NMR (300 MHz, C_6D_6, δ) −1.27 (s, 3H, Ni−CH_3), 1.04 (d, $^3J_{HH} = 6.60$ Hz, 6H, CH$(CH_3)_2$), 1.37 (d, $^3J_{HH} = 6.60$ Hz, 6H, CH$(CH_3)_2$), 3.66 (s, 6H, NCH_2N), 3.82 (t, $^3J_{HH} = 6.90$ Hz, 2H, C$H$$(CH_3)_2$), 3.91 (dd, $^2J_{HP} = 42.29$ Hz, $^2J_{HH} = 13.20$ Hz, 6 H, PCH_2N), 6.54 (t, $^3J_{HH} = 7.50$ Hz, 1H, Ar), 6.94 (d, $^3J_{HH} = 7.80$ Hz, 1H, Ar), 7.07−7.22 (m, 6H, Ar), 7.29 (d, $^3J_{HH} = 6.90$ Hz, 1H, Ar), 7.48 (d, $^3J_{HH} = 6.90$ Hz, 2H, Ar), 7.90 (s, 1H, HC═N); ^{13}C NMR (75 MHz, C_6D_6, δ) −19.43 (d, $^2J_{CP} = 4.22$ Hz, Ni−CH_3), 21.08, 22.87, 26.51, 48.08 (d, $^1J_{CP} = 12.22$ Hz, P−C−N), 71.12 (d, $^3J_{CP} = 4.60$ Hz, N−C−N), 112.14, 117.81, 121.63, 124.64, 126.21, 128.35, 132.51, 133.10, 133.67,

(12) Casiraghi, G.; Casnati, G.; Puglia, G.; Sartori, G.; Terenghi, G. *J. Chem. Soc., Perkin Trans. 1* **1980**, 1862.

(13) (a) Kaschube, W.; Pörschke, K. R.; Wilke, G. *J. Organomet. Chem.* **1988**, *355*, 525. (b) Byers, P. K.; Canty, A. J.; Jin, H.; Kruis, D.; Markies, B. A.; Boersma, J.; Koten, G. V.; Hill, G. S.; Irwin, M. J.; Rendina, L. M.; Puddephatt, R. J. *Inorg. Synth.* **1998**, *32*, 167.

139.31, 139.86, 147.01, 162.98, 163.90; ^{31}P NMR (121 MHz, C_6D_6, δ) −55.34; yield 69.7%. Anal. Calcd for $C_{32}H_{41}N_4OPNi$: C, 65.47; H, 6.98; N, 9.55. Found: C, 65.49; H, 6.95; N, 9.42.

4a ($R_3 = NO_2$, $R_1 = R_2 = R_4 = H$): ^{1}H NMR (300 MHz, C_6D_6, δ) −0.19 (d, $^3J_{HP} = 3.28$ Hz, 3H, Pd−CH_3), 1.00 (d, $^3J_{HH} = 6.90$ Hz, 6H, CH(CH_3)$_2$), 1.32 (d, $^3J_{HH} = 6.90$ Hz, 6H, CH(CH_3)$_2$), 3.29 (sept, $^3J_{HH} = 6.90$ Hz, 2H, CH(CH$_3$)$_2$), 3.83 (s, 6H, NCH_2N), 3.99 (dd, $^2J_{HP} = 30.59$ Hz, $^2J_{HH} = 13.50$ Hz, 6H, PCH_2N), 6.65 (d, $^3J_{HH} = 9.60$ Hz, 1H, Ar), 7.14 (d, $^3J_{HH} = 3.00$ Hz, 1H, Ar), 7.21−7.17 (m, 2H, Ar), 7.53 (d, $^4J_{HP} = 10.20$ Hz, 1H, HC═N), 8.11 (d, $^3J_{HH} = 2.70$ Hz, 1H, Ar), 8.22 (dd, $^3J_{HH} = 3.00$ Hz, $^3J_{HH} = 9.60$ Hz, 1H, Ar); ^{13}C NMR (75 MHz, C_6D_6, δ) −7.88 (d, $^2J_{CP} = 17.73$ Hz, Pd−CH_3), 23.32, 25.00, 28.73, 50.95 (d, $^1J_{CP} = 16.74$ Hz, P−C−N), 73.60 (d, $^3J_{CP} = 6.11$ Hz, N−C−N), 118.54, 123.90, 127.44, 130.15, 135.21, 136.30, 141.02, 147.35, 166.63, 173.39; ^{31}P NMR (121 MHz, C_6D_6, δ) −46.18; yield 95.7%. Anal. Calcd for $C_{26}H_{36}N_5O_3PPd$: C, 51.71; H, 5.96; N, 11.60. Found: C, 52.16; H, 6.30; N, 11.63.

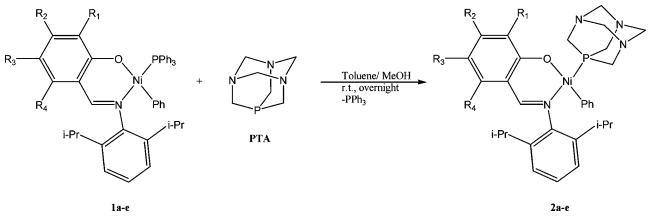
4b ($R_1 = OCH_3$, $R_2 = R_3 = R_4 = H$): ^{1}H NMR (300 MHz, C_6D_6, δ) −0.18 (d, $^3J_{HP} = 3.60$ Hz, 3H, Pd−CH_3), 1.01 (d, $^3J_{HH} = 6.90$ Hz, 6H, CH(CH_3)$_2$), 1.32 (d, $^3J_{HH} = 6.60$ Hz, 6H, CH(CH_3)$_2$), 3.47 (sept, $^3J_{HH} = 6.90$ Hz, 2H, CH(CH$_3$)$_2$), 3.54 (s, 3H, OCH_3), 3.98−4.08 (m, 12H, PCH_2N, NCH_2N), 6.43 (t, $^3J_{HH} = 7.21$ Hz, 1H, Ar), 6.71 (m, 2H, Ar), 7.92 (d, $^4J_{HH} = 11.43$ Hz, 1H, HC═N); ^{13}C NMR (75 MHz, C_6D_6, δ) −9.33 (d, $^2J_{CP} = 13.80$ Hz, Pd−CH_3), 23.36, 25.14, 28.62 51.28 (d, $^1J_{CP} = 15.24$ Hz, P−C−N), 56.46 (OCH_3), 73.83 (d, $^3J_{CP} = 7.62$ Hz, N−C−N), 112.57, 115.46, 119.49, 123.94, 126.93, 128.61, 141.70, 148.46, 154.17, 161.82, 166.45; ^{31}P NMR (121 MHz, C_6D_6, δ) −44.74; yield 91.2%. Anal. Calcd for $C_{27}H_{39}N_4O_2PPd$: C, 54.97; H, 6.61; N, 9.50. Found: C, 55.21; H, 6.50; N, 9.41.

4c ($R_3 = CH(CH)_2CH = R_4$, $R_1 = R_2 = H$): ^{1}H NMR (300 MHz, C_6D_6, δ) −0.20 (d, $^3J_{HP} = 3.90$ Hz, 3H, Pd−CH_3), 1.02 (d, $^3J_{HH} = 6.90$ Hz, 6H, CH(CH_3)$_2$), 1.30 (d, $^3J_{HH} = 6.90$ Hz, 6 Hz, CH(CH_3)$_2$), 3.54 (sept, $^3J_{HH} = 7.20$ Hz, 2H, CH(CH$_3$)$_2$), 3.85 (s, 6H, N−C−N), 3.93 (dd, $^2J_{HP} = 29.39$ Hz, $^2J_{HH} = 13.20$ Hz, 6H, PCH_2N), 6.95−7.13 (m, 5H, Ar), 7.45(d, $^3J_{HH} = 8.10$ Hz, 1H, Ar), 7.52 (d, $^3J_{HH} = 9.30$ Hz, 1H, Ar), 7.57 (d, $^3J_{HH} = 8.70$ Hz, 1H, Ar), 8.95 (d, $^4J_{HP} = 11.95$ Hz, 1H, HC═N); ^{13}C NMR (75 MHz, C_6D_6, δ) −8.88 (d, $^2J_{CP} = 15.31$ Hz, Pd−CH_3), 23.45, 25.37, 28.63, 51.05 (d, $^1J_{CP} = 15.31$ Hz, P−C−N), 73.74 (d, $^3J_{CP} = 7.62$ Hz, N−C−N), 119.23, 122.10, 124.04, 126.95, 127.38, 127.46, 128.92, 129.69, 129.89, 136.38, 137.29, 142.13, 149.39, 160.09; ^{31}P NMR (121 MHz, C_6D_6, δ) −47.18; yield 98.5%. Anal. Calcd for $C_{30}H_{39}N_4OPPd$: C, 59.20; H, 6.41; N, 9.21. Found: C, 60.01; H, 6.48; N, 8.81.

4d ($R_1 = R_3 = Cl$, $R_2 = R_4 = H$): ^{1}H NMR (300 MHz, C_6D_6, δ) −0.19 (d, $^3J_{HP} = 3.30$ Hz, 3H, Pd−CH_3), 1.00 (d, $^3J_{HH} = 6.90$ Hz, 6H, CH(CH_3)$_2$), 1.34 (d, $^3J_{HH} = 6.90$ Hz, 6H, CH(CH_3)$_2$), 3.34 (sept, $^3J_{HH} = 6.60$ Hz, 2H, CH(CH$_3$)$_2$), 3.98 (s, 6H, NCH_2N), 3.99 (d, $^2J_{HP} = 20.39$ Hz, $^2J_{HH} = 12.90$ Hz, 6H, PCH_2N), 6.77 (d, $^3J_{HH} = 2.70$ Hz, 1H, Ar), 7.13−7.18 (m, 3H, Ar), 7.51 (d, $^3J_{HH} = 3.00$ Hz, 1H, Ar), 7.57 (d, $^4J_{HP} = 10.50$ Hz, 1H, HC═N); ^{13}C NMR (75 MHz, C_6D_6, δ) −8.40 (d, $^2J_{CP} = 13.73$ Hz, Pd−CH_3), 23.33, 25.07, 28.67, 51.24 (d, $^1J_{CP} = 16.82$ Hz, P−C−N), 73.66 (d, $^3J_{CP} = 7.62$ Hz, N−C−N), 116.66, 120.34, 124.04, 127.32, 129.40, 133.93, 134.72, 141.16, 147.69, 162.56, 166.02; ^{31}P NMR (121 MHz, C_6D_6, δ) −44.54; yield 82.8%. Anal. Calcd for $C_{26}H_{35}N_4OPCl_2Pd$: C, 49.69; H, 5.57; N, 8.92. Found: C, 50.49; H, 5.59; N, 8.92.

4e ($R_1 = C_6H_5$, $R_2 = R_3 = R_4 = H$): ^{1}H NMR (300 MHz, C_6D_6, δ) −0.17 (d, $^3J_{HP} = 3.60$ Hz, 3H, Pd−CH_3), 1.02 (d, $^3J_{HH} = 6.90$ Hz, 6H, CH(CH_3)$_2$), 1.31 (d, $^3J_{HH} = 6.90$ Hz, 6H, CH(CH_3)$_2$), 3.47 (sept, $^3J_{HH} = 7.20$ Hz, 2H, CH(CH$_3$)$_2$), 3.70 (s, 6H, NCH_2N), 3.91 (dd, $^2J_{HP} = 20.09$ Hz, $^2J_{HH} = 13.50$ Hz, 6H, PCH_2N), 6.54 (t, $^3J_{HH} = 6.90$ Hz, 1H, Ar), 6.93 (m, 1H, Ar), 7.12 (m, 1H, Ar), 7.24 (t, $^3J_{HH} = 7.20$ Hz, 2H, Ar), 7.40 (m, 1H, Ar), 7.59−7.62 (m, 2H, Ar), 7.93 (d, $^4J_{HP} = 11.70$ Hz, 1H, HC═N); ^{13}C NMR (75 MHz, C_6D_6, δ) −7.88 (d, $^2J_{CP} = 54.59$ Hz, Pd−CH_3), 23.98, 25.82, 29.22, 51.50 (d, $^1J_{CP} = 15.23$ Hz, P−C−N), 73.70(d, $^3J_{CP} = 7.62$ Hz, N−C−N), 113.53, 120.07, 123.61, 126.42, 126.64, 130.45, 135.83, 136.56, 141.17, 142.02, 147.67, 166.53, 166.34; ^{31}P NMR (121 MHz, C_6D_6, δ) −46.16; yield 67.6%.

Scheme 1



Polymerization of Ethylene Using 2a. To a 100 mL glass miniclave reactor was added approximately 10 mL of degassed water, followed by the addition of **2a** (100 mg, 0.162 mmol) in 10 mL of toluene. Ethylene was added until the total pressure was 8 atm. The mixture was stirred for approximately 5 h at ambient temperature. After the system was vented, the toluene layer was separated and toluene was removed by rotoevaporation leaving behind *no* polyethylene.

Results and Discussion

Initially, we attempted the synthesis of the PTA derivatives of nickel salicylaldiminato complexes using the commonly employed protocol of rapidly stirring a biphasic mixture consisting of the PPh_3 analogue complex (e.g., **1a**) in toluene with excess PTA in water at ambient temperature. However, under these reaction conditions no ligand substitution occurred. This procedure is generally successful since PTA has smaller steric requirements and is a more donating ligand than PPh_3.[14,15] Evidently, in this instance there is little PTA in the organic phase and vice versa. This conclusion is supported upon carrying out the reaction in a homogeneous toluene/methanol mixture in which **1a** and PTA were first dissolved in toluene and methanol, respectively (Scheme 1). That is, upon addition of the concentrated PTA solution to a solution of **1a** in toluene, a yellow precipitate formed immediately. The identity of this yellow derivative (**2a**) was confirmed to be the PTA analogue of **1a** by NMR spectroscopy, elemental analysis, and X-ray crystallography.

The ^{1}H NMR spectrum of **2a** in CD_2Cl_2 displayed many characteristic resonances. Importantly, the signals corresponding to the terminal isopropyl groups (CH(CH_3)$_2$) were split into two sets of doublets indicating a rotation barrier of the aniline moiety upon ligand coordination, consistent with what is observed for other salicylaldiminato complexes.[16,17] Hydrogen resonances due to the PTA ligand are located between 3.7 and 4.2 ppm, with the NCH_2N hydrogens

(14) DeLerno, J. R.; Trefonas, L. M.; Darensbourg, M. Y.; Majeste, R. J. *Inorg. Chem.* **1976**, *15*, 816.
(15) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.
(16) Darensbourg, D. J.; Rainey, P.; Yarbrough, J. *Inorg. Chem.* **2001**, *40*, 986.
(17) Klein, H.; Bickelhaupt, A. *Inorg. Chim. Acta* **1996**, *248*, 111.

Table 1. Crystallographic data for complexes **1a**, **2a**, **4a**,**b**, and **3b′**

	1a	2a	4a	4b	3b′
empirical formula	$C_{43}H_{41}O_3N_2PNi$	$C_{32}H_{40}O_3N_5Cl_2PNi$	$C_{26}H_{36}O_3N_5PPd$	$C_{27}H_{39}O_2N_4PPd$	$C_{40}H_{48}O_4N_2Ni$
fw	723.46	703.27	603.99	588.99	679.08
cryst syst	triclinic	monoclinic	triclinic	orthorhombic	monoclinic
space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	*Pbca*	$P2_1/n$
V, Å^3	1780.6(4)	3169.3(5)	1336.4(18)	5384(4)	3947.3(8)
Z	2	4	2	8	4
a, Å	9.5718(12)	10.1182(9)	9.127(7)	12.249(6)	8.9737(11)
b, Å	12.0581(16)	20.5266(18)	10.888(8)	18.457(8)	20.255(3)
c, Å	15.784(2)	15.5267(13)	15.293(14)	23.812(11)	21.720(3)
α, deg	90.158(2)		69.195(14)		
β, deg	99.214(3)	100.643(2)	76.151(19)		90.919(3)
γ, deg	97.906(3)		71.950(12)		
T, K	110	110	110	110	110
d(calc), g/cm^3	1.349	1.474	1.501	1.453	1.286
abs coeff, mm^{-1}	0.633	0.874	0.791	0.780	0.669
R,[a] % [$I > 2\sigma(I)$]	4.79	8.10	8.00	3.43	6.11
R_w,[a] %	8.79	19.85	9.41	5.23	14.62

[a] $R = \sum||F_o| - |F_c||/\sum F_o$ and $R_{wF} = \{[\sum w(F_o - F_c)^2]/\sum wF_o^2\}^{1/2}$.

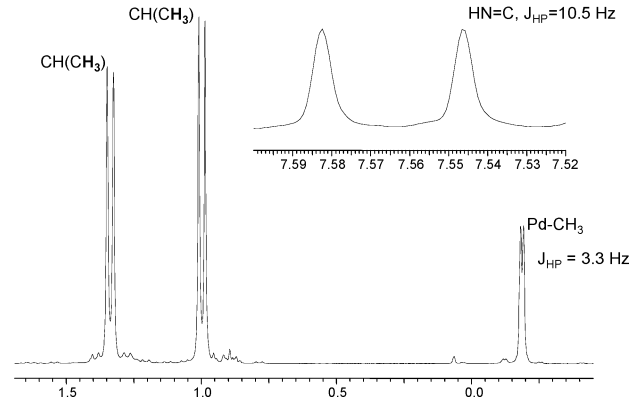
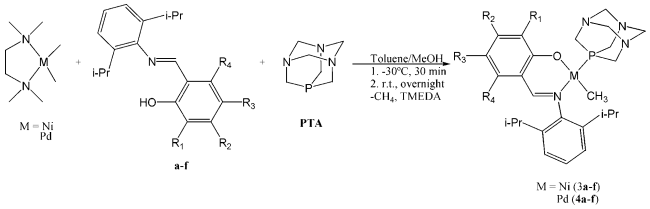


Figure 3. Representative ^{1}H NMR spectrum of **4d**.

Scheme 2



appearing as singlets. The resonance due to the PCH_2N hydrogen is observed as a doublet of doublets as a result of coupling to phosphorus and the geminal proton ($^2J_{HP} \sim 25$ Hz and $^2J_{HH} \sim 13$ Hz). The ketimine (*H*C═N) hydrogen is displayed as a doublet near 8.0 ppm with phosphorus coupling on the order of 8.1 Hz, as previously reported for the PPh_3 derivatives (**1**).[6] The ^{31}P NMR resonance in **2a** (−57.76 ppm) is shifted in CD_2Cl_2 40.5 ppm downfield from free PTA at −98.3 ppm in water.

Alternatively, salicylaldiminato PTA complexes may be prepared via a direct synthetic approach in which (TMEDA)M-$(CH_3)_2$ (M = Ni, Pd) is used as the metal precursor.[13] With liberation of methane in the process, the metal precursor is reacted with PTA and the corresponding salicylaldimine at −30 °C to yield the nickel and palladium complexes (**3** and **4**) in moderate to quantitative yields (Scheme 2). The ^{1}H NMR resonance of the ketimine hydrogen in **4** displays phosphorus coupling ($J_{HP} \sim 11$ Hz) with chemical shift values similar to those observed for **1**.[6] Resonances due to the M−CH_3 protons are consistent with other group 10 complexes, occurring in the 0 to −1 ppm range.[17,18] Interestingly, the nickel derivatives, **3**, do not exhibit ^{31}P coupling of the methyl and ketimine hydrogen atoms to PTA. This is in contrast to the SHOP catalyst developed by Keim and co-workers, where ^{31}P coupling to the methyl hydrogens was observed ($J_{HP} \sim 7.4$ Hz).[18a] Complex **4**, however, does exhibit ^{31}P coupling ($J_{HP} \sim 5$ Hz) of the Pd−CH_3 hydrogen atoms to PTA. A representative ^{1}H NMR spectrum of **4d** is presented in Figure 3.

The ^{13}C NMR spectra of complexes **3** and **4** also display unique resonances. The Ni−CH_3 carbon resonances are observed in the −15 to −20 ppm range with ^{31}P coupling on the order of 4 Hz. In contrast, the Pd−CH_3 carbon resonances are displayed further downfield (−7 to −9 ppm) with a larger ^{31}P coupling ($J_{CP} \sim 15$ Hz). The NCH_2N and PCH_2N carbons of the PTA ligand are observed in the 50 and 70 ppm region, respectively. ^{31}P coupling is also observed for the PCH_2N carbons with approximate values of 8 and 15 Hz for **3** and **4**, respectively. As expected, a smaller ^{31}P coupling constant is associated with the NCH_2N carbon, with J_{CP} values on the order of 5−7 Hz for **3** and **4**, respectively. The ^{31}P NMR resonances for these complexes are observed at approximately −60 and −45 ppm for **3** and **4**, respectively.

The solid-state structure of the nickel(II) salicylaldimato derivative containing the PPh_3 ligand (complex **1e** in Figure 1) has been reported by Grubbs and co-workers.[6a] Herein, we describe the solid-state structure of an analogous complex, **1a**, for comparative purposes. Crystals of **1a** suitable for X-ray analysis were obtained from a solution of **1a** in toluene maintained at −20 °C for approximately 2 weeks. Tables 1 and 2 contain the crystallographic data and selected bond distances and angles, whereas a thermal ellipsoid representation of complex **1a** may be found in Figure 4. As expected for four-coordinate d^8 metal complexes, the structure of **1a** adopts a nearly ideal square planar geometry with N−Ni−P and C−Ni−O bond angles of 176.61(7) and 171.64(10)°,

(18) (a) Klein, H.; Keim, W.; Heinicke, J.; He, M.; Dal, A.; Hetche, O.; Flörke, U.; Haupt, H. *Eur. J. Inorg. Chem.* **2000**, 431. (b) Klein, H.; Wiemer, T. *Inorg. Chim. Acta* **1988**, *154*, 21.

Table 2. Selected Bond Distances (Å) and Angles of Complexes **1a**, **2a**, **4a**,**b**, and **3b′**[a]

	1a	2a	4a	4b	3b′
			Bond Distances		
M(1)−C(1)	1.893(3)	1.893(6)	2.024(9)	2.036(4)	
M(1)−P(1)	2.1754(8)	2.1345(18)	2.199(3)	2.1995(12)	
M(1)−O(1)	1.9141(19)	1.888(4)	2.094(5)	2.068(2)	1.827(3)
M(1)−N(1)	1.947(2)	1.964(5)	2.097(6)	2.087(3)	1.907(3)
			Bond Angles		
C(1)−M(1)−O(1)	171.64(10)	169.7(2)	176.1(3)	177.13(13)	
P(1)−M(1)−C(1)	84.86(8)	83.85(18)	87.7(3)	86.26(11)	
O(1)−M(1)−N(1)	92.86(4)	87.68(13)	88.6(2)	89.67(11)	93.37(12)
P(1)−M(1)−O(1)	89.65(6)	92.99(18)	90.44(17)	90.98(8)	
P(1)−M(1)−N(1)	176.61(7)	173.33(15)	175.82(19)	173.27(8)	
N(1)−M(1)−N(2)					178.04(12)

[a] Estimated standard deviations are given in parentheses.

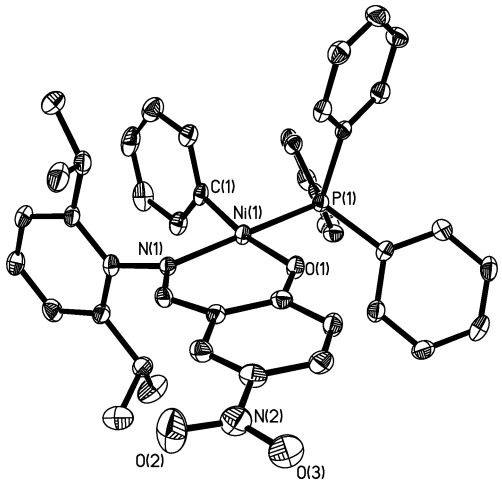


Figure 4. Thermal ellipsoid representation of **1a** showing 50% probability ellipsoids.

respectively. The isopropyl groups on the 2,6-diisopropylbenzimine lie perpendicular to the plane created by the N, P, O, and C atoms. Such positioning allows these groups to effectively shield the axial faces of the metal center to enhance the rate of enchainment relative to chain transfer.[4,6] The positioning is also in accord with the solution spectroscopic data where two sets of doublets are observed for the terminal isopropyl hydrogens in the ^{1}H NMR spectrum. The Ni−C bond distance was found to be nearly identical with that observed in **1e**, having a value of 1.893(3) Å. Consistent with the Ni−P bond distance of **1e** (2.172(2) Å), in **1a**, the distance associated with this bond was found to be 2.1754(8) Å, indicating little steric interaction of large groups in the R_1 position with PPh_3.

Using the same crystal growth technique as described for **1a**, suitable crystals for X-ray analysis of several of the other derivatives were obtained. The thermal ellipsoid drawings of two such complexes (**2a** and **4a**) are shown in Figures 5 and 6, respectively. Selected bond lengths and angles are listed in Table 2. Similar to the solid-state structures of **1a**,**e**, these complexes adopt the typical square planar geometry (e.g., N−M−P angles in **2a** and **4a** were found to be 173.33(15) and 173.27(8)°). The nickel−carbon bond distance to the phenyl ligand in **2a** at 1.893(6) Å is identical to that seen in complex **1a**. Comparing the Ni−P bond distances in **1a** of 2.1754(8) Å to that seen in **2a** of 2.1345(18) Å, we notice a shortening of the bond distance in **2a** of approximately 0.05 Å. This decrease in Ni−P bond length upon going from PPh_3 to PTA is consistent with the smaller cone angle (103°) and more basic nature of PTA as compared to PPh_3. The Pd−P bond distance in **4a** was found to be 2.199(3) Å, which is slightly shorter than that observed in *cis*-$PdCl_2(PTA)_2$ of 2.226(5) Å.[19] The difference in the Pd−P bond length in **4a** vs the corresponding Ni−P bond distance in **2a** of 0.07 Å is less than the covalent radii difference in nickel and palladium of 0.11 Å. The Pd−C(methyl) bond

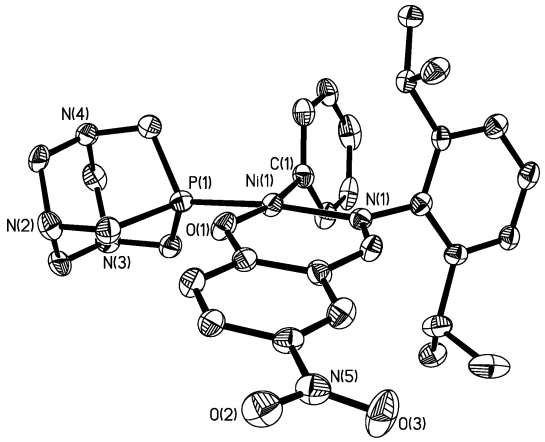


Figure 5. Thermal ellipsoid representation of **2a** showing 50% probability ellipsoids.

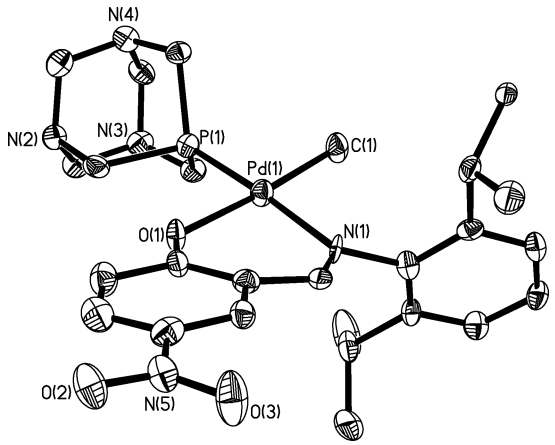


Figure 6. Thermal ellipsoid representation of **4a** showing 50% probability ellipsoids.

(19) Darensbourg, D. J.; Decuir, T. J.; Stafford, N. W.; Robertson, J. B.; Draper, J. D.; Reibenspies, J. H.; Kathó, A.; Joó, F. *Inorg. Chem.* **1997**, *36*, 4218.

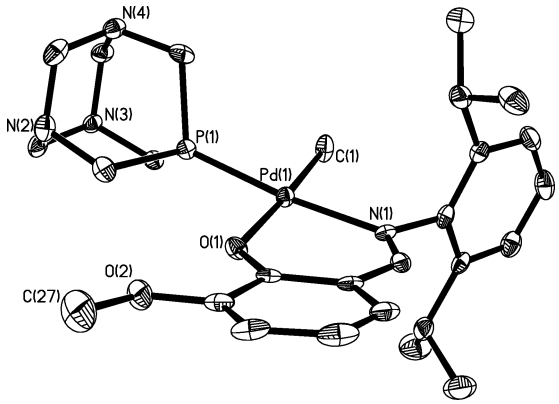


Figure 7. Thermal ellipsoid representation of **4b** showing 50% probability ellipsoids.

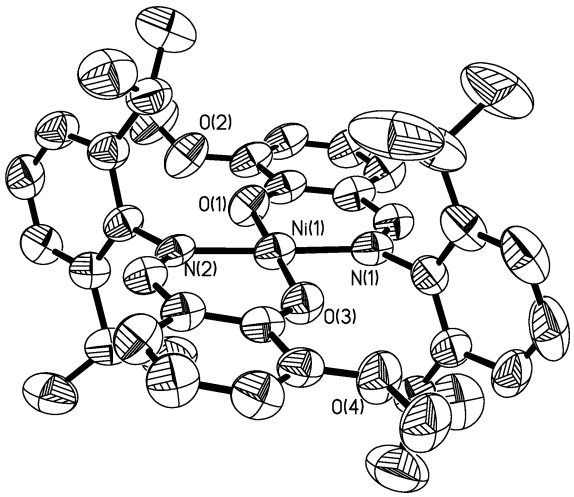


Figure 8. Thermal ellipsoid representation of **3b′** showing 50% probability ellipsoids.

length was determined to be 2.024(9) Å in **4a**. The solid-state structure of the methoxy derivative, complex **4b**, was also determined, and its structure is depicted in the thermal ellipsoid representation in Figure 7. In this instance, the electron-donating ability of the OCH_3 group is not reflected in the Pd−P bond distance of 2.1995(12) Å, which is the same as that observed in **4a** (Table 2). However, the Pd−C bond distance increases by approximately 0.025 Å. Nevertheless, electron-donating effects have been shown to greatly decrease the activity of the catalyst as evident in a decrease in the reported turnover number from 253 kg of polyethylene/mol of Ni for **1a** to 13.3 kg of polyethylene/mol of Ni for **1b**.[6a] X-ray structural data for other closely related (salicylaldiminato)M(methyl)(PTA) derivatives (M = Ni, **3b**,**d**; M = Pd, **4c**,**d**) are included in the Supporting Information.

In a few cases during crystal growth over extended periods of time, ligand redistribution occurred with concomitant formation of the thermodynamically stable bis(salicylaldiminato) complexes. These crystals are black in color and appear to be relatively stable in air. The solid-state structure of one such isolated species, **3b′**, has been determined by X-ray crystallography. A thermal ellipsoid drawing of **3b′** is shown in Figure 8.

The Ni−N and Ni−O bond distances observed in complex **3b′** of 1.907(3) and 1.827(3)Å are slightly shorter than the corresponding parameters found in the parent (salicylaldiminato)Ni(methyl)(PTA) derivative, **3b**, of 1.931(6) and 1.881(5) Å, respectively. These decreases in bond lengths are anticipated upon loss of the electron-donating phosphine ligand. The formation of such bis complexes is clearly undesirable in polymerization processes and has been an issue for SHOP-type systems which utilize higher temperatures and pressure to produce high molecular weight polyethylene.[20]

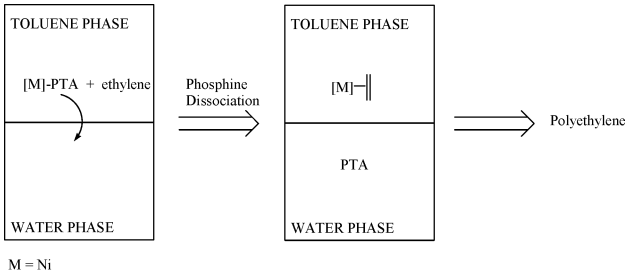


Figure 9. Polymerization of ethylene using **2a** in a biphasic toluene/water biphasic solvent system.

Ethylene Polymerization. The polymerization of ethylene using **1** was first reported in 1998.[6] Although derivatives incorporating large groups in the R_1 position of the salicylaldimine (e.g. **1e**) did not require a phosphine scavenger, other active derivatives such as **1a** did in fact necessitate the use of the air-sensitive cocatalyst, $Ni(COD)_2$. Our approach to bypass the need for a cocatalyst involves the use of water-soluble phosphines to facilitate the dissociation process illustrated in Figure 9. The dissociation of PTA into the aqueous phase would effectively allow the formation of the active catalyst in the organic phase, initiating the polymerization. Furthermore, upon PTA dissociation, reentering of this phosphine into the organic phase would not occur, since PTA is not soluble in toluene. This was previously quite evident upon failing to synthesize **2** via a biphasic toluene/water ligand replacement process (vide supra).

For all attempts to polymerize ethylene at ambient temperature using **2a** as catalyst utilizing a biphasic toluene/water (1/1) solvent system under 8 atm of ethylene pressure, *no* polymer formation was observed. Raising the temperature to 70 °C resulted in Ni(0) formation, and analysis of the water phase revealed the presence of the phosphine oxide, PTA═O. The formation of phosphine oxide has also been observed in other rhodium and ruthenium catalytic systems.[11c]

Concluding Remarks

Herein, we have reported the synthesis of methyl and phenyl derivatives of nickel and palladium salicylaldiminato complexes containing the water-soluble phosphine (PTA) in excellent yields. These complexes have all been structurally characterized in the solid state by X-ray crystallography. Thus far, we have been unproductive in catalyzing the polymerization of ethylene with (salicylaldiminato)Ni(Ph)(PTA) in

(20) Ittel, S. D.; Calabrese, J.; Klabunde, U.; Mulhaupt, R.; Herskovitz, T.; Janowicz, A. H. *J. Polym. Sci., Part A: Polym. Chem.* **1987**, *25*, 1989.

a biphasic medium. This is undoubtedly due to the stability of the Ni−PTA bond, i.e., the high temperature required to effect phosphine dissociation in this instance.

With regard to this latter point, we have attempted to determine the rate of Ni−PTA bond dissociation in **2a** initially utilizing a large excess (10 equiv) of PPh_3 as incoming ligand. At ambient temperature, as well as at 35 °C, the ^{31}P signal of PTA in **2a** at −57.8 ppm was unaffected over an extended reaction period. On the other hand, a similar experiment involving the use of the more basic and less sterically hindered phosphine, PMe_3, as entering ligand resulted in immediate displacement of the PTA ligand at ambient temperature. This latter process is evidently taking place via an associative mechanism, a common occurrence in square-planar nickel(II) complexes. Hence, qualitatively it is apparent that the dissociation of PTA from **2a** is not a facile process at modest reaction temperatures.

The slow initiation step when employing complex **2a** as catalyst precursor for the polymerization of ethylene might be overcome by preparing nickel(II) derivatives bearing other water-soluble phosphines. For example, the water-soluble *meta*-TPPTS ligand, which is electronically almost identical with PPh_3 and thereby expected to have similar or enhanced Ni−PR_3 dissociation rates, would seem to be quite appropriate.[21] Unfortunately, we have thus far been unsuccessful at preparing the *meta*-TPPTS analogue of complex **2a**. This is most likely due to the significantly larger cone angle in *meta*-TPPTS of 170° [22] vs that of PPh_3 (145°).[15] In principle the approach outlined in Figure 9 appears to be fundamentally sound if a set of suitable conditions can be found. It is probable that employing less sterically encumbered water-soluble triphenylphosphine derivatives as ligands will lead to metal complexes which have metal−PR_3 bond dissociation energies similar to that for metal−PPh_3, thereby making them effective catalysts for this polymerization process.[23]

Acknowledgment. Financial support from the National Science Foundation (Grants CHE 99-10342 and CHE 02-34222; Grant CHE 98-07975 for the purchase of X-ray equipment) and the Robert A. Welch Foundation is greatly appreciated.

Supporting Information Available: Tables of anisotropic thermal parameters, bond distances, and bond angles for complexes **1a**, **2a**, **3b**, **3b′**, **3d**, and **4a**−**d**, in CIF format, and selected crystallographic data, bond distances and angles, and thermal ellipsoid representations for complexes **3b**,**d** and **4c**,**d**, in pdf format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC0341284

(21) Darensbourg, D. J.; Bischoff, C. J. *Inorg. Chem.* **1993**, *32*, 47.

(22) Darensbourg, D. J.; Bischoff, C. J.; Reibenspies, J. H. *Inorg. Chem.* **1991**, *30*, 1144.

(23) Stelzer, O.; Sheldrick, W. S.; Weferling, N.; Herd, O.; Hebler, A.; Langhans, K. P. *J. Organomet. Chem.* **1994**, *475*, 99.