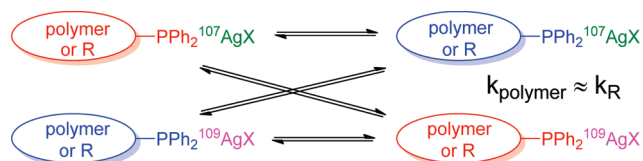# Variable-Temperature NMR Studies of Soluble Polymer-Supported Phosphine−Silver Complexes

David E. Bergbreiter* and Yun-Chin Yang

Department of Chemistry, Texas A&M University, P.O. Box 30012, College Station, Texas 77842-3012

bergbreiter@tamu.edu

The use of polymers as supports for organometallic catalysts has received wide attention. However, catalyst reactivity is sometimes altered as a consequence of catalyst immobilization by a polymeric ligand and such altered reactivity can complicate such supported catalysts' use. The results in this study show that heptane phase selectively soluble polyisobutylene (PIB)-bound phosphine ligands have essentially identical kinetic behavior when compared to electronically similar isobutyldiphenylphosphine analogues in phosphine coordination and exchange in silver(I) halide complexes. These studies used variable-temperature ^{31}P NMR spectroscopy to probe the silver−phosphine exchange processes for both AgI and AgCl complexes of these polymeric and low molecular weight phosphine ligands. The results show that the dynamic behavior of the PIB- and isobutyldiphenylphosphine−AgX complexes is nearly identical based on line-shape analysis of these ^{31}P NMR spectra as a function of temperature. Similar studies of more polar poly(ethylene glycol)triarylphosphine-bound AgX complexes and electronically analogous low molecular weight AgX complexes have similar behavior in variable-temperature ^{31}P NMR spectroscopy.

Introduction

Strategies that use ligands on polymer supports to immobilize and recover homogeneous transition metal catalysts have attracted attention ever since Merrifield introduced the concept of solid phase synthesis.[1] While much of this work has involved insoluble cross-linked polymer supports, soluble supports have received attention as well.[2] In recent years, interest in these supports has increased as new procedures have been developed that facilitate separation of soluble polymer-bound catalysts from products.[3] For example, our group has emphasized the advantages of terminally functionalized nonpolar polyisobutylene (PIB) supports that readily separate in a liquid/liquid biphasic system after a homogeneous reaction.[4] These supports are analogous to established more polar end-functionalized poly(ethylene glycol) (PEG) supports.[2b] We and others have argued that these soluble polymer supports lead to polymer-supported metal catalysts that have reactivity directly analogous to that of a more conventional low molecular weight catalyst. This argument has been substantiated in a number of studies where the yields of product or product selectivity for reactions of soluble polymer-bound catalysts have been compared with

(1) (a) Lu, J.; Toy, P. H. *Chem. Rev.* **2009**, *109*, 815. (b) *The Power of Functional Resins in Organic Synthesis*; Tulla-Puche, J., Albericio, F., Eds.; Wiley-VCH: Weinheim, Germany, 2008. (c) *Combinatorial Chemistry on Solid Supports*; Bräse, S., Ed.; Springer Verlag: New York, 2007.

(2) (a) Barrett, A. G. M.; Hopkins, B. T.; Köbberling, J. *Chem. Rev.* **2002**, *102*, 3301. (b) Dickerson, T. J.; Reed, N. N.; Janda, K. D. *Chem. Rev.* **2002**, *102*, 3325. (c) Fan, Q.-H.; Li, Y.-M.; Chan, A. S. C. *Chem. Rev.* **2002**, *102*, 3385. (d) Yoshida, J.-I.; Itami, K. *Chem. Rev.* **2002**, *102*, 3693. (e) Buchmeiser, M. R. *Chem. Rev.* **2009**, *109*, 303. (f) Trindade, A. F.; Gois, P. M. P.; Afonso, C. A. M. *Chem. Rev.* **2009**, *109*, 418. (g) Ikegami, S.; Hamamoto, H. *Chem. Rev.* **2009**, *109*, 583.

(3) (a) Bergbreiter, D. E. *Chem. Rev.* **2002**, *102*, 3345. (b) Bergbreiter, D. E.; Tian, J.; Hongfa, C. *Chem. Rev.* **2009**, *109*, 530.

(4) (a) Bergbreiter, D. E.; Li, J. *Chem. Commun.* **2004**, 42. (b) Bergbreiter, D. E.; Sung, S. D.; Li, J.; Ortiz, D.; Hamilton, P. N. *Org. Process Res. Dev.* **2004**, *8*, 461. (c) Li, J.; Sung, S.; Tian, J.; Bergbreiter, D. E. *Tetrahedron* **2005**, *61*, 12081. (d) Hongfa, C.; Tian, J.; Bazzi, H. S.; Bergbreiter, D. E. *Org. Lett.* **2007**, *9*, 3259. (e) Bergbreiter, D. E.; Tian, J. *Tetrahedron Lett.* **2007**, *48*, 4499. (f) Bergbreiter, D. E.; Hamilton, P. N.; Koshti, N. M. *J. Am. Chem. Soc.* **2007**, *129*, 10666. (g) Hongfa, C.; Tian, J.; Andreatta, J.; Darensbourg, D. J.; Bergbreiter, D. E. *Chem. Commun.* **2008**, 975. (h) Bergbreiter, D. E.; Ortiz-Acosta, D. *Tetrahedron Lett.* **2008**, *49*, 5608. (i) Hongfa, C.; Su, H.-L.; Bazzi, H. S.; Bergbreiter, D. E. *Org. Lett.* **2009**, *11*, 665.

those of low molecular weight homogeneous catalysts. In this study, we examined the similarity of low molecular weight and high molecular weight phosphine ligands by studying the dynamics of phosphine ligand exchange at an NMR-active silver metal center.

SCHEME 1. Polymer- or Alkyldiphenylphosphine Exchange Processes of [107]AgX and [109]AgX Complexes
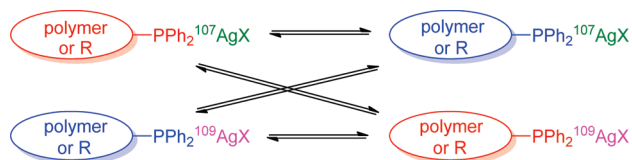
^{31}P NMR spectroscopy is generally useful as a tool to study ligand metal interactions in phosphine complexes of transition metals. Phosphine–silver complexes are particularly useful subjects in this regard because the phosphine ligand exchange can often be studied by variable-temperature (VT) dynamic NMR spectroscopy.[5] Specifically, at low temperature, the ^{31}P NMR spectrum of a slowly exchanging phosphine ligand in a silver–phosphine complex is seen as a doublet of doublets because silver exists as a nearly equally abundant mixture of ^{107}Ag and ^{109}Ag isotopes each with nuclear spin quantum number (I) of $^{1}/_{2}$. In such cases, exchange of a phosphine ligand from a ^{107}Ag to a ^{109}Ag or of a ^{107}Ag or ^{109}Ag from one phosphine to another as shown in Scheme 1 can then be studied in detail as a function of temperature. In the case of complexes like Bu$_3$PAgI, this temperature-dependent ligand exchange can be monitored by ^{31}P NMR spectroscopy (Figure 1). These spectra show a temperature-dependent chemical shift for the phosphine ligand. More importantly, the kinetics of the phosphine
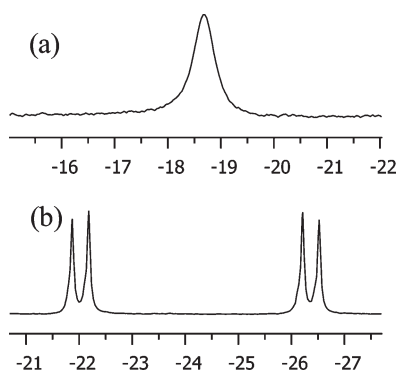
FIGURE 1. ^{31}P NMR spectra of Bu$_3$PAgI in THF at (a) 52 and (b) −87 °C.

ligand exchange process can be analyzed by line shape analysis because the low temperature (−87 °C) doublet of doublets (Figure 1b) evolves to a singlet (Figure 1a) at higher temperature (52 °C) due to the rapid exchange of phosphine from one silver to another.[6] The rate of this exchange as a function of temperature can then be used to determine the activation energy for this ligand exchange by using the Eyring equation (eq 1).

$$\ln\left(\frac{k}{T}\right) = \frac{\Delta S^{\ddagger}}{R} + \ln\left(\frac{k_B}{h}\right) - \frac{\Delta H^{\ddagger}}{R}\frac{1}{T} \qquad (1)$$

The studies reported below use variable-temperature ^{31}P NMR spectroscopy to study and compare the dynamic behavior of silver complexes of both terminally functionalized PIB-PPh$_2$ and PEG-PPh$_2$ ligated silver complexes with silver complexes prepared from electronically similar low molecular weight phosphine ligands. The results of these studies show that both terminally functionalized soluble PIB-PPh$_2$ and PEG-PPh$_2$ phosphine ligands behave like electronically similar low molecular weight phosphine ligands in phosphine metal exchange. This similarity of a soluble polymeric ligand and a low molecular weight ligand is consistent with the idea that solutions of these homogeneous catalysts bound to these soluble ligands will generally behave like solutions of their low molecular weight analogues in catalytic processes.

Results and Discussion

The PIB-bound alkyldiphenylphosphine ligand (**1**) and its complexes with AgI or AgCl (**2** and **3**, respectively) were synthesized from PIB-CH$_2$Br by using LiPPh$_2$ following chemistry previously reported (Scheme 2).[4] A lower molecular weight electronically similar phosphine (**4**) was also synthesized by reaction of isobutylmagnesium bromide with chlorodiphenylphosphine and similar AgI and AgCl complexes (**5** and **6**, respectively) were in turn prepared from **4**. Polyisobutyldiphenyl- and isobutyldiphenylphosphine (**1** and **4**, respectively) had identical ^{31}P NMR spectra with a singlet at −19.5 ppm (Figure 2). The AgI complexes (**2** and **5**) had similar more complex NMR spectra at room temperature in C$_6$D$_6$. The ^{31}P NMR spectra of the AgCl complexes **3** and **6** were likewise similar in C$_6$D$_6$ at room temperature.

The AgI complexes **2** and **5** so formed were then dissolved in CD$_2$Cl$_2$ and their ^{31}P NMR spectra were recorded from −64 to 30 °C as shown in Figure 3. Because the PIB-PPh$_2$ ligand is soluble at low temperature, high-quality spectra were obtained even at −64 °C. As shown, these PIB-PPh$_2$AgI and isobutyl-PPh$_2$AgI complexes have nearly identical dynamic NMR behavior with both the changes in line shape

SCHEME 2. Synthetic Route to Polymeric PIB-Bound Ag Complexes and Their Lower Molecular Weight Analogues
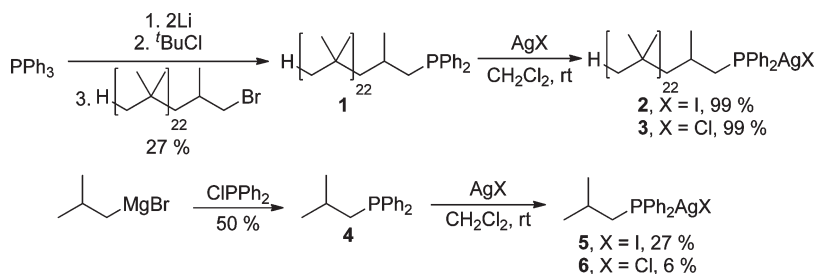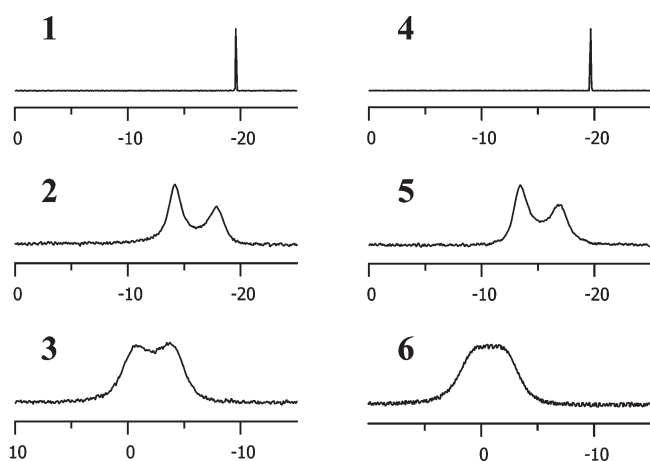
FIGURE 2. ^{31}P NMR spectra of phosphines (**1** and **4**) and corresponding silver complexes **2**, **3**, **5**, and **6** in C$_6$D$_6$ at room temperature.

and the temperature-dependent chemical shifts being very similar.

The variable-temperature NMR spectra for **2** and **5** can be used to calculate the rate of silver and phosphine exchange (Table 1). Below −33 °C, the exchange process is slow on the NMR time scale and a doublet of doublets was observed. The coupling constant of 464 Hz of inner doublet corresponds to ^{107}Ag−^{31}P coupling, and the outer doublet has a coupling constant of 536 Hz due to ^{109}Ag−^{31}P. The ratio of these coupling constants is 0.866, which corresponds to a gyromagnetic ratio of ^{107}Ag/^{109}Ag of 0.870. Integration of inner/outer doublets is 52/48, which corresponds to the isotopic ratio of ^{107}Ag/^{109}Ag of 51.8/48.2. Using line shape analysis,[7] the rate of phosphine ligand exchange for **2** and **5** was then calculated at each temperature. These rate constants were then used to calculate the $\Delta G^{\ddagger}$ for the exchange process at 20 °C, using the Eyring equation (Table 2).

Similar analyses were also carried out in other solvents to afford a list of activation energies for PIB-PPh$_2$AgI (**2**), PIB-PPh$_2$AgCl (**3**), (CH$_3$)$_2$CHCH$_2$PPh$_2$AgI (**5**), and (CH$_3$)$_2$-CHCH$_2$PPh$_2$AgCl (**6**) phosphine exchange in various solvents. Exchange behavior of **2** and **3** was studied in THF, CD$_2$Cl$_2$, and heptane. Heptane was not used for **5** or **6** because the silver halide complexes have limited solubility in this solvent. A slightly higher activation energy is seen in the less polar solvent heptane for both **2** and **3**. However, the differences in activation energy for the PIB− and the isobutylphosphine−silver complexes are minimal. While the observed differences were often within experimental error, in most cases the calculated $\Delta G^{\ddagger}$ of the low molecular weight phosphine complex was consistently less than or equal to the $\Delta G^{\ddagger}$ of the polymer-bound species.

(5) (a) Muetterties, E. L.; Alegranti, C. W. *J. Am. Chem. Soc.* **1970**, *92*, 4115. (b) Muetterties, E. L.; Alegranti, C. W. *J. Am. Chem. Soc.* **1972**, *94*, 6386. (c) Bergbreiter, D. E.; Lynch, T. J.; Shimazu, S. *Organometallics* **1983**, *2*, 1354.

(6) Triaryl- and trialkylphosphine silver(I) complexes usually exist in tetrameric form in both solution and the solid state. VT NMR studies of these complexes showed that the ligand exchange process occurs intermolecularly. (a) Shimazu, S. Ph.D. Dissertation, Texas A&M University, December, **1983**; Appendix I. (b) Teo, B.-K.; Calabrese, J. C. *Inorg. Chem.* **1976**, *15*, 2474.

(7) Line-shape simulations were performed with the computer program WINDNMR: Reich, H. J. *J. Chem. Educ., Software* **1996**, *3D*, 2.
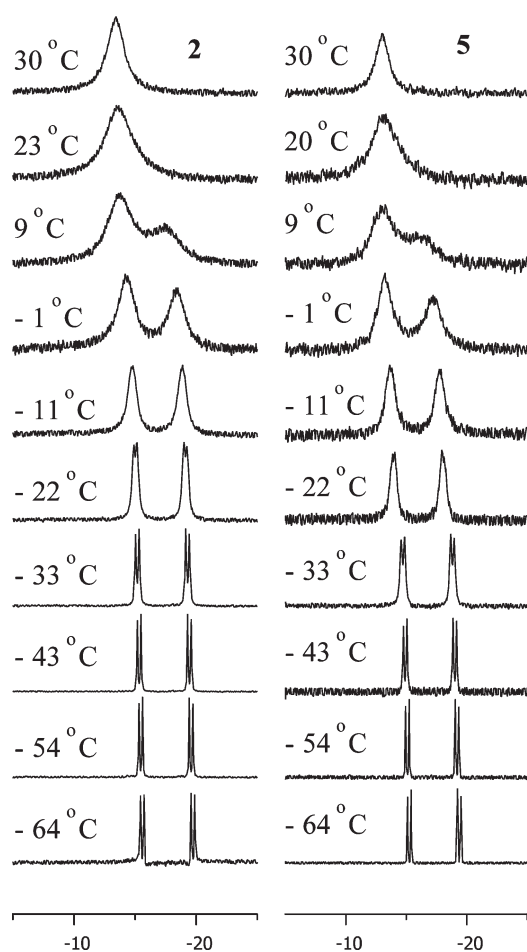
FIGURE 3. VT ^{31}P NMR spectra of **2** and **5** in CD$_2$Cl$_2$ at temperatures from −64 to 30 °C.

TABLE 1. Calculated Rate Constants for Phosphine Exchange in 2 and 5 in CD$_2$Cl$_2$ at Various Temperatures

temp, °C	2	5
30	4331	5215
20	2598	3012
9	1352	1731
−1	743	865
−11	361	510
−22	163	238
−33	57	124
−43	24	56
−54	9	21
−64	3	8

TABLE 2. Activation Energies (kcal/mol, 20 °C) for PIB- and Isobutylphosphine−Ag(I) Exchange in Various Solvents[a]

	2	5	3	6
THF[b]	12.9	12.7	12.3	11.9
CD$_2$Cl$_2$	12.6	12.5	11.5	11.5
heptane[b]	13.4		13.0	

[a]Activation energies were derived from at least seven individual rate constants measured over a range of −64 to 52 °C. [b]10% C$_6$D$_6$ was added.

While our recent work has focused on using soluble nonpolar PIB-bound ligands as catalyst supports, PEG derivatives are more common as soluble polymer supports.[2b] Thus, we extended our studies of phosphine ligand exchange

SCHEME 3. Synthesis of PEG-Bound Ag Complexes and Their Lower Molecular Weight Analogues
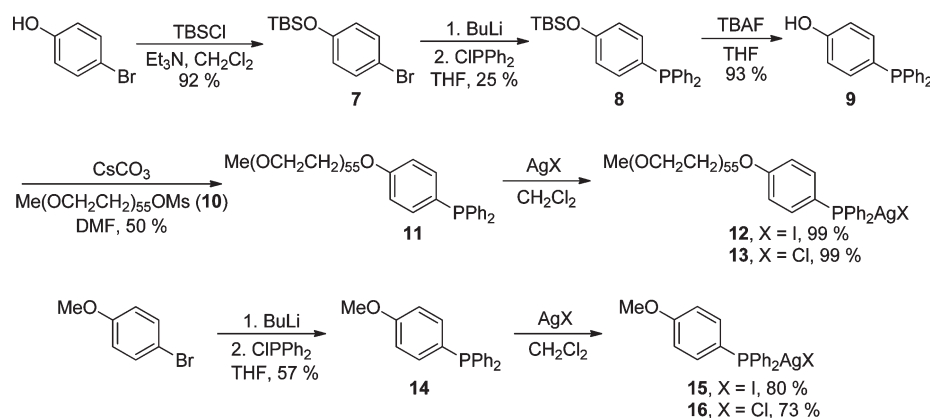
to include PEG-triarylphosphine-bound silver halide complexes too. These ^{31}P NMR spectroscopy studies showed that phosphine silver halide complexes bound to the terminus of a polar polymer, PEG, also have variable-temperature NMR behavior and exchange kinetics similar to those of an electronically analogous low molecular weight phosphine ligand.

In these studies, we first synthesized PEG-supported phosphine silver halide complexes (Scheme 3). Electronically similar low molecular weight phosphines and silver complexes were then also prepared. The comparative dynamic variable-temperature ^{31}P NMR spectra of these polymeric and low molecular weight silver phosphine complexes were again found to be very similar (the ^{31}P NMR spectra are provided as Supporting Information). The free energies of activation for phosphine exchange at 20 °C were again calculated from the rate constants measured by line shape analysis at various temperatures over a −76 to 30 °C range for **12**, **15**, **13**, and **16**. These $\Delta G^{\ddagger}$ values were 12.3, 12.3, 11.1, and 10.8 kcal/mol, respectively. As was true for the less polar terminally substituted PIB-phosphines, the PEG-bound phosphine and low molecular weight phosphine ligands have similar behavior.

Conclusions

Dynamic NMR studies of phosphine exchange in PIB-bound, PEG-bound, and low molecular weight phosphine silver halide complexes show that terminal phosphine ligands on polar and nonpolar polymers have exchange behavior that is very similar to that seen with low molecular weight phosphine ligands. Line shape analyses show that the rates and activations energies are nearly the same. This similar dynamic behavior in a ligand exchange process for either a polymer or a nonpolymer silver complex supports the assumption that soluble end-functionalized polymer-supported metal complexes can be used to prepare soluble polymer-bound organometallic catalysts whose reactivity and selectivity will be exactly like that of lower molecular weight analogues.

Experimental Section

Vinyl-terminated PIB oligomers (Glissopal 1300) were obtained from BASF Co. and had a M_n of 1300 based on ^1H NMR end group analysis of the terminal vinyl group. All other reagents were purchased from commercial sources and used

without further purification unless otherwise specified. CH_2Cl_2 was degassed with three freeze−pump−thaw cycles before being used in the preparation of silver complexes. Isobutylmagnesium bromide solution was prepared from 2-bromo-2-methylpropane and magnesium turnings in THF; the concentration was determined by titration.[8] ^1H NMR spectra were recorded on Varian Inova 500 or Inova 300 spectrometers at 499.834 or 299.959 MHz, respectively. ^{13}C NMR spectra were recorded on Varian Inova 500 or Inova 300 spectrometers at 125.695 or 75.432 MHz, respectively. ^1H and ^{13}C NMR chemical shifts are reported in ppm and referenced to CDCl$_3$, CD$_2$Cl$_2$, or C$_6$D$_6$. ^{31}P NMR spectra were obtained on an Inova 300 spectrometer at 121.425 MHz and chemical shifts were reported in ppm and were referenced to external 85% H$_3$PO$_4$ at room temperature. When THF or heptane was used for VT NMR experiments, 10% C$_6$D$_6$ was added as internal lock. Coupling constants (J values) were reported in Hertz (Hz), and spin multiplicities are indicated by the following symbols: s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet). All reactions were carried out under nitrogen atmosphere unless otherwise noted. Temperatures recorded for VT-NMR experiments were calibrated with 100% MeOH. High-resolution MS data were collected from Applied Biosystems Voyager STR MALDI/TOF mass spectrometer with 2,4,6-trihydroxyacetophenone (THAP) as matrix. Melting points were measured by Stanford Research Systems OptiMelt apparatus and uncorrected. PIB-CH$_2$Br, 4-(diphenylphosphinyl)phenol (**9**), and Me(OCH$_2$CH$_2$)$_{55}$OMs (**10**) were prepared according to literature procedures.[4,9]

Synthesis of PIB-CH$_2$PPh$_2$ (1). Lithium (0.058 g, 8.36 mmol) was cut and pressed into rods and placed in a 50-mL round-bottomed flask equipped with a reflux condenser and a magnetic stir bar. Triphenylphosphine (1.1 g, 4.2 mmol) was dissolved in THF (10 mL) and introduced into the reaction flask at room temperature. The reaction flask was immersed in an oil bath whose temperature was kept at 70 °C. The reaction mixture was stirred for 4 h and then cooled to room temperature. At this point *tert*-butyl chloride was added (0.46 mL, 4.2 mmol). The reaction mixture was then stirred at room temperature for 10 min before it was transferred by forced siphon with a cannula to a 100-mL round-bottomed flask containing PIB-CH$_2$Br (6.54 g, 4.7 mmol in 25 mL THF). The resulting reaction mixture was further stirred at room temperature for 14 h. Then saturated aqueous NH$_4$Cl (50 mL) and hexanes (50 mL) were added to the reaction mixture and the aqueous phase was separated. The nonpolar phase was washed with H$_2$O (2 × 50 mL), 90%

(8) Krasovskiy, A.; Knochel, P. *Synthesis* **2006**, 890.
(9) (a) Sieber, F.; Wentworth, P. Jr.; Toker, J. D.; Wentworth, A. D.; Metz, W. A.; Reed, N. N.; Janda, K. D. *J. Org. Chem.* **1999**, *64*, 5188. (b) Köllhofer, A.; Plenio, H. *Chem.—Eur. J.* **2003**, *9*, 1416.

aqueous EtOH (3 × 50 mL), and acetonitrile (7 × 20 mL), then dried over anhydrous MgSO$_4$. The solvent was evaporated under reduced pressure to afford a crude product that was purified by silica gel column chromatography with hexane as eluting solvent to afford a colorless oil (1.84 g, 1.1 mmol, 26% yield). ^{1}H NMR (300 MHz, C$_6$D$_6$): δ 0.80−1.90 (m, 183 H), 1.90−2.00 (dd, J = 13.4, 8.1 Hz, 1 H), 2.06−2.18 (dd, J = 13.4, 5.5 Hz, 1 H), 7.02−7.13 (m, 6 H), 7.43−7.54 (m, 4 H). ^{13}C NMR (125 MHz, C$_6$D$_6$): δ 14.4, multiple peaks between 20 and 41, 55−61, 128.4, 128.6 (d, $J_{^{31}P-^{13}C}$ = 6.2 Hz), 128.7 (d, $J_{^{31}P-^{13}C}$ = 5.1 Hz), 133.0 (d, $J_{^{31}P-^{13}C}$ = 18.5 Hz), 133.6 (d, $J_{^{31}P-^{13}C}$ = 19.3 Hz), 140.0 (d, $J_{^{31}P-^{13}C}$ = 15.2 Hz), 140.2 (d, $J_{^{31}P-^{13}C}$ = 14.4 Hz). ^{31}P NMR (121 MHz, C$_6$D$_6$): δ −19.5.

Synthesis of Polyisobutyldiphenylphosphine Silver Iodide (PIB-CH$_2$PPh$_2$AgI) (2). The PIB phosphine **1** (0.041 g, 0.03 mmol) and silver iodide (0.013 g, 0.05 mmol) were placed in a 25-mL round-bottomed flask equipped with a magnetic stir bar. Then CH$_2$Cl$_2$ (3 mL) was added to the flask and the reaction mixture was stirred at room temperature for 54 h in the dark. The suspension was filtered and the solvent was evaporated under reduced pressure to afford a colorless oil (0.048 g, 0.03 mmol, 99% yield). ^{1}H NMR (300 MHz, C$_6$D$_6$): δ 0.77−2.38 (m, 185 H), 7.03−7.25 (m, 6 H), 7.74−8.00 (m, 4 H). ^{13}C NMR (75 MHz, C$_6$D$_6$): δ 14.4, 15.2, multiple peaks between 24 and 41, 55−60, and 128−136. ^{31}P NMR (121 MHz, C$_6$D$_6$): δ −15.6.

Synthesis of Polyisobutyldiphenylphosphine Silver Chloride (PIB-CH$_2$PPh$_2$AgCl) (3). The same procedure used to prepare **2** was used substituting AgCl (0.010 g, 0.07 mmol) for AgI. The product was isolated as a colorless oil (0.052 g, 0.03 mmol, 99% yield). ^{1}H NMR (300 MHz, C$_6$D$_6$): δ 0.70−1.97 (m, 183 H), 2.00−2.43 (m, 2 H), 6.98−7.14 (m, 6 H), 7.75−8.09 (m, 4 H). ^{13}C NMR (75 MHz, C$_6$D$_6$): δ multiple peaks between 24 and 38, 55−60, and 128−134. ^{31}P NMR (121 MHz, C$_6$D$_6$): δ −2.0.

Synthesis of Isobutyldiphenylphosphine (4). Isobutylmagnesium bromide (30 mL, 1.25 M in THF) was cooled to 0 °C and chlorodiphenylphosphine (6.9 mL, 37.6 mmol) was added drop-wise. The reaction mixture was warmed to room temperature and stirred for 24 h. Then saturated aqueous NH$_4$Cl (50 mL) was added to quench the reaction mixture followed by addition of ethyl acetate (50 mL). The organic layer was separated and washed with H$_2$O (50 mL) and brine (50 mL) and dried over anhydrous MgSO$_4$. The solvent was evaporated under reduced pressure to afford the crude product, which was further purified by vacuum distillation to give a colorless liquid (4.55 g, 18.8 mmol, 50% yield). ^{1}H NMR (300 MHz, C$_6$D$_6$): δ 0.98 (d, J = 6.3 Hz, 6 H), 1.55−1.77 (m, 1 H), 1.89 (d, J = 7.0 Hz, 2 H), 7.00−7.12 (m, 6 H), 7.39−7.47 (m, 4 H). ^{13}C NMR (75 MHz, C$_6$D$_6$): δ 24.3 (d, $J_{^{31}P-^{13}C}$ = 9.6 Hz), 26.4 (d, $J_{^{31}P-^{13}C}$ = 14.0 Hz), 38.9 (d, $J_{^{31}P-^{13}C}$ = 13.8 Hz), 128.5, 128.6 (d, $J_{^{31}P-^{13}C}$ = 6.6 Hz), 133.1 (d, $J_{^{31}P-^{13}C}$ = 18.8 Hz), 140.2 (d, $J_{^{31}P-^{13}C}$ = 14.3 Hz). ^{31}P NMR (121 MHz, C$_6$D$_6$): δ −19.5.

Synthesis of Isobutyldiphenylphosphine Silver Iodide ((CH$_3$)$_2$CHCH$_2$PPh$_2$AgI) (5). The same procedure used to prepare **2** was used. The product was recrystallized from a mixture of EtOH and CH$_2$Cl$_2$ to give a white solid (0.51 g, 1.1 mmol, 27% yield). ^{1}H NMR (500 MHz, C$_6$D$_6$): δ 1.02 (dd, J = 6.7, 0.5 Hz, 6 H), 2.15 (t, J = 7.0 Hz, 2 H), 2.31−2.46 (m, 1 H), 7.01−7.06 (m, 2 H), 7.06−7.12 (m, 4 H), 7.81−7.88 (m, 4 H). ^{13}C NMR (125 MHz, C$_6$D$_6$): δ 25.2 (d, $J_{^{31}P-^{13}C}$ = 9.2 Hz), 26.9 (d, $J_{^{31}P-^{13}C}$ = 9.2 Hz), 31.9 (d, $J_{^{31}P-^{13}C}$ = 8.9 Hz), 128.7 (d, $J_{^{31}P-^{13}C}$ = 9.2 Hz), 129.6 (d, $J_{^{31}P-^{13}C}$ = 1.5 Hz), 133.9 (d, $J_{^{31}P-^{13}C}$ = 15.3 Hz), 135.3 (d, $J_{^{31}P-^{13}C}$ = 20.1 Hz). ^{31}P NMR (121 MHz, C$_6$D$_6$): δ −15.3. Mp 260−264 °C. HRMS calcd for [(C$_{16}$H$_{19}$PAg)$_2$I]$^+$ 824.9595, found 824.9785.

Synthesis of Isobutyldiphenylphosphine Silver Chloride ((CH$_3$)$_2$CHCH$_2$PPh$_2$AgCl) (6). The same procedure used to prepare **5** was used substituting AgCl (0.72 g, 5.0 mmol) for AgI. The product was recrystallized from an EtOH/CH$_2$Cl$_2$

mixture to give a white solid (0.10 g, 0.26 mmol, 6% yield). ^{1}H NMR (500 MHz, C$_6$D$_6$): δ 0.99 (d, J = 6.6 Hz, 6 H), 1.97 (t, J = 7.4 Hz, 2 H), 2.22−2.34 (m, 1 H), 6.94−7.04 (m, 6 H), 7.91−7.97 (m, 4 H). ^{13}C NMR (125 MHz, C$_6$D$_6$): δ 24.8 (d, $J_{^{31}P-^{13}C}$ = 10.0 Hz), 27.2 (d, $J_{^{31}P-^{13}C}$ = 10.0 Hz), 37.1 (d, $J_{^{31}P-^{13}C}$ = 13.7 Hz), 128.8 (d, $J_{^{31}P-^{13}C}$ = 9.8 Hz), 129.8, 133.9 (d, $J_{^{31}P-^{13}C}$ = 16.7 Hz), 135.2 (d, $J_{^{31}P-^{13}C}$ = 26.1 Hz). ^{31}P NMR (121 MHz, C$_6$D$_6$): δ −0.7. Mp 191−193 °C. HRMS calcd for [(C$_{16}$H$_{19}$-PAg)$_2$Cl]$^+$ 733.0239, found 733.0394.

Synthesis of Poly(ethylene glycol)triarylphosphine (11). This phosphine was prepared by a literature procedure.[9] The product was precipitated with diethyl ether (500 mL) and was characterized by ^{1}H and ^{31}P NMR spectroscopy. The product was collected by filtration as a white solid and contaminated with 20% phosphine oxide. ^{1}H NMR (500 MHz, CDCl$_3$): δ 3.32, (s, 3 H), 3.42−3.83 (m, 218 H), 4.04−4.08 (m, 2H), 6.79−6.85 (m, 2 H), 7.16−7.28 (m, 12 H). ^{31}P NMR (121 MHz, CDCl$_3$): δ −6.5.

Poly(ethylene glycol)triarylphosphine Complexes of Silver Iodide and Silver Chloride (12 and 13, respectively). Complexes **12** and **13** were prepared from the phosphine **11** and AgI or AgCl with use of a procedure analogous to that used to prepare PIB-PPh$_2$ complexes of AgI and AgCl. The silver halide complexes so formed were characterized by ^{1}H and ^{31}P NMR spectroscopy and were contaminated with up to 25% phosphine oxide. **12:** ^{1}H NMR (500 MHz, CD$_2$Cl$_2$): δ 3.33, (s, 3 H), 3.42−3.86 (m, 218 H), 4.06−4.10 (m, 2H), 6.83−6.88 (m, 2 H), 7.26−7.33 (m, 4 H), 7.35−7.41 (m, 2 H), 7.43−7.51 (m, 6 H). ^{31}P NMR (121 MHz, CD$_2$Cl$_2$): δ −3.4. **13:** ^{1}H NMR (300 MHz, CD$_2$Cl$_2$): δ 3.32, (s, 3 H), 3.32−3.84 (m, 218 H), 4.02−4.09 (m, 2 H), 6.80−6.88 (m, 2 H), 7.24−7.50 (m, 12 H). ^{31}P NMR (121 MHz, CD$_2$Cl$_2$): δ 7.7.

Synthesis of (4-Methoxyphenyl)diphenylphosphine (14). To a 250-mL round-bottomed flask equipped with a magnetic stirrer was added 4-bromoanisole (5.61 g, 30.0 mmol) and THF (100 mL). The flask was immersed in a dry ice−acetone bath for 30 min before BuLi (20 mL, 1.6 M in hexanes, 32.0 mmol) was added. The reaction mixture was stirred at −78 °C for 60 min at which point chlorodiphenylphosphine (7.2 mL, 40 mmol in 20 mL of THF) was added. The reaction mixture was stirred at −78 °C for 3 h and then warmed to room temperature and stirred overnight. Then saturated aqueous NH$_4$Cl (50 mL) and H$_2$O (50 mL) were added to quench the reaction and the organic phase was separated. The organic phase was washed with H$_2$O (50 mL) and brine (50 mL) and dried over anhydrous MgSO$_4$. The solvent was removed under reduced pressure to afford a crude product that was purified by silica gel column chromatography with use of hexane and CH$_2$Cl$_2$ (hexane:CH$_2$Cl$_2$ = 4:1) to afford a colorless oil that turned into a solid on standing. The solid was further recrystallized from ethanol to give colorless prisms (5.04 g, 17.2 mmol, 57% yield). ^{1}H NMR (500 MHz, CDCl$_3$): δ 3.82, (s, 3 H), 6.89−6.95 (m, 2 H), 7.28−7.43 (m, 12 H). ^{13}C NMR (75 MHz, CDCl$_3$): δ 55.1, 114.2 (d, $J_{^{31}P-^{13}C}$ = 8.1 Hz), 127.3 (d, $J_{^{31}P-^{13}C}$ = 6.8 Hz), 128.4 (d, $J_{^{31}P-^{13}C}$ = 6.8 Hz), 128.5, 133.4 (d, $J_{^{31}P-^{13}C}$ = 19.0 Hz), 135.6 (d, $J_{^{31}P-^{13}C}$ = 21.3 Hz), 137.6 (d, $J_{^{31}P-^{13}C}$ = 9.3 Hz), 160.4. ^{31}P NMR (121 MHz, CDCl$_3$): δ −6.5. Mp 65−66 °C (lit.[10] mp 64.5−65.5 °C).

(4-Methoxyphenyl)diphenylphosphine Silver Iodide and Silver Chloride (15 and 16). **15** and **16** were prepared from (4-methoxyphenyl)diphenylphosphine and AgI or AgCl. The product CH$_3$OC$_6$H$_4$PPh$_2$AgI was isolated as white needles in 80% yield. ^{1}H NMR (300 MHz, CD$_2$Cl$_2$): δ 3.80 (s, 3 H), 6.86−6.93 (m, 2 H), 7.31−7.39 (m, 4 H), 7.40−7.47 (m, 2 H), 7.54−7.64 (m, 6 H). ^{13}C NMR (75 MHz, CD$_2$Cl$_2$): δ 55.8, 114.8 (d, $J_{^{31}P-^{13}C}$ = 10.8 Hz), 123.3 (d, $J_{^{31}P-^{13}C}$ = 28.7 Hz), 129.1 (d, $J_{^{31}P-^{13}C}$ = 9.5 Hz),

(10) McEwen, W. E.; Shiau, W.-I.; Yeh, Y.-I.; Schulz, D. N.; Pagilagan, R. U.; Levy, J. B.; Symmes, C. Jr.; Nelson, G. O.; Granoth, I. *J. Am. Chem. Soc.* **1975**, 97, 1787.

130.3 (d, $J_{31_P-13_C}$ = 1.6 Hz), 133.8 (d, $J_{31_P-13_C}$ = 24.9 Hz), 134.5 (d, $J_{31_P-13_C}$ = 15.7 Hz), 136.7 (d, $J_{31_P-13_C}$ = 17.6 Hz), 161.9 (d, $J_{31_P-13_C}$ = 1.5 Hz). ^{31}P NMR (121 MHz, CD$_2$Cl$_2$): δ −6.5. Mp 188−189 °C. HRMS calcd for [(C$_{19}$H$_{17}$OPAg)$_2$I]$^+$ 924.9181, found 924.8835. The product CH$_3$OC$_6$H$_4$PPh$_2$AgCl was isolated as a white solid in 73% yield. ^{1}H NMR (300 MHz, CD$_2$Cl$_2$): δ 3.75 (s, 3 H), 6.81−6.88 (m, 2 H), 7.27−7.35 (m, 4 H), 7.36−7.44 (m, 2 H), 7.50−7.62 (m, 6 H). ^{13}C NMR (75 MHz, CD$_2$Cl$_2$): δ 55.7, 114.9 (d, $J_{31_P-13_C}$ = 11.2 Hz), 123.1 (d, $J_{31_P-13_C}$ = 32.6 Hz), 129.2 (d, $J_{31_P-13_C}$ = 9.8 Hz), 130.4 (d, $J_{31_P-13_C}$ = 1.7 Hz), 133.6 (d, $J_{31_P-13_C}$ = 28.7 Hz), 134.2 (d, $J_{31_P-13_C}$ = 16.5 Hz), 136.5 (d, $J_{31_P-13_C}$ = 18.5 Hz), 161.9 (d, $J_{31_P-13_C}$ = 1.4 Hz). ^{31}P NMR (121 MHz, CD$_2$Cl$_2$): δ 6.5. Mp 97−100 °C. HRMS calcd for [(C$_{19}$H$_{17}$OPAg)$_2$Cl]$^+$ 832.9824, found 833.0092.

Supporting Information Available: NMR spectra and structures with peak assignments. This material is available free of charge via the Internet at http://pubs.acs.org.