

Cationic Nickel Complexes Containing Bulky Phosphine Ligands: Catalyst Precursors for Styrene Polymerization

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Received February 13, 2004

The cationic complexes $[\text{Ni}(\eta^3\text{-CH}_2\text{C(R)CH}_2)(\text{P})_2][\text{BPh}_4]$ ($\text{R} = \text{Me, H}$; $(\text{P})_2 = (\text{PMe}^i\text{Pr}_2)_2$, $(\text{PPh}^i\text{Pr}_2)_2$, 1,2-bis(diisopropylphosphino)ethane (dippe)) and $[\text{Ni}(\eta\text{-2-MeInd})(\text{P})_2][\text{BPh}_4]$ ($2\text{-MeInd} = 2\text{-methylindenyl}$; $(\text{P})_2 = (\text{PMe}^i\text{Pr}_2)_2$, $(\text{PPh}^i\text{Pr}_2)_2$, dippe) have been prepared and characterized. These materials are catalyst precursors for the nonliving polymerization of styrene to polystyrene without the need of a cocatalyst such as methylaluminoxane. The polymerization reactions are carried out in refluxing 1,2-dichloroethane, using a 1:1000 catalyst to styrene ratio, yielding essentially atactic polystyrenes with M_n in the range 14 500–155 000 Da and polydispersities between 1.89 and 9.70. The mass properties of the polymers and the overall yield depend much on the nature of the catalyst precursor.

Introduction

The field of catalytic olefin oligomerization and polymerization mediated by late-transition-metal complexes¹ has been renewed following the reports by Brookhart and co-workers of a family of new cationic Ni^{II} and Pd^{II} catalysts containing α -diimine ligands.^{2–9} These complexes are very effective catalysts for the polymerization of ethylene and α -olefins, as well as the copolymerization of ethylene with α -olefins and polar comonomers.^{4,6,9–12} In most cases, the term “catalyst” applies to the catalyst precursor, which, in general, is a complex that ought to undergo activation by use of a cocatalyst to generate the actual catalytically active

cationic species. Among several activators, methylaluminoxane (MAO) is widely used as cocatalyst.¹³ However, there are also cationic or neutral Ni^{II} and Pd^{II} systems capable of olefin polymerization without the need of a cocatalyst.¹⁴

Concerning the polymerization of styrene, the reactions mediated by the aluminum-free cationic complex $[\text{Ni}(\eta^3\text{-CH}_2\text{C}(\text{CH}_3)\text{CH}_2)(\text{COD})][\text{PF}_6]$ have been studied in detail.¹⁵ This compound is a very active homogeneous catalyst precursor for the low-molecular-weight ($M_n = 1000\text{--}3000$ Da) polymerization of styrene. The addition of phosphine ligands¹⁶ to this system causes an increase in the catalytic activity, which is dramatic in some instances (e.g. upon addition of 1 equiv of PPh_3).¹⁷ The activity increase is less pronounced when the incoming phosphine has larger cone angles. An important increase in the stereoregularity of the resulting polymers is also observed upon addition of bulky monodentate phosphine ligands, e.g. PCy_3 , since the isotactic content

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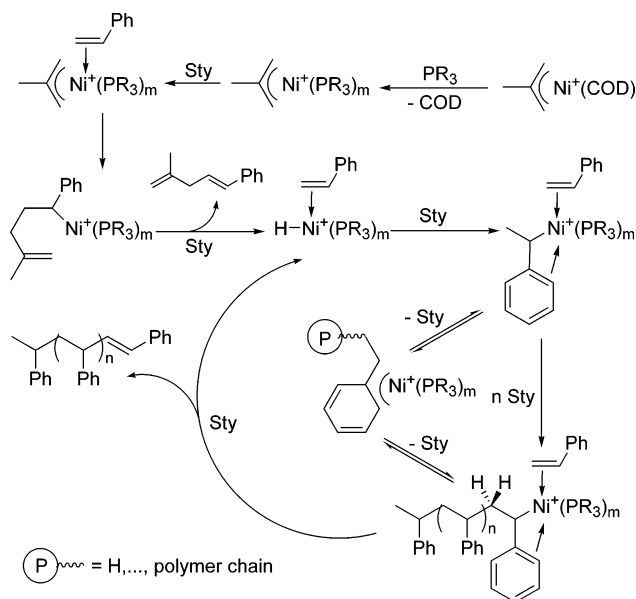
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Scheme 1



P_m may change from 0.65 to 0.90.^{17,18} However, the values of M_n for the polymers remain low (below 2000 Da). NMR data have shown the in situ formation of cationic complexes of the type $[\text{Ni}(\eta^3\text{-CH}_2\text{C}(\text{CH}_3)\text{CH}_2)(\text{PR}_3)_2]^+$ ($\text{PR}_3 = \text{PPh}_3, \text{P}(\text{OPh})_3, \text{P}(\text{o-Tol})_3, \text{PMe}_3, \text{P}^n\text{Bu}_3, \text{PCy}_3$). A mechanism has been proposed involving addition of styrene to a Ni-H bond, due to either phosphine dissociation or exchange with the monomer, to yield a styryl complex, bound to the nickel center in an η^3 -benzyl fashion, which by multiple insertion and subsequent β -hydride elimination gives rise to regio-regular head-to-tail polystyrene chains containing methyl and unsaturated end groups (Scheme 1). Strong evidence in favor of this mechanism was provided by the NMR detection and isolation of a cationic η^3 - α -methylbenzyl nickel species, catalytic studies on structurally characterized cationic η^3 -benzyl nickel complexes, and microstructural studies of the polymers obtained.^{15,17-19}

Indenyl complexes, capable of undergoing facile ring slippage of the indenyl ligand (Ind) involving change from η^5 to a η^3 allyl-like coordination (indenyl effect), have also shown to be active in olefin oligomerization and polymerization.²⁰⁻²⁶ Thus, Zargarian and co-workers have reported that the neutral complexes $[\text{Ni}(\eta^3\text{-1-R-indenyl})\text{X}(\text{PR}_3)]$ ($\text{R} = \text{Me}, \text{iPr}$; $\text{X} = \text{Cl}, \text{Me}, \text{C}\equiv\text{CPh}$; $\text{PR}_3 = \text{PPh}_3, \text{PMe}_3$) in combination with MAO are capable of polymerizing ethylene to fairly high molecular weight polyethylene at a modest level of activity.²² Interestingly, these authors have reported that the cationic derivatives $[\text{Ni}(\eta\text{-indenyl})(\text{PR}_3)_2]^+$ are quite

inert toward phosphine substitution and as such cannot be used in catalysis in the absence of cocatalysts, although a moderate level of catalytic activity can be induced at higher temperatures.²⁰ Monophosphine Ni(η -indenyl) complexes are therefore more reactive than the bis(phosphine) derivatives. However, in contrast with this, it has been reported very recently that the complexes $[\text{Ni}(\eta\text{-1-R-Ind})\text{Cl}(\text{PPh}_3)]$ ($\text{R} = \text{cyclopentyl}, \text{benzyl}$) are able to catalyze the polymerization of styrene effectively in the presence of NaBPh_4 and PPh_3 , at 80 °C, in toluene, to give atactic polystyrenes with M_n values in the range 4000–7000 Da.²⁷ The cationic indenyl complexes $[\text{Ni}(\eta\text{:}\sigma\text{-1-IndCH}_2\text{CH}_2\text{NMe}_2)(\text{PR}_3)]^+$ ($\text{R} = \text{Ph}, \text{Me}, \text{Cy}$) contain an amine group tethered to the indenyl ligand, which is hemilabile. These compounds are capable of initiating styrene polymerization at 80 °C, yielding polystyrenes with M_n values of 24 500 Da ($\text{R} = \text{Ph}$), 35 000 Da ($\text{R} = \text{Cy}$), and 61 000 Da ($\text{R} = \text{Me}$), whereas at 20 °C these values are lower, 6500 Da ($\text{R} = \text{Cy}$) and 13 000 Da ($\text{R} = \text{Me}$), with narrower molecular weight distributions.^{23,25} The complexes $[\text{Ni}(\eta\text{:}\sigma\text{-1-IndCH}_2\text{Y})(\text{PPh}_3)]^+$ bearing different amino tethers ($\text{Y} = 2\text{-pyridyl}, \text{CH}_2\text{-pyrrolidine}, \text{CH}_2\text{N}^i\text{Pr}_2$) were also employed as catalysts in the polymerization of styrene, demonstrating that the nature of the N moiety influences the catalytic activity.²⁶

We have described the preparation of cationic 2-methylallyl, allyl, and 2-methylindenyl nickel complexes bearing the bulky phosphine ligand 1,2-bis(diisopropylphosphino)ethane (dippe).²⁸ We have now prepared new derivatives containing the bulky monodentate phosphine ligands PR^iPr_2 ($\text{R} = \text{Me}, \text{Ph}$). All these complexes have been tested as catalysts for the polymerization of styrene. These catalytic reactions, together with the characterization of the new complexes and of the resulting polystyrenes, are described in the present work.

Experimental Section

All synthetic operations were performed under a dry dinitrogen or argon atmosphere following conventional Schlenk techniques. Tetrahydrofuran, diethyl ether, and petroleum ether (boiling point range 40–60 °C) were distilled from the appropriate drying agents. All solvents were deoxygenated immediately before use. PMe^iPr_2 and PPh^iPr_2 , as well as the complexes $[\text{Ni}(\text{COD})_2]$, $[\text{Ni}(\eta\text{-2-MeInd})\text{Br}(\text{PPh}_3)]$, $[\text{Ni}(\eta^3\text{-CH}_2\text{C}(\text{R})\text{CH}_2)(\text{dippe})][\text{BPh}_4]$ ($\text{R} = \text{Me}$ (**1c**), H (**2c**)), and $[\text{Ni}(\eta\text{-2-MeInd})(\text{dippe})][\text{BPh}_4]$ (**4c**) were obtained according to the literature.²⁸ Styrene was dried by stirring over CaH_2 and then purified by trap-to-trap distillation. NMR spectra were taken on Varian Unity 400 MHz or Varian Gemini 200 MHz equipment. Microanalysis was performed by the Serveis Científico-Tècnics, Universitat de Barcelona. Molecular weight distributions were determined at 35 °C by GPC/SEC using a Waters 150 CV equipment fitted with three serial-mounted Ultrastayragel columns: HR1, HR3, HR4 (10 μm ; 7.8 \times 300 mm). The polymer samples were eluted with THF at a flow rate of 1 $\text{cm}^3 \text{min}^{-1}$. The system was calibrated using polystyrene standards (TSK Tosoh Co.).

$[\text{Ni}(\eta^3\text{-CH}_2\text{C}(\text{R})\text{CH}_2)(\text{PMe}^i\text{Pr}_2)_2][\text{BPh}_4]$ ($\text{R} = \text{Me}$ (1a**), H (**2a**)).** To a slurry of $[\text{Ni}(\text{COD})_2]$ (0.54 g, 2 mmol) in diethyl ether (20 mL) cooled to -80 °C using a liquid N_2 -ethanol bath

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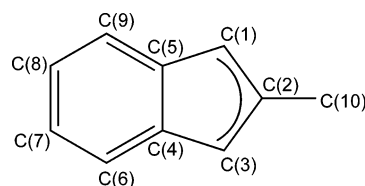
was added 3-bromo-2-methylpropene (for **1a**) or allyl bromide (for **2a**) (2 mL of a stock 1 M solution in diethyl ether, 2 mmol). The mixture was warmed to room temperature and stirred for 1 h. During this time it changed from yellow to red. At this stage PMe^iPr_2 (0.3 mL, 2 mmol) was added. The mixture was stirred for 15 min, and then the solvent was removed under vacuum. The residue was extracted with methanol. The orange-brown solution was filtered through Celite in order to remove finely divided black metallic nickel, not always but very often present in the reaction mixture. An excess of solid NaBPh_4 (ca. 0.4 g) was added to the filtered solution. The yellow or orange microcrystalline precipitate generated was filtered off, washed with ethanol and petroleum ether, and dried under vacuum. The complexes were recrystallized from acetone–ethanol. Data for **1a**: yield 0.52 g, 75% based on the starting amount of PMe^iPr_2 . Anal. Calcd for $\text{C}_{42}\text{H}_{61}\text{BNiP}_2$: C, 72.3; H, 8.82. Found: C, 72.0; H, 8.58. $^1\text{H NMR}$ (CDCl_3 , 298 K): δ 0.92 (m, 24 H, $\text{P}(\text{CH}(\text{CH}_3)_2)_2$); 0.97 (m, 6 H, PCH_3); 1.63 (s, 3 H, $\text{CH}_2\text{C}(\text{CH}_3)\text{CH}_2$); 1.81 (m, 4 H, $\text{P}(\text{CH}(\text{CH}_3)_2)_2$); 1.96 (s br, 2 H, $\text{CH}^{\text{anti}}\text{C}(\text{CH}_3)\text{CH}^{\text{anti}}$); 3.57 (s br, 2 H, $\text{CH}^{\text{syn}}\text{C}(\text{CH}_3)\text{CH}^{\text{syn}}$); 6.76 (t, $^3J_{\text{HH}} = 7.3$ Hz, 4 H), 6.91 (t, $^3J_{\text{HH}} = 7.3$ Hz, 8 H), 7.33 (br, 8 H), $\text{B}(\text{C}_6\text{H}_5)_4$. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 298 K): δ 28.3 s. $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 298 K): δ 5.5 (PCH_3); 17.7, 18.2, 19.7, 19.8 (s, $\text{P}(\text{CH}(\text{CH}_3)_2)_2$); 23.1 (s, $\text{CH}_2\text{C}(\text{CH}_3)\text{CH}_2$); 27.5 (m, $\text{P}(\text{CH}(\text{CH}_3)_2)_2$); 63.1 (m, $\text{CH}_2\text{C}(\text{CH}_3)\text{CH}_2$); 127.3 (s, $\text{CH}_2\text{C}(\text{CH}_3)\text{CH}_2$). Data for **2a**: yield 0.48 g, 70% based on the starting amount of PMe^iPr_2 . Anal. Calcd for $\text{C}_{41}\text{H}_{59}\text{BNiP}_2$: C, 72.1; H, 8.70. Found: C, 71.9; H, 8.52. $^1\text{H NMR}$ (CDCl_3 , 298 K): δ 1.09 (m, 6 H, PCH_3); 1.49 (m, 24 H, $\text{P}(\text{CH}(\text{CH}_3)_2)_2$); 1.94 (m, 4 H, $\text{P}(\text{CH}(\text{CH}_3)_2)_2$); 2.14 (d, $^3J_{\text{HH}} = 16$ Hz, 2 H, $\text{CH}^{\text{anti}}\text{CHCH}^{\text{anti}}$); 3.92 (br, 2 H, $\text{CH}^{\text{syn}}\text{CHCH}^{\text{syn}}$); 4.85 (m, 1 H, CH_2CHCH_2); 6.76 (t, $^3J_{\text{HH}} = 7.3$ Hz, 4 H), 6.91 (t, $^3J_{\text{HH}} = 7.3$ Hz, 8 H), 7.33 (br, 8 H), $\text{B}(\text{C}_6\text{H}_5)_4$. $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 298 K): δ 27.5 s. $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 298 K): δ 8.75 (PCH_3); 17.9, 18.2, 19.8 (s, $\text{P}(\text{CH}(\text{CH}_3)_2)_2$); 27.5 (m, $\text{P}(\text{CH}(\text{CH}_3)_2)_2$); 66.4 (t, $J_{\text{CP}} = 3$ Hz, CH_2CHCH_2); 114.9 (s, CH_2CHCH_2).

[Ni($\eta^3\text{-CH}_2\text{C}(\text{CH}_3)\text{CH}_2$)(PPh^iPr_2) $_2$][BPh_4] (1b**). This compound was prepared by following a procedure identical with that for **1a**, using PPh^iPr_2 (0.42 mL, 2 mmol) instead of PMe^iPr_2 . Yield: 0.49 g, 60% based on the starting amount of PPh^iPr_2 . Anal. Calcd for $\text{C}_{52}\text{H}_{65}\text{BNiP}_2$: C, 76.0; H, 7.97. Found: C, 75.9; H, 7.69. $^1\text{H NMR}$ (CD_2Cl_2 , 298 K): δ 1.24 (m, 24 H, $\text{P}(\text{CH}(\text{CH}_3)_2)_2$); 2.06 (s, 3 H, $\text{CH}_2\text{C}(\text{CH}_3)\text{CH}_2$); 2.50 (m, 4 H, $\text{P}(\text{CH}(\text{CH}_3)_2)_2$); 2.89 (s br, 2 H, $\text{CH}^{\text{anti}}\text{C}(\text{CH}_3)\text{CH}^{\text{anti}}$); 4.07 (s br, 2 H, $\text{CH}^{\text{syn}}\text{C}(\text{CH}_3)\text{CH}^{\text{syn}}$); 6.80–7.30 (m, 10 H, PC_6H_5); 6.76 (t, $^3J_{\text{HH}} = 7.3$ Hz, 4 H), 6.91 (t, $^3J_{\text{HH}} = 7.3$ Hz, 8 H), 7.33 (br, 8 H), $\text{B}(\text{C}_6\text{H}_5)_4$. $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 298 K): δ 38.0 s. $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 298 K): δ 14.9, 15.0, 18.4, 19.9 (s, $\text{P}(\text{CH}(\text{CH}_3)_2)_2$); 20.2 (s, $\text{CH}_2\text{C}(\text{CH}_3)\text{CH}_2$); 23.3 (m, $\text{P}(\text{CH}(\text{CH}_3)_2)_2$); 67.6 (m, $\text{CH}_2\text{C}(\text{CH}_3)\text{CH}_2$); 128.2 (s, $\text{CH}_2\text{C}(\text{CH}_3)\text{CH}_2$); 129–132 (s, $\text{P}(\text{C}_6\text{H}_5)_4$).**

[NiBr $_2$ (PR^iPr_2) $_2$] (R = Me (3a), Ph (3b)**). To a slurry of anhydrous NiBr_2 (0.22 g, ca. 1 mmol) in ethanol (20 mL) was added either PMe^iPr_2 (0.3 mL, 2 mmol) or PPh^iPr_2 (0.42 mL, 2 mmol). The color immediately changed to dark purple upon addition of PMe^iPr_2 , with precipitation of a crystalline material, whereas upon addition of PPh^iPr_2 the mixture became orange. In the latter case, the mixture was gently heated for several minutes using a warm water bath. Both reaction mixtures were stirred at room temperature for 12 h. The resulting crystalline precipitate, dark purple in the case of **3a** and brown in the case of **3b**, was filtered off, washed with ethanol and petroleum ether, and dried under vacuum. Yields: 0.36 g, 80% for **3a**; 0.46 g, 75% for **3b**. Data for **3a** are as follows. Anal. Calcd for $\text{C}_{14}\text{H}_{34}\text{Br}_2\text{NiP}_2$: C, 34.8; H, 7.10. Found: C, 35.1; H, 6.99. $^1\text{H NMR}$ (CD_3COCD_3 , 298 K): very broad signals. $^1\text{H NMR}$ (CD_3COCD_3 , 193 K): δ 1.05 (br, 6 H, PCH_3); 1.23 (d br, 12 H, $\text{P}(\text{CH}(\text{CH}_3)_2)_2$); 1.41 (d, br, 12 H, $\text{P}(\text{CH}(\text{CH}_3)_2)_2$); 2.24 (br, 4 H, $\text{P}(\text{CH}(\text{CH}_3)_2)_2$). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_3COCD_3 , 298 K): featureless. $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_3COCD_3 , 188 K): δ 13.9 s. $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 228 K): δ 2.13 (s br,**

PCH_3); 17.71, 19.03 (s, $\text{P}(\text{CH}(\text{CH}_3)_2)_2$); 23.93 (br, $\text{P}(\text{CH}(\text{CH}_3)_2)_2$). Data for **3b** are as follows. Anal. Calcd for $\text{C}_{24}\text{H}_{38}\text{Br}_2\text{NiP}_2$: C, 47.5; H, 6.31. Found: C, 47.1; H, 6.24. $^1\text{H NMR}$ (CD_3COCD_3 , 298 K): very broad signals. $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_3COCD_3 , 298 K): featureless. $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_3COCD_3 , 223 K): δ 26.2 s. $^{13}\text{C}\{^1\text{H}\}$ NMR: not recorded.

[Ni($\eta^2\text{-MeInd}$)(PR^iPr_2) $_2$][BPh_4] (R = Me (4a), Ph (4b)**). To a solution of $[\text{Ni}(\eta^2\text{-MeInd})\text{Br}(\text{PPh}_3)]$ (0.53 g, 1 mmol) in methanol (20 mL) was added PMe^iPr_2 (0.3 mL, 2 mmol) or PPh^iPr_2 (0.42 mL, 2 mmol). The mixture was stirred for 12 h at room temperature. Addition of an excess of solid NaBPh_4 (ca. 0.4 g) yielded a brown-orange precipitate, which was filtered off, washed with ethanol and petroleum ether, and dried under vacuum. The numbering scheme used for the identification of the NMR signals for these compounds are based on the atom labeling**



Data for **4a**: yield 0.46 g, 60%. Anal. Calcd for $\text{C}_{48}\text{H}_{63}\text{BNiP}_2$: C, 74.7; H, 8.23. Found: C, 74.6; H, 8.11. $^1\text{H NMR}$ (CD_3COCD_3 , 298 K): δ 0.90 (br, 6 H, PCH_3); 0.95 (m, 24 H, $\text{P}(\text{CH}(\text{CH}_3)_2)_2$); 1.80 (m, 4 H, $\text{P}(\text{CH}(\text{CH}_3)_2)_2$); 2.32 (s, 3 H, $\text{H}^{\text{C}(10)}$); 5.33 (s, 2 H, $\text{H}^{\text{C}(1)-\text{C}(3)}$); 7.05 (m, 2 H, $\text{H}^{\text{C}(6)-\text{C}(9)}$); 7.44 (m, 2 H, $\text{H}^{\text{C}(7)-\text{C}(8)}$); 6.76 (t, $^3J_{\text{HH}} = 7.3$ Hz, 4 H), 6.91 (t, $^3J_{\text{HH}} = 7.3$ Hz, 8 H), 7.33 (br, 8 H), $\text{B}(\text{C}_6\text{H}_5)_4$. $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_3COCD_3 , 298 K): δ 28.5 s. $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_3COCD_3 , 298 K): δ 6.2 (PCH_3); 15.6 (s, $\text{C}(10)$); 17.5, 18.2, 19.7, 20.0 (s, $\text{P}(\text{CH}(\text{CH}_3)_2)_2$); 28.1 (m, $\text{P}(\text{CH}(\text{CH}_3)_2)_2$); 80.8 (br, $\text{C}(1)$, $\text{C}(3)$); 117.6 (s, $\text{C}(2)$); 119.2 (s, $\text{C}(6)$, $\text{C}(9)$); 121.8 (s, $\text{C}(4)$, $\text{C}(5)$); 127.7 (s, $\text{C}(7)$, $\text{C}(8)$). Data for **4b**: yield 0.49 g, 55%. Anal. Calcd for $\text{C}_{58}\text{H}_{67}\text{BNiP}_2$: C, 77.8; H, 7.54. Found: C, 77.6; H, 7.39. $^1\text{H NMR}$ (CDCl_3 , 298 K): δ 1.43 (m, 24 H, $\text{P}(\text{CH}(\text{CH}_3)_2)_2$); 2.39 (m, 4 H, $\text{P}(\text{CH}(\text{CH}_3)_2)_2$); 2.59 (s, 3 H, $\text{H}^{\text{C}(10)}$); 5.87 (s, 2 H, $\text{H}^{\text{C}(1)-\text{C}(3)}$); 6.95 (m, 2 H, $\text{H}^{\text{C}(6)-\text{C}(9)}$); 7.43 (m, 2 H, $\text{H}^{\text{C}(7)-\text{C}(8)}$); 6.80–7.30 (m, 10 H, PC_6H_5); 6.76 (t, $^3J_{\text{HH}} = 7.3$ Hz, 4 H), 6.91 (t, $^3J_{\text{HH}} = 7.3$ Hz, 8 H), 7.33 (br, 8 H), $\text{B}(\text{C}_6\text{H}_5)_4$. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 298 K): δ 33.6 s. $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 298 K): δ 14.5 (s, $\text{C}(10)$); 15.0, 18.1, 19.5 (s, $\text{P}(\text{CH}(\text{CH}_3)_2)_2$); 23.3 (m, $\text{P}(\text{CH}(\text{CH}_3)_2)_2$); 87.9 (br, $\text{C}(1)$, $\text{C}(3)$); 116.9 (s, $\text{C}(2)$); 119.2 (s, $\text{C}(6)$, $\text{C}(9)$); 121.8 (s, $\text{C}(4)$, $\text{C}(5)$); 125.7 (s, $\text{C}(7)$, $\text{C}(8)$), 129–132 (s, $\text{P}(\text{C}_6\text{H}_5)_4$).

X-ray Structure Determinations. Crystal data and experimental details are given in Table 1. X-ray data were collected on a MSC-RIGAKU AFC6S diffractometer (graphite-monochromated $\text{Mo K}\alpha$ radiation, $\lambda = 0.71073$ Å). Corrections for Lorentz and polarization effects, for crystal decay, and for absorption were applied. All structures were solved by direct methods using the program SHELXS97.^{29a} Structure refinement on F^2 was carried out with the program SHELXL97.^{29b} ORTEP³⁰ was used for plotting. All non-hydrogen atoms were anisotropically refined. Hydrogen atoms were refined in idealized positions riding on the atoms to which they were bonded.

General Procedure for Styrene Polymerization Reactions. A Schlenk tube was loaded with styrene (10 g), 1,2-dichloroethane (2 mL), and the corresponding catalyst (0.1% mol) under dinitrogen. The system was heated to the point of reflux using an oil bath. The temperature of the bath was maintained in the interval 90–95 °C. The reaction time was

(29) (a) SHELXS97, Program for Crystal Structure Solution; University of Göttingen, Göttingen, Germany, 1990. (b) SHELXL97, Program for Crystal Structure Refinement; University of Göttingen, Göttingen, Germany, 1997.

(30) Farruggia, L. J. ORTEP-3 for Windows, version 1.076. *J. Appl. Crystallogr.* **1997**, *30*, 565.

Table 1. Summary of Crystallographic Data for 1b and 3a

	1b	3a
formula	C ₅₂ H ₆₅ BNiP ₂	C ₁₄ H ₃₄ Br ₂ NiP ₂
fw	821.54	482.88
T (K)	293(2)	293(2)
cryst size (mm)	0.40 × 0.18 × 0.12	0.32 × 0.25 × 0.20
cryst syst	triclinic	orthorhombic
space group	<i>P</i> 1 (No. 2)	<i>Pna</i> 2 ₁ (No. 33)
cell params		
<i>a</i> (Å)	13.233(3)	18.871(5)
<i>b</i> (Å)	14.501(7)	7.516(2)
<i>c</i> (Å)	12.416(3)	14.330(5)
α (deg)	99.22(3)	
β (deg)	94.25(2)	
γ (deg)	101.47(3)	
<i>V</i> (Å ³)	2290(1)	2032(2)
<i>Z</i>	2	4
ρ _{calcd} (g cm ⁻³)	1.221	1.578
μ (Mo Kα) (cm ⁻¹)	5.40	5.03
<i>F</i> (000)	880	984
max and min transmissn factors	1–0.82	1.44–0.79
θ range for data collectn (deg)	2.57 < θ < 26.82	2.58 < θ < 25.05
no. of rflns collected	6667	1642
no. of unique rflns	6667 (<i>R</i> _{int} = 0.110)	1642 (<i>R</i> _{int} = 0.000)
no. of obsd rflns (<i>I</i> > 3σ)	4013	1024
no. of parameters	514	182
final <i>R</i> ₁ , <i>wR</i> ₂ values (<i>I</i> > 3σ)	0.063, 0.154	0.065, 0.156
final <i>R</i> ₁ , <i>wR</i> ₂ values (all data)	0.116, 0.182	0.113, 0.179
residual electron density peaks (e Å ⁻³)	+1.361, -0.616	+1.002, -0.963

measured from the moment in which the reflux was initiated. Two milliliter aliquots of the reaction mixture were taken every 1 h, for an extended period of 6 h. The reaction was quenched by addition of methanol to every aliquot. The volatiles were pumped off, and the residue was treated with methanol to yield a white precipitate of polystyrene, which was filtered off and dried under vacuum. The polystyrene was dissolved in dichloromethane (10 mL) and filtered through a silica gel plug. The silica gel was washed with several small portions of dichloromethane in order to remove all traces of polystyrene. The solvent was removed from the combined filtrate. The resulting residue was crushed with methanol, and the polystyrene was filtered off, washed with petroleum ether, and dried under vacuum to constant weight.

In some instances, the reaction was left running for a period of 19 h. At the end of this period, the reaction mixture was treated also as described above.

In all cases, the polymerization reactions were contrasted against a blank consisting of a reaction mixture identical with the system under study, but with no catalyst added. The small amounts of polystyrene obtained in the blank reaction (only significant in a few instances, usually after long reaction times) were discounted from the amounts of polystyrene obtained in the catalyzed reactions, and the resulting corrected figures were used for the calculation of the yields.

Results and Discussion

Preparation of the Complexes. The 2-methylallyl derivatives [Ni(η^3 -CH₂C(CH₃)CH₂)(PMeⁱPr₂)₂][BPh₄] (**1a**) and [Ni(η^3 -CH₂C(CH₃)CH₂)(PPhⁱPr₂)₂][BPh₄] (**1b**), as well as the allyl complex [Ni(η^3 -CH₂CHCH₂)(PMeⁱPr₂)₂][BPh₄] (**2a**), were prepared as described for the related dippe derivatives [Ni(η^3 -CH₂C(CH₃)CH₂)(dippe)][BPh₄] (**1c**) and [Ni(η^3 -CH₂CHCH₂)(dippe)][BPh₄] (**2c**): by reaction of [Ni(COD)₂] with either 3-bromo-2-methylpropene or allyl bromide and the corresponding phosphine in diethyl ether, followed by extraction

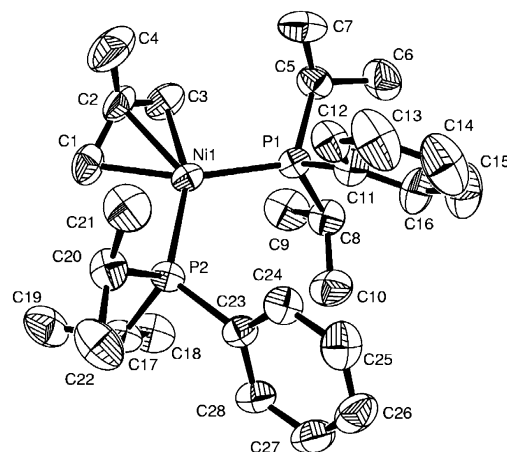
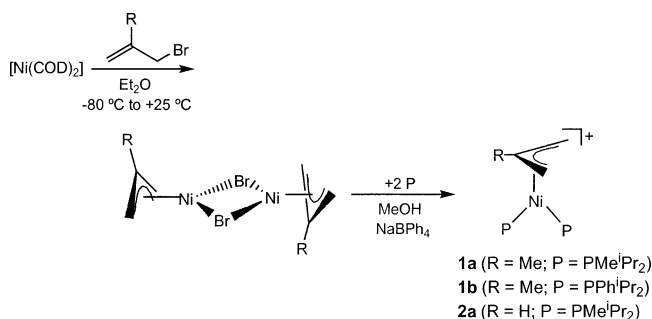


Figure 1. ORTEP drawing (30% thermal ellipsoids) of the cation [Ni(η^3 -CH₂C(CH₃)CH₂)(PPhⁱPr₂)₂]⁺ in complex **1b**. Hydrogen atoms have been omitted. Selected bond lengths (Å) and angles (deg) with estimated standard deviations in parentheses: Ni(1)–C(1), 2.035(5); Ni(1)–C(2), 2.079(5); Ni(1)–C(3), 2.137(6); Ni(1)–P(1), 2.245(2); Ni(1)–P(2), 2.334(2); C(1)–C(2), 1.417(9); C(2)–C(3), 1.361(9); C(2)–C(4), 1.426(9); P(1)–Ni(1)–P(2), 111.29(6); C(1)–C(2)–C(3), 119.9(6).

with MeOH and addition of NaBPh₄.²⁸



This method did not work for the preparation of the allyl complex [Ni(η^3 -CH₂CHCH₂)(PPhⁱPr₂)₂][BPh₄]. In this case, the only isolated product was the allyl-phosphonium salt [CH₂=CHCH₂PPhⁱPr₂][BPh₄]. The ³¹P-{¹H} NMR spectra of **1a**, **1b** and **2a** consist of one singlet, whereas the ¹H NMR spectra display separated resonances corresponding to the anti and syn protons of the 2-methylallyl or allyl ligands. A reexamination of the ¹H NMR spectrum of compound **2c** showed that the assignments previously reported for this derivative were in error.²⁸ Separated resonances for the anti and syn protons of the allyl ligand in the [Ni(η^3 -CH₂CHCH₂)(dippe)]⁺ cation at 2.72 ppm (H^{anti}, d, ³J_{HH} = 10.2 Hz) and 4.61 ppm (H^{syn}, d, ³J_{HH} = 7.2 Hz) are present in the spectrum, together with one multiplet at 5.31 ppm corresponding to the proton attached to the central allyl carbon atom. No coalescence is observed for the resonances of the anti and syn protons when the temperature is raised to 60 °C for any of the derivatives **1a–c** and **2a,c**. This suggests a relatively high energy barrier for the H^{syn}/H^{anti} exchange process in all these compounds, and also in the case of compound **2c**, in contrast with the earlier report.²⁸ The crystal structure of **1b** was determined. An ORTEP view of the complex cation [Ni(η^3 -CH₂C(CH₃)CH₂)(PPhⁱPr₂)₂]⁺ is shown in Figure 1, together with the most relevant bond distances and

angles. This complex displays a pseudo-square-planar "two-legged piano stool" structure, very similar to that of compound **1c**.²⁸ The angle formed by the least-squares plane defined by the 2-methylallyl carbon atoms and the plane defined by the NiP₂ moiety has a value of 64.6°. The bond lengths C(1)–C(2) and C(2)–C(3) are not equal and are intermediate between single and double bonds, as expected. The variation sequence observed for the Ni–C separations suggests an unsymmetric bonding mode for the methylallyl ligand. The P(1)–Ni(1)–P(2) angle of 111.29(6)° is significantly larger than the value of 90.6(2)° found in the dippe derivative **1c**, due to the absence of the backbone carbon chain between the two phosphorus atoms. In addition, the Ni–P bonds are ca. 0.1 Å longer than in **1c**, suggesting an increased steric hindrance for PPhⁱPr₂ compared to dippe. The torsion angle C(23)–P(2)–P(1)–C(11) has a value of 38.7°, which indicates a staggered conformation of the PPhⁱPr₂ ligands with respect to each other.

The preparation of the neutral 2-methylindenyl derivatives [Ni(η -2-MeInd)Br(PR₃)] (PR₃ = PMeⁱPr₂, PPhⁱPr₂) was attempted, since these materials are precursors for the synthesis of cationic complexes by halide abstraction. The intended synthetic route to these neutral compounds was the metathetical exchange of bromide in [NiBr₂(PR₃)₂] using Li(2-MeInd).

The complexes [NiBr₂(PR₃)₂] (PR₃ = PMeⁱPr₂ (**3a**), PPhⁱPr₂ (**3b**)) were obtained by reaction of anhydrous NiBr₂ with the corresponding phosphine in ethanol. These compounds are crystalline materials and are diamagnetic in solution (Evans method³¹) that, however, display broad resonances in their ¹H NMR spectra, whereas their ³¹P{¹H} NMR spectra are featureless at room temperature. At low temperature, a broad resonance appears and sharpens as the temperature gets lower. Thus, at 188 K in CD₃COCD₃, the ³¹P{¹H} NMR of **3a** consists of one relatively sharp singlet at 13.5 ppm (Figure 2), or at 26.5 ppm in the case of **3b**. This behavior can be interpreted in terms of a rapid phosphine dissociation equilibrium which occurs at a lower rate and to a lesser extent as the temperature is lowered. The fact that both PMeⁱPr₂ and PPhⁱPr₂ in these complexes are easily exchanged by other phosphines, e.g. PET₃, is consistent with this hypothesis. The crystal structure of **3a** was determined. An ORTEP view of the molecular structure of [NiBr₂(PMeⁱPr₂)₂] is shown in Figure 3.

The structure consists of a packing of discrete [NiBr₂(PMeⁱPr₂)₂] molecules interacting through van der Waals forces. Each of the molecules is square planar, with a trans arrangement of bromide and phosphine ligands. This structure is very similar to that adopted by the related compounds *trans*-[NiBr₂(PⁱPr₃)₂]³² and *trans*-[NiBr₂(PPhMe₂)₂].³³ All distances and angles in this complex are within the expected ranges, being unexceptional.

The reactions of **3a,b** with Li(2-MeInd) failed to give the desired complexes. The starting materials are recovered back from these reactions. One possible

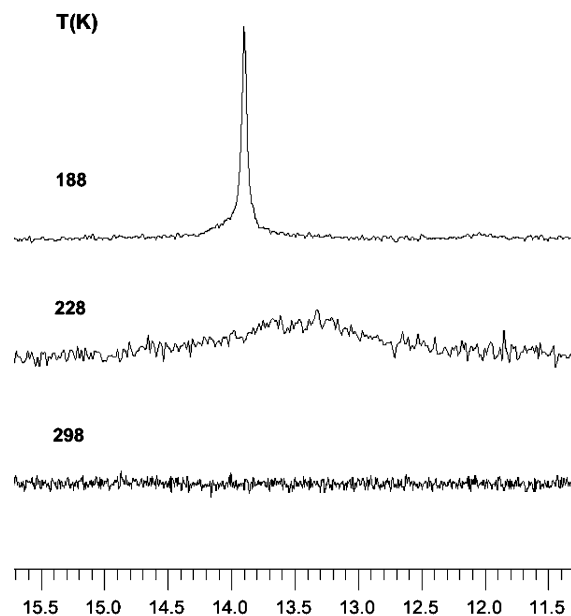


Figure 2. VT ³¹P{¹H} NMR spectra of compound **3a** in CD₃COCD₃.

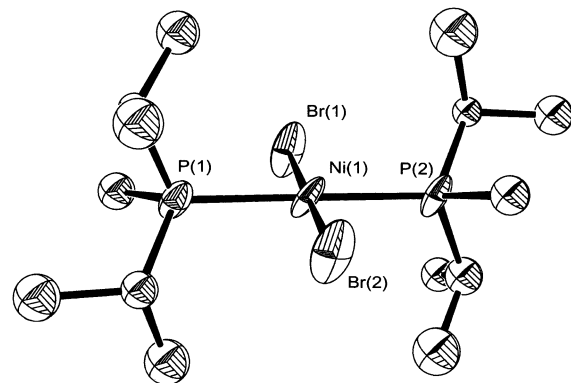


Figure 3. ORTEP drawing (30% thermal ellipsoids) of the complex [NiBr₂(PMeⁱPr₂)₂] (**3a**). Hydrogen atoms have been omitted. Selected bond lengths (Å) and angles (deg) with estimated standard deviations in parentheses: Ni(1)–P(1), 2.254(6); Ni(1)–P(2), 2.251(6); Ni(1)–Br(1), 2.300(3); Ni(1)–Br(2), 2.301(3); P(1)–Ni(1)–P(2), 179.1(2); Br(1)–Ni(1)–Br(2), 179.6(2); Br(1)–Ni(1)–P(1), 89.4(2); Br(2)–Ni(1)–P(2), 88.6(2).

explanation for this behavior might be that the complexes [Ni(η -2-MeInd)Br(PR₃)], once generated, undergo a disproportionation reaction, yielding [NiBr₂(PR₃)₂] (isolated) plus [Ni(η -2-MeInd)₂] (not detected). In any case, since the desired products were not obtained, these reactions were not investigated any further.

The complexes [Ni(η -2-MeInd)(PR₃)₂][BPh₄] (PR₃ = PMeⁱPr₂ (**4a**), PPhⁱPr₂ (**4b**)) were prepared in a fashion analogous to that for the dippe derivative [Ni(η -2-MeInd)(dippe)][BPh₄] (**4c**).²⁸ The procedure is an adaptation of the method used by Zargarian and co-workers for the synthesis of indenyl and 1-methylindenyl nickel phosphine derivatives,³⁴ which consists of the reaction of [Ni(η -2-MeInd)Br(PPh₃)] with 2 equiv of the corresponding phosphine in MeOH, followed by addition of NaBPh₄.

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(32) Wunderlich, H. *Z. Kristallogr.* **1997**, *212*, 381.

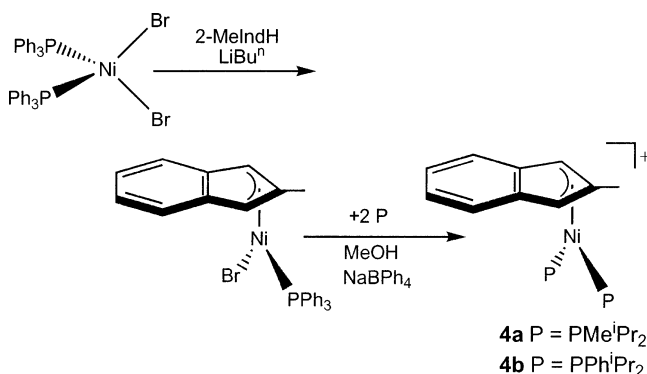
(33) Godfrey, S. M.; McAuliffe, C. A.; Pritchard, R. G. *J. Chem. Soc., Dalton Trans.* **1993**, 2875.

(34) Huber, T. A.; Bélanger-Gariépy, F.; Zargarian, D. *Organometallics* **1995**, *14*, 4997.

Table 2. Polymerization of Styrene Catalyzed by Complexes **1**, **2**, and **4**

entry ^a	cat.	time (h)	yield (%)	N_t^b (h ⁻¹)	polymer ^c				
					type of distribn	$10^{-3}M_w$	$10^{-3}M_n$	M_w/M_n	distribn, wt % ^d
1	1a	6	59	102	bimodal ^e	111.5 ^e	47.6 ^e	2.34 ^e	
2	1a	19	67	35					
3	1b	6	45	78	unimodal	152.8	33.8	4.52	
4	1b	19	50	27					
5	1c	6	35	60	unimodal	262.1	134.4	1.95	
6	1c	19	81	43					
7	2a	5	42	84	bimodal	43.4	31.7	1.37	39
						226.2	175.3	1.29	61
8	2a	19	88	46					
9	2c	5	66	132	unimodal	100.5	47.0	2.14	
10	2c	19	89	48					
11	4a	6	60	102	bimodal	4.2	3.0	1.40	40
						39.0	22.4	1.74	60
12	4a	19	92	48					
13	4b	6	25	42	unimodal	140.7	14.5	9.70	
14	4b	19	43	23					
15	4c	19	94	48	unimodal	293.3	155.2	1.89	

^a Experimental conditions: styrene (10 g), solvent 1,2-dichloroethane (2 mL), [sty]/[Ni] = 1000, $T = 90-95^\circ\text{C}$. ^b See ref 36. ^c Determined by GPC/SEC. ^d Estimated by area integration of both distributions in the GPC/SEC chromatogram. ^e A unimodal distribution is apparently observed, but a shift from the typical Schulz–Flory shape on the low-molecular-weight side of the GPC/SEC chromatogram denotes the presence of a superimposed small fraction of low-molecular-weight polystyrene of difficult quantification; the values presented correspond to the integration of the whole sample.



The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **4a,b** consist of one singlet, whereas the ^1H NMR spectra show signals characteristic of the 2-MeInd ligand. The hapticity in solution was estimated by means of $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy.³⁵ The parameter $\Delta\delta$, which represents the difference in chemical shift between the $^{13}\text{C}\{^1\text{H}\}$ NMR resonances of the ring-junction carbon atoms C(4)–C(5) in the indenyl complexes **4a,b** and in “free” indenyl (i.e. sodium indenyl, δ 130.7 ppm), has a value at 298 K of -8.9 ppm for **4a** and -9.0 ppm for **4b**. These values indicate an intermediate η^3/η^5 hapticity in solution for both compounds, as has also been previously found for **4c**, suggesting that slip-fold distortions are also present in the 2-MeInd ligand in these complexes.²⁰

Polymerization Reactions. The cationic methylallyl, allyl, and indenyl derivatives **1a–c**, **2a,c** and **4a–c** are catalytic precursors for the polymerization of styrene to polystyrene in the absence of a cocatalyst such as MAO. A range of reaction conditions (solvent, temperature, catalyst/styrene ratio, reaction time) were evaluated. The best results were obtained using 1,2-dichloroethane as solvent at the reflux temperature ($T = 90-95^\circ\text{C}$), with a catalyst to styrene molar ratio of 1:1000 under a dinitrogen atmosphere. No catalytic effect was observed for the molar ratio 1:10 000. Interestingly, the 18-electron pentamethylcyclopentadienyl complex $[\text{Cp}^*\text{Ni}$

(dippe)][BPh₄], also reported by our research group,²⁸ is not catalytically active under these conditions. The amount of polystyrene increases steadily with the reaction time, although the overall yield depends much on the particular catalyst used. Most often, after a period of 5–6 h the increase in the viscosity of the reaction mixture led us to terminate the reaction at this point by quenching with MeOH and exposure to air. In general, the rate of polystyrene formation decreases after this period, although in some cases a significant increase in the overall polystyrene yield was observed when the mixture was allowed to react for an extended period of time of 19 h under reflux. Thus, for instance, when **4c** was used as catalyst, extremely low amounts of polystyrene were obtained after 6 h. However, after 19 h the conversion into polystyrene was over 90%. The individual yields of polystyrene obtained using each of the catalysts after the appropriate reaction times and the resulting turnover frequency (N_t)³⁶ are listed in Table 2. For reaction times of 5–6 h, the yields are between 25% and 66%. Depending on the catalyst, the yields increase up to 43%, to 94% after 19 h. We have measured the individual polystyrene yields as a function of time for each catalyst. This has allowed us to evaluate the variation of the cumulated turnover number (TON) with the reaction time, as shown in Figure 4, as well as the variation of the turnover frequency. The variation of the cumulated TON with the reaction time shows clearly a sigmoid profile in all cases. After 5–6 h, the increase in TON is very smooth, approaching a plateau. With respect to the variation of the turnover frequency, N_t increases to a maximum in the first 1 h, after which the activity decreases. Hence, all of the systems behave similarly in terms of polystyrene yields, **4b** being the least efficient. It is possible that in this case the catalytically active species do not survive in solution for a prolonged period of time.

The polystyrenes obtained in these catalytic reactions were characterized by GPC/SEC, and their mass fea-

(35) Huber, T. A.; Bayraktarian, M.; Dion, S.; Dubuc, I.; Bélanger-Gariépy, F.; Zargarian, D. *Organometallics* **1997**, *16*, 5811.

(36) The turnover frequency is defined as $N_t = (\text{moles of converted styrene})/[(\text{moles of catalyst})(\text{time})]$.

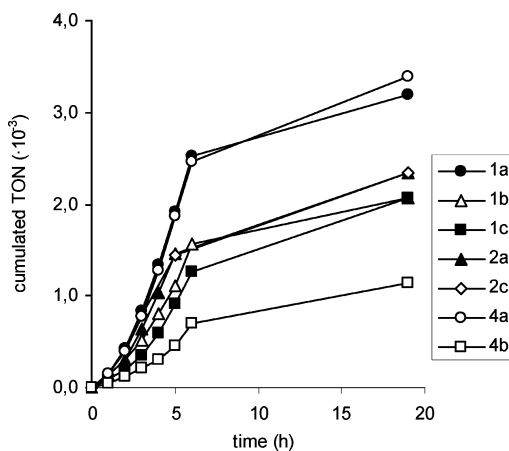


Figure 4. Variation of the cumulated turnover number (TON) with time for the polymerization of styrene catalyzed by complexes **1**, **2**, and **4**.

tures, at the end of the polymerization reaction, are listed in Table 2. The GPC traces indicate rather broad molecular weight distributions, which apparently can be treated as unimodal with three exceptions (see below). The values of M_n range from 14 500 to 155 200 Da in the case of the unimodal distributions, with polydispersity indexes (M_w/M_n) varying inversely. The lower polydispersity values ($M_w/M_n \approx 2$) are observed for the polystyrenes obtained using as catalysts compounds containing the bidentate phosphine dippe (**1c**, **2c**, and **4c**), which also led to polymers having the highest values of M_n and unimodal distributions. The largest polydispersity values correspond to the polystyrenes obtained using complexes containing PPh^iPr_2 as coligand (**1b** and **4b**). However, the polystyrenes resulting from the reactions catalyzed by compounds containing the monodentate ligand PMe^iPr_2 (**1a**, **2a**, and **4a**) are clearly bimodal at the end of 6 h.

In fact, we carried out a study of the variation of the molecular weight distributions with the reaction time and found out that only the catalysts containing the bidentate phosphine dippe (**1c**, **2c**, and **4c**) give rise to polystyrenes having unimodal distributions along the course of the reaction. For all the other cases, the presence of low-molecular-weight polystyrene at short reaction times is always visible. As the reaction goes on, a new fraction of much higher M_n gradually appears. This is shown in Figure 5, as an example corresponding to the polymerization of styrene catalyzed by **4a**. The variation of M_n with the conversion into polystyrene for each of the catalysts indicates that the polymerization processes hereby considered are not living. The general trend is that M_n increases initially with conversion to a value which, after that, remains more or less stable when the conversion increases. All these facts might indicate the simultaneous occurrence of two different polymerization pathways, one of them leading rapidly (i.e. less than 1 h) to polymers of low molecular weight and another one which leads to polymers of higher molecular weight. The latter apparently requires an induction time to be effective, but it would continue to be operative for longer reaction times. This would be also consistent with the observed variation of the cumulated turnover number with the reaction time (Figure 4). A similar behavior was also reported in a

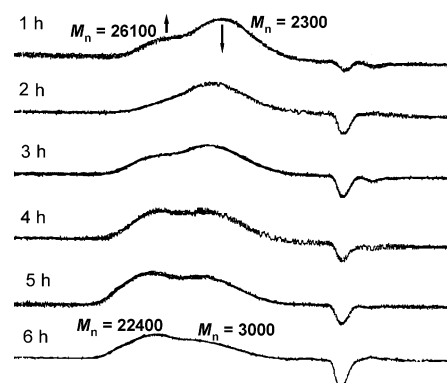


Figure 5. GPC chromatograms of polystyrenes obtained using compound **4a** as catalyst after the reaction times shown.

recently published work on the polymerization of styrene catalyzed by related cationic indenyl nickel complexes.²⁶

The polystyrenes obtained in the catalytic runs were also characterized by means of ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy (1,1,2,2-tetrachloroethane- d_2 , 120 °C). According to the literature, the analysis of the intensity distribution of the $^{13}\text{C}\{^1\text{H}\}$ NMR resonances corresponding to the ipso-carbon atoms of the phenyl groups of polystyrene gives information relevant to the tacticity of polystyrenes.^{15,17,18} The isotactic contents, P_m , calculated from the $^{13}\text{C}\{^1\text{H}\}$ NMR data for all of the polymers obtained in this work fall in the range 0.57–0.63. Since pure atactic polystyrene should have $P_m = 0.50$, and for isotactic polystyrene $P_m = 1.00$, it can be concluded that the polystyrenes resulting from the catalytic reactions under study are essentially atactic.

In summary, the compounds **1a–c**, **2a,c** and **4a–c** exhibit a moderate catalytic activity for the nonliving polymerization of styrene in refluxing 1,2-dichloroethane. The resulting polystyrenes are essentially atactic and have rather high molecular weights, with the sole exception of the polymers obtained using **4a** as catalyst. Either bimodal molecular weight distributions or larger polydispersities are generally obtained when the catalytic precursors contain monodentate phosphine as coligands. The variation with time of the cumulated TON and turnover frequencies, as well as the variation of the values of M_n , seem to indicate the occurrence of more than one single pathway for the formation of the polymers.

Comparing our results with the data in the literature for the polymerization of styrene mediated by related allyl complexes,^{15,17,18} working at much lower temperatures, we can see that in general there are important differences in the polymerization products, despite the existing similarities between the catalytic systems. The proposed insertion mechanism leads to styrene oligomers ranging from dimers to low-molecular-weight unimodal polymers, usually containing a certain degree of stereoregularity, both features depending on the basicity and bulk of the phosphine ligand used, whereas in the present work, essentially atactic, rather high molecular weight bimodal polystyrenes are obtained. It seems reasonable to think of at least two different polymerization pathways, as has been mentioned earlier. Initially, the reaction would take place by an insertion mechanism essentially analogous to that

proposed for the oligomerization/polymerization of styrene catalyzed by cationic allyl nickel phosphine derivatives at lower temperatures.^{17–19} In this fashion, low-molecular-weight polystyrenes would be generated. After approximately 1 h, a second mechanism is active, leading to atactic, high-molecular-weight polystyrenes. This could be just a simple cationic polymerization process or a free-radical mechanism operating at higher temperatures.²⁶ For instance, the reaction of the metal complex with 1,2-dichloroethane used as solvent at high temperature, or even its mere decomposition, might generate free radicals which initiate a radical polymerization of styrene, leading to atactic high-molecular-weight polystyrenes. In this sense, we have monitored by ³¹P{¹H} NMR the initial stages of the polymerization reaction using **2a** as catalyst in 1,2-dichloroethane/tetrachloroethane-*d*₂. When the temperature is raised to 80 °C, the resonance at ca. 27.5 ppm corresponding to **2a** disappears, and the spectrum becomes featureless. The ¹H NMR spectrum showed formation of polystyrene. Cooling to room temperature did not restore the original ³¹P{¹H} NMR spectrum. The ³¹P{¹H} NMR spectrum of a blank sample of **2a**, identical with the previous one but without styrene, showed an identical behavior. These observations are consistent with the postulated formation of radical species at high temperature. Thus, the final product of the polymerization reaction should be a mixture containing one fraction of low-molecular-weight polystyrenes of higher isotactic content plus another fraction of high-molecular-weight atactic polystyrenes. The second fraction becomes more important with longer reaction times, whereas the lighter fraction would be the main component at the beginning of the

reaction. The insertion mechanism does not necessarily require phosphine dissociation, since all of the precatalysts are formally 16-electron species. However, phosphine dissociation might in fact occur for complexes containing monodentate phosphine ligands, leading to multiple active sites. This is less likely to occur in the case of complexes containing bidentate dippe as coligand, and hence the polymerization takes place mainly through the alternative pathway. This might also account for the lack of catalytic activity observed for the 18-electron complex [Cp*Ni(dippe)][BPh₄]. In any case, we must remark that this is just a hypothesis, based upon experimental observations and the comparison of our results with catalytic polymerization reactions using closely related systems which have been mechanistically studied more in detail.

Acknowledgment. We thank the Ministerio de Ciencia y Tecnología (DGICYT, Project BQU2001-4026, Accion Integrada HP2001-0064) and Junta de Andalucía (PAI FQM188) for financial support. Thanks are also due to the CRUP (Acção Integrada E-30/02) and to the Fundação para a Ciência e Tecnologia for financial support (Project POCTI/QUI/42015/2001, cofinanced by FEDER) and for fellowships PRAXIS XXI/BD/19638/99 (to S.I.C.) and SSRH/BD/9127/2002 (to L.C.S.).

Supporting Information Available: Figures giving relevant GPC/SEC chromatograms and CIF files giving X-ray structural data, including data collection parameters, positional and thermal parameters, and bond distances and angles for complexes **1b** and **3a**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OM049883J