Synthesis of Polysiloxane-Bound (Ether−phosphine)palladium Complexes. Stoichiometric and Catalytic Reactions in Interphases[1]

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Received April 6, 1995⊗

The reaction of two equiv of the monomeric ether−phosphine O,P ligand $(MeO)_3Si(CH_2)_3(Ph)PCH_2-Do$ [**1a(T^0), 1b(T^0)**] {Do = CH_2OCH_3 [**1a(T^0)**], $\overline{CHCH_2CH_2CH_2O}$ [**1b(T^0)**]} with $PdCl_2(COD)$ yields the monomeric palladium(II) complexes $Cl_2Pd(P{\sim}O)_2$ [**2a(T^0)$_2$**, **2b(T^0)$_2$**]. The compounds **2a(T^0)$_2$** and **2b(T^0)$_2$** are sol−gel processed with variable amounts (*y*) of $Si(OEt)_4$ (**Q^0**) to give the polysiloxane-bound complexes **2a(T^n)$_2$(Q^k)$_y$, 2b(T^n)$_2$(Q^k)$_y$** (Table 1) {$P{\sim}O = \eta^1$-P-coordinated ether−phosphine ligand; for T^n and Q^k, y = number of condensed T type (three oxygen neighbors), Q type (four oxygen neighbors) silicon atoms; n and k = number of Si−O−Si bonds; $n = 0-3$; $k = 0-4$; **2a(T^n)$_2$(Q^k)$_y$, 2b(T^n)$_2$(Q^k)$_y$** = $\{[M]\text{-}SiO_{n/2}(OX)_{3-n}\}_2[SiO_{k/2}\,(OX)_{4-k}]_y$, $[M] = (Cl_2Pd)_{1/2}\text{-}(Ph)P(CH_2Do)(CH_2)_3-$, X = H, Me, Et}. The complexes **2b(T^n)$_2$(Q^k)$_y$** (y = 4, 12, 36) show high activity and selectivity in the hydrogenation of 1-hexyne and tolan. The dicationic complexes $[Pd(P\frown O)_2][SbF_6]_2$ [**3a(T^0)$_2$, 3b(T^0)$_2$**] are formed by reacting $Cl_2Pd(P{\sim}O)_2$ with 2 equiv of a silver salt {$P\frown O = \eta^2$-$O\frown P$-coordinated ether−phosphine ligand; **3a(T^0)$_2$, 3b(T^0)$_2$** = $[M]-SiOMe_3$; $[M] = \{[\overline{Pd^{2+}]_{1/2}P(Ph)(CH_2CH_2O}CH_3)(CH_2)_3-\}\{SbF_6\}$ (**a**), $\{[\overline{Pd^{2+}]_{1/2}P(Ph)(CH_2\underline{CHCH_2CH_2CH_2O}})(CH_2)_3-\}\{SbF_6\}$ **(b)**}. Their polysiloxane-bound congeners **3a(T^n)$_2$, 3b-(T^n)$_2$** $\{[M]\text{-}SiO_{n/2}(OX)_{3-n}\}$ are obtained if a volatile, reversible bound ligand like acetonitrile is employed during the sol−gel process. The bis(chelate)palladium(II) complexes **3a(T^n)$_2$**, **3b(T^n)$_2$** are catalytic active in the solvent-free CO−ethene copolymerization, producing polyketones with chain lengths comparable to those obtained with chelating diphosphine ligands. The polysiloxane-bound palladium(0) complexes **5a(T^n)$_2$(Q^k)$_4$, 5b(T^n)$_2$(Q^k)$_4$** $\{\text{-}[M]\text{-}SiO_{n/2}(OX)_{3-n}\}_2[SiO_{k/2}(OX)_{4-k}]_4$, $[M] = [(dba)Pd]_{1/2}P(Ph)(CH_2Do)(CH_2)_3-\}$ undergo an oxidative addition reaction with iodobenzene in an interphase with formation of the complexes $PhPd(I)(P{\sim}O)_2{\cdot}4SiO_2$ [**6a(T^n)$_2$-(Q^k)$_4$, 6b(T^n)$_2$(Q^k)$_4$**] $\{[M]\text{-}SiO_{n/2}(OX)_{3-n}]_2[SiO_{k/2}(OX)_{4-k}]_4$, $[M] = [PhPd(I)]_{1/2}P(Ph)(CH_2Do)(CH_2)_3-\}$, which insert carbon monoxide into the palladium−aryl bond even in the solid state.

Introduction

Over the past few years there has been an increasing interest in the preparation of hybrid inorganic−organic materials,[2−8] nanocomposites,[9−12] glasses,[13] ceramics,[14−16] and aerogels.[17] Catalytic, enzymatic, and stoichiometric reactions are performed at the inorganic or at the organic parts of such materials. The sol−gel process[18,19] has been proved to offer a possibility for the preparation of such polymer frameworks under smooth and low temperature conditions. The hydrolysis and polycondensation of silicon alkoxides provided with a transition metal functionalized organic spacer R is of particular interest, because

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⊗ Abstract published in *Advance ACS Abstracts*, December 15, 1995.

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0020-1669/96/1335-0514$12.00/0

it allows the preparation of transition metal modified polymers as stationary phases with a wide variety of anchored metal complexes.[6,20−25] The resulting polymers are functionalized with immobilized homogeneous catalysts.[21,26−34]

$$x\,\mathrm{RSi(OR')_3} + y\,\mathrm{Si(OR')_4} \xrightarrow[-\mathrm{R'OH}]{\mathrm{H_2O}} \underset{\text{T units}\quad\text{Q units}}{[\mathrm{RSiO_{3/2}}]_x[\mathrm{SiO_{4/2}}]_y} \qquad (1)$$

The characteristics of the matrix can be varied by the simultaneous cocondensation of D, T, or Q type alkoxy silanes [$D = R_2Si(OR')_2$, $T = RSi(OR')_3$, $Q = Si(OR')_4$] (eq 1). These novel frameworks have desirable and tunable mechanical, chemical, and physical properties such as adjustable porosity, chemical inertness, and a defined swelling capacity of the final polysiloxane matrices. In the presence of a mobile phase (solvent, gaseous, or liquid reactant) the networks (stationary phases) are able to swell, forming interphases.[35−37] In recent investigations, we examined the mobility of the silicon matrix components (Q, T, and D type silicon substructures) and the flexibility of polysiloxane bound ether−phosphines and their ruthenium and palladium complexes.[38] Of particular interest was the fluxional behavior of the nonrigid complex $HRuCl(P{\sim}O)_2(P\frown O)$ containing two monodentate ether−phosphine ligands ($P{\sim}O$) and one bidendate ($P\frown O$) ligand. By VT $^{31}P\{^1H\}$ NMR spectroscopic investigations in solution[39,40] and by corresponding ^{31}P CP MAS NMR measurements in the solid state, it was found that not only the monomeric but also the polymer supported ruthenium complex undergoes a chemical exchange.[1] In the latter case, this happens only in the interphase. All three ether oxygen atoms of the phosphine ligands compete for one coordination site. This is a nice example for the opening and closing mechanism, which is a favorable precondition for the catalytic activity of a complex. In continuation of this work we examined the possibility to synthesize different types of (ether−phosphine)palladium(II) complexes with monodentate ($P{\sim}O$) and bidentate ($P\frown O$) ligands. It was planned to anchor these complexes on a matrix by sol−gel processing. Further goals are catalytic and stoichiometric model reactions which will be carried out at the transition metal center of the stationary phase. Therefore several types of complexes were applied in catalytic hydrogenation, alkene insertion, and alkene−CO copolymerization reactions. The CO insertion and the opening of an η^2-$P\frown O$-chelate by nitrogen donor ligands have been selected as stoichiometric reactions in the interphase. Moreover, we wanted to test whether the reactivity of the polysiloxane-bound complexes depends on the solvent polarity (mobile phase) during the chemical reactions. IR and heteronuclear solid state NMR spectroscopy establish the degree of condensation of the matrix components (^{29}Si), the stereochemistry of the transition metal complex (^{31}P and ^{13}C), and the integrity of the ligand backbone (^{13}C), respectively.

Experimental Section

A. Reagents and Physical Measurements. $PdCl_2$ was a gift from Degussa AG. $AgSbF_6$ and $Si(OEt)_4$ were obtained from Aldrich. Dibenzylideneacetone (dba),[41] $Pd(dba)_2$,[42] $PhPd(I)(PPh_3)_2$,[43] $Cl_2Pd(P{\sim}O)_2$ [**2a(T^0)$_2$**, **2b(T^0)$_2$**],[24] and the ether−phosphine ligands **1a(T^0)** and **1b(T^0)**[44] were synthesized as described previously. C_2H_4 and CO were of commercial grade and were used without further purification. All manipulations were performed under argon by employing the usual Schlenk techniques. Methanol was dried with magnesium and distilled, ethanol was distilled from NaOEt. *n*-Hexane and toluene were distilled from sodium benzophenone ketyl. H_2O, $Si(OEt)_4$ (**Q^0**) were distilled under inert gas prior to use. All reagents were stored under argon. The elemental analyses were carried out on a Carlo Erba analyzer, Model 1106. Mass spectra were acquired on a Finnigan Mat 711 A modified by AMD and are reported as mass/charge (*m/z*). GC analysis were carried out on a Carlo Erba GC 6000 VEGA SERIES 2 gas chromatograph equipped with a DBWAX column (i.d. 0.3 mm × 50 m) or with a SP 1000 column (i.d. 0.3 mm × 25 m). As internal standards butanone and tetradecane were used, respectively. The catalytic hydrogenations were carried out in a 100 mL stainless steel autoclave. To keep the hydrogen pressure in the reaction autoclave at a constant level, a second autoclave (hydrogen stock) is combined with the reaction vessel by a pressure reducing valve. The pressure decrease in the hydrogen stock and the temperature in the reaction vessel were recorded continuously during the whole reaction. The surface areas were determined by analyzing the N_2 adsorption isotherms according to the BET method using a Micromeritics Gemini II and a Micromeritics ASAP 2000. IR data were obtained on a Bruker IFS 48 FT-IR spectrometer. $^{31}P\{^1H\}$ NMR spectra were recorded at 32.391 MHz on a Bruker AC 80, $^{13}C\{^1H\}$ NMR spectra at 62.89 MHz (100.622 MHz) on a Bruker AC 250 (AMX 400). The ^{13}C and ^{31}P CP MAS solid state NMR spectra were recorded on a Bruker ASX 300 multinuclear spectrometer with a 4 mm probehead. The silicon 29 NMR spectra were measured with a MSL 200 spectrometer (4.7 T) with a 7 mm wide bore probehead. The rotor was filled with the sample, using the normal Schlenk technique. Frequencies and standards: ^{31}P, 121.49 MHz ($NH_4H_2PO_4$); ^{13}C, 75.46 MHz [TMS, carbonyl resonance of glycine ($\delta = 170.09$) as the second standard]; ^{29}Si, 39.75 MHz (Q_8M_8).[45] Typically, contact times T_c of 4 ms (^{29}Si), 2 ms (^{31}P), and 2 ms (^{13}C), respectively, were applied to routine CP MAS NMR spectra. Peak deconvolution of the spectra were performed with the Bruker software GLINFIT using Gaussian line shapes. For a more detailed description of other solid state NMR parameters, see ref 20. Kinetic energies of the photoelectrons in the XPS measurements were analyzed with a concentric hemispherical analyzer (VSW HA 150) at a pass energy of 50 eV. The resolution was determined by fwhm of the incident Mg Kα radiation (0.7 eV). A clean silver sample was used for the energy calibration.

B. Preparation of Compounds 2−7. Formation of the Polysiloxane-Bound Complexes 2a(T^n)$_2$(Q^k)$_4$ and 2b(T^n)$_2$(Q^k)$_y$ ($y = 4, 12,$

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36). To a solution of 1.0 mmol Cl$_2$Pd(P$\sim$O)$_2$ [**2a(T^0)$_2$** (830 mg), **2b(T^0)$_2$** (890 mg)] were added the selected amount of Si(OEt)$_4$ (**Q^0**) (y = 4, 12, 36 equiv), 1.5-fold of the stoichiometric amount of water [y = 4, 297 mg (16.5 mmol); y = 12, 730 mg (40.5 mmol); y = 36, 2.02 g (113 mmol)], and 60 mg of the catalyst (n-Bu)$_2$Sn(OAc)$_2$. The mixture was stirred for 8 h at room temperature until a gel was formed. The solvent was removed under reduced pressure and the gel was extracted with ethanol (3 × 20 mL), ether (2 × 10 mL), and hexane (5 mL) and dried in vacuo. The polysiloxane-bound complexes were obtained as yellow powders in quantitative yields.

***cis/trans*-Dichlorobis[(2-methoxyethyl)phenyl(polysiloxanylpropyl)-phosphine-*P*]palladium(II) [2a(T^n)$_2$(Q^k)$_4$].** Anal. Calcd for C$_{24}$H$_{36}$-Cl$_2$O$_{13}$P$_2$PdSi$_6$:[46] C, 30.66; H, 3.86; Cl, 7.54; Pd, 11.32. Found: C, 29.65; H, 3.73; Cl, 8.10; Pd, 10.75. ^{31}P CP MAS NMR: δ 20, 8.3. ^{13}C CP MAS NMR: δ 129.7 (C−Ph), 67.9 (C-6), 58.3 (C-7), 30.5 (C-5), 26.6−19 (C-4,3), 12.7 (C-2). ^{29}Si CP MAS NMR: δ −51.2 (T^1), −58.7 (T^2), −64.4 (T^3), −92.3 (Q^2), −100.4 (Q^3), −107.6 (Q^4). N$_2$ surface area: 2.1 m^2 g^{-1}.

***cis/trans*-Dichlorobis[phenyl(polysiloxanylpropyl)(tetra-hydrofuranyl-2-methyl)phosphine-*P*]palladium(II) [2b(T^n)$_2$(Q^k)$_4$].** Anal. Calcd for C$_{28}$H$_{40}$Cl$_2$O$_{13}$P$_2$PdSi$_6$:[46] C, 33.89; H, 4.06; Cl, 7.15; Pd, 10.72. Found: C, 34.41; H, 5.61; Cl, 7.64; Pd, 11.45. ^{31}P CP MAS NMR: δ 20.5, 8.5. ^{13}C CP MAS NMR: δ 130.2 (C-Ph), 78.2 (C-6), 68.4 (C-9), 33.8−30.0 (C-7, 5), 26.8 (C-4), 24.5 (C-8), 17.4 (C-3), 10.8 (C-2). ^{29}Si CP MAS NMR: δ −51.6 (T^1), −58.3 (T^2), −64.1 (T^3), −91.9 (Q^2), −100.4 (Q^3), −108.0 (Q^4). N$_2$ surface area: 2.8 m^2 g^{-1}.

***cis/trans*-Dichlorobis[phenyl(polysiloxanylpropyl)(tetra-hydrofuranyl-2-methyl)phosphine-*P*]palladium(II) [2b(T^n)$_2$(Q^k)$_{12}$].** Anal. Calcd for C$_{28}$H$_{40}$Cl$_2$O$_{29}$P$_2$PdSi$_{14}$:[46] C, 23.34; H, 2.80; Cl, 4.92; Pd, 7.38. Found: C, 24.42; H, 3.27; Cl, 4.21; Pd, 8.24. ^{31}P CP MAS NMR: δ 20.2, 7.9. ^{13}C CP MAS NMR: δ 130.2 (C−Ph), 78.4 (C-6), 68.6 (C-9), 34.0−30.5 (C-7, 5), 26.3 (C-4), 24.1 (C-8), 18.0 (C-3), 10.1 (C-2). ^{29}Si CP MAS NMR: δ −51.6 (T^1), −59.1 (T^2), −64.8 (T^3), −91.7 (Q^2), −101.3 (Q^3), −109.5 (Q^4). N$_2$ surface area: 3.5 m^2 g^{-1}.

***cis/trans*-Dichlorobis[phenyl(polysiloxanylpropyl)(tetra-hydrofuranyl-2-methyl)phosphine-*P*]palladium(II) [2b(T^n)$_2$(Q^k)$_{36}$].** Anal. Calcd for C$_{28}$H$_{40}$Cl$_2$O$_{77}$P$_2$PdSi$_{38}$:[46] C, 11.73; H, 1.41; Cl, 2.47, Pd, 3.71. Found: C, 10.36; H, 2.56; Cl, 1.52; Pd, 4.71. ^{31}P CP MAS NMR: δ 21.0, 9.0. ^{13}C CP MAS NMR: δ 130.2 (C−Ph), 78.8 (C-6), 68.2 (C-9), 33.1−29.7 (C-7, 5), 26.5 (C-4), 24.5 (C-8), 16.9 (C-3), 11.5 (C-2). ^{29}Si CP MAS NMR: δ −50.7 (T^1), −58.6 (T^2), −64.1 (T^3), −92.6 (Q^2), −101.0 (Q^3), −108.5 (Q^4). N$_2$ surface area: 280 m^2 g^{-1}.

Bis(chelate)palladium(II) Complexes [Pd($\overset{\frown}{\mathrm{PO}}$)$_2$][SbF$_6$]$_2$ [3a(T^0)$_2$, 3b(T^0)$_2$]. A sample of AgSbF$_6$ (3 mmol, 1.03 g) dissolved in 5 mL of THF was added with stirring to a solution of 1.5 mmol of the palladium complex **2a(T^0)$_2$** (1.26 g) or **2b(T^0)$_2$** (1.33 g) in THF (25 mL). After the mixture was stirred for 4 h in the dark at room temperature the precipitate (AgCl) was removed by centrifugation. The solvent was evaporated under reduced pressure, and the product was extracted with 10 mL of n-hexane. The palladium complexes **3a(T^0)$_2$** and **3b(T^0)$_2$** were isolated as yellow oils and dried in vacuo.

***cis*-Bis[(2-methoxyethyl)phenyl(3-(trimethoxysilyl)propyl)phosphine-*O,P*]palladium(II) Bis(hexafluoroantimonate) [3a(T^0)$_2$].** **3a(T^0)$_2$** was obtained as a yellow oil in 92% yield. FD-MS: m/z 767 [M$^+$ − 2SbF$_6$]. Anal. Calcd for C$_{30}$H$_{54}$F$_{12}$O$_8$P$_2$PdSb$_2$Si$_2$: C, 29.09; H, 4.39; F, 18.71. Found: C, 29.30; H, 4.63; F, 18.97. ^{31}P{^{1}H} NMR (32.391 MHz, THF, −30 °C): δ 47.21 (s), 45.02 (s). ^{13}C{^{1}H} NMR (75.46 MHz, CDCl$_3$): δ 134.0−122.0 (m, C−Ph), 72.36 (m, C-6), 64.76 (m, C-7), 50.08 (s, C-1), 28.61 (d, $^1J_{\mathrm{PC}}$ = 29 Hz, C-4), 23.01 (m, C-5), 18.14−17.49 (m, C-3), 10.31 (m, C-2).

***cis*-Bis[phenyl(tetrahydrofuranyl-2-methyl)(3-(trimethoxysilyl)-propyl)phosphine-*O,P*]palladium(II) Bis(hexafluoroantimonate) [3b(T^0)$_2$].** **3b(T^0)$_2$** was obtained as a yellow oil in 85% yield. FD-MS: m/z 819 [M$^+$ − 2SbF$_6$]. Anal. Calcd for C$_{34}$H$_{58}$F$_{12}$O$_8$P$_2$PdSb$_2$-Si$_2$: C, 31.64; H, 4.53; F, 17.66. Found: C, 29.98; H, 3.71; F, 18.58. ^{31}P{^{1}H} NMR (32.391 MHz, THF, −30 °C): δ 47.35 (s), 47.19 (s), 45.11 (s), 44.25 (s), 43.71 (s), 43.19 (s), 42.45 (s), 41.18 (s), 40.53 (s). ^{13}C{^{1}H} NMR (75.46 MHz, CDCl$_3$): δ 133.6−123.0 (m, C−Ph), 83.9−82.5 (m, C-6), 76.2−75.8 (m, C-9), 49.7 (s, C-1), 36.4−35.4 (m, C-4), 30.8 (m, C-5, C-7), 26.5 (m, C-8), 20.3 (C-3), 13.2 (m, C-2).

Bis(acetonitrile)bis(ether−phosphine)palladium(II) Complexes 4a(T^0)$_2$, 4b(T^0)$_2$. Argon was bubbled through a solution of the bis-(chelate)palladium(II) complex **3a(T^0)$_2$** (1.24 g, 1.0 mmol) or **3b(T^0)$_2$** (1.29 g, 1.0 mmol) dissolved in a mixture of diethyl ether (5 mL) and acetonitrile (1 mL). After the solvent was removed, each complex was dried for 2 min under reduced pressure.

***cis*-Bis(acetonitrile)bis[(2-methoxyethyl)phenyl(3-(trimethoxy-silyl)propyl)phosphine-*P*]palladium(II) Bis(hexafluoroantimonate) [4a(T^0)$_2$].** **4a(T^0)$_2$** was quantitatively obtained as a yellow oil. ^{31}P{^{1}H} NMR (32.391 MHz, THF, −30 °C): δ 25.91 (s), 24.22 (s). ^{13}C{^{1}H} NMR (75.46 MHz, CDCl$_3$): δ 138.3−128.4 (m, C−Ph), 120.1 (m, C≡N) 68.1 (m, C-6), 58.1 (m, C-7), 50.9 (s, C-1), 31.8 (m, C-4), 28.7 (m, C-5), 19.4 (m, C-3), 11.0 (m, C-2). IR (film on NaCl): 2317, 2296 ν(C≡N) cm^{-1}.

***cis*-Bis(acetonitrile)bis[phenyl(tetrahydrofuranyl-2-methyl)(3-(tri-methoxysilyl)propyl)phosphine-*P*]palladium(II) Bis(hexafluoro-antimonate) [4b(T^0)$_2$].** **4b(T^0)$_2$** was quantitatively obtained as a yellow oil. ^{31}P{^{1}H} NMR (32.391 MHz, THF, −30 °C): δ 26.87 (s), 26.36 (s), 25.23 (s), 24.83 (s), 24.18 (s), 23.71 (s). ^{13}C{^{1}H} NMR (75.46 MHz, CDCl$_3$): δ 140.6−129 (m, C−Ph), 119.3 (C≡N), 78.2 (m, C-6), 68.3 (m, C-9), 50.72 (s, C-1), 35.9 (m, C-4), 33.2 (m, C-5, C-7), 26.0 (m, C-8), 20.1 (m, C-3), 11.34 (s, C-2); IR (film on NaCl): 2322, 2294 ν(C≡N) cm^{-1}.

Preparation of the Dicationic Complexes 3a(T^n)$_2$ and 3b(T^n)$_2$ by Polycondensation. First, 0.4 mmol of the monomeric precursors **3a(T^0)$_2$** (0.495 mg) or **3b(T^0)$_2$** (0.516 mg) was dissolved in a minimum of CH$_3$CN (2 mL) (to form the above-mentioned complex **4**) and then a 1.5-fold excess of the stoichiometric amount of water (32 mg, 1.8 mmol) was added while stirring. After 3 h a gel was formed, and the reaction mixture was evaporated to dryness. The resulting yellow powder was extracted three times with toluene (5 mL) to remove acetonitrile, washed two times with diethyl ether (5 mL), and dried in vacuo.

***cis*-Bis[(2-methoxyethyl)phenyl(3-polysiloxanylpropyl)phosphine-*O,P*]palladium(II) Bis(hexafluoroantimonate) [3a(T^n)$_2$].** **3a(T^n)$_2$** was obtained as a yellow powder in 70% yield. Anal. Calcd for C$_{24}$H$_{36}$F$_{12}$O$_5$P$_2$PdSb$_2$Si$_2$:[46] C, 26.2; H, 3.32; F, 20.71, Pd, 9.67. Found: C, 28.66; H, 3.85; F, 18.65, Pd, 10.73. ^{31}P CP MAS NMR: δ 49.7. ^{13}C CP MAS NMR: δ 130.6 (C−Ph), 72.7 (C-6), 65.5 (C-7), 30.9 (C-4), 26.8 (C-5), 18.0 (C-3), 14.3 (C-2). ^{29}Si CP MAS NMR: δ −49.9 (T^1), −58.2 (T^2), −64.8 (T^3). N$_2$ surface area: 257 m^2 g^{-1}.

***cis*-Bis[phenyl(3-polysiloxanylpropyl)(tetrahydrofuranyl-2-meth-yl)phosphine-*O,P*]palladium(II) Bis(hexafluoroantimonate) [3b(T^n)$_2$].** **3b(T^n)$_2$** (380 mg, 0.33 mmol) was obtained as a yellow powder in 82% yield. Anal. Calcd for C$_{28}$H$_{40}$F$_{12}$O$_5$P$_2$PdSb$_2$Si$_2$:[46] C, 29.18; H, 3.50; F, 19.78, Pd, 9.23. Found: C, 29.79; H, 3.73; F, 20.11, Pd, 9.90. ^{31}P CP MAS NMR: δ 44. ^{13}C CP MAS NMR: δ 130.2 (C−Ph), 83.3 (C-6), 75.0 (C-9), 30.5 (C-4, 5, 7), 26.6 (C-8), 21.3 (C-3), 13.7 (C-2). ^{29}Si CP MAS NMR: δ −50.8 (T^1), −59.7 (T^2), −66.1 (T^3). N$_2$ surface area: 259 m^2 g^{-1}.

Formation of the Ethene−CO Copolymer. In a typical reaction 15 mg (0.013 mmol) of the powdery compound **3a(T^n)$_2$** or **3b(T^n)$_2$** was placed into an 100 mL autoclave, which was sealed after flushing with argon and hydrogen. The autoclave was charged with 30 bar of ethene and 30 bar of carbon monoxide, bringing the total pressure to 60 bar. After the autoclave was heated for 3 d at the selected temperature, the unreacted gases were released and the insoluble polymer (5.3 g, mp 256 °C) was analyzed without any further purification. Anal. Calcd for (C$_3$H$_4$O)$_n$:[46] C, 64.27; H, 7.19. Found: C, 64.81; H, 7.34. ^{13}C CP MAS NMR: δ 209.9 (C=O), 35.51 (CH$_2$), 7.30 (CH$_3$). ^{13}C{^{1}H} NMR (100.63 MHz, C$_6$D$_6$/CF$_3$CHOHCF$_3$): δ 217.1 (CH$_3$CH$_2$*C*O), 212.6 (CH$_2$CH$_2$*C*OCH$_2$CH$_2$), 35.21 (CH$_2$), 3.5 (CH$_2$*C*H$_3$). IR (KBr): 1691 ν(C=O) cm^{-1}.

Formation of the Polysiloxane-Bound Complexes 6a(T^n)$_2$(Q^k)$_4$ and 6b(T^n)$_2$(Q^k)$_4$. Three different methods according to eqs 2−4 (Scheme 4) were employed.

1. Via Equation 4: (a) Preparation of the Monomeric Palladium(0) Complexes (dba)Pd(P$\sim$O)$_2$ [5a(T^0)$_2$, 5b(T^0)$_2$]. A solution containing 2.0 mmol of the corresponding O,P ligand **1a(T^0)$_2$** (661.5

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[46] The given formula is the repeating unit of a polymer.

mg) or **1b(T^0)$_2$** (713 mg) in benzene (10 mL) was slowly added to a red-brown suspension of Pd(dba)$_2$ (574.5 mg, 1.0 mmol) in benzene (30 mL) at −10 °C. After stirring 8 h at −10 °C the volume was reduced to 3 mL in vacuo at ambient temperature. To remove palladium metal, the mixture was filtered through cellulose, and the resulting orange solution was stored 10 h at −70 °C. The solvent was separated from the precipitated, orange oily crude product (73% yield), which can be used in the polycondensation reaction. For further purification of **5a(T^0)$_2$** or **5b(T^0)$_2$** the crude product was dissolved in diethyl ether (5 mL) and reprecipitated twice at −70 °C.

(Dibenzylideneacetone)bis[(2-methoxyethyl)phenyl(3-(trimethoxysilyl)propyl)phosphine-*P*]palladium(II) [5a(T^0)$_2$]. Pure **5a(T^0)$_2$** was obtained as a yellow oil in 35% yield. FD-MS: *m/z* 1002.5 [M$^+$], 765 [M$^+$ − dba]. Anal. Calcd for $C_{47}H_{68}O_9P_2PdSi_2$: C, 56.34; H, 6.84, Pd, 10.62. Found: C, 54.98; H, 7.09; Pd, 10.11. $^{31}P\{^1H\}$ NMR (32.391 MHz, THF, −30 °C): δ 9.65 (m), 6.93 (m), 5.3 (m), 4.46 (m), 3.42 (m), 1.61 (m). $^{13}C\{^1H\}$ NMR (75.46 MHz, C_6D_6): δ 185.6 (s, C═O), 136.3−125.2 (m, C−Ph, ═CH), 68.5 (m, C-6), 58.3 (m, C-7), 50.92 (s, C-1), 31.8 (m, C-4), 28.7 (m, C-5), 19.4 (m, C-3), 11.0 (m, C-2). IR (film on NaCl): 1644 ν(>C═O). cm^{-1}

(Dibenzylideneacetone)bis[phenyl(tetrahydrofuranyl-2-methyl)-(3-(trimethoxysilyl)propyl)phosphine-*P*]palladium(II) [5b(T^0)$_2$]. Pure **5b(T^0)$_2$** was obtained as a yellow oil in 30% yield. FD-MS: *m/z* 1053 [M$^+$], 820 [M$^+$ − dba]. Anal. Calcd for $C_{51}H_{72}O_9P_2PdSi_2$: C, 58.14; H, 6.89; Pd, 10.10. Found: C, 57.40; H, 7.35; Pd, 9.21. $^{31}P\{^1H\}$ NMR (32.391 MHz, THF, −30 °C): δ 18.9 (m), 14.7 (m), 11.02 (m), 10.48 (m), 9.74 (m), 8.86 (m), 8.31 (m), 7.75 (m), 7.51 (m), 6.91 (m), 6.13 (m), 5.28 (m), 4.85 (m), 4.51 (m), 4.23 (m), 2.48 (m), 2.32 (m), 1.74 (m). $^{13}C\{^1H\}$ NMR (75.46 MHz, C_6D_6): δ 185.3 (s, C═O), 136.8−125.1 (m, C−Ph, ═CH), 78.5 (m, C-6), 68.3 (m, C-9), 50.4 (s, C-1), 33.5 (m, C-7), 30.5 (m, C-5), 27.2 (m, C-4), 24.9 (m, C-8), 17.4 (m, C-3), 10.81 (s, C-2). IR (film on NaCl): 1645 ν(>C═O) cm^{-1}.

(b) Preparation of the Polysiloxane-Bound Palladium(0) Complexes 5a(T^n)$_2$(Q^k)$_4$ and 5a(T^n)$_2$(Q^k)$_4$. To a solution of 1.0 mmol pure (dba)Pd(P∼O)$_2$ [**5a(T^0)$_2$** (1.001 g), **5b(T^0)$_2$** (1.053 g)] in ethanol or THF (3 mL) were added Si(OEt)$_4$ (**Q^0**) (4.0 mmol, 833 mg), 1.5-fold of the stoichiometric amount of water (16.5 mmol, 297 mg), and one drop (20 mg) of the catalyst (*n*-Bu)$_2$Sn(OAc)$_2$. The homogeneous solution was stirred at 20 °C in the dark. After 8 h, a yellow gel was formed. The solvent was removed under reduced pressure, and the obtained powder was extracted twice with ethanol (10 mL), ether, and hexane and subsequently dried in vacuo. The collected washing fractions do not contain any dibenzylideneacetone, indicating the absence of a Pd(0) oxidation. The polysiloxane-bound complexes **5a(T^n)$_2$(Q^k)$_4$**, **5b(T^n)$_2$(Q^k)$_4$** are light sensitive and decompose within a few days at room temperature, but they are stable at −30 °C.

(Dibenzylideneacetone)bis[(2-methoxyethyl)phenyl(3-polysiloxanylpropyl)phosphine-*P*]palladium(II) [5a(T^n)$_2$(Q^k)$_4$]. 5a(T^n)$_2$(Q^k)$_4$ was obtained as a pale brown powder in 85% yield. Anal. Calcd for $C_{41}H_{50}O_{14}P_2PdSi_6$:[46] C, 44.62; H, 4.57; Pd, 9.64. Found: C, 44.89; H, 5.63; Pd, 10.45. ^{31}P CP MAS NMR: δ 2.1. ^{13}C CP MAS NMR: δ 186.6 (C═O), 129.3 (Ph, ═CH), 68.6 (C-6), 58.1 (C-7), 30.4 (C-5), 25.5 (C-4), 18.0 (C-3), 10.0 (C-2). ^{29}Si CP MAS NMR: δ −50.6 (T^1), −59.9 (T^2), −65.4 (T^3), −91.1 (Q^2), −102.1 (Q^3), −110.1 (Q^4). IR (KBr): 1640 ν(>C═O) cm^{-1}. N$_2$ surface area: 3.3 m^2 g^{-1}.

(Dibenzylideneacetone)bis[phenyl(3-polysiloxanylpropyl)(tetrahydrofuranyl-2-methyl)phosphine-*P*]palladium(II) [5b(T^n)$_2$(Q^k)$_4$]. 5b(T^n)$_2$(Q^k)$_4$ was obtained as a pale-brown powder in 92% yield. Anal. Calcd for $C_{45}H_{54}O_{14}P_2PdSi_6$:[46] C, 46.77; H, 4.71; Pd, 9.21. Found: C, 47.54; H, 5.20; Pd, 9.31. ^{31}P CP MAS NMR: δ 1.6. ^{13}C CP MAS NMR: δ 185.9 (C═O), 130.4 (Ph, ═CH), 78.2 (C-6), 68.4 (C-9), 33.8−30.0 (C-7, 5), 27.2 (C-4), 24.5 (C-8), 17.4 (C-3), 10.8 (C-2). ^{29}Si CP MAS NMR: δ −50.7 (T^1), −58.8 (T^2), −63.1 (T^3), −90.2 (Q^2), −101.2 (Q^3), −109.1 (Q^4). IR (KBr): 1645 ν(>C═O) cm^{-1}. N$_2$ surface area: 5.2 m^2 g^{-1}.

(c) Preparation of the Polysiloxane-Bound Palladium Aryl Complexes 6. 0.8 mmol of the powdery complexes **5a(T^n)$_2$(Q^k)$_4$** (800 mg) and **5a(T^n)$_2$(Q^k)$_4$** (842 mg) were suspended in a solution of the stoichiometric amount of PhI (0.8 mmol, 163 mg) in THF. After the mixture was stirred for 10 h at ambient temperature in the dark, the swollen, pale brown gels were filtered off (or centrifugated) and were washed three times with ethanol (5 mL) and once with diethyl ether (10 mL) and dried in vacuo. The entire amount of released dba (0.78 mmol) was isolated quantitatively from the collected washing fractions.

Iodo-*trans*-bis[(2-methoxyethyl)phenyl(3-polysiloxanylpropyl)-phosphine-*P*](phenyl)palladium(II) [6a(T^n)$_2$(Q^k)$_4$]. Anal. Calcd for $C_{30}H_{41}IO_{13}P_2PdSi_6$:[46] C, 33.57; H, 3.85; I, 11.82; Pd, 9.91. Found: C, 34.74; H, 4.41; I, 12.04; Pd, 10.70. ^{31}P CP MAS NMR: δ 2.4. ^{13}C CP MAS NMR: δ 155.6 (Pd−C), 128.3 (C−Ph), 68.0 (C-6), 58.6 (C-7), 30.4 (C-5), 26.8 (C-4), 18.1 (C-3), 10.0 (C-2). ^{29}Si CP MAS NMR: δ −51.6 (T^1), −59.9 (T^2), −64.8 (T^3), −91.7 (Q^2), −100.5 (Q^3), −108.9 (Q^4). N$_2$ surface area: 3.4 m^2 g^{-1}.

Iodo(phenyl)-*trans*-bis[phenyl(3-polysiloxanylpropyl)(tetrahydrofuranyl-2-methyl)phosphine-*P*]palladium(II) [6b(T^n)$_2$(Q^k)$_4$]. Anal. Calcd for $C_{34}H_{45}IO_{13}P_2PdSi_6$:[46] C, 36.29; H, 4.03; I, 11.28; Pd, 9.45. Found: C, 38.99; H, 6.23; I, 11.91, Pd, 9.98. ^{31}P CP MAS NMR: δ 2.2. ^{13}C CP MAS NMR: δ 156.6 (Pd−C), 128.7 (C−Ph), 75.6 (C-6), 67.6 (C-9), 33.8−30.0 (C-7, 5), 26.1 (C-4, 8), 18.3 (C-3), 9.8 (C-2). ^{29}Si CP MAS NMR: δ −50.1 (T^1), −58.9 (T^2), −63.5 (T^3), −90.9 (Q^2), −101.1 (Q^3), −110.2 (Q^4). N$_2$ surface area: 5.2 m^2 g^{-1}.

2. Via Equation 2: (a) Preparation of the Monomeric Palladium Aryl Complexes 6a(T^0)$_2$ and 6b(T^0)$_2$. A solution of 2.0 mmol of the corresponding O,P ligand **1a(T^0)$_2$** (661.5 mg), **1b(T^0)$_2$** (713 mg) in toluene (3 mL) was added to a solution of 1.0 mmol (834 mg) PhPd(I)(PPh$_3$)$_2$ in toluene (10 mL). After the mixture had been stirred 3 h in the dark the solvent was evaporated. The oily product was dissolved in *n*-pentane (10 mL) and the solution was cooled down to −70 °C. The oily product which precipitated within 2 h was separated from the *n*-pentane/PPh$_3$ mixture. This procedure was repeated three times. The light sensitive compounds **6a(T^0)$_2$**, **6b(T^0)$_2$** were obtained as yellow oils.

Iodo-*trans*-bis[(2-methoxyethyl)phenyl(3-(trimethoxysilyl)propyl)phosphine-*P*](phenyl)palladium(II) [6a(T^0)$_2$]. FD-MS: *m/z* 970 [M$^+$], 893 [M$^+$ − Ph], 843.1 [M$^+$ − I]. Anal. Calcd for $C_{36}H_{59}IO_8P_2PdSi_2$:[46] C, 44.52; H, 6.12; I, 13.07; Pd, 10.95. Found: C, 43.06; H, 6.37; I, 11.53; Pd, 10.18. $^{31}P\{^1H\}$ NMR (32.391 MHz, THF, −30 °C): δ 1.62 (s), 1.37 (s). $^{13}C\{^1H\}$ NMR (75.46 MHz, CDCl$_3$): δ 154.9 (Pd−C), 135.93−122.9 (m, C−Ph), 68.64 (s, C-6), 58.34 (s, C-7), 50.52 (s, C-1), 29.1 (m, C-5), 25.5 (m, C-4), 17.78 (s, C-3), 10.92 (s, C-2).

Iodo(phenyl)-*trans*-bis[phenyl(tetrahydrofuranyl-2-methyl)(3-(trimethoxysilyl)propyl)phosphine-*P*]palladium(II) [6b(T^0)$_2$]. FD-MS: *m/z* 951.4 [M$^+$ − Ph], 894.9 [M$^+$ − I]. Anal. Calcd for $C_{40}H_{63}IO_8P_2PdSi_2$:[46] C, 46.95; H, 6.21; I, 12.40; Pd, 10.40. Found: C, 48.48; H, 6.58; I, 10.99; Pd, 9.70. $^{31}P\{^1H\}$ NMR (32.391 MHz, THF, −30 °C): δ 4.15 (s), 3.81 (s), 2.51 (s), 1.85 (s), 1.31 (s), 1.12 (s), 0.81 (s), 0.55 (s). $^{13}C\{^1H\}$ NMR (75.46 MHz, CDCl$_3$): δ 155.3 (Pd−C), 135.93−122.7 (m, C−Ph), 76.05 (s, C-6), 67.52 (s, C-9), 50.43 (s, C-1), 33.32 (s, C-7), 30.4 (m, C-5), 26.9 (m, C-4), 25.58 (s, C-8), 17.5 (m, C-3), 11.06 (s, C-2).

(b) Polycondensation of 6a(T^0)$_2$ and 6b(T^0)$_2$ to 6a(T^n)$_2$(Q^k)$_4$ and 6b(T^n)$_2$(Q^k)$_4$. First 0.5 mmol of the monomeric precursors **6a(T^0)$_2$** (485 mg) and **6b(T^0)$_2$** (512 mg) were dissolved in THF (3 mL). Then 4 equiv of Si(OEt)$_4$ (**Q^0**) (2 mmol, 416 mg), water (8.2 mmol, 147 mg), and two drops (40 mg) of (*n*-Bu)$_2$Sn(OAc)$_2$ were added. After the mixture was stirred for 8 h in the dark, the gels precipitated. The solvent was removed under reduced pressure, and the resulting yellow-brown powders were washed with THF (3 × 10 mL), ether (1 × 10 mL), and *n*-pentane (5 mL). Drying the gels in vacuo yielded the slightly brown, light sensitive polysiloxane-bound compounds **6a(T^n)$_2$(Q^k)$_4$** and **6b(T^n)$_2$(Q^k)$_4$**.

6a(T^n)$_2$(Q^k)$_4$. Anal. Calcd for $C_{30}H_{41}IO_{13}P_2PdSi_6$:[46] C, 33.57; H, 3.85; I, 11.82; Pd, 9.91. Found: C, 33.93; H, 4.70; I, 12.04; Pd, 10.42.

6b(T^n)$_2$(Q^k)$_4$: Anal. Calcd for $C_{34}H_{45}IO_{13}P_2PdSi_6$:[46] C, 36.29; H, 4.03; I, 11.28; Pd, 9.45. Found: C, 37.10; H, 5.21; I, 12.15, Pd, 10.45.

To form the polysiloxane-bound complexes **6a(T^n)$_2$(Q^k)$_4$**, **6b(T^n)$_2$(Q^k)$_4$** it is also possible to use the crude product from the oxidative addition reaction with PhI (vide infra).

3. Via Equation 3. Oxidative Addition of PhI to form the Complexes 6a(T^0)$_2$ and 6b(T^0)$_2$. First 1.0 mmol of (dba)Pd(P∼O)$_2$ [**5a(T^0)$_2$** (1.001 g), **5b(T^0)$_2$** (1.053 g)] was dissolved in a solution of PhI (1.0 mmol, 204 mg) in THF (10 mL). After the mixture was stirred for 8 h in the dark, the solvent was removed under reduced pressure. The crude product was dissolved in *n*-hexane (10 mL) and the solution was cooled to −10 °C. At this temperature dba precipitates slowly and was separated by centrifugation. This procedure was repeated four times.

$6a(T^0)_2$: **$6a(T^0)_2$** was obtained in 25% yield. Anal. Calcd for $C_{36}H_{59}IO_8P_2PdSi_2$: C, 44.52; H, 6.12; I, 13.07; Pd, 10.95. Found: C, 44.16; H, 5.70; I, 12.40; Pd, 10.32.

$6b(T^0)_2$: **$6b(T^0)_2$** was obtained in 42% yield. Anal. Calcd for $C_{40}H_{63}IO_8P_2PdSi_2$: C, 46.95; H, 6.21; I, 12.40; Pd, 10.40. Found: C, 47.37; H, 6.23; I, 9.70; Pd, 9.40.

Carbon Monoxide Insertion in an Interphase. An autoclave (100 mL) was charged with 0.15 mmol of the powdery gel **$6a(T^n)_2(Q^k)_4$** (160 mg) or **$6b(T^n)_2(Q^k)_4$** (169 mg) and purged with argon. The autoclave was pressurized with 20 bar of carbon monoxide and was heated to 40 °C. After 1 h the pressure was released and the yellow gels were removed without further washing or drying.

Benzoyl(iodo)-*trans*-bis[(2-methoxyethyl)phenyl(3-polysiloxanylpropyl)phosphine-*P*](phenyl)palladium(II) [$7a(T^n)_2(Q^k)_4$]. Anal. Calcd for $C_{31}H_{41}IO_{14}P_2PdSi_6$:[46] C, 33.81; H, 3.75; I, 11.52; Pd, 9.66. Found: C, 34.05; H, 4.53; I, 10.17; Pd, 8.90. ^{31}P CP MAS NMR: δ 2.1. ^{13}C CP MAS NMR: δ 235 (C═O), 140.2 (Pd−C), 129.1 (C−Ph), 67.7 (C-6), 57.5 (C-7), 30.4 (C-5), 26.9 (C-4), 18.2 (C-3), 14.0 (C-2). ^{29}Si CP MAS NMR: δ −51.3 (T^1), −59.4 (T^2), -64.7 (T^3), −91.1 (Q^2), −101.6 (Q^3), -109.1 (Q^4). IR (KBr): 1646 ν(CO) cm^{-1}.

Benzoyl(iodo)-*trans*-bis[phenyl(3-polysiloxanylpropyl)(tetrahydrofuranyl-2-methyl)phosphine-*P*]palladium(II) [$7b(T^n)_2(Q^k)_4$]. Anal. Calcd for $C_{35}H_{45}IO_{14}P_2PdSi_6$:[46] C, 36.45; H, 3.93; I, 11.00; Pd, 9.22. Found: C, 37.53; H, 5.49; I, 9.42; Pd, 8.40. ^{31}P CP MAS NMR: δ 1.9. ^{13}C CP MAS NMR: δ 234.8 (C═O), 139.1 (Pd−C), 129.3 (C−Ph), 76.0 (C-6), 67.8 (C-9), 33.3 (C-7), 30.4−25.5 (C-5, 4, 8), 17.7 (C-3), 10.6 (C-2). ^{29}Si CP MAS NMR: δ −50.4 (T^1), −58.7 (T^2), −63.1 (T^3), −90.4 (Q^2), −101.8 (Q^3), −109.5 (Q^4). IR (KBr): 1640 ν(CO) cm^{-1}.

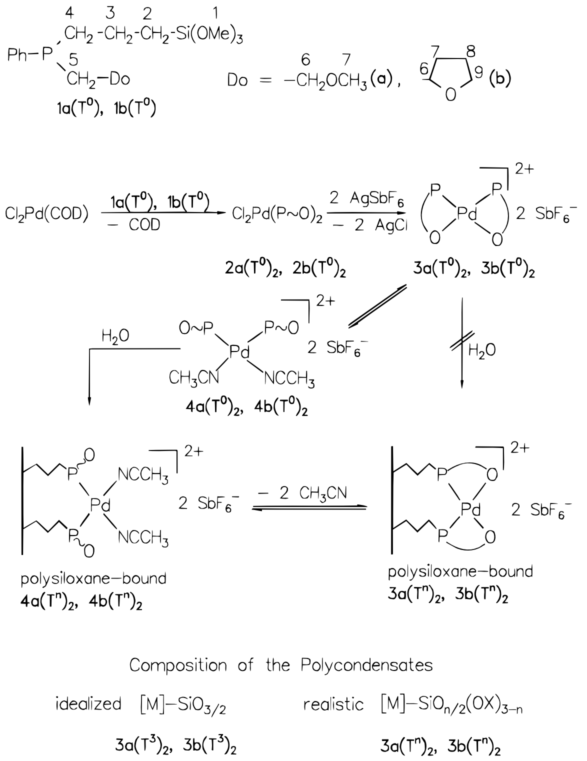
C. Hydrogenation of 1-Hexyne. In a typical reaction, an autoclave was charged with $Cl_2Pd(P{\sim}O)_2$ [**$5b(T^n)_2(Q^k)_y$**: 172.6 mg, 0.174 mmol] and 1-hexyne (10.0 g, 0.12 mol). After the autoclave was flushed twice with hydrogen the mixture was heated to the selected temperature (Figure 8). The hydrogen pressure was adjusted to 50 bar within a few seconds. The reaction starts immediately, which was observed by the decrease of the pressure and by the rising of the temperature. After the hydrogen uptake had been finished, the catalyst was separated from the reaction mixture by centrifugation, washed with *n*-hexane, and dried for reuse in further catalytic runs. The reaction mixture was analyzed by GC.

Hydrogenation of Tolan. The catalyst $Cl_2Pd(P{\sim}O)_2$ [**$5b(T^n)_2(Q^k)_4$**, 1.6×10^{-2} mmol, 16.0 mg] was suspended in a solution of 2.85 g (16.0 mmol) of tolan in a mixture of toluene/ethanol (60 mL; see Results and Discussion). The autoclave was flushed with hydrogen and heated as mentioned above. When the hydrogen uptake is completed the catalyst was recovered by centrifugation and was washed. The conversion and selectivity was determined by GC.

Results and Discussion

Synthesis of the Bis(chelate)palladium Complexes $3a(T^0)_2$ and $3b(T^0)_2$. Reaction of the organosilyl (T)-functionalized ether−phosphines **$1a(T^0)$** and **$1b(T^0)$**[47] (Scheme 1) with Cl_2-Pd(COD) in CH_2Cl_2 or THF results in the formation of a mixture of *cis/trans*-$Cl_2Pd(P{\sim}O)_2$ [**$2a(T^0)_2$** and **$2b(T^0)_2$**] ($P{\sim}O = \eta^1$-P coordinated ether−phosphine ligand; T^0 = T type silicon atom without Si−O−Si bonds). The $^{31}P\{^1H\}$ NMR and IR data are in agreement with those of similar palladium complexes.[24,48,49] Treatment of a THF solution of the neutral palladium complexes **$2a(T^0)_2$**, **$2b(T^0)_2$** with 2 equiv of a silver salt in the dark leads to the cationic bis(chelate)palladium complexes $[Pd(P⌒O)_2]$-$[SbF_6]_2$ [**$3a(T^0)_2$**, **$3b(T^0)_2$**] (P⌒O = η^2-O⌒P-coordinated ether−phosphine ligand). In the $^{31}P\{^1H\}$NMR spectrum of **$3a(T^0)_2$** two resonances [two diastereomers due to the chirality of **$1a(T^0)$**] are observed, whereas the signals of the diastereomers of **$3b(T^0)_2$** are not completely resolved. The ^{31}P downfield shift of about 40 ppm in the spectra of **$3a(T^0)_2$** and **$3b(T^0)_2$** compared to the neutral complexes $Cl_2Pd(P{\sim}O)_2$ is caused by the ring contribution to the chemical shift of a five-membered ring[50,51] and by the deshielding of the phosphorus nucleus due to the cationic palladium center. Compared to those for $Cl_2Pd(P{\sim}O)_2$, the $^{13}C\{^1H\}$ NMR resonances of the OCH_2, OCH_3, and OCH groups of $[Pd(P⌒O)_2]^{2+}$ are also shifted to lower field. This shift is typical of an η^2-P⌒O-coordinated ether−phosphine ligand.[40,52,53] The signals of the OCH_2 [**$3a(T^0)_2$**] and OCH [**$3b(T^0)_2$**] units are observed as multiplets (diastereomers). The carbon-13 resonance of the PCH_2 spacer unit (C-4, Scheme 1) is split by the adjacent phosphorus nuclei into a doublet ($^1J_{P-C}$ = 29 Hz). $^{13}C\{^1H\}$ NMR spectra at a different magnetic field strength ensure that not the diastereomers but the P-C interaction is responsible for the splitting of the carbon 13 resonance of the C-4 nucleus. The small value of the P−P coupling constant

Scheme 1. Synthesis and Composition of the Polymeric Complexes $[Pd(P⌒O)_2]^{2+}$, **3**[a]



[a] T^n: T type silicon atom (three oxygen neighbors); n = 0−3, number of Si−O−Si bonds. P∼O: η^1-P-coordinated ligand. P⌒O: η^2-O⌒P-coordinated ligand. X = H, Me; [M] = $[Pd^{2+}]_{1/2}P(Ph)(CH_2CH_2OCH_3)(CH_2)_3-\}\{SbF_6\}$; $\{[Pd^{2+}]_{1/2}P(Ph)(CH_2CHCH_2CH_2CH_2O)$-$(CH_2)_3-\}\{SbF_6\}$.

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(47) The numbers of the compounds (**1**−**7**) represents the stereochemistry of the complexes and the ligands, respectively. The letters **a**, **b** designate the type of the ligand. The silicon units involved in the complex are outlined by the letters **T** and **Q**. Their stoichiometric amounts are described by a subscript. The letters *n* and *m* or the numbers 0−4 define whether the compound is polycondensed (*n*, *m* or 1−4) or not (0); see Table 1.

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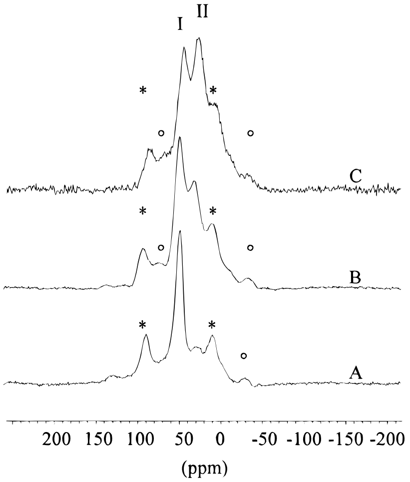

Figure 1. Formation of the decomposition products (**II**) at various stages of the hydrolysis and polycondensation of the cationic complex (**I**) **3b(T⁰)₂** (^{31}P CP MAS NMR spectra, 81 MHz, rf = 3.3 kHz). Asterisks and small circles denote the spinning side bands of **I** and of **II**, respectively. Time applied to the polycondensation: A, 10 min; B, 30 min; C, 3 h.

points to *cis* phosphines.[54] An analogous, previously published *cis*-bis(chelate)palladium(II) complex of the type $[Pd(P^\frown O)_2]^{2+}$ (O,P = $Ph_2PCH_2\overline{CHOCH_2CH_2CH_2O}$), the structure of which was proven by an X-ray structural analysis,[48] shows comparable ^{31}P and $^{13}C\{^1H\}$ NMR data. At ambient temperatures **$3a(T^0)_2$** and **$3b(T^0)_2$** do not react with olefins or alkynes like C_2H_4, COD, PhC≡CPh, or PhC≡CH with cleavage of the weak palladium−oxygen bond.

If the bis(chelate) complexes **3** are subjected to hydrolysis and polycondensation with water in THF or ethanol, they undergo a partial or complete decomposition. The course of the disintegration was followed by recording ^{31}P CP MAS NMR spectra at several stages of the hydrolysis and condensation reaction (Figure 1). The occurrence of a ^{31}P resonance at ≈ 25 ppm is typical of a nonchelating η^1-P-coordinated ether−phosphine ligand bound to a cationic palladium center. Obviously another ligand (probably H_2O or an OH^- residue) from the reaction mixture is able to cleave one oxygen−palladium bond or even two oxygen-palladium bonds with the formation of the complexes[24,48,49] $[Pd(X)(P{\sim}O)(P^\frown O)]^+$ or of the types previously reported: $[Pd(\mu\text{-OH})(PR_3)(R')]_2^{2+}$ [55] and $[Pd(\mu\text{-OH})(dppe)]_2^{2+}$,[56−58] respectively. The removal of the above-mentioned additional ligand by washing and/or drying of the polymer was not successful.

Formation of the Polycondensed Bis(chelate)palladium Complexes with the Assistance of a Labile Bound Ligand. To prevent such a decomposition (vide supra) we tried to use the effect that the cationic bis(chelate)palladium(II) complexes $[Pd(P^\frown O)_2]^{2+}$ [**$3a(T^n)_2$**, **$3b(T^n)_2$**] are able to add reversibly other donor ligands by cleaving both oxygen−palladium bonds. Therefore the palladium complexes **$4a(T^0)_2$** and **$4b(T^0)_2$** have been synthesized (Scheme 1), which contain two weakly bound, volatile acetonitrile ligands. Due to the opening of the ether−phosphine $P^\frown O$ chelates the $^{31}P\{^1H\}$ NMR signals are shifted to higher field (diastereomers). In the IR spectra of **$4a(T^0)_2$** and **$4b(T^0)_2$** two absorptions for the C≡N groups are in agreement with a *cis*-arrangement of both phosphine ligands. Owing to the lability of the palladium-acetonitrile bond the monomeric complexes **$4a(T^0)_2$** and **$4b(T^0)_2$** are not accessible to a correct elemental analysis. As soon as they are washed a few times with ligroin (60/90) and/or dried in vacuo, the starting bis(chelate) complexes **$3a(T^0)_2$** and **$3b(T^0)_2$** are formed again.

The intact polymer-supported analogues **$4a(T^n)_2$** and **$4b(T^n)_2$** (Table 1; Scheme 1; T^n = T type silicon atom, three oxygen neighbors; n = 0−3, number of Si−O−Si bonds) are formed by treating a solution of **$4a(T^0)_2$** and **$4b(T^0)_2$**, respectively, in CH_3CN with an excess of water without using any catalyst. The transition from the sol to the gel state requires about 3 h. The IR spectra of the crude products reveal two C≡N absorptions at 2321 and 2292 cm^{-1}, respectively. Continued washing with ligroin and drying of the polysiloxane gels resulted in a complete elimination of the coordinated acetonitrile ligand and in the formation of the dicationic bis(chelate)palladium(II) complexes **$3a(T^n)_2$**, **$3b(T^n)_2$** (Scheme 1; Table 1). One isotropic signal in the ^{31}P CP MAS NMR spectra, with the same chemical shift as that of the monomeric species **$3a(T^0)_2$** and **$3b(T^0)_2$**, is characteristic for the presence of two chemically equivalent chelating phosphines in $[Pd(P^\frown O)_2]^{2+}$ (Figure 2). No phosphine oxides,[23] which are known to be formed easily during the sol−gel processing, or other metal−phosphine species are detected. The ^{13}C CP MAS NMR spectra show the typical downfield shift of the ^{13}C signals of the OCH_2, OCH, and OCH_3 groups incorporated in an η^2-$O^\frown P$-chelating ether−phosphine ligand (Figure 3) and the resonances of the C-2 to C-5 [**$3a(T^n)_2$**] and of the C-2 to C-8 [**$3b(T^n)_2$**] carbon atoms (Scheme 1), respectively. Therefore a cleavage of the Si-C bonds of the spacer moieties can be excluded from these sets of data.

The method of introducing volatile ligands like acetonitrile, stabilizing labile transition metal complexes during the sol−gel processing, was found to be of general applicability.[59]

Behavior of the Polymer-Supported Palladium Cations $3a(T^n)_2$ and $3b(T^n)_2$ toward Ethene and Carbon Monoxide. Cationic palladium complexes of the type $[Pd(L\text{-}L)][X]_2$ (L-L = monodentate or bidentate phosphorus or nitrogen ligands; X = noncoordinating or weakly coordinating monovalent anion) have been found to catalyze the alternating copolymerization of alkenes and carbon monoxide.[60−70] Catalytic systems with monodentate ligands such as $[(Ph_3P)_2Pd(CH_3CN)_2]^{2+}$ are able to convert carbon monoxide and ethene favorably in methanol into methylpropionate and low-molecular-weight keto−ester oligomers. The incorporation of bidentate diphosphine ligands $Ph_2P(CH_2)_xPPh_2$ dramatically enhances the production of high-molecular-weight copolymers if x = 2, 3.[60] The weakly coordinating ligand X is necessary for an efficiently working catalyst. This was found by comparing the catalytic activities of the palladium complexes $XPd(PR_3)_2(R')$ and $[Pd(PR_3)_2(R')(solvent)]^+$,[69−71] respectively. From these points of view

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(54) Only a few *trans*-phosphine palladium complexes exhibit small P−P coupling constants.

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Table 1. Labeling of the Polycondensation Products

educt	cocondensation agent	amount of the cocondensate	product labeling
$Cl_2Pd(P{\sim}O)_2$ [$\mathbf{2a(T^0)_2}$]	$Si(OEt)_4$ ($\mathbf{Q^0}$)	4	$\mathbf{2a(T^n)_2(Q^k)_{4,6}}$
$Cl_2Pd(P{\sim}O)_2$ [$\mathbf{2b(T^0)_2}$]	$Si(OEt)_4$ ($\mathbf{Q^0}$)	4, 12, 36	$\mathbf{2b(T^n)_2(Q^k)_4}$, $\mathbf{2b(T^n)_2(Q^k)_{12}}$, $\mathbf{2b(T^n)_2(Q^k)_{36}}$
$[Pd(P^\frown O)_2][SbF_6]_2$ [$\mathbf{3a(T^0)_2}$, $\mathbf{3b(T^0)_2}$]			$\mathbf{3a(T^n)_2}$, $\mathbf{3b(T^n)_2}$
$[(CH_3CN)_2Pd(P{\sim}O)_2][SbF_6]_2$ [$\mathbf{4a(T^0)_2}$, $\mathbf{4b(T^0)_2}$]			$\mathbf{4a(T^n)_2}$, $\mathbf{4b(T^n)_2}$
$Pd(dba)(P{\sim}O)_2$ [$\mathbf{5a(T^0)_2}$, $\mathbf{5b(T^0)_2}$]	$Si(OEt)_4$ ($\mathbf{Q^0}$)	4	$\mathbf{5a(T^n)_2(Q^k)_4}$, $\mathbf{5b(T^n)_2(Q^k)_4}$
$IPd(Ph)(P{\sim}O)_2$ [$\mathbf{6a(T^0)_2}$, $\mathbf{6b(T^0)_2}$]	$Si(OEt)_4$ ($\mathbf{Q^0}$)	4	$\mathbf{6a(T^n)_2(Q^k)_4}$, $\mathbf{6b(T^n)_2(Q^k)_4}$
$(PhCO)PdI(P{\sim}O)_2$ [$\mathbf{7a(T^0)_2}$, $\mathbf{7b(T^0)_2}$]	$Si(OEt)_4$ ($\mathbf{Q^0}$)	4	$\mathbf{7a(T^n)_2(Q^k)_4}$, $\mathbf{7b(T^n)_2(Q^k)_4}$

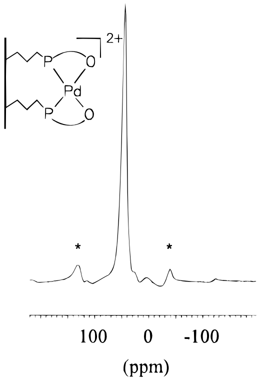

Figure 2. ^{31}P CP MAS NMR spectrum (121.5 MHz, $\nu_r = 10$ kHz) of the polysiloxane-bound bis(chelate)palladium(II) complex $[Pd(P^\frown O)_2]^{2+}$ [$\mathbf{3b(T^n)_2}$].

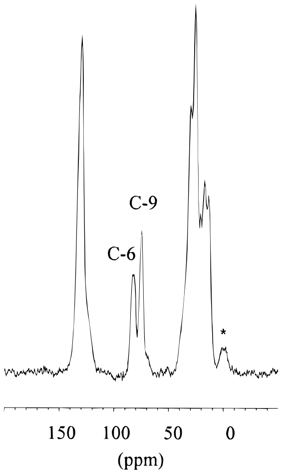

Figure 3. ^{13}C CP MAS NMR spectrum (75.46 MHz, $\nu_r = 10$ kHz) of the polysiloxane-bound bis(chelate)palladium(II) complex $[Pd(P^\frown O)_2]^{2+}$ [$\mathbf{3b(T^n)_2}$]. The spinning side band is labeled with an asterisk.

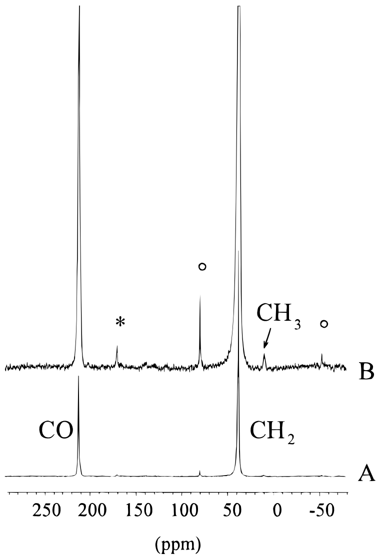

Figure 4. ^{13}C CP MAS NMR spectrum (75.46 MHz, $\nu_r = 10$ kHz) of the untreated copolymer of ethene and carbon monoxide prepared by using $[Pd(P^\frown O)_2]^{2+}$ [$\mathbf{3a(T^n)_2}$] as the catalyst. The reaction was carried out without any solvent. The spinning side bands of the CO and the CH_2 group are labeled with an asterisk and and a small circle, respectively.

we were interested in whether the complexes $\mathbf{3a(T^n)_2}$ and $\mathbf{3b(T^n)_2}$ provided with hemilabile $O^\frown P$ ether−phosphine ligands could afford a product composition like the analogous complexes with monophosphine or with diphosphine ligands.[60] In the present case the copolymerization of CO and C_2H_4 has been carried out without any solvent. Protic components (alcohols, acids), which decompose eventually forming intermediates like spiroketals, are thus avoided. The reaction between C_2H_4 and CO was performed at 40, 70, 100, and 130 °C. At 100 °C we received a white powder as the product. At lower temperatures, no reaction occurred; at higher temperatures, only a small amount of a dark solid product was isolated. A typical ^{13}C CP MAS NMR spectrum of the crude, colorless, untreated solid ethene−CO copolymer displays two signals due to the CH_2 and the carbonyl carbon atoms (Figure 4A). The carbon resonance (7 ppm) of the terminal CH_2CH_3 group is also visible in the solid state spectra (Figure 4B). In contrast to Batistini et al.,[61] who have synthesized a propylene−carbon monoxide copolymer, in the ^{13}C NMR spectrum of our ethylene−CO copolymer no signals for OCH_3 groups or spiroketal units[72] could be detected. From an end group analysis, which has been carried out by the aid of solid state ^{13}C NMR spectra,[73] a ratio of CH_3:CH_2 = 1:130 [$n = 130$ ($\pm$ 30), Scheme 2] is derived.[74]

The chain length of the polymers produced with the polysiloxane supported cations $\mathbf{3a(T^n)_2}$ and $\mathbf{3b(T^n)_2}$ is therefore comparable to those copolymers, which have been obtained with the catalysts $[(CH_3CN)_2Pd(Ph_2P(CH_2)_xPPh_2)]^{2+}$ ($x = 2-4$).[75] Thus the η^2-$O^\frown P$-chelating ether−phosphines behave more like

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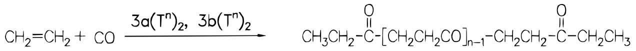
(72) Spiroketals are supposed to be converted thermally to the analogous polyketones at the applied temperatures. Van Doorn, J. A.; Wong, P. K.; Sudmeier, O. Eur. Pat. Appl. 376, 364, 1989; *Chem. Abstr.* **1991**, *114*, 24797.

(73) A quantification of the ratio by a contact time variation was not practicable, due to the low signal intensity of CH_3 ^{13}C signal.

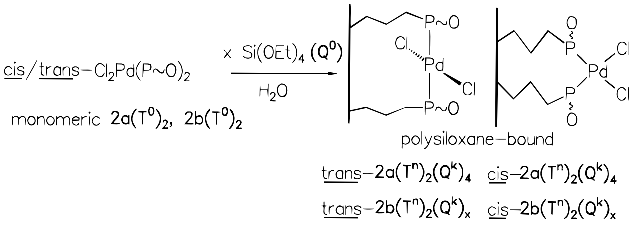
(74) The determination of the ratio of the terminal carbonyl groups (CH_3-CH_2*C*O, 117 ppm) and the internal carbonyl units (CH_2CH_2*C*OCH_2-CH_2, 112 ppm) is inferred from the $^{13}C\{^1H\}$ NMR (inverse gate decoupled) spectra of the same polymer dissolved in $CF_3CHOHCF_3$/C_6D_6 and was found to be 1:42. The ratio CH_3:CH_2 was estimated to be 1:60 by employing the same methods. These results are equivalent with a chain length of approximately $n = 60-85$ (Scheme 2). However, principally two errors have to be taken into account if the NMR signals are utilized to estimate the chain length of the polymer: The integration of the end group $^{13}C\{^1H\}$ NMR (inverse gate decoupled) signals is more accurate than the integration of a ^{13}C resonance, which has been obtained from a solid state NMR spectrum. This is because an error in the integration of the latter is caused due to different $T_{1\rho H}$ and TCH times. Performing a contact time variation to overcome this error is too time consuming. But the "solution NMR" method is less precise than the solid state NMR method, since only the soluble and low-molecular-weight part of the copolymer is detectable. But by employing a reasonable contact time, we minimized the error in the solid state NMR method. Therefore the result of this method is more reliable in contrast to the data extracted from the $^{13}C\{^1H\}$ NMR spectra.

Scheme 2. Reaction in an Interphase: The Ethene−Carbon Monoxide Copolymerization.



$$CH_2{=}CH_2 + CO \xrightarrow{3a(T^n)_2,\ 3b(T^n)_2} CH_3CH_2-\overset{O}{\overset{\|}{C}}-[CH_2CH_2CO]_{n-1}-CH_2CH_2-\overset{O}{\overset{\|}{C}}-CH_2CH_3$$

Scheme 3. Polycondensation of *cis*/*trans*-$Cl_2Pd(P{\sim}O)_2$ [**$2a(T^0)_2$, $2b(T^0)_2$**][a]



[a] P∼O: η^1-P coordinated ether−phosphine ligand. T^n, Q^k: T, Q type silicon atom (three or four oxygen neighbors). $n = 0-3$; $k = 0-4$; n, k = number of Si−O−Si bonds. The heavy lines represent the polysiloxane matrices. $x = 4, 12, 36$ is the amount of the cocondensate.

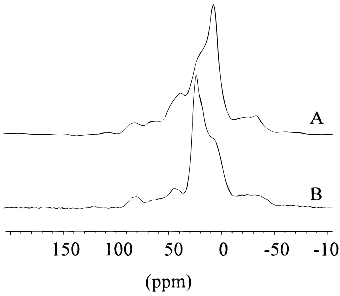


Figure 5. Decomposition of the complex *cis/trans*-**$2b(T^n)(Q^k)_4$** during the catalytic hydrogenation of 1-hexyne (^{31}P CP MAS NMR spectra, 81 MHz, rf = 3 kHz). Key: A, Complex **$2b(T^n)(Q^k)_4$** before the catalytic run. B, decomposition products after four catalytic runs.

the diphosphine ligands with a C_2, C_3, or C_4 bridge than like the monophosphine ligands. This demonstrates the outstanding behavior of this type of ligands.

Preparation of the Polymer Supported Palladium Complexes *trans-/cis-*$2a(T^n)_2(Q^k)_4$ and *trans-/cis-*$2b(T^n)_2(Q^k)_x$ ($x = 4, 12, 36$). The monomeric precursors **$2a(T^0)_2$**, **$2b(T^0)_2$** were sol−gel processed (Scheme 3, Table 1) with water, variable amounts of $Si(OEt)_4$ (**Q^0**; Q type silicon atom; four oxygen neighbors), and the assistance of the catalyst $(AcO)_2Sn(n\text{-}Bu)_2$. The resulting yellow gels were characterized by ^{31}P, ^{13}C, and ^{29}Si CP MAS NMR spectroscopy (Experimental Section). As a result of the presence of a *cis-/trans*-isomeric mixture of the palladium complexes **$2a(T^n)_2(Q^k)_4$** and **$2b(T^n)_2(Q^k)_x$** ($k = 0-4$, number of Si−O−Si bonds), the ^{31}P solid state NMR spectra display two not entirely resolved signals (Figure 5A). The *cis:trans* ratio of the polysiloxane-bound complexes was determined to be 40:60. This result is in contrast to the values obtained for several T/D polymers like **$2a(T^n)_2(D^i)_y$** [$D^i = (CH_3)_2SiO_{i/2}$, D type silicon atom; two oxygen neighbors; $i = 0-2$, number of Si−O−Si bonds] in which *cis-trans* ratios of 20:80 have been obtained.[38] The different polarities of the matrices (T/D or T/Q) are supposed to cause the differences in the position of the *cis−trans* equilibrium. Phosphine palladium complexes like $Cl_2Pd(PR_3)_2$ are known to be selective hydrogenation catalysts. Therefore the ether−phosphine palladium complexes **$2b(T^n)_2(Q^k)_x$** ($x = 4, 12, 36$) were employed in the catalytic hydrogenation of 1-hexyne and diphenylacetylene.

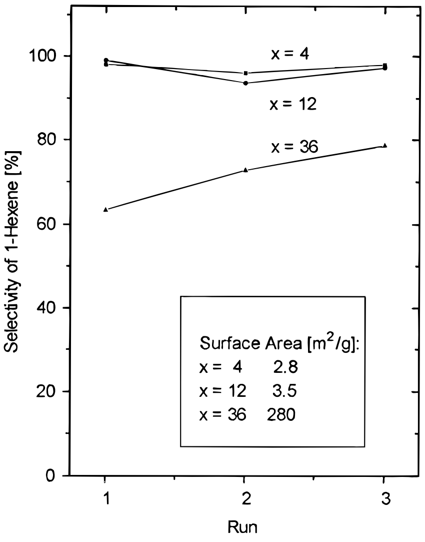


Figure 6. Selectivity of the catalytic hydrogenation of 1-hexyne to 1-hexene and hexane and its relation to the surface area of the activated polysiloxane bound catalysts $Cl_2Pd(P{\sim}O)_2{\cdot}x\ SiO_2$ [**$2b(T^n)_2(Q^k)_x$**].

Hydrogenation of 1-Hexyne. In preliminary experiments we perceived that a rapid hydrogenation was only achieved if the complexes $Cl_2Pd(P{\sim}O)_2{\cdot}xSiO_2$ [**$2b(T^n)_2(Q^k)_x$**] have been activated for 5 h in toluene at 80 °C under an atmosphere of hydrogen (20 bar). Predieri et al.[34] reported the same experiences with thioureapalladium(II)-functionalized polysiloxane matrices. After the activation period the recovered gels **$2b(T^n)_2(Q^k)_x$** are still yellow and show the same spectroscopic data (^{31}P, ^{13}C, ^{29}Si CP MAS NMR) and elemental analysis as the starting materials.

Since all the reactants and possible products (1-hexyne, 1-hexene, 2-hexene, 3-hexene, and hexane) are liquids, the hydrogenation of 1-hexyne was carried out without any solvent. A solvent-free implementation of a reaction would have favorable advantages with regard to economical and environmental aspects.

No discernible reaction occurs when the temperature is kept below 60 °C during the first run. Between 65 and 70 °C the H_2 uptake is finished within 10−20 min (conversion: > 99%). The turnover frequency (TON = 1.15 $mol_{sub}\ mol_{cat}^{-1}\ s^{-1}$ − 0.6 $mol_{sub}\ mol_{cat}^{-1}\ s^{-1}$) depends on the hydrogen pressure at the beginning of the reaction. The catalyst was reused up to 10 times, but no loss of the activity was detected. By determination of the palladium content in the reaction solution after each run a leaching of 0.2−1% of the original palladium quantity was found. Since the recovered reaction solution is inactive for the catalytic hydrogenation of 1-hexyne it is assumed, that the palladium still embedded in the polysiloxane matrix is the active catalyst rather than the palladium species in the reaction solution.

By employment of smaller amounts of the cocondensation agent $Si(OEt)_4$ (**Q^0**) ($x = 4, 12$) the selectivity with respect to 1-hexene ranges from 96 to 98% (2−4% hexane; no isomerization products like 2- or 3-hexene were formed) during seven runs. In contrast to this observation the selectivity is decreased to 62% (in the first run, Figure 6) taking a high amount of $Si(OEt)_4$ (**Q^0**) ($x = 36$) and is increased to a constant value of 78% in runs 3−7. The high and low selectivities are related to low and high BET (N_2) surface areas of the polysiloxane gels, respectively. Subsequently added silica gel, which has been synthesized according to the method of the polycondensed complex **$2b(T^n)_2(Q^k)_4$** or commercially available silica gel show no influence on the high selectivity of the activated complex **$2b(T^n)_2(Q^k)_4$**. Therefore we exclude any hydrogenation activity of the cocondensation component.

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(75) With $x = 1, 2, 3, 4, 5$, and 6 the obtained chain lenghts are $n = 2$, 100, 180, 45, 6, and 2, respectively (see ref 60).

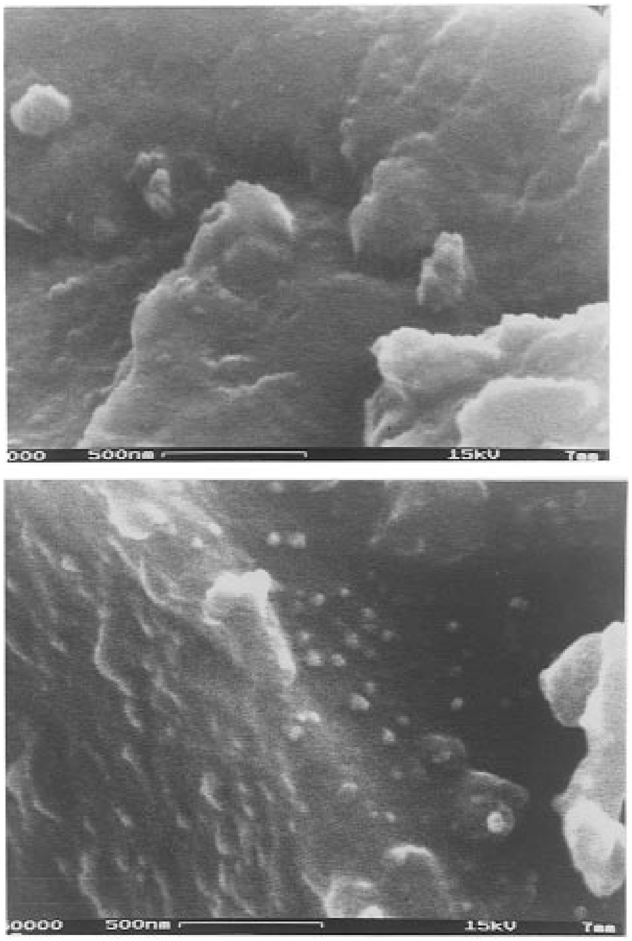

Figure 7. SEM of the catalyst $Cl_2Pd(P{\sim}O)_2{\cdot}4SiO_2$ [$\mathbf{2b(T^{\mathit{n}})_2(Q^{\mathit{k}})_4}$] after the activation cycle (top) and after seven runs (bottom) in 1-hexyne hydrogenation at 70 °C. Figure was reduced to 68% of original size.

No difference in the distribution of the polysiloxane particle size of the polycondensed complex $PdCl_2(P{\sim}O)_2{\cdot}xSiO_2$ [$\mathbf{2b(T^{\mathit{n}})_2(Q^{\mathit{k}})_x}$, x = 4, 12, 36] was detected by scanning electron microscopic (SEM) investigations (magnified 1000×) before and after the catalytic runs. A high-resolution SEM illustration (Figure 7, figure reduced to 68% of original size) reveals palladium particles uniformly dispersed on the surface of the matrix. The size of the spherically shaped palladium particles ranges from about 12 to 20 nm (particles with a lower diameter than 10 nm would certainly not be detected).

The assumption that the existence of these particles is a question of palladium metal is supported by ^{31}P CP MAS NMR spectra. If palladium metal agglomerates to form small particles, ^{31}P resonances should point either to a noncoordinated or a chemically modified phosphine ligand. Figure 5 displays the change of the ^{31}P chemical shifts before and after four catalytic runs. The two signals of the *cis/trans* mixture (Figure 5A) are replaced by a new signal at δ 28 after the catalytic application (Figure 5B). Only a small amount of the original portion of the *trans*-complex was detected. A thermally induced shift of the *cis/trans* equilibrium during the catalysis in favor of the *cis*-complex was excluded by measuring ^{31}P NMR spectra after heating the complex $\mathbf{2b(T^{\mathit{n}})_2(Q^{\mathit{k}})_4}$. No changes could be observed. Investigations of J. Blümel[23] point to the formation of a silica bound pentacoordinated phosphorane(V) species [$R_3P(OSi{\equiv})_2$]. Possibly the new signal could be assigned to such a phosphine−oxygen compound, which is consistent with the cleavage of the palladium−ligand bond. The formation of a simple phosphine oxide ($R_3P{=}O$) is not taken into consideration, because of the lack of a corresponding ^{31}P NMR signal at δ 36. The decomposition of the polymer-bound palladium complex $\mathbf{2b(T^{\mathit{n}})_2(Q^{\mathit{k}})_4}$ during the hydrogenation results in a reaction at the phase boundary solid−liquid. The desired reaction in the interphase failed.

At 80 °C an exothermic reaction takes place and the temperature of the reaction mixture rises up to ≈200 °C within a few seconds although the heater has been removed. Remarkably the H_2 pressure is decreased simultaneously. After 5 min the H_2 uptake is complete and the reaction mixture cools down to room temperature. In conclusion, if no solvent is used, the hydrogenation of 1-hexyne is fast *and* controllable only in a small temperature region. Therefore a solvent-free process is very difficult to handle, which is an important hindrance for a technical application of this class of reaction.

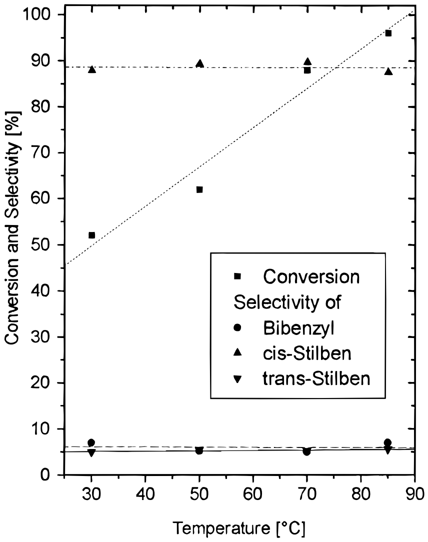

Figure 8. Temperature dependency of selectivity and of the educt conversion of the catalytic hydrogenation of 1,2-diphenylacetylene with $\mathbf{2b(T^{\mathit{n}})_2(Q^{\mathit{k}})_4}$ as the catalyst [p(H_2) at the beginning: 50 bar; catalyst: substrate = 1:1000; reaction time = 1 h; solvent = toluene:ethanol = 57:5].

XPS Study. The XPS spectra of the heterogeneous catalyst after seven catalytic runs showed two signals according to the binding energies of Pd(II) $3d_{5/2}$ (337.5 eV) and Pd(0) $3d_{5/2}$ (335.5 eV).[76] The ratio of Pd(0):Pd(II) was determined to be 1:1. The difference of the observed ratio Pd:P:Si (1:2.7:6.9) to the idealized stoichiometry (1:2:6) is within the experimental error. The signal of Cl 3p was completely decreased, implying that a replacement of Cl^- by another ligand (probably OH^- from the matrix components) has taken place, which is in agreement with the observation of other authors.[77] Two phosphorus species in a ratio of $[P(V)]:[P(III)_{complex}] = 1:1$ were assigned[76,78] to the photoelectron signals at 132.1 and 130.7 eV. In summary, the XPS spectra are supporting the results obtained by solid state NMR spectroscopy, that the polysiloxane-bound starting complex $\mathbf{2b(T^{\mathit{n}})_2(Q^{\mathit{k}})_4}$ was reduced to Pd(0) and that a phosphorus(V) species was formed during the catalytic utilization.

Hydrogenation of Tolan. Since tolan and some of the products (*trans*-stilbene, bibenzyl) are solids, the hydrogenation was carried out in toluene, employing the complex $Cl_2Pd(P{\sim}O)_2{\cdot}4SiO_2$ [$\mathbf{2b(T^{\mathit{n}})_2(Q^{\mathit{k}})_4}$] as a catalyst. Moreover the presence of the solvent facilitates the control of the reaction temperature.

Within a limited reaction time (1 h, Figure 8) the conversion

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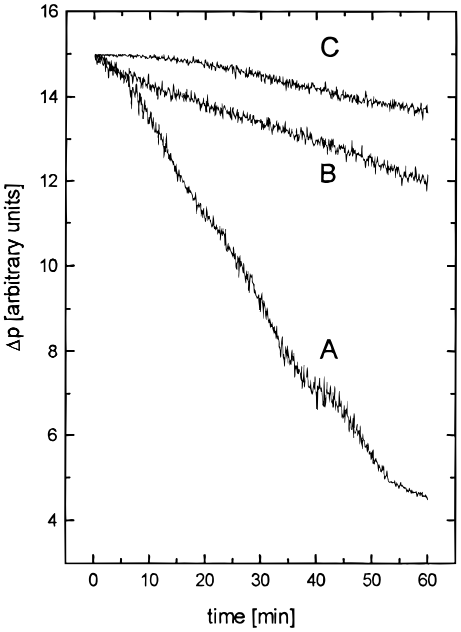


Figure 9. Dependency of the rate of the catalytic hydrogenation on the ratio ethanol:toluene of the solvent. Key: A, 10:50; B, 3:57; C, 0:60 ($T = 40$ °C, $p = 30$ bar). Δp represents the pressure decrease in the autoclave connected to the reaction vessel by a pressure reduction valve.

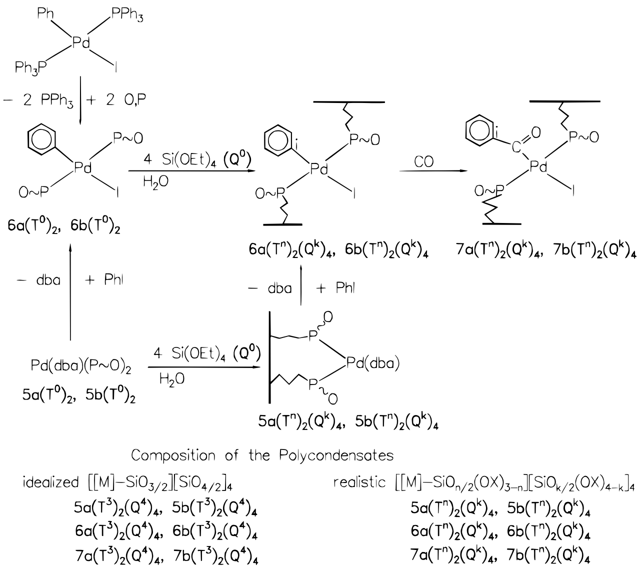
of diphenylacetylene is strongly dependent on the temperature, but simultaneously no change in the selectivities was found. In each case the selectivities are 89% *cis*-stilbene, 5% *trans*-stilbene, and 6% of the fully hydrogenated product (bibenzyl). Regarding Figure 8, it is concluded that bibenzyl is formed continuously from the beginning of the reaction, but the percentage remains the same. With the above-mentioned catalyst the *cis:trans* selectivities are comparable to those obtained with the thiourea-functionalized heterogeneous catalyst[34] but somewhat lower (95%) than another silicate bound palladium catalyst.[79]

It is deduced from the pressure decrease in the hydrogen supply (Figure 9A), that the hydrogenation of tolan is of virtually zero order with respect to the concentration of the substrate up to high conversions of tolan. It was found, that the solvent ratio ethanol:toluene strongly influences the reaction rate (Figure 9A−C). Higher amounts of ethanol accelerates the conversion. But no further increase of the hydrogenation rate was observed if the amount of ethanol exceeds the ratio 10:50. Thus the better solubility of hydrogen in ethanol is not the deciding factor, but the swelling ability of the matrix. If the matrix is swollen optimally (at a ratio of about 10:50), a further addition of ethanol exerts no effect on the reaction rate.

Formation of the Monomeric Palladium(0) and Palladium(II) Complexes 5a(T^0)$_2$, 5b(T^0)$_2$, 6a(T^0)$_2$, and 6b(T^0)$_2$ and Their Polycondensation to the Polysiloxane-Bound Species 5a(T^n)$_2$(Q^k)$_4$, 5b(T^n)$_2$(Q^k)$_4$, 6a(T^n)$_2$(Q^k)$_4$, and 6b(T^n)$_2$(Q^k)$_4$. Due to similar ^{31}P and ^{13}C solid state NMR spectra of the products and the educts **5**−**7** (Scheme 4) the polysiloxane-bound (ether−phosphine)palladium(II) complexes **6a(T^n)$_2$(Q^k)$_4$, 6b(T^n)$_2$(Q^k)$_4$** have been synthesized by three independent methods.

The reaction of Pd(dba)$_2$ (dba = dibenzylideneacetone = 1,5-diphenylpenta-1,5-dien-3-one) with 2 equiv of the monomeric ligand **1a(T^0)$_2$** or **1b(T^0)$_2$** leads to the formation of the palladium complex Pd(dba)(P∼O)$_2$ [**5a(T^0)$_2$ or 5b(T^0)$_2$**] with liberation of dba. In the ^{31}P{^{1}H} NMR spectra of the reaction mixture a multiplet is observed, which can be traced back to the chirality of the ether−phosphines and to the asymmetrically bonded dba ligand.[80,81] Upon addition of a further O,P ligand to **5a(T^0)$_2$, 5b(T^0)$_2$** the same signal pattern and noncomplexed ligand is discernible. No evidence was found for a similar reaction as in the system Pd(dba)(PPh$_3$)$_2$/PPh$_3$ [82] in which Pd(PPh$_3$)$_{3,4}$ is formed. Pursuant to the ^{13}C{^{1}H} NMR spectra the Si(OCH$_3$)$_3$ functions and the propyl spacer are still preserved. A band at 1637 cm^{-1} in the IR spectra of **5a(T^0)$_2$** and **5b(T^0)$_2$** is assigned to the >C=O group of coordinated dba.[80−82] Since dba shows similar solubility, pure **5a(T^0)$_2$, 5b(T^0)$_2$** can be obtained only in low yields.

Scheme 4. Synthesis and Reactivity of the Polysiloxane-Bound Pd−Aryl Complexes **6**[a]



[a] dba = dibenzylideneacetone; see the Experimental Section; O,P = free ether−phosphine ligand. P∼O: η^1-P coordinated ligand. T^n, Q^k: T, Q type silicon atom (three or four oxygen neighbors). $n = 0{-}3$; $k = 0{-}4$; n, k = number of Si−O−Si bonds. The bold-faced bars represent the polysiloxane matrices. X = H, Me, Et. [M] = [(dba)Pd]$_{1/2}$P(Ph)(CH$_2$Do)(CH$_2$)$_3$− (**5a,b**), [(Ph)PdI]$_{1/2}$P(Ph)(CH$_2$Do)(CH$_2$)$_3$− (**6a,b**), [(PhCO)PdI]$_{1/2}$P(Ph)(CH$_2$Do)(CH$_2$)$_3$− (**7a,b**).

Treating the monomeric precursors **5a(T^0)$_2$ or 5b(T^0)$_2$** with 4 equiv of Si(OEt)$_4$ (**Q^0**), excess of water, and the catalyst (*n*-Bu)$_2$Sn(OAc)$_2$ (Scheme 4) results in the formation of the polymer-bound palladium complex **5a(T^n)$_2$(Q^k)$_4$** or **5b(T^n)$_2$(Q^k)$_4$**. One broad signal in the ^{31}P CP MAS NMR spectra with the same chemical shift as the monomeric precursors and a characteristic >C=O IR absorption are indicative of the successful sol−gel processing of the palladium(0) complexes **5a(T^n)$_2$(Q^k)$_4$, 5b(T^n)$_2$(Q^k)$_4$**. Of further significance are the ^{13}C resonances in the ^{13}C CP MAS spectra of both compounds at δ 186 being attributed to the >C=O (dba) group. The other carbon resonances of the coordinated dba ligand are located in the same region as those of the phenyl carbon atoms of the phosphine ligand. Because of the insufficient resolution of the signals in the solid state spectra no specific assignment is possible. Better total yields are obtained if the cocondensation reactions were carried out with the crude products **5a(T^0)** and

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$\mathbf{5b(T^0)_2}$, since released dba is separable more easily from the polycondensed complexes.

In a subsequent experiment an oxidative addition reaction in the interphase liquid−solid was carried out to check the reactivity of the polysiloxane-bound complexes $\mathbf{5a(T^{\mathit{n}})_2(Q^{\mathit{k}})_4}$ and $\mathbf{5b(T^{\mathit{n}})_2(Q^{\mathit{k}})_4}$. Stirring of a suspension of $\mathbf{5a(T^{\mathit{n}})_2(Q^{\mathit{k}})_4}$ or $\mathbf{5b(T^{\mathit{n}})_2(Q^{\mathit{k}})_4}$ in toluene with iodobenzene (Scheme 4) yields the palladium(II) aryl complexes $\mathbf{6a(T^{\mathit{n}})_2(Q^{\mathit{k}})_4}$ or $\mathbf{6b(T^{\mathit{n}})_2(Q^{\mathit{k}})_4}$. Compared to the starting materials **5** the ^{31}P CP MAS NMR resonances of the products **6** show a downfield shift of only about 1 ppm. A definite characterization is therefore impossible. But the disappearance of the >C═O (^{13}C CP MAS NMR) resonance (δ 186) and the simultaneous occurrence of a signal at δ 156.6 (ipso carbon atom, Figure 10A) support the assumption that the complexes $\mathbf{6a(T^{\mathit{n}})_2(Q^{\mathit{k}})_4}$ and $\mathbf{6b(T^{\mathit{n}})_2(Q^{\mathit{k}})_4}$ were formed. Moreover, we isolated an equimolar amount of released dba from the reaction mixture, which is a further evidence for the successful and complete oxidative addition of iodobenzene. Finally $\mathbf{6a(T^{\mathit{n}})_2(Q^{\mathit{k}})_4}$ and $\mathbf{6b(T^{\mathit{n}})_2(Q^{\mathit{k}})_4}$ were also generated by oxidative addition of C_6H_5I at the monomeric precursor Pd(dba)(P∼O)$_2$ [$\mathbf{5a(T^0)_2}$ and $\mathbf{5b(T^0)_2}$] (Scheme 4) and subsequent polycondensation of the T-functionalized monomeric products $\mathbf{6a(T^0)_2}$ and $\mathbf{6b(T^0)_2}$ with Si(OEt)$_4$ ($\mathbf{Q^0}$). Another method to synthesize IPd(Ph)(P∼O)$_2$·4SiO$_2$ [$\mathbf{6a(T^{\mathit{n}})_2(Q^{\mathit{k}})_4}$, $\mathbf{6b(T^{\mathit{n}})_2(Q^{\mathit{k}})_4}$] is the replacement of PPh$_3$ from IPd(Ph)(PPh$_3$)$_2$ by the more basic ether−phosphine ligands $\mathbf{1a(T^0)_2}$ and $\mathbf{1b(T^0)_2}$, followed by a polycondensation (Scheme 4) with Si(OEt)$_4$ ($\mathbf{Q^0}$). In conclusion it can be established, that all three reaction pathways (eqs 2−4, Scheme 4) are independent from each other

$$(\mathrm{Ph})\mathrm{PdI}(\mathrm{PPh_3})_2 \rightarrow \mathbf{6a(T^0)_2,\ 6b(T^0)_2} \rightarrow \mathbf{6a(T^{\mathit{n}})_2(Q^{\mathit{k}})_4,\ 6b(T^{\mathit{n}})_2(Q^{\mathit{k}})_4} \quad (2)$$

$$\mathbf{5a(T^0)_2,\ 5b(T^0)_2} \rightarrow \mathbf{6a(T^0)_2,\ 6b(T^0)_2} \rightarrow \mathbf{6a(T^{\mathit{n}})_2(Q^{\mathit{k}})_4,\ 6b(T^{\mathit{n}})_2(Q^{\mathit{k}})_4} \quad (3)$$

$$\mathbf{5a(T^0)_2,\ 5b(T^0)_2} \rightarrow \mathbf{5a(T^{\mathit{n}})_2(Q^{\mathit{k}})_4,\ 5b(T^{\mathit{n}})_2(Q^{\mathit{k}})_4} \rightarrow \mathbf{6a(T^{\mathit{n}})_2(Q^{\mathit{k}})_4,\ 6b(T^{\mathit{n}})_2(Q^{\mathit{k}})_4} \quad (4)$$

and lead to the same final products $\mathbf{6a(T^{\mathit{n}})_2(Q^{\mathit{k}})_4}$ and $\mathbf{6b(T^{\mathit{n}})_2(Q^{\mathit{k}})_4}$. This is also an indirect evidence for the existence of the intermediates $\mathbf{5a(T^{\mathit{n}})_2(Q^{\mathit{k}})_4}$ and $\mathbf{5b(T^{\mathit{n}})_2(Q^{\mathit{k}})_4}$.

Attempts to apply the polymeric palladium(II) complex $\mathbf{6a(T^{\mathit{n}})_2(Q^{\mathit{k}})4}$ to the Heck reaction[83,84] were not successful. Compared to the literature (98%) the selectivity in the arylation of iodobenzene to *trans*-stilbene was only 90% (10% *cis*-stilbene), and a leaching of the catalyst from the matrix was observed.

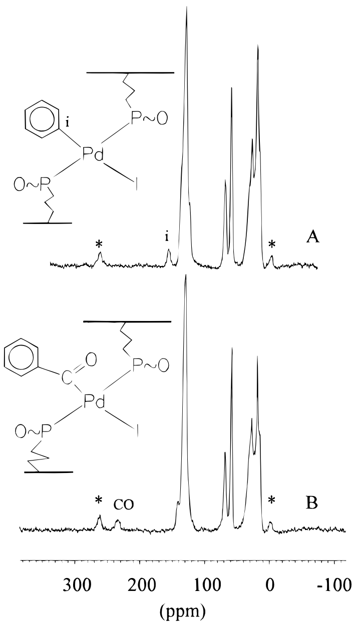

Figure 10. Carbon monoxide insertion in the interphase. ^{13}C CP MAS NMR spectra (75.46 MHz, $\nu_r = 10$ kHz) of $\mathbf{6a(T^{\mathit{n}})_2(Q^{\mathit{k}})_4}$ (A, before CO insertion) and $\mathbf{7a(T^{\mathit{n}})_2(Q^{\mathit{k}})_4}$ (B, after CO insertion).

Solvent-Free Carbon Monoxide Insertion in an Interphase. Since palladium aryl complexes are known to take up carbon monoxide at ambient temperature and atmospheric pressure,[85−87] we have been interested whether this type of reaction takes place in a solvent-free process. If the polysiloxane-bound palladium complexes **6** are exposed to an atmosphere of carbon monoxide at 40 °C (Scheme 4) for several hours, a broad absorption is observed in the IR spectra ($\approx$ 1650 cm^{-1}) indicating the formation of a Pd(COPh) structural unit. No change of the ^{13}C and ^{31}P CP MAS NMR spectra happened. Thus the CO insertion starts already at mild conditions, but it proceeds relatively slowly. When the carbon monoxide pressure is increased to 20 bar, the reaction can be brought to completeness (Scheme 4). In the ^{13}C CP MAS NMR spectra the resonances for the ipso carbon atoms of the Pd−C$_6$H$_5$ units of $\mathbf{6a(T^{\mathit{n}})_2(Q^{\mathit{k}})_4}$, $\mathbf{6b(T^{\mathit{n}})_2(Q^{\mathit{k}})_4}$ (δ 156) disappear during the CO insertion, whereas simultaneously new signals of the corresponding ipso carbon atoms (δ 140, Figure 10) and of the acyl carbonyl groups (δ 234) in the polymeric complexes **7** are observed. The chemical shifts of the carbon resonances of the ether−phosphine ligands are not affected by the carbon monoxide insertion. Because iodine is highly polarizable, this reaction exerts no influence upon the chemical shifts in the ^{31}P solid state NMR spectra according to the observations of other authors.[55,85] Like the ethylene−CO copolymerization, this CO insertion is a nice example of an organometallic reaction type in the interphase. To study the potential of such interphase systems in detail, further fundamental model reactions of other (ether−phosphine)metal complexes are in progress.

Conclusion

The polycondensation of trimethoxysilyl-functionalized palladium complexes allows a general and easy access to polymer-supported complexes. Even monomeric precursor complexes

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in low oxidation states [palladium(0)] or with chelating η^2-P$\frown$O ligands are stable enough to survive such a procedure. Specific reaction conditions are necessary in the case of the dicationic bis(chelate)palladium(II) complexes [**3a(T^n)$_2$**, **3b(T^n)$_2$**] to prevent chemical modifications. The irreversible opening of the P$\frown$O-chelates by water or OH$^-$ in the course of the sol−gel processing is avoided by the assistance of volatile, reversibly bound donors like acetonitrile. The metal complexes incorporated in the gels are well accessible for liquid or gaseous reactants, which is deduced from the behavior of the compounds **6a(T^n)$_2$(Q^k)$_4$, 6b(T^n)$_2$(Q^k)$_4$** and **5a(T^n)$_2$(Q^k)$_4$**, **5b(T^n)$_2$(Q^k)$_4$**, respectively, toward carbon monoxide and PhI in stoichiometric reactions. At elevated pressure or if the polar gels are swollen in polar solvents fast reactions between the catalyst **2b(T^n)$_2$(Q^k)$_y$** and the substrate (1-hexyne, tolan) are possible. Preparation of gels with more flexible matrix properties and with the ability to swell also in nonpolar solvents or substrates are in progress. When the reactivity of the polysiloxane-bound complexes **6a(T^n)$_2$(Q^k)$_4$** and **2b(T^n)$_2$(Q^k)$_y$** in catalytic cycles was tested, it was found that in a reductive reaction medium (arylation of styrene, hydrogen atmosphere) the contact of the palladium to the phosphine ligands is lost. Palladium metal highly dispersed in the gels is therefore the active hydrogenation agent. In other fundamental kinds of organometallic reactions like CO insertion, oxidative addition, and CO−olefin copolymerization no leaching was observed. In the latter case, the behavior of the complexes with ether−phosphine ligands [Pd(P$\frown$O)$_2$]$^{2+}$ [**3a(T^n)$_2$**, **3b(T^n)$_2$**] is different from that of complexes with common monophosphine ligands, which was concluded from the chain length of the produced polyketones.

Acknowledgment. We are grateful to Degussa AG, Germany, for a generous gift of PdCl$_2$ and to Fa. Micromeritics for the disposal of a Gemini II for the gas adsorption analysis. The support of this research by the Fonds der Chemischen Industrie, Frankfurt/Main, Germany, and by the Deutsche Forschungsgemeinschaft (Forschergruppe, Grant No. Li 154/41-1), Bonn/Bad Godesberg, Germany, is gratefully acknowledged. We would also like to acknowledge Prof. K. Unger and M. Hallmann, University of Mainz, for their assistance in the gas adsorption analysis and to E. Nadler, University of Tübingen, for SEM micrographs. R.S. thanks the University of Tübingen and the Land Baden-Württemberg for a scholarship (Landesgraduiertenförderungsgesetz).

Supporting Information Available: SEM illustration (magnified by a factor of 1000) of the catalyst after the activation cycle (A) and after seven catalytic runs (B) (1 page). Ordering information is given on any current masthead page.

IC950412M