ORGANOMETALLICS

Volume 27, Number 19, October 13, 2008

Communications

Base-Free Phosphine−Sulfonate Nickel Benzyl Complexes

Xiaoyuan Zhou, Sébastien Bontemps, and Richard F. Jordan*

Department of Chemistry, The University of Chicago, 5735 South Ellis Avenue, Chicago, Illinois 60637

Received July 31, 2008

*Summary: Base-free [2-PR$_2$-4-Me-benzenesulfonate)]Ni(η^3-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 the ethylene pressure (60−300 psi).* **4b** *is less active than* **4a** *and produces a polymer with higher M_n, fewer branches, and a higher fraction of terminal olefin units.*

Palladium alkyl complexes that contain *o*-phosphinoarenesulfonate ligands ([PO]$^-$) catalyze the copolymerization of ethylene and polar monomers to linear functionalized polyethylenes. In-situ-generated and discrete [PO]PdR species copolymerize ethylene with carbon monoxide,[1] alkyl acrylates,[2] acrylonitrile,[3] vinyl ethers,[4] vinyl fluoride,[5] functionalized norborenes,[6] *N*-vinylpyrrolidinone and *N*-isopropylacrylamide,[7] and copolymerize vinyl acetate with carbon monoxide.[8] Analogous [PO]NiR species are of interest because nickel catalysts are often more reactive and are less expensive than palladium catalysts and thus are more attractive for practical applications.[9,10]

In-situ-generated [PO]NiR species were reported to oligomerize ethylene to C_4−C_{20} α-olefins[11] and to polymerize ethylene.[2a] Rieger showed that discrete (2-PAr$_2$-benzenesulfonate)Ni(Ph)(PPh$_3$) complexes (Ar = Ph, 2-Me-Ph, 2-OMe-Ph) polymerize ethylene to low-molecular-weight (M_w = 1000−4000), moderately branched (15−25 branches/10^3 C) polymers in the presence of phosphine scavengers (B(C$_6$F$_5$)$_3$ or Ni(COD)$_2$, where COD = 1,5-cyclooctadiene).[12] Low activities were observed in the absence of a scavenger. [PO]NiR catalysts are inhibited by methyl methacrylate and poisoned by

---

* E-mail: rfjordan@uchicago.edu.

(1) (a) Drent, E.; Dijk, R.; Ginkel, R.; Oort, B.; Pugh, R. I. *Chem. Commun.* **2002**, 964. (b) Hearley, A. K.; Nowack, R. J.; Rieger, B. *Organometallics* **2005**, *24*, 2755. (c) Newsham, D. K.; Borkar, S.; Sen, A.; Conner, D. M.; Goodall, B. L. *Organometallics* **2007**, *26*, 3636. (d) Bettucci, L.; Bianchini, C.; Claver, C.; Suarez, E. J. G.; Ruiz, A.; Meli, A.; Oberhauser, W. *Dalton Trans.* **2007**, 5590.

(2) (a) Drent, E.; Dijk, R.; Ginkel, R.; Oort, B.; Pugh, R. I. *Chem. Commun.* **2002**, 744. (b) Drent, E.; Pello, D. H. L. European Patent 0632084, 1995. (c) Kochi, T.; Yoshimura, K.; Nozaki, K. *Dalton Trans.* **2006**, 25. (d) Skupov, K. M.; Marella, P. R.; Simard, M.; Yap, G. P. A.; Allen, N.; Conner, D.; Goodall, B. L.; Claverie, J. P. *Macromol. Rapid Commun.* **2007**, *28*, 2033.

(3) Kochi, T.; Noda, S.; Yoshimura, K.; Nozaki, K. *J. Am. Chem. Soc.* **2007**, *129*, 8948.

(4) Luo, S.; Vela, J.; Lief, G. R.; Jordan, R. F. *J. Am. Chem. Soc.* **2007**, *129*, 8946.

(5) Weng, W.; Shen, Z.; Jordan, R. F. *J. Am. Chem. Soc.* **2007**, *129*, 15450.

(6) (a) Liu, S.; Borkar, S.; Newsham, D.; Yennawar, H.; Sen, A. *Organometallics* **2007**, *26*, 210. (b) Skupov, K. M.; Marella, P. R.; Hobbs, J. L.; McIntosh, L. H.; Goodall, B. L.; Claverie, J. P. *Macromolecules* **2006**, *39*, 4279.

(7) Skupov, K. M.; Piche, L.; Claverie, J. P. *Macromolecules* **2008**, *41*, 2309.

(8) Kochi, T.; Nakamura, A.; Ida, H.; Nozaki, K. *J. Am. Chem. Soc.* **2007**, *129*, 7770.

(9) (a) Ittel, S. D.; Johnson, L. K.; Brookhart, M. *Chem. Rev.* **2000**, *100*, 1169. (b) Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F. *Angew. Chem., Int. Ed.* **1999**, *38*, 429. (c) Gibson, V. C.; Spitzmesser, S. K. *Chem. Rev.* **2003**, *103*, 283.

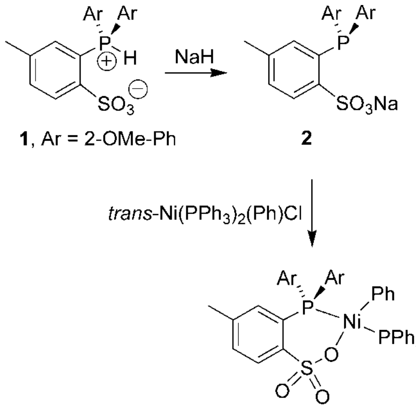
(10) (a) Johnson, L. K.; Killian, C. M.; Brookhart, M. *J. Am. Chem. Soc.* **1995**, *117*, 6414. (b) Liu, W.; Malinoski, J. M.; Brookhart, M. *Organometallics* **2002**, *21*, 2836. (c) Malinoski, J. M.; Brookhart, M. *Organometallics* **2003**, *22*, 5324. (d) Daugulis, O.; Brookhart, M. *Organometallics* **2002**, *21*, 5926. (e) Kim, J. S.; Pawlow, J. H.; Wojcinski, L. M., II; Murtuza, S.; Kacker, S.; Sen, A. *J. Am. Chem. Soc.* **1998**, *120*, 1932.

(11) Murray, R. E. U.S. Patent 4,689,437, 1987.

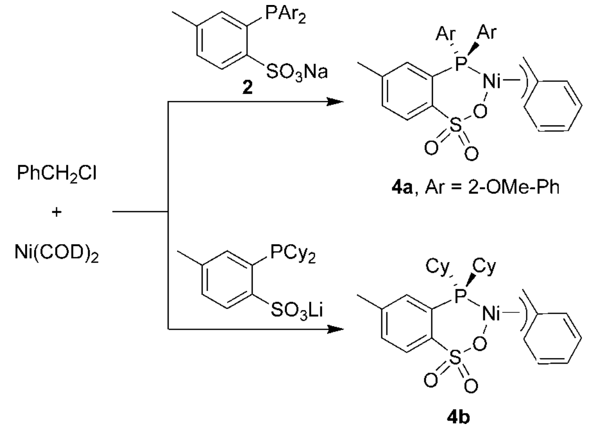
(12) Nowack, R. J.; Hearley, A. K.; Rieger, B. *Z. Anorg. Allg. Chem.* **2005**, *631*, 2775.

10.1021/om800741w CCC: $40.75 © 2008 American Chemical Society
Publication on Web 09/11/2008

Scheme 1



Scheme 2



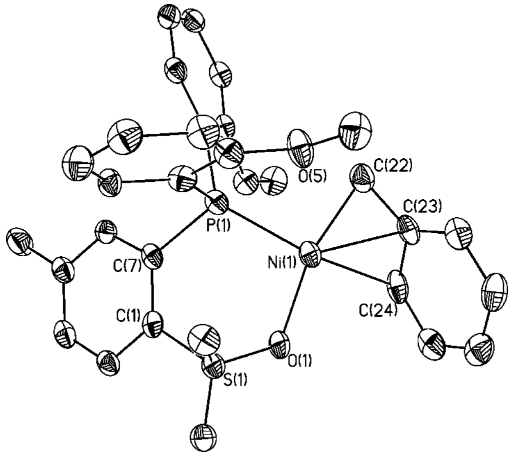


Figure 1. Molecular structure of **4a**. Hydrogen atoms are omitted. Selected bond distances (Å) and angles (deg): Ni(1)−P(1) 2.163(1), Ni(1)−O(1) 1.938(3), Ni(1)−C(22) 1.949(4), Ni(1)−C(23) 2.066(4), Ni(1)−C(24) 2.191(4), S(1)−O(1) 1.499(3), S(1)−O(2) 1.443(3), S(1)−O(3) 1.446(3); O(1)−Ni(1)−P(1) 99.34(8), P(1)−Ni(1)−C(22) 96.8(1), O(1)−Ni(1)−C(24) 91.7(1), C(22)−Ni(1)−C(24) 71.8(2).

methyl acrylate.[2a,12] Similar SHOP-type nickel catalysts that contain phosphine−enolate, phosphine−phenolate, or related ligands have been studied extensively.[13,14]

We are interested in base-free [PO]NiR complexes to simplify mechanistic studies and avoid the use of scavengers, which, in addition to sequestering L ligands of [PO]M(R)(L) species, might also react with the $[PO]^-$ ligand.[15] Here we report the syntheses of base-free [PO]Ni(η^3-CH_2Ph) complexes and their behavior in ethylene polymerization.

We first prepared [PO-OMe]Ni(Ph)(PPh_3) (**3**; $[PO\text{-}OMe]^-$ = 2-P(2-OMe-Ph)$_2$-4-Me-benzenesulfonate) for use as a benchmark PPh_3-stabilized catalyst. Following Rieger's synthesis of the parent benzenesulfonate analogue,[12] the zwitterion [PO-OMe]H (**1**)[16] was deprotonated with NaH to afford Na[PO-OMe] (**2**), which was reacted with *trans*-Ni(PPh_3)$_2$(Ph)Cl[17] to afford **3** in 87% yield (Scheme 1). The $^{31}P\{^1H\}$ NMR spectrum of **3** contains doublets for the PPh_3 (δ 17.1) ligand and the P(2-OMe-Ph)$_2$ unit (δ −4.1) with a large $^2J_{PP}$ value (283 Hz) characteristic of a trans arrangement of the phosphines.

Bazan showed that the reaction of Na[2-PPh$_2$-benzoate], benzyl chloride, and Ni(COD)$_2$ produces [κ^2-*P*,*O*-2-PPh$_2$-$C_6H_4CO_2$]Ni(CH_2Ph) in high yield.[18] We used this method to synthesize [PO]Ni(η^3-CH_2Ph) complexes (Scheme 2). The reaction of **2** with benzyl chloride and Ni(COD)$_2$ gives [PO-OMe]Ni(η^3-CH_2Ph) (**4a**) in 29% yield as a deep-red powder. The analogous reaction of in-situ-generated [PO-Cy]Li ($[PO\text{-}Cy]^-$ = 2-PCy$_2$-4-Me-benzenesulfonate) gives the deep-red product [PO-Cy]Ni(η^3-CH_2Ph) (**4b**) in 11% yield after multiple recrystallizations.

The molecular structures of **4a** and **4b** were determined by X-ray diffraction (Figures 1 and 2).[19] Complex **4a** features an approximately square-planar Ni center. The [PO]Ni chelate ring adopts a boat conformation, with an angle of 129.7° between the S(1)−O(1)−Ni(1)−P(1) and S(1)−C(1)−C(7)−P(1) planes.

---

[13] Review: Kuhn, P.; Semeril, D.; Matt, D.; Chetcuti, M. J.; Lutz, P. *Dalton Trans.* **2007**, 515.

[14] Leading references: (a) Peuckert, M.; Keim, W. *Organometallics* **1983**, *2*, 594. (b) Starzewski, K. A. O.; Witte, J. *Angew. Chem., Int. Ed.* **1987**, *26*, 63. (c) Klabunde, U.; Ittel, S. D. *J. Mol. Catal.* **1987**, *41*, 123. (d) Kuhn, P.; Semeril, D.; Jeunesse, C.; Matt, D.; Neuburger, M.; Mota, A. *Chem.—Eur. J.* **2006**, *12*, 5210. (e) Soula, R.; Broyer, J. P.; Llauro, M. F.; Tomov, A.; Spitz, R.; Claverie, J.; Drujon, X.; Malinge, J.; Saudemont, T. *Macromolecules* **2001**, *34*, 2438. (f) Soula, R.; Saillard, B.; Spitz, R.; Claverie, J.; Llaurro, M. F.; Monnet, C. *Macromolecules* **2002**, *35*, 1513. (g) Gibson, V. C.; Tomov, A.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **2001**, 719. (h) Heinicke, J.; Koehler, M.; Peulecke, N.; He, M.; Kindermann, M. K.; Keim, W.; Fink, G. *Chem.—Eur. J.* **2003**, *9*, 6093. (i) Monteiro, A. L.; de Souza, M. O.; de Souza, R. F. *Polym. Bull.* **1996**, *36*, 331. (j) Pietsch, J.; Braunstein, P.; Chauvin, Y. *New J. Chem.* **1998**, *22*, 467. (k) Heinicke, J.; He, M.; Dal, A.; Klein, H. F.; Hetche, O.; Keim, W.; Flörke, U.; Haupt, H. *Eur. J. Inorg. Chem.* **2000**, 431. (l) Heinicke, J.; Peulecke, N.; Kindermann, M. K.; Jones, P. G. *Z. Anorg. Allg. Chem.* **2005**, *631*, 67.

[15] (a) Chen, Y.; Boardman, B. M.; Wu, G.; Bazan, G. C. *J. Organomet. Chem.* **2007**, *692*, 4745. (b) Chen, Y.; Wu, G.; Bazan, G. C. *Angew. Chem., Int. Ed.* **2005**, *44*, 1108. (c) Kim, Y. H.; Kim, T. H.; Lee, B. Y.; Woodmansee, D.; Bu, X.; Bazan, G. C. *Organometallics* **2002**, *21*, 3082. (d) Lee, B. Y.; Bu, X.; Bazan, G. C. *Organometallics* **2001**, *20*, 5425.

[16] (a) McIntosh, L. H., III; Allen, N. T.; Kirk, T. C.; Goodall, B. L. Can. Pat. Appl. 2556356, 2007. (b) Vela, J.; Lief, G. R.; Shen, Z.; Jordan, R. F. *Organometallics* **2007**, *26*, 6624.

[17] Zeller, A.; Herdtweck, E.; Strassner, T. *Eur. J. Inorg. Chem.* **2003**, 1802.

[18] (a) Komon, Z. J. A.; Bu, X.; Bazan, G. C. *J. Am. Chem. Soc.* **2000**, *122*, 12379. (b) Rojas, R. S.; Wasilke, J.; Wu, G.; Ziller, J. W.; Bazan, G. C. *Organometallics* **2005**, *24*, 5644.

[19] (a) Crystal data for **4a**: $C_{28}H_{27}NiO_5PS$, $M = 565.24$, triclinic, $P\bar{1}$, $a = 9.566(2)$ Å, $b = 9.877(2)$ Å, $c = 15.129(4)$ Å, $\alpha = 104.407(4)°$, $\beta = 95.245(4)°$, $\gamma = 112.580(4)°$, $V = 1250.2(5)$ Å^3, $Z = 2$, $T = 100$ K, Mo Kα radiation (0.710 73 Å), absorption coefficient 0.962 mm^{-1}, 12 010 reflections collected, 4416 independent reflections, $R_{int} = 0.0313$; R indices $[I > 2\sigma(I)]$ R1 = 0.0488, wR2 = 0.1136; R indices (all data) R1 = 0.0687, wR2 = 0.1204. (b) **4b** crystallizes with two independent molecules in the unit cell, which have similar structures; one molecule is shown in Figure 2. Crystal data for **4b**: $2C_{26}H_{35}NiO_3PS + C_7H_8$, $M = 1126.69$, triclinic, $P\bar{1}$, $a = 10.524(3)$ Å, $b = 14.941(4)$ Å, $c = 17.791(5)$ Å, $\alpha = 87.493(5)°$, $\beta = 85.024(5)°$, $\gamma = 81.311(5)°$, $V = 2753(1)$ Å^3, $Z = 2$, $T = 100$ K, Mo Kα radiation (0.710 73 Å), absorption coefficient 0.868 mm^{-1}, 26 770 reflections collected, 9780 independent reflections, $R_{int} = 0.0370$; R indices $[I > 2\sigma(I)]$ R1 = 0.0514, wR2 = 0.0973; R indices (all data) R1 = 0.0877, wR2 = 0.1075.

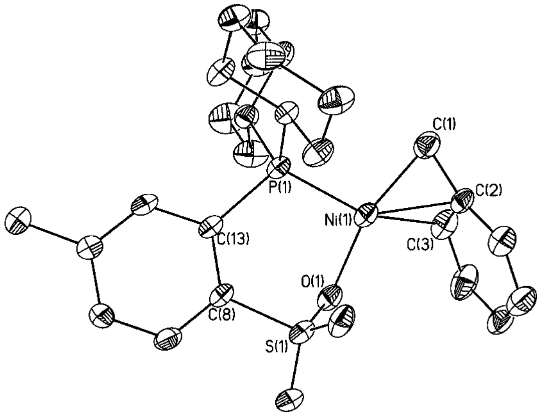


Figure 2. Molecular structure of **4b**. Hydrogen atoms are omitted. Selected bond distances (Å) and angles (deg): Ni(1)−P(1) 2.149(1), Ni(1)−O(1) 1.922(3), Ni(1)−C(1) 1.919(4), Ni(1)−C(2) 2.023(4), Ni(1)−C(3) 2.260(4), S(1)−O(1) 1.477(3), S(1)−O(2) 1.442(3), S(1)−O(3) 1.442(3); O(1)−Ni(1)−P(1) 98.10 (8), P(1)−Ni(1)−C(1) 98.9 (1), O(1)−Ni(1)−C(3) 96.1(1), C(1)−Ni(1)−C(3) 69.8(2).

The methoxy group of the axial 2-OMe-Ph ring [O(5)] sits above an axial coordination site, but the Ni−O distance (Ni(1)−O(5), 3.25 Å) is too long for a significant Ni−O interaction.[20] The benzyl group is coordinated in a η^3 fashion with the methylene group cis to the phosphine. The Ni−$C_{methylene}$ distance is ca. 0.24 Å shorter than the Ni−C_{ortho} distance, as expected based on the greater trans influence of the phosphine compared to the sulfonate ligand and the greater negative charge on the methylene carbon compared to the *o*-carbon of the benzyl anion.[21] Similar features were observed for other η^3-benzyl nickel complexes.[18a,22] The structure of **4b** is similar to that of **4a** except that the [PO]Ni chelate ring in **4b** adopts an envelope conformation, with O(1) lying 0.81 Å out of the Ni(1)−P(1)−C(13)−C(8)−S(1) plane.

The NMR spectra of **4a** and **4b** show that the η^3-benzyl structures are retained in solution. The ^{13}C NMR $-C$H$_2$Ph resonances (**4a**, δ 25.8, J_{CP} = 8 Hz; **4b**, δ 18.1, J_{CP} = 9 Hz) are typical for η^3-benzyl nickel complexes (δ 15−35) and are downfield from the position expected for η^1-benzyl nickel complexes (ca. δ 10).[18,22,23] Additionally, the $^1J_{CH}$ value (157 Hz) for the $-CH_2$Ph groups of **4a** and **4b** is indicative of η^3 coordination. The ambient temperature ^{13}C NMR spectra contain one set of 2-OMe-Ph resonances for **4a** and one set of Cy resonances for **4b**, indicative of fast inversion of the [PO]Ni rings. Also, the ambient temperature ^{1}H NMR spectra of both complexes contain one doublet for the $-CH_2$Ph hydrogens (**4a**, J_{HP} = 5.0 Hz; **4b**, J_{HP} = 3.5 Hz) and one set of $-$CH$_2$*Ph* resonances, which shows that in both cases the edges of the benzyl ligand are equivalent on the NMR time scale. These observations can be accounted for by fast η^3/η^1-benzyl isomerization or fast suprafacial shifting of the [PO]Ni unit across the η^3-benzyl ligand.[22c,23,24]

Ethylene polymerization results for **3**, **4a**, and **4b** at 25 °C and 60−300 psi of ethylene pressure are summarized in Table 1. Comparison of entry 1 versus 2 and entry 4 versus 5 shows that **4a** is ca. 4 times more active and produces polymers with slightly higher M_n compared to **3**. Both **3** and **4a** produce polyethylenes with ca. 10 methyl branches per 1000 carbon atoms, which corresponds to 0.5−1 Me branch/chain. Longer branches were not observed by ^{13}C NMR.[25] The polymers produced by **3** and **4a** contain terminal and internal olefin units, with the terminal/internal ratio being higher for **3** than **4a**. ^{1}H and ^{13}C NMR analysis of polymers produced by **3** shows that the internal olefins are mainly 2-olefins (85%), with small amounts of 2^+-olefins (15%), and that the *E*/*Z* ratio is ca. 1/1.[16b] For the polymers produced by **4a**, 67% of the internal olefins are 2-olefins (*E*/*Z* = 1/1). Increasing the ethylene pressure from 60 to 300 psi results in a higher yield and M_n for **3** but has little influence on the performance of **4a** (entries 7 and 8). The polymer microstructures are not influenced by the pressure in either case. The ethylene polymerization behavior of **4a** is very similar to that of (2-PAr$_2$-benzenesulfonate)Ni(Ph)(PPh$_3$) complexes in the presence of phosphine scavengers.[12]

Comparison of entry 2 versus 3 and entry 5 versus 6 shows that **4b** is ca. 10 times less active but produces polymer with higher M_n compared to **4a**. The polymer produced by **4b** is highly linear (1 Me branch/1000 C) with a high level (91%) of terminal unsaturation. The small fraction of internal olefins contains only 2-olefins.

NMR monitoring of the reaction of **4a** with ethylene (30 equiv) at 25 °C shows that ethylene is immediately and rapidly polymerized but that a minimal amount of **4a** is consumed, showing that the initial insertion is slower than subsequent insertions. For all three catalysts, polymer yields increase by only a factor of 2−3 when the polymerization time is extended from 2 to 18 h (entries 1−3 vs 4−6), indicating that significant catalyst deactivation occurs under these conditions.

These results are consistent with the mechanism in Scheme 3, which is analogous to that established for related (phosphinosulfonamide)nickel catalysts.[26] The lack of a pressure dependence of the polymer yield, M_n, and microstructure for **4a** suggests that the catalyst resting state is the alkyl olefin adduct **II** and that chain transfer occurs by β-H transfer to metal followed by associative olefin exchange of **III** or β-H transfer to monomer and olefin exchange of **IV**. 2,1-Insertion of **III** would generate secondary alkyl species **V**, which can insert ethylene to form Me branches, undergo chain transfer to form internal olefins, or undergo further chain walking, leading to 2^+-olefins.

---

[20] Σ(Ni and O covalent radii) = 1.94 Å; Σ(Ni and O van der Waals radii) = 3.15 Å. Radii are taken from Webelements. See: http://www.webelements.com/.

[21] Bushby, R. J.; Tytko, M. P. *J. Organomet. Chem.* **1984**, *270*, 265.

[22] (a) Lee, B. Y.; Bazan, G. C.; Vela, J.; Komon, Z. J. A.; Bu, X. *J. Am. Chem. Soc.* **2001**, *123*, 5352. (b) Albers, I.; Álvarez, E.; Cámpora, J.; Maya, C. M.; Palma, P.; Sánchez, L. J.; Passaglia, E. *J. Organomet. Chem.* **2004**, *689*, 833. (c) Ascenso, J. R.; Carrondo, M. A.; Dias, A. R.; Gomes, P. T.; Piedade, M. F. M.; Romão, C. C. *Polyhedron* **1989**, *8*, 2449.

[23] (a) Shim, C. B.; Kim, Y. H.; Lee, B. Y.; Dong, Y.; Yun, H. *Organometallics* **2003**, *22*, 4272. (b) S, S.; Joe, D. J.; Na, S. J.; Park, Y.; Choi, C. H.; Lee, B. Y. *Macromolecules* **2005**, *38*, 10027.

[24] (a) Carmona, E.; Paneque, M.; Poveda, M. L. *Polyhedron* **1989**, *8*, 285. (b) Becker, Y.; Stille, J. K. *J. Am. Chem. Soc.* **1978**, *100*, 845. (c) Cotton, F. A.; Marks, T. J. *J. Am. Chem. Soc.* **1969**, *91*, 1339.

[25] Galland, G. B.; de Souza, R. F.; Mauler, R. S.; Nunes, F. F. *Macromolecules* **1999**, *32*, 1620.

[26] Rachita, M. J.; Huff, R. L.; Bennett, J. L.; Brookhart, M. *J. Polym. Sci., Part A* **2000**, *38*, 4627.

[27] PPh$_3$ might also induce chain transfer by the formation of [PO]Ni(R)(ethylene)(PPh$_3$) species as suggested in refs 14d and 14i.

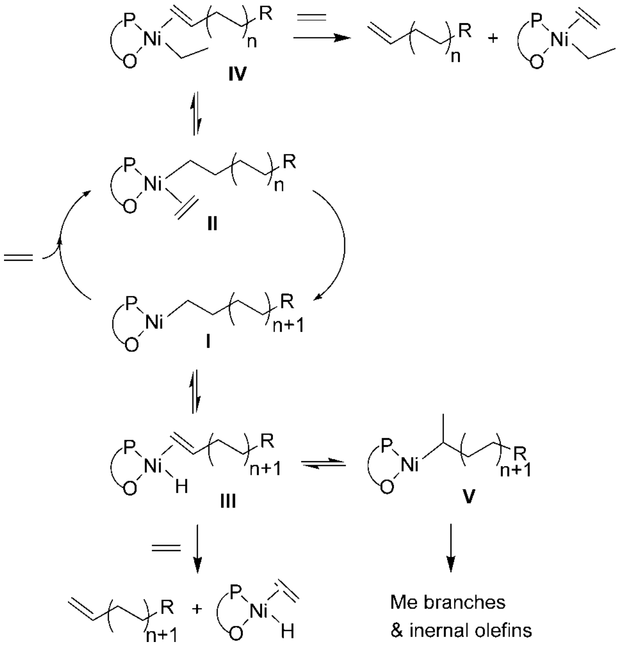
[28] Two isomers and two modes of insertion are possible for [PO]Ni(R)(ethylene) species **II** in Scheme 3. As a result of trans-influence effects, the *cis*-P,R-**II** isomer shown in Scheme 3 is probably more stable than *trans*-P,R-**II**, in which the alkyl is trans to the PR$_2$ unit, but the ethylene insertion barrier is probably higher for *cis*-P,R-**II** than for *trans*-P,R-**II**. A similar situation arises in other unsymmetrical catalysts. It has been proposed that in such systems chain growth proceeds by isomerization of the more stable (LL′)M(R)(olefin) isomer to the less stable isomer, followed by migratory insertion. Thus, chain growth in Scheme 3 may occur by isomerization of *cis*-P,R-**II** to *trans*-P,R-**II** followed by insertion to form **I**; however, further studies are required to fully understand the chain growth mechanism in this system. For discussions of this issue, see refs 13 and 14d and (a) Jenkins, J. C.; Brookhart, M. *J. Am. Chem. Soc.* **2004**, *126*, 5827. (b) Haras, A.; Anderson, G. D. W.; Michalak, A.; Rieger, B.; Ziegler, T. *Organometallics* **2006**, *25*, 4491. (c) Michalak, A.; Ziegler, T. *Organometallics* **2003**, *22*, 2069. (d) Chan, M. S. W.; Deng, L.; Ziegler, T. *Organometallics* **2000**, *19*, 2741.

Table 1. Ethylene Polymerization Results

entry	catalyst	$P(C_2H_4)$ (psi)	time (h)	yield (g)	activity[b]	M_n[c]	Me branches[d]	Ter./Int.[e]
1[a]	**3**	60	2	1.2	30	760	9	68/32
2[a]	**4a**	60	2	5.6	140	1300	11	35/65
3[a]	**4b**	60	2	0.4	11	2100	1	91/9
4[a]	**3**	60	18	2.4	6.5	920	7	78/22
5[a]	**4a**	60	18	9.5	26.3	1200	10	32/68
6[a]	**4b**	60	18	1.3	3.6	2100	1	91/9
7[f]	**3**	300	2	2.2	55	1300	12	69/31
8[f]	**4a**	300	2	6.5	163	1500	11	36/64

[a] Polymerization conditions for entries 1−6: Fisher-Porter glass pressure bottle, 20 μmol catalyst, 60 psi of ethylene pressure, T = 25 °C, solvent = 25 mL of toluene and 5 mL of CH_2Cl_2 (added to dissolve compound **4a**). [b] (g of PE)(mmol of Ni)$^{-1}$ h^{-1}. [c] Determined by ^{1}H NMR assuming that each chain contains one C=C unit. [d] Number of Me branches per 10^3 C, determined by ^{13}C NMR. [e] Ratio of terminal olefins to internal olefins. [f] Polymerization conditions for entries 7 and 8: 300 mL glass-lined stainless steel Parr autoclave equipped with a water cooling loop, a thermocouple, and a magnetically coupled stirrer and controlled by a Parr 4842 controller. Other conditions were the same as entries 1−6.

Scheme 3[a]



[a] R = polymer chain.

The lower polymer yield and M_n observed for PPh_3 complex **3** compared to base-free **4a** reflect competitive binding of PPh_3 to the active nickel species.[12−14] PPh_3 may also displace olefin from **III**, resulting in the observed lower M_n and higher terminal/internal olefin ratio for **3** versus **4a**.[27] The lower activity and higher M_n observed for **4b** compared to **4a** probably reflect the difference in the trans influence of the diaryl- and dialkylphosphino units in these catalysts. The strong trans influence of the PCy_2 unit of **4b** should disfavor structures in which an alkyl or hydride ligand is trans to the PCy_2 unit, raising the barriers for insertion and chain transfer.[14h,28] The differences in the overall electron-donating ability and steric bulk of $-PCy_2$ and $-PAr_2$ may also be important.

This work shows that base-free [PO]Ni(η^3-benzyl) complexes are readily accessible and function as single-component ethylene polymerization catalysts. Studies of the reactions of these and related [PO]Ni(η^3-benzyl) species with polar monomers are in progress.

Acknowledgment. This work was supported by the U.S. Department of Energy (Grant DE-FG-02-00ER15036). We thank Jacqueline DeFoe for assistance with the synthesis of **1** and Ian Steele for assistance with X-ray crystallography.

Supporting Information Available: Experimental procedures, characterization data for new compounds, and crystallographic data for **4a** and **4b** including CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

OM800741W