5176 *Organometallics* **2004,** *23,* 5176−5181

Poly(dimethylsiloxane)-Derived Phosphine and Phosphinite Ligands: Synthesis, Characterization, Solubility in Supercritical Carbon Dioxide, and Sequestration on Silica

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Received May 25, 2004

The synthesis and characterization of eight macromolecular phosphorus-containing ligands are presented ($\mathrm{Ph_2PR}$ (**1a**), $(\overline{\mathrm{OCH_2CH_2O)P}}\mathrm{R}$ (**1b**), $\mathrm{PhPR_2}$ (**1c**); $\mathrm{Ph_2PC(CH_3)_2COR}$ (**2a**), $(\overline{\mathrm{OCH_2CH_2O)P}}\mathrm{C(CH_3)_2COR}$ (**2b**), $\mathrm{PhP\{C(CH_3)_2COR\}_2}$ (**2c**), t-$\mathrm{Bu_2PC(CH_3)_2COR}$, (**2d**), $\mathrm{Cy_2PC(CH_3)_2COR}$ (**2e**); $\mathrm{R = OCH_2CH_2OCH_2CH_2CH_2[SiMe_2O]_{\mathit{n}}SiMe_2Bu}$, $n = 15{-}20$). They contain low-molecular-weight poly(dimethylsiloxane) tags, and their molecular weights have been determined using a number of methods, including GPC and MALDI-TOF mass spectrometry. Solubility studies of **1a**,**b** in supercritical carbon dioxide are described. Reaction of **2a** with $\mathrm{PdCl_2(MeCN)_2}$ yields the air-stable complex *trans*-Pd(**2a**)$_2$Cl$_2$ (**3**) as a yellow oil. Catalytic studies using these ligands in cross-coupling reactions in toluene and supercritical carbon dioxide are reported. The ligands and **3** adsorb reversibly on silica, thus resulting in a method for recycling catalytic species by using a solvent trigger.

Introduction

Phosphines are often the ligands of choice in homogeneous catalysis, as they can be easily prepared and modified. They have been used to prepare catalysts for a wide range of reactions such as hydrogenation and C−C coupling.[1] There is growing interest in the recyclability of such catalysts, due to environmental concerns and the ever-rising costs of precious metals.[2] This can involve the use of green solvents such as supercritical carbon dioxide ($\mathrm{scCO_2}$). Fluorous ligands, such as tris(4-(1*H*,1*H*,2*H*,2*H*-perfluorodecyl)phenyl)phosphine, have been particularly successful in this area but are expensive. We have addressed this issue by preparing a new family of cheaper ligands tagged with a poly(dimethylsiloxane) (PDMS) chain that are soluble in $\mathrm{scCO_2}$. Generally, low-molecular-weight siloxane-based polymers are soluble in supercritical carbon dioxide.[3] More recently discovered $\mathrm{CO_2}$-philes include poly(ether-carbonate) copolymers and peracetylated sugars,[4] which could also be used in this area. In some cases, trimethylsilyl-subsituted ligands and their complexes are also soluble in $\mathrm{scCO_2}$.[5]

PDMS possesses high chemical and physical stability, and therefore, these tags will be inert under typical reaction conditions and should not unduly affect catalysis. PDMS derivatives have been used as stabilizers in dispersion polymerizations in $\mathrm{scCO_2}$[6] but have not been used for catalytic applications. From a sustainability perspective, it is interesting to look at the life cycles of perfluorocarbons and PDMS. There is some concern about the environmental persistence of perfluorocarbons and other fluorinated compounds. It has been suggested that the products of their breakdown can be environmentally damaging in the long term.[7] PDMS derivatives ultimately degrade to silicates, carbon dioxide, and small amounts of methane.[8] The synthesis of fluorocarbons is technically challenging, can involve large amounts of solvent, and employ hazardous reagents such as molecular fluorine and HF. PDMS is manufactured via the hydrolysis of dimethyldichlorosilane, which in turn is prepared from silicon and methyl chloride. The process of PDMS manufacture is self-contained: the chloride ion is recycled with the regeneration of methyl chloride via the reaction of methanol and HCl. This

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10.1021/om0496277 CCC: $27.50

comparatively “green” reaction results in functionalized PDMS-based materials that are cheaper than their perfluorocarbon analogues.

Experimental Section

All reactions were performed under an inert atmosphere using standard Schlenk line procedures or a glovebox with an O_2 level below 10 ppm. Reagents were purchased from Aldrich or Lancaster, distilled or recrystallized, and subsequently deoxygenated by three freeze−pump−thaw cycles. Poly(dimethylsiloxane) monocarbinol was purchased from Gelest and degassed prior to use; it was converted to an ester by using a literature procedure.[10] Solvents (toluene, diethyl ether, THF, hexane) were dried over sodium−benzophenone and distilled under argon. Deuterated chloroform was dried over CaH_2 and then trap-to-trap distilled and freeze−pump−thaw degassed three times. Compounds were analyzed on a JEOL EX 270 NMR spectrometer (^1H, 270 MHz; $^{13}C\{^1H\}$, 67.5 MHz; $^{31}P\{^1H\}$, 109 MHz) and a Bruker AMX-500 NMR spectrometer (^1H, 500 MHz; $^{13}C\{^1H\}$, 125 MHz). ^1H NMR spectra were referenced to residual protons in the deuterated solvent and ^{13}C NMR spectra to the ^{13}C atoms therein. $^{31}P\{^1H\}$ NMR spectra were referenced to external $P(OMe)_3$ (141.0 ppm with respect to 85% H_3PO_4 at 0.0 ppm). $^{13}C\{^1H\}$ NMR resonances were assigned on the basis of their chemical shifts and by DEPT NMR experiments. The observed signals in the NMR spectra were characterized as follows: singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), broad (br), and complex area (ca). A complex area is an area of a spectrum containing overlapping multiplets. Elemental analyses were performed by Elemental Microanalysis Ltd., Devon, U.K. GPC analyses (using monodisperse polystyrene standards) were performed by Rapra Technology Ltd., Shrewsbury, U.K. MALDI-TOF mass spectra were obtained by the EPSRC National Mass Spectrometry Service Centre at Swansea using an Applied Biosystems Voyager instrument. Quantities of reagents and yields were calculated based on a value of $n = 15$ for the poly(dimethylsiloxane) monocarbinol reagent; however, the molecular weight of this monodisperse reagent varied with batches purchased, from $n = 15$ to $n = 20$.

Preparation of PDMS-Tagged Phosphinite Ligands 1a−c. Poly(dimethylsiloxane) monocarbinol (4.0 g, 3 mmol), triethylamine (1.7 mL, 12 mmol), and anhydrous diethyl ether (50 mL) were charged in a dry Schlenk tube. Chlorophosphine (3 mmol in 20 mL of Et_2O; in the case of dichlorophenylphosphine 1.5 mmol in 20 mL of Et_2O) was added dropwise at 0 °C. The mixture was warmed to room temperature overnight. The triethylamine hydrochloride salt was extracted by addition of degassed water, and after separation of the layers under argon, the ethereal layer was dried over anhydrous $MgSO_4$. After filtration, the solvent and any unreacted reagents were removed under vacuum to yield colorless oils.

For **1a**: yield 3.9 g (85%). For **1b**: yield 4.0 g (70%). For **1c**: yield 3.1 g (73%).

For **1a**: ^1H NMR (270 MHz, $CDCl_3$) δ −0.14 to +0.29 (br, 127 H, $C_4H_9Si(CH_3)_2[OSi(CH_3)_2]_{18}$), 0.46−0.52 (m, 2H, $Si(CH_3)_2\mathit{CH_2}CH_2CH_2O$), 1.55−1.67 (m, 2H, $Si(CH_3)_2CH_2\mathit{CH_2}CH_2O$), 3.36 (m, 2H, $Si(CH_3)_2CH_2CH_2\mathit{CH_2}O$), 3.63 (m, 2H, $-O\mathit{CH_2}CH_2OP$), 4.01 (m, 2H, $-O-CH_2\mathit{CH_2}OP$), 7.2−7.7 (br, 10H, Ph); $^{13}C\{^1H\}$ NMR δ 0.9, 1.0, 1.7 (s, $C_4H_9Si(CH_3)_2[OSi(CH_3)_2]_{18}$), 14.8, 24.0 (s, $Si(CH_3)_2\mathit{CH_2CH_2}CH_2$), 68.0, 70.2, 74.7 (s, $-\mathit{CH_2}O\mathit{CH_2CH_2}O$), 128.9, 129.8, 130.8, 131.1, 142.6 (s, *Ph*); $^{31}P\{^1H\}$ NMR δ 115.2; GPC $M_w = 2090$, $M_n = 1660$, polydispersity 1.25, calculated by NMR $M_w = 1882$ ($n = 19$). Anal. Calcd for $n = 18$: C, 41.50; H, 8.39. Found: C, 41.68; H, 8.36.

For **1b**: ^1H NMR (270 MHz, $CDCl_3$) δ −0.14 to +0.288 (br, 122 H, $C_4H_9Si(CH_3)_2[OSi(CH_3)_2]_{18}$), 0.52−0.59 (m, 2H, $Si(CH_3)_2\mathit{CH_2}CH_2CH_2O$), 1.61−1.67 (m, 2H, $Si(CH_3)_2CH_2\mathit{CH_2}CH_2O$), 3.45−4.23 (ca, 10H, $Si(CH_3)_2CH_2CH_2\mathit{CH_2}O$, $-O\mathit{CH_2}\mathit{CH_2}O$, $PO_2C_2H_4$); $^{13}C\{^1H\}$ NMR δ 0.9, 1.0, 1.7 (s, $C_4H_9Si(CH_3)_2[OSi(CH_3)_2]_{18}$), 14.7, 23.9 (s, $Si(CH_3)_2\mathit{CH_2CH_2}CH_2$), 68.0, 70.9, 74.7 (s, $-\mathit{CH_2}O\mathit{CH_2CH_2}O$), 64.5, 66.5 ($PO_2\mathit{C_2}H_4$); $^{31}P\{^1H\}$ NMR δ 135.8; GPC $M_w = 1770$, $M_n = 1450$, polydispersity 1.2, calculated by NMR $M_w = 1640$ ($n = 18$); Maldi-TOF (dithranol matrix with added LiCl) $M_w = 1860$, $M_n = 1740$, polydispersity 1.23. Anal. Calcd for $n = 20$: C, 34.91; H, 8.24. Found: C, 34.73; H, 8.82.

For **1c**: ^1H NMR (270 MHz, $CDCl_3$) δ −0.14 to +0.29 (br, 250 H, $C_4H_9Si(CH_3)_2[OSi(CH_3)_2]_{18}$), 0.42−0.61 (m, 4H, $Si(CH_3)_2\mathit{CH_2}CH_2CH_2O$), 1.45−1.65 (br, 4H, $Si(CH_3)_2CH_2\mathit{CH_2}CH_2O$), 3.27−4.32 (ca, 12H, $Si(CH_3)_2CH_2CH_2\mathit{CH_2}O$, $-O\mathit{CH_2}\mathit{CH_2}O$), 7.30−7.90 (m, 5H, *Ph*); $^{13}C\{^1H\}$ NMR δ 0.9, 1.0, 1.7 (s, $C_4H_9Si(CH_3)_2[OSi(CH_3)_2]_{18}$), 14.0, 23.3 (s, $Si(CH_3)_2\mathit{CH_2CH_2}CH_2$), 65.7, 70.6, 74.0 (s, $-\mathit{CH_2}O\mathit{CH_2CH_2}O$), 128, 128.06, 129.63, 129.93, 132.03 (*Ph*); $^{31}P\{^1H\}$ NMR δ 159.3; GPC $M_w = 3520$, $M_n = 1590$, polydispersity 2.3, calculated by NMR $M_w = 3396$ ($n = 20$). Anal. Calcd for $n = 20$: C, 36.97; H, 8.47. Found: C, 36.59; H, 8.49.

Preparation of Esterified PDMS-Tagged Phosphine Ligands 2a−e. A dry Schlenk tube was charged with diethyl ether (40 mL) and the previously prepared brominated ester of the poly(dimethylsiloxane) monocarbinol (1.5 g, 1 mmol).[10] nBuLi (0.6 mL of a 1.6 M solution in *n*-hexane) was added dropwise under argon at −78 °C. After the mixture had been stirred for 2 h, the phosphine chloride compound (1 mmol in 10 mL of diethyl ether or 0.5 mmol in the case of Cl_2PPh) was added. The mixture was warmed to room temperature and stirred for a further 18 h at this temperature. The mixture was hydrolyzed with a saturated ammonium chloride solution (5 mL) and extracted with diethyl ether. The organic layer was dried over $MgSO_4$, filtered, and evaporated under vacuum to yield the product as a colorless oil.

For **2a**: yield 1.29 g (78%). For **2b**: yield 1.32 g (76%). For **2c**: yield 1.20 g (83%). For **2d**: yield 0.99 g (61%). For **2e**: yield 0.98 g (61%).

For **2a**: ^1H NMR (270 MHz, $CDCl_3$) δ −0.22 to +0.04 (br, 100 H, $C_4H_9Si(CH_3)_2[OSi(CH_3)_2]_n$), 0.44 (br, 2H, $Si(CH_3)_2\mathit{CH_2}CH_2CH_2OCH_2CH_2O$), 1.50 (br, 2H, $Si(CH_3)_2CH_2\mathit{CH_2}CH_2OCH_2CH_2O$), 1.87 (s, 6H $OCOC(\mathit{CH_3})_2$), 3.17−4.24 (ca, 6H, $Si(CH_3)_2CH_2CH_2\mathit{CH_2}O\mathit{CH_2CH_2}$), 7.20−7.70 (br, 10H, *Ph*); $^{13}C\{^1H\}$ NMR δ 0.94, 0.98, 1.04, 1.68 ($(\mathit{CH_3})_3CSi(\mathit{CH_3})_2[OSi(\mathit{CH_3})_2]_n$), 14.0 ($Si(CH_3)_2\mathit{CH_2}CH_2CH_2O$), 23.3 ($Si(CH_3)_2CH_2\mathit{CH_2}CH_2O$), 41.8 ($OCO\mathit{C}(CH_3)_2$), 63.7 ($Si(CH_3)_2CH_2CH_2\mathit{CH_2}O$), 67.9 ($-CH_2O\mathit{CH_2}CH_2O$), 73.9 ($-CH_2OCH_2\mathit{CH_2}O$), 24.7 ($OCOC(\mathit{CH_3})_2$), 127.9, 128.1, 128.9, 134.3, 134.6 (s, *Ph*), 175 ($O\mathit{C}OC(CH_3)_2$); $^{31}P\{^1H\}$ NMR δ 18.7; FT-IR ν_{max} 1720 cm^{-1} (s) C=O, 1257 cm^{-1} (s) Si−O; GPC $M_w = 1950$, $M_n = 1580$, polydispersity 1.2, calculated by NMR $M_w = 1585$. Anal. Calcd for $n = 18$: C, 41.86; H, 8.31. Found: C, 42.00; H, 8.33.

For **2b**: ^1H NMR (270 MHz, $CDCl_3$) δ −0.22 to +0.04 (br, 100 H, $C_4H_9Si(CH_3)_2[OSi(CH_3)_2]_n$), 0.50 (br, 2H, $Si(CH_3)_2\mathit{CH_2}CH_2CH_2OCH_2CH_2O$) 1.50 (br, 2H, $Si(CH_3)_2CH_2\mathit{CH_2}CH_2OCH_2CH_2-$), 1.87 (s, 6H, $OCOC(\mathit{CH_3})_2$), 3.35−4.27 (ca, 10H, $Si(CH_3)_2CH_2CH_2\mathit{CH_2}O\mathit{CH_2CH_2}OCOC(CH_3)_2PO_2\mathit{C_2H_4}$); $^{13}C\{^1H\}$ NMR δ 0.9, 0.98, 1.04, 1.68 ($(\mathit{CH_3})_3CSi(\mathit{CH_3})_2[OSi(\mathit{CH_3})_2]_n$), 14.0 ($Si(CH_3)_2\mathit{CH_2}CH_2CH_2O$), 24.0 ($Si(CH_3)_2CH_2\mathit{CH_2}CH_2O$), 65.0 ($Si(CH_3)_2CH_2CH_2\mathit{CH_2}O$), 68.2 ($-CH_2O\mathit{CH_2}CH_2O$), 74.0 ($-CH_2OCH_2\mathit{CH_2}O$), 30.7 ($OCOC(\mathit{CH_3})_2$), 62.0, 70.9 ($PO_2\mathit{C_2}H_4$); $^{31}P\{^1H\}$ NMR δ 45.5; FT-IR ν_{max} 1745 cm^{-1} (s) C=O, 1265 cm^{-1} (s) Si−O; GPC $M_w = 1800$, $M_n = 1470$, polydispersity 1.2, calculated by NMR $M_w = 1491$. Anal. Calcd for $n = 17$: C, 37.37; H, 8.42. Found: C, 36.93, H; 8.40.

For **2c**: ^1H NMR (270 MHz, $CDCl_3$) δ −0.36 to +0.03 (br, 257 H, $C_4H_9Si(CH_3)_2[OSi(CH_3)_2]_n$), 0.54 (br, 4H, $Si(CH_3)_2\mathit{CH_2}CH_2CH_2OCH_2CH_2O$), 1.13−2.14 (ca, 16H, $Si(CH_3)_2CH_2\mathit{CH_2}CH_2O$, $OCOC(\mathit{CH_3})_2$), 3.34−4.31 (br, 12H, $Si(CH_3)_2CH_2$-

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(9) As with all processes under high pressure, appropriate safety precautions must be taken.

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$\mathrm{CH_2}\mathit{CH_2}\mathrm{O}\mathit{CH_2CH_2}$), 7.2−7.7 (br, 5H, *Ph*); ^{13}C{^{1}H} NMR δ 0.11, 1.13, 1.16, 1.77 (($\mathit{CH_3}$)$_3$$\mathit{C}$Si($\mathit{CH_3}$)$_2$[OSi($\mathit{CH_3}$)$_2$]$_n$), 14.1 ($\mathrm{Si(CH_3)_2}\mathit{CH_2}\mathrm{CH_2CH_2O}$), 20.5 ($\mathrm{OCO}\mathit{C}\mathrm{(CH_3)_2}$), 23.3 ($\mathrm{Si(CH_3)_2CH_2}\mathit{CH_2}\mathrm{CH_2O}$), 64.8 ($\mathrm{Si(CH_3)_2CH_2CH_2}\mathit{CH_2}\mathrm{O}$), 68.0 ($-\mathrm{CH_2O}\mathit{CH_2}\mathrm{CH_2O}$), 74.1 ($-\mathrm{CH_2OCH_2}\mathit{CH_2}\mathrm{O}$), 30.8 ($\mathrm{OCOC(}\mathit{CH_3}\mathrm{)_2}$), 128.6, 128.8, 131.0, 131.1, 133.1 (s, *Ph*);. ^{31}P{^{1}H} NMR δ 39.2; FT-IR ν_{max} 1745 cm^{-1} (s) C═O, 1274 cm^{-1} (s) Si−O; GPC $M_w = 2800$, $M_n = 2325$, polydispersity 1.2. Anal. Calcd for $n = 17$: C, 38.98; H, 8.52. Found: C, 39.11; H, 8.53.

For **2d**: ^{1}H NMR (270 MHz, CDCl$_3$) δ −0.22to +0.25 (br, 107 H, $\mathrm{C_4H_9Si(CH_3)_2[OSi(CH_3)_2]}_n$), 0.48 (br, 2H, $\mathrm{Si(CH_3)_2}\mathit{CH_2}\mathrm{CH_2CH_2OCH_2CH_2O}$), 1.10−1.90 (ca, 26H, $\mathrm{Si(CH_3)_2CH_2}\mathit{CH_2}\mathrm{CH_2O}$, $\mathrm{PC(}\mathit{CH_3}\mathrm{)_3}$, $\mathrm{OCOC(}\mathit{CH_3}\mathrm{)_2}$), 3.31−4.22 (ca, 6H, $\mathrm{Si(CH_3)_2CH_2CH_2}\mathit{CH_2}\mathrm{O}\mathit{CH_2CH_2}$); ^{13}C{^{1}H} NMR δ 0.9, 1.0, 1.1, 1.6 (s, ($\mathit{CH_3}$)$_3$$\mathit{C}$Si($\mathit{CH_3}$)$_2$[OSi(CH$_3$)$_2$]$_n$), 14.2 (s, $\mathrm{Si(CH_3)_2}\mathit{CH_2}\mathrm{CH_2CH_2O}$), 23.4 (s, $\mathrm{Si(CH_3)_2CH_2}\mathit{CH_2}\mathrm{CH_2O}$), 25.8, 22.0, 20.4 (s, $\mathrm{OCO}\mathit{C}\mathrm{(}\mathit{C}\mathrm{H_3)_2}$, $\mathrm{PC(}\mathit{C}\mathrm{H_3)_3}$), 36.9 (s, $\mathrm{P}\mathit{C}\mathrm{(CH_3)_3}$), 61.6 (s, $\mathrm{Si(CH_3)_2CH_2CH_2}\mathit{CH_2}\mathrm{O}$), 71.6 (s, $-\mathrm{CH_2O}\mathit{CH_2}\mathrm{CH_2O}$), 74.1 ($-\mathrm{CH_2OCH_2}\mathit{CH_2}\mathrm{O}$), 173.7 ($\mathrm{O}\mathit{C}\mathrm{OC(CH_3)_2}$); ^{31}P{^{1}H} NMR δ 66.8; FT-IR ν_{max} 1747 cm^{-1} (s) C═O, 1263 cm^{-1} (s) Si−O; GPC $M_w = 1800$, $M_n = 1510$, polydispersity 1.2, calculated by NMR $M_w = 1545$. Anal. Calcd for $n = 17$: C, 40.43; H, 8.99. Found: C, 39.93; H, 9.08.

For **2e**: ^{1}H NMR (270 MHz, CDCl$_3$): δ −0.22 to +0.20 (br, 110 H, $\mathrm{C_4H_9Si(CH_3)_2[OSi(CH_3)_2]}_n$), 0.50 (br, 2H, $\mathrm{Si(CH_3)_2}\mathit{CH_2}\mathrm{CH_2CH_2OCH_2CH_2O}$), 1.10−1.80 (ca, 24H, $\mathrm{Si(CH_3)_2CH_2}\mathit{CH_2}\mathrm{CH_2O}$, *Cy*), 1.88 (s, 6H $\mathrm{OCOC(}\mathit{CH_3}\mathrm{)_2}$), 3.31−4.22 (ca, 6H, $\mathrm{Si(CH_3)_2CH_2CH_2\text{-}}\mathit{CH_2}\mathrm{O}\mathit{CH_2CH_2}$); ^{13}C{^{1}H} NMR δ 1.03, 1.09, 1.11, 1.62 (s, ($\mathit{CH_3}$)$_3$$\mathit{C}$Si($\mathit{CH_3}$)$_2$[OSi($\mathit{CH_3}$)$_2$]$_n$), 14.3 (s, $\mathrm{Si(CH_3)_2}\mathit{CH_2}\mathrm{CH_2CH_2O}$), 23.7 (s, $\mathrm{Si(CH_3)_2CH_2}\mathit{CH_2}\mathrm{CH_2O}$), 64.2 (s, $\mathrm{Si(CH_3)_2CH_2CH_2}\mathit{CH_2}\mathrm{O}$), 68.1 (s, $-\mathrm{CH_2O}\mathit{CH_2}\mathrm{CH_2O}$), 73.7 ($-\mathrm{CH_2OCH_2}\mathit{CH_2}\mathrm{O}$), 31.9 (s, $\mathrm{OCOC(}\mathit{CH_3}\mathrm{)_2}$), 36.0 ($\mathrm{OCO}\mathit{C}\mathrm{(CH_3)_2}$), 26.0 (ca, CH$_2$, *Cy*); ^{31}P{^{1}H} NMR δ 52.1; FT-IR ν_{max} 1737 cm^{-1} (s) C═O, 1265 cm^{-1} (s) Si−O; GPC $M_w = 2420$, $M_n = 1860$, polydispersity 1.3, calculated by NMR $M_w = 1600$. Anal. Calcd for $n = 18$: C, 41.59; H, 8.92. Found: C, 41.77; H, 8.95.

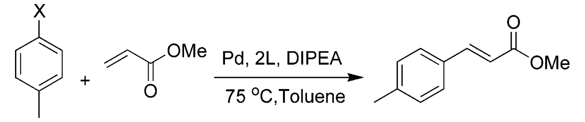
Synthesis of the Palladium Complex *trans*-Pd(2a)$_2$Cl$_2$ (3). In a dry Schlenk tube were placed **2a** (2.00 g, 1.26 mmol), [PdCl$_2$(MeCN)$_2$] (0.16 g, 0.63 mmol), and dichloromethane (30 mL). The orange solution was stirred at room temperature for 4 h. The solvent was removed under vacuum to give *trans*-Pd(**2a**)$_2$Cl$_2$ (**3**) in quantitative yield.

For **3**: ^{1}H NMR (270 MHz, CDCl$_3$) δ −0.03 to +0.04 (br, 130 H, $\mathrm{C_4H_9Si(CH_3)_2[OSi(CH_3)_2]}_n$), 0.43−0.47 (br, 2H, $\mathrm{Si(CH_3)_2}\mathit{CH_2}\mathrm{CH_2CH_2OCH_2CH_2O}$), 1.501 (br, 2H, $\mathrm{Si(CH_3)_2CH_2}\mathit{CH_2}\mathrm{CH_2OCH_2CH_2O}$), 1.87 (s, 6H, $\mathrm{OCOC(}\mathit{CH_3}\mathrm{)_2}$), 3.3−4.3 (ca, 6H, $\mathrm{Si(CH_3)_2CH_2CH_2}\mathit{CH_2}\mathrm{O}\mathit{CH_2CH_2}$), 7.3−8 (br, 10H, Ph); ^{13}C{^{1}H} NMR δ −0.7, 0.3, 0.9, 1.7 (($\mathit{CH_3}$)$_3$$\mathit{C}$Si($\mathit{CH_3}$)$_2$[OSi($\mathit{CH_3}$)$_2$]$_n$), 13.3 ($\mathrm{Si(CH_3)_2}\mathit{CH_2}\mathrm{CH_2CH_2O}$), 23.3 ($\mathrm{Si(CH_3)_2CH_2}\mathit{CH_2}\mathrm{CH_2O}$), 29.9 ($\mathrm{OCOC(}\mathit{CH_3}\mathrm{)_2}$), 46.6 ($\mathrm{OCO}\mathit{C}\mathrm{(CH_3)_2}$), 64.4 ($\mathrm{Si(CH_3)_2CH_2CH_2}\mathit{CH_2}\mathrm{O}$), 67.3 ($-\mathrm{CH_2O}\mathit{CH_2}\mathrm{CH_2O}$), 73.3 ($-\mathrm{CH_2OCH_2}\mathit{CH_2}\mathrm{O}$), 127.6, 128.1, 130.6, 135.7, 135.8 (s, *Ph*), 173.5 ($\mathrm{O}\mathit{C}\mathrm{OC(CH_3)_2}$).; ^{31}P{^{1}H} NMR δ 39.3. Anal. Calcd for $n = 18$: C, 39.91; H, 7.92. Found: C, 40.16; H, 7.93.

Synthesis of Supported Catalyst. A 2.00 g amount of silica gel (K 100, 0.063−0.2 mm) that had been maintained at 200 °C for 48 h was placed in a dry Schlenk tube and degassed. **3** (0.20 g, 0.06 mmol) was dissolved in 10 mL of dry toluene and then added to the tube containing silica with stirring. The mixture was stirred for 1 h and filtered via cannula. The silica-supported material was dried under vacuum. The solvent was removed under vacuum, and any residues were analyzed. The Pd complex quantitatively adsorbed onto the silica, to give a bright yellow powder, as evidenced by mass difference and analysis of the supernatant toluene.

Preliminary Catalytic Studies. Using a glovebox and a standard Schlenk line, Carousel tubes (Radleys) were charged with the phosphine ligands (0.06 mmol) (Table 1), anhydrous toluene (15 mL), 4-halotoluene compound (1.2 mmol), methyl acrylate (0.5 g, 5 mmol), Pd(OCOCH$_3$)$_2$ or Pd(OCOCF$_3$)$_2$ (0.03 mmol) or Pd$_2$(dba)$_3$ (0.02 mmol), and *N*,*N*-diisopropylethylamine (DIPEA) (0.23 g, 1.78 mmol) (Scheme 1). The reaction mixtures were stirred for 18 h at 75 °C. After they were cooled to room temperature, the mixtures were filtered to remove any palladium black particles, and after the solvent was removed, samples were analyzed by ^{1}H NMR spectroscopy. Conversion values were obtained by comparing relative quantities of the halotoluene starting material and the desired product. Stille reactions using phenyltributyltin and Suzuki reactions using phenylboronic acid were performed under similar conditions. Yields of between 3 and 100% were obtained after column chromatography.

Scheme 1. Palladium-Catalyzed C−C Couplings of Methyl Acrylate and 4-Halotoluenes



X = I or Br; Pd = Pd(OCOCH$_3$)$_2$ or Pd(OCOCF$_3$)$_2$
L = **1a, 1b, 1c, 2a, 2b, 2c, 2d** or **2e**
DIPEA = N,N-Diisopropylethylamine

Representative Reaction in Supercritical Carbon Dioxide.[9] **3** (0.10 g, 0.03 mmol), 4-iodotoluene compound (1.2 mmol), methyl acrylate (0.5 g, 5 mmol), *N*,*N*-diisopropylethylamine (0.23 g, 1.78 mmol), and a stir bar were placed in a 25 mL stainless steel pressure vessel (Thar Technologies). The oily catalyst was spread onto the upper surface of the pressure vessel to prevent catalysis before a homogeneous solution had formed. The vessel was pressurized to 100 bar, sealed, and heated to 75 °C. The mixture was stirred magnetically for 3 h. Upon cooling, the cell was vented into toluene (50 mL) and washed out with toluene (10 mL). No palladium black particles were observed. The organic fractions were combined, concentrated in vacuo, and analyzed by ^{1}H NMR spectroscopy. Conversion: 91%.

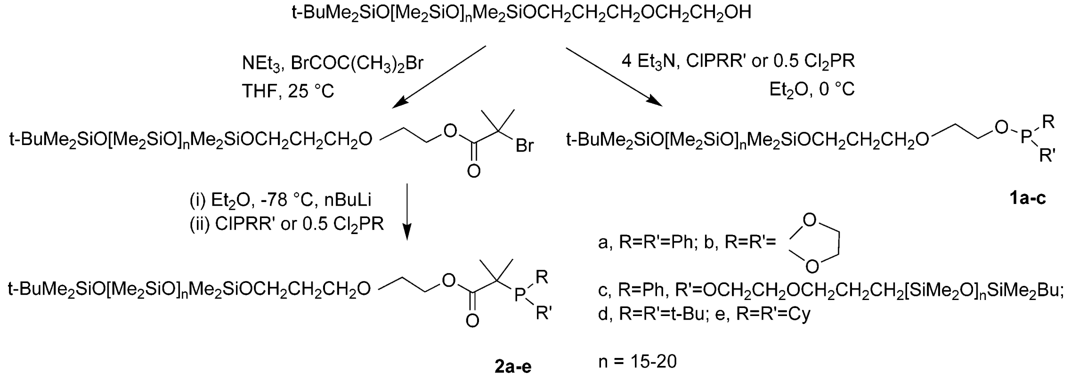
The reaction above was repeated using the supported catalyst (same mole ratio of reagents to Pd). However, upon depressurization negligible amounts of chemicals left the pressure vessel; washing the pressure vessel and catalyst with toluene, concentration in vacuo, and purification via flash column chromatography gave the coupled product in a yield of 55%.

Stille and Suzuki reactions were also performed in scCO$_2$ using **3** under similar conditions and yields of between 58 and 100% achieved. These reactions were not performed using the supported catalyst in scCO$_2$.

Catalysis using Silica-Adsorbed Complex. A Schlenk tube was charged with the supported catalyst (0.80 g, 2 mol % Pd), toluene (15 mL), 4-iodotoluene (0.26 g, 1.2 mmol), methyl acrylate (0.50 g, 5 mmol), and *N*,*N*-diisopropylethylamine (0.23 g, 1.78 mmol). The reaction mixture was stirred for 3 h at 75 °C. After it was cooled to room temperature, the mixture was filtered and the solvent removed in vacuo. Samples were analyzed by ^{1}H NMR spectroscopy. The residual orange-brown silica was reused under the same conditions and gave negligible conversions. Conversion was 45% in run 1, 3% in run 2, and 2% in run 3. Stille and Suzuki reactions were also performed using the supported catalyst under similar conditions and yields of between 3% and 30% achieved.

A Schlenk tube was charged with the supported catalyst (0.80 g, 2 mol % Pd), toluene (9 mL), diethyl ether (1 mL), 4-iodotoluene (0.26 g, 1.2 mmol), methyl acrylate (0.50 g, 5 mmol), and *N*,*N*-diisopropylethylamine (0.23 g, 1.78 mmol). The reaction mixture was stirred for 3 h at 75 °C. After the mixture was cooled to room temperature, approximately 2 mL of solvent was removed in vacuo and the remaining toluene solution decanted and analyzed. Further reagents and solvents were added to the residual silica and reactions repeated under the same conditions. Samples were analyzed by ^{1}H NMR spectroscopy. The conversion was 59% in run 1, 50% in run 2, and 49% in run 3.

Scheme 2. Synthetic Route to PDMS-Tagged Ligands

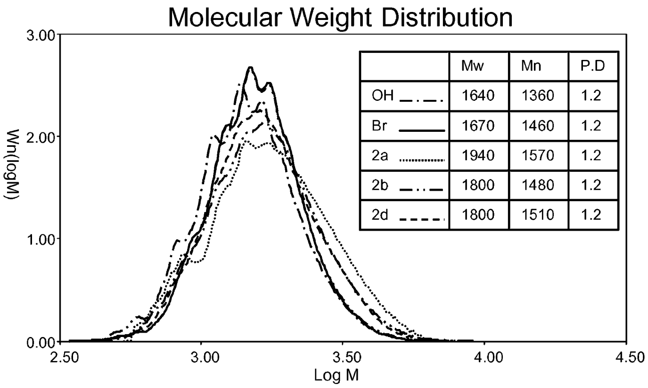


Results and Discussion

Ligand Syntheses and Characterization. The phosphinite ligands **1a**−**c** were prepared in good yields from a commerically available monocarbinol-terminated PDMS and chlorophosphines in the presence of triethylamine (Scheme 2). Ligands containing less electron rich donors were prepared by incorporating a linker unit. Lithiation of the previously prepared bromide[10] was achieved in diethyl ether at −78 °C. Subsequent addition of chlorophosphines gave ligands **2a**−**e** in good yields. All of these air-sensitive macromolecular ligands were characterized by ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectroscopy and their molecular weights determined (vide infra).

The ^{31}P chemical shifts for **1a**−**c** are observed at high frequency (>100 ppm), as expected for such species. The ^{31}P NMR spectra of **2a**−**e** exhibit resonances at lower frequency, between 19 and 67 ppm. Therefore, a range of macromolecular ligands with varying donor properties can be obtained easily and used to give optimum reactivity for a particular process. In addition to NMR data, molecular weight determinations were undertaken using a range of techniques such as end-group analysis of the molecules' ^{1}H NMR spectra, elemental analysis, and GPC (Figure 1). Maldi-TOF mass spectrometric data obtained in duplicate for **1b** showed good agreement with the corresponding GPC data.

Solubility in Supercritical Carbon Dioxide and Common Laboratory Solvents. Pd(**2a**)$_2$Cl$_2$ (**3**), a yellow air-stable oil, was prepared quantitatively by reacting **2a** with Pd(MeCN)$_2$Cl$_2$ in dichloromethane. The colored metal complex **3** was used to assess the solubility of these species in common organic solvents such as alcohols, ethers, halogenated solvents, and hydrocarbons. It was completely miscible in all solvents at a concentration of 0.4 g mL^{-1}. However, the complex is insoluble in ethylene glycol and water. **3** was also soluble in perfluorocarbons, e.g. perfluoromethylcyclohexane, and partitioned equally between the fluorous phase and organic phase in typical fluorous biphasic systems. Therefore, it is essential that synthetic routes to these ligands and their complexes are high-yielding, as their extraordinary solubility and noncrystalline nature would make purification difficult.



	Mw	Mn	P.D
OH — · —	1640	1360	1.2
Br ——	1670	1460	1.2
2a ········	1940	1570	1.2
2b — · · —	1800	1480	1.2
2d - - - -	1800	1510	1.2

Figure 1. Molecular weight distributions of starting materials and phosphines **2a**,**b**,**d**.

Studies were conducted to investigate the solubility of **1a**,**b** in supercritical carbon dioxide. A 20 mL high pressure view cell was charged with 200 mg of ligand and liquid carbon dioxide added to fill approximately one-third of the reaction vessel.[9] The vessel was warmed to 40 °C and the pressure increased to 80 bar. The sample was left to equilibrate for 10 min and observed visually via a remote camera. The pressure was increased at 10 bar intervals, followed by observations after equilibration. At a pressure of 110 bar both ligands were at least partially insoluble; however, at 120 bar complete dissolution of both ligands was observed in the carbon dioxide. This corresponds to a concentration of 5.5 × 10^{-3} mol L^{-1} for both **1a** and **1b**. This is comparable to the case for fluorinated ligands that have been used for catalysis in this medium.[11] However, it is worth noting that these ligands cost approximately one-tenth of the price of such fluorinated ligands. Upon depressurization of the view cell, the siloxane-based ligand deposits at the bottom of the vessel and could be redissolved. Although recycling catalysts through varying pressure in supercritical systems has been discussed extensively,[12] to date results have not been as promising as anticipated. From this observation, these macromolecular ligands and their catalysts may be recyclable in this way.

Sequestration on Silica. Another approach to recycling catalysts is their heterogenization and, more recently, "interphase" catalysis, which combines the benefits of homogeneous catalysis (e.g. selectivity and activity) with the separability of heterogeneous systems. The use of perfluorinated ligands and their complexes with fluorous reversed-phase silica gel or polymers to aid recycling without fluorous solvents has recently been

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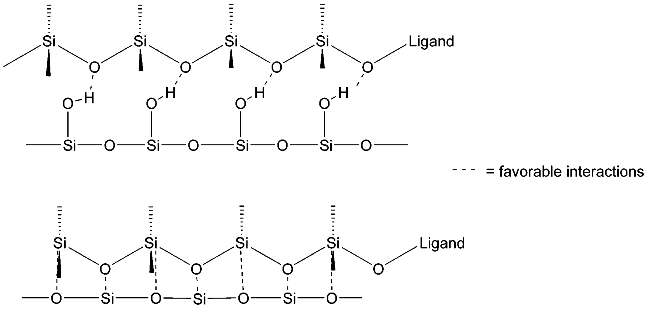

Figure 2. Adsorption of PDMS on silica.

reported.[13] Our ligands possess an affinity for unmodified silica, which may provide an opportunity for recycling future catalytic species. PDMS is known to adsorb onto silica through a variety of mechanisms (Figure 2).[14] Upon addition of oven-dried silica to a hexane solution of **3**, the solvent became colorless and the silica turned yellow. No free ligand or complex was present in the supernatant solvent when analyzed by ^{1}H NMR, ^{31}P NMR, and FT-IR spectroscopy. The degree of desoprtion in the presence of solvents of different polarities was assessed using FT-IR spectroscopy ($\nu_{C=O}$ 1720 cm^{-1}). The complex remains adsorbed in toluene, hexane, and cyclohexane, whereas it quantitatively desorbs in diethyl ether, THF, 1,4-dioxane, ethanol, and acetonitrile. Subtle differences in the heats of sorption for different solvents and types of silica have been reported[15] and will have a significant effect on the choice of solvent and silica used when trying to control the sequestration of these ligands. If trimethylsilyl-modified silica was used, the amount of adsorbed complex decreased by 50%, indicating the crucial role of the silanol residues in the adsorption process.

Catalytic Studies in Toluene and Supercritical Carbon Dioxide. Data on the coupling of halotoluenes with methyl acrylate in toluene are presented in Table 1. It should be noted that the electron-rich phosphinite ligands **1a**−**c** gave low conversions, whereas the least electron rich phosphine, **2a**, affords catalyst systems with activities similar to that of triphenylphosphine under comparable conditions. Parallel reactions without any ligand were also performed. Generally, palladium fluoroacetate gave superior conversions compared with palladium acetate; however, use of a palladium(0) source did not increase the conversions. Somewhat surprisingly, conversions using the *t*-Bu- and Cy-substituted ligands **2d**,**e** were comparatively poor. Palladium-catalyzed coupling reactions using P(*t*-Bu)$_3$ and PCy$_3$ in a range of conventional solvents have afforded some of the most reactive systems to date.[16]

Table 1. Summary of Results from Heck Reactions in Toluene

entry	ligand	X[a]	Pd[b]	conversn (%)
1	**1a**	I	H	11
2	**1a**	I	F	23
3	**1a**	Br	F	14
4	**1b**	I	H	16
5	**1b**	I	F	12
6	**1b**	Br	F	12
7	**1c**	I	H	25
8	**1c**	I	F	22
9	**1c**	Br	F	14
10	**2a**	I	H	90
11	**2a**	I	F	100
12	**2a**	Br	F	52
13	**2a**	I	dba	91
14	**2a**	Br	dba	31
15	**2b**	I	H	33
16	**2b**	I	F	10
17	**2b**	Br	F	20
18	**2c**	I	H	59
19	**2c**	I	F	90
20	**2c**	Br	F	27
21	**2d**	I	H	18
22	**2d**	I	F	30
23	**2d**	Br	F	0
24	**2e**	I	H	30
25	**2e**	I	F	70
26	**2e**	Br	F	3
27	PPh$_3$	I	H	73
28	PPh$_3$	I	F	80
29	PPh$_3$	Br	F	59
30	no ligand	I	F	6
31	no ligand	I	H	6
32	no ligand	Br	F	0
33	no ligand	Br	H	0

[a] X = substituent in halotoluene. [b] Legend: Pd = palladium source; H = Pd(OAc)$_2$; F = Pd(OCOCF$_3$)$_2$; dba = Pd$_2$(dba)$_3$.

Table 2. Effect of Catalyst Loading Using 3 in Heck Coupling of Iodotoluene and Methyl Acrylate at 75 °C in Toluene

catalyst loading (mol %)	conversn (%)	catalyst loading (mol %)	conversn (%)
0.05	19	0.5	63
0.1	34	1	71
0.2	43	2	95

Catalytic studies show that **3** performs the Heck reaction as well as previously reported systems in scCO$_2$ (Table 3) at similar or lower temperatures.[17] The formation of a deep red solution was noted, which is comparable with observations made when using fluorinated ligands.[17a] No palladium black particles were seen upon depressurization, in contrast to the situation when toluene was used as a solvent. This would be a benefit when attempting to recycle the active palladium-containing species.

Stille reactions were performed without base, whereas Suzuki couplings were performed in the presence of 1 equiv of *N*,*N*-diisopropylamine. Yields for these reactions (Table 4) were similar to those previously reported in scCO$_2$.[17]

Catalysis using Silica-Supported Catalyst and Catalyst Recycling. The silica−**3** material was used as a catalyst in a range of solvents. Conversions for the Heck reaction were lower than those obtained for the homogeneous system in toluene (45% compared to 95%). Under typical reaction conditions, some ligand leaching

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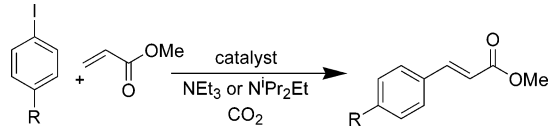
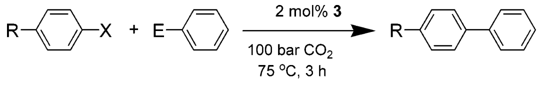
Table 3. Heck Cross-Coupling in $scCO_2$



entry	catalyst	T (°C)/P (bar)	yield (%)	amt of Pd (mol %)	TON (h^{-1})[d]	ref
1	**3**[a]	75/117	91[c]	2.5	12.1	this work
2	$Pd(OAc)_2$[b]/$(C_6F_{13}CH_2CH_2)_2PPh$	100/70−140	91	5.0		17a
3	$Pd(OAc)_2$[b]/$P[3,5\text{-}(CF_3)_2C_6H_3]_3$	90/345	94[c]	3.0	2.6	17b
4	$Pd(F_6OAc)_2$[b]/P(2-furyl)$_3$	80/110	96	2.0	2.8	17c

[a] R = Me; reaction carried out in 25 mL pressure vessel (Thar Technologies). [b] R = H. [c] Conversion. [d] TON h^{-1} = [(moles of iodobenzene) × (% conversion)]/[(moles of catalyst added) × (hours of reaction)].

Table 4. Stille and Suzuki Coupling Reactions in $scCO_2$



E	R	X	yield (%)
Bu_3Sn	Me	Br	70
Bu_3Sn	OMe	I	100
$B(OH)_3$	Me	Br	59
$B(OH)_3$	OMe	I	58

occurred, when using toluene and an organic base. Catalyst recycling was not fruitful, as silica reuse gave 2−3% conversions. Recently, a number of supported palladium catalysts have been developed,[18] some of which have been used in $scCO_2$.[18a,b] When our supported catalyst was used in $scCO_2$, 55% yield was obtained. Unfortunately, the organic product remained trapped on the silica surface upon depressurization. However, optimization of this system, for example using a flow reactor or employing an adsorption/desorption trigger, may facilitate catalyst recovery in this benign solvent. The use of carbon dioxide as a solubility switch that can be used to recycle fluorous silica/fluorous catalyst combinations has recently been reported.[19] In toluene, a small amount of diethyl ether can be used as a homogenizing trigger for our supported catalysts and increases the conversion to 59%. Removal of the diethyl ether in vacuo allows the catalyst to readsorb onto the silica from the remaining toluene solution, and the organic mixture can be separated by filtration. Second and third runs in toluene/diethyl ether (90/10 v/v) using this catalyst recycling approach gave conversions of 50% and 49%. The small amount of polar trigger solvent can be recycled between catalytic runs. The significant reduction in yield when using the silica-adsorbed complex was also seen during Suzuki and Stille couplings in toluene. For example, the Stille coupling of bromotoluene and phenyltributyltin gave a 25% yield for the heterogeneous system, compared to 89% for the unsupported complex **3**. However, for all examples studied, the addition of a small amount of polar cosolvent “homogenized” the catalyst and conversions approached those obtained using the unsupported complex **3**.

Conclusions

In conclusion, a commercially available PDMS reagent can be used to prepare a series of novel phosphorus-containing ligands at a reasonable price, 5−20 times cheaper than fluorous ligands. They have potential applications in reactions using environmentally friendly methods, including immobilization and $scCO_2$ as a solvent. They have a wide range of electron densities on the phosphorus atom, as evidenced by ^{31}P NMR data. Overall, siloxane tagging of ligands in combination with silica or modified silica might provide a suitable method of recycling many types of homogeneous catalysts, while still allowing a direct correlation with data obtained in homogeneous solution. However, there is much work to be done in pursuit of this end goal, and therefore, we intend to extend this tagging technique to other catalytic reactions. In addition to metal complexation, these macromolecular ligands, or copolymers thereof, may be useful in the synthesis of polymer−organometallic blends and the preparation of metallic colloids and nanoparticles, which have wide-ranging uses in catalysis, electronics, and medicine.

Acknowledgment. We thank the Universities of York and Leeds for a White Rose studentship and additional support from the Iranian IROST (S.S.M.). The Royal Society is gratefully acknowledged for a University Research Fellowship (F.M.K.) and Johnson-Matthey for the loan of metal salts. The EPSRC National Mass Spectrometry Service Centre at Swansea is thanked for mass spectra and RAPRA Technology Ltd. for GPC data.

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