Chemistry in Interphases: Chemical Exchange in a Polysiloxane-Bound Chlorohydridotris(ether–phosphine)ruthenium(II) Complex. An Investigation by Solid-State NMR Spectroscopy[1,2]

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The reaction between $HRuCl(PPh_3)_3$ (**2**) and the ether–phosphine ligands $R(Ph)PCH_2CH_2OCH_3$ [**1a, 1b(T°)**], $R(Ph)PCH_2$–tetrahydrofuryl [**1c, 1d(T°)**] (R = Ph (**a,c**), $CH_2CH_2CH_2Si(OMe)_3$ [**b(T°), d(T°)**]) (for labeling see Table 1) affords the monomeric ruthenium complexes $HRuCl(P{\sim}O)_2(P{\frown}O)$ [**3a,c, 3b(T°)₃, 3d(T°)₃**] [P~O: η^1-P-coordinated, P⌢O: η^2-P⌢O-coordinated; T° = T type (T° = –Si(OMe)₃) silicon atoms without Si–O–Si bonds]. Variable temperature $^{31}P\{^1H\}$ NMR spectroscopic investigations, which have been carried out in detail in the case of **3a**, give evidence of fluxional behavior. In the presence of water and catalytic amounts of NEt₃ the monomeric precursors $HRuCl(P{\sim}O)_2(P{\frown}O)$ [**3b(T°)₃, 3d(T°)₃**] are subjected to a polycondensation (sol–gel process) to give the corresponding polysiloxane- (T-) bound (ether–phosphine)ruthenium(II) complexes **3b′(Tⁿ)₃** and **3d′(Tⁿ)₃** [(Tⁿ): T type silicon atoms; n = 1–3 (number of Si–O–Si bonds)]. Solid-state ^{29}Si CP-MAS NMR spectroscopy has been used to establish a highly cross-linked polysiloxane matrix in the case of the polycondensated complex $HRuCl(P{\sim}O)_2(P{\frown}O)$ [**3d′(Tⁿ)₃**]. According to $^{31}P\{^1H\}$ NMR and ^{31}P CP-MAS NMR spectra the complex geometry is retained on going from the monomers $HRuCl(P{\sim}O)_2(P{\frown}O)$ [**3b(T°)₃, 3d(T°)₃**] to the corresponding polymers **3b′(Tⁿ)₃, 3d′(Tⁿ)₃**. If $HRuCl(P{\sim}O)_2(P{\frown}O)$ [**3d′(Tⁿ)₃**] (stationary phase) is treated with methanol (mobile phase) a swollen gel is formed. The ruthenium complex in this interphase [**3d′(Tⁿ)₃** + CH₃OH] shows a chemical exchange of the three ether oxygen donors (equivalence of all three P atoms) which has been demonstrated by ^{31}P and ^{13}C solid-state NMR spectroscopy. Temperature dependent measurements establish these findings. If $HRuCl(P{\sim}O)_2(P{\frown}O)$ [**3b(Tⁿ)₃** and **3d′(Tⁿ)₃**] are reacted with acetic acid and carbon monoxide to give the polysiloxane-bound complexes $ClRu(O_2CMe)(P{\sim}O)_3$ [**4b′(Tⁿ)₃, 4d′(Tⁿ)₃**] and $HRuCl(CO)$-$(P{\sim}O)_3$ [**5b′(Tⁿ)₃, 5d′(Tⁿ)₃**], respectively, the exchange process is prevented by cleavage of the Ru–O bond. The complexes $HRuCl(CO)(P{\sim}O)_3$ [**5b(Tⁿ)₃** and **5d′(Tⁿ)₃**] reversibly take up carbon monoxide with formation of the supported complexes $HRuCl(CO)_2(P{\sim}O)_2$ [**6b′(Tⁿ)₂, 6d′(Tⁿ)₂**].

Introduction

In recent investigations we have been concerned with transition metal complexes containing monodentate (P~O) and bidentate (P⌢O) ether phosphine ligands.[3] The interest in such "hemilabile" ligands stems from the fact that the coordinated oxygen can dissociate from the metal in solution, leaving a vacant coordination site for substrate-binding catalytic action. On coordination of the oxygen to the metal, a chelate is formed. The dissociation and association of the weak donor leads to an "opening and closing mechanism".[4–7] In complexes with two or three "hemilabile" phosphine oxygen ligands the oxygen donors compete for one coordination site. This reveals a fluxional behavior in solution that has been studied in detail by variable temperature ^{31}P NMR spectroscopy in the case of the examples depicted in Scheme 1.[5] Line shape analyses has enabled the calculation of thermodynamic parameters, e.g. the
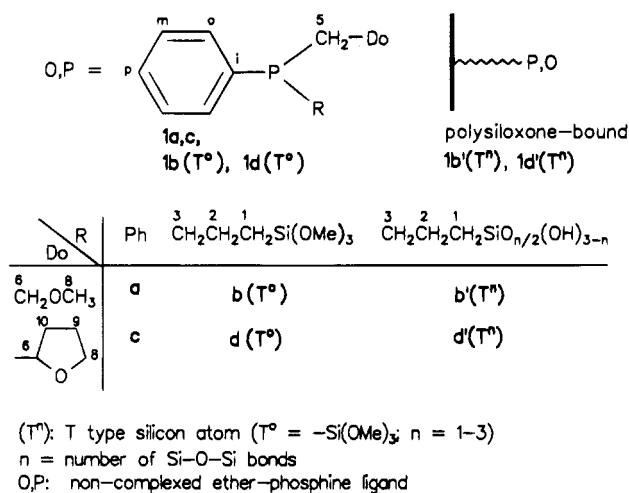
Scheme 1
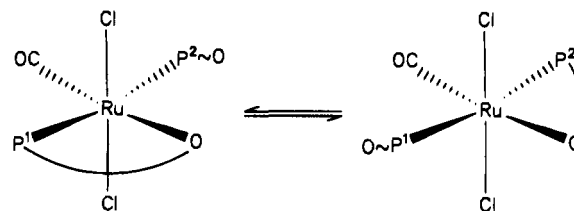
determination of the ruthenium-oxygen bond strengths in dependence on the kind of the different ether moieties.[8]

Chemical systems in which the reactive center is fixed to polymeric matrices are gaining increasing significance.[2,9–25] In this context the simultaneous cocondensation of organo- (T-)

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(1) Dedicated to Professor W. C. Kaska on the occasion of his 60th birthday.
(2) Supported Organometallic Complexes. 8. Part 7: Lindner, E.; Schreiber, R.; Kemmler, M.; Schneller, T.; Mayer, H. A. *Chem. Mater.* **1995**, *7*, 951.
(3) Bader, A.; Lindner. E. *Coord. Chem. Rev.* **1991**, *108*, 27–110.
(4) Lindner, E.; Karle, B. *Chem. Ber.* **1990**, *123*, 1469–1473.
(5) Lindner, E.; Mayer H. A.; Möckel A. In *Phosphorus-31 NMR Spectral Properties in Compound Characterization and Structural Analysis*; Quin, L. D., Verkade, J. G., Eds.; VCH: Weinheim, Germany, 1994.
(6) McCann, G. M.; Carvill, A.; Lindner, E.; Karle, B.; Mayer, H. A. *J. Chem. Soc., Dalton Trans.* **1990**, 3107–3115.
(7) Lindner, E.; Schober, U. *Inorg. Chem.* **1988**, *27*, 212–214.

(8) Lindner, E.; Möckel, A.; Mayer, H. A.; Kühbauch, H.; Fawzi, R.; Steimann, M. *Inorg. Chem.* **1993**, *32*, 1266–1271.
(9) Lindner, E.; Kemmler, M.; Mayer, H. A. *Z. Anorg. Allg. Chem.* **1994**, *620*, 1142–1150.
(10) Deschler, U.; Kleinschmit, P.; Panster, P. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 236.
(11) Eckert, H. *Prog. Nucl. Magn. Reson. Spectrosc.* **1992**, *24*, 159–293.
(12) Maciel, G.; Sindorf, D. W.; Bartuska, V. *J. Chromatogr.* **1981**, *205*, 438–443.
(13) Sindorf, D. W.; Maciel, G. E. *J. Am. Chem. Soc.* **1983**, *105*, 3767–3776.
(14) Bayer, E.; Albert, K.; Reiners, J.; Nieder, M.; Müller, D. *J. Chromatogr.* **1983**, *264*, 197–213.
(15) Khatib, I. S.; Parish, R. V. *J. Organomet. Chem.* **1989**, *369*, 9–12.
(16) Lindner, E.; Bader, A.; Mayer, H. A. *Z. Anorg. Allg. Chem.* **1991**, *598/599*, 235–252.
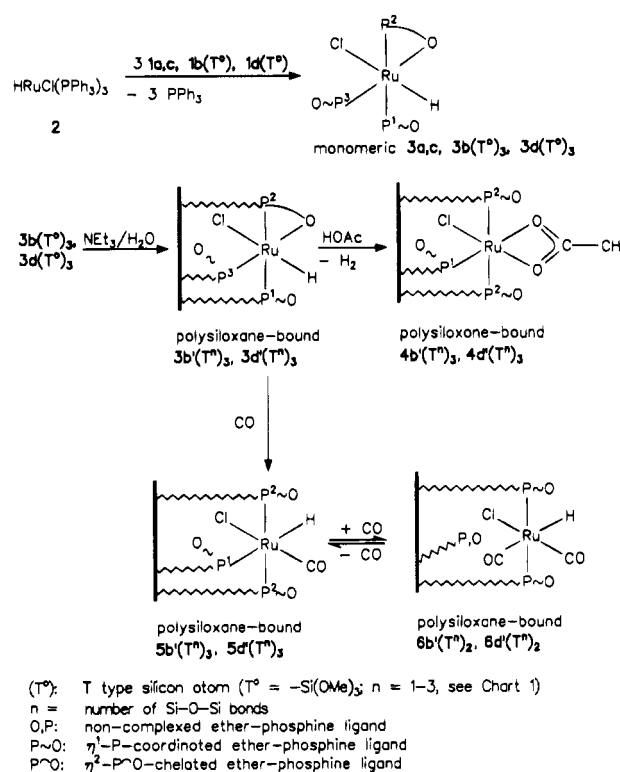
Chart 1

(T^n): T type silicon atom (T^0 = $-$Si(OMe)$_3$; n = 1$-$3)
n = number of Si$-$O$-$Si bonds
O,P: non$-$complexed ether$-$phosphine ligand

silyl functionalized transition metal complexes with D, T, or Q alkoxy silanes [D = R$_2$Si(OR')$_2$, T = RSi(OR')$_3$, Q = Si(OR')$_4$; R, R' = Me, Et] affords a possibility to modify the materials extensively.[2,15-19] These novel networks have preferable mechanical and chemical properties, e.g. a high degree of flexibility and high density as well as a reduced leaching of the functional groups.[16,17,19] In the presence of an adequate solvent (mobile phase) the polymers (stationary phase) are able to swell forming an interphase. These systems are capable to combine the advantages of the homogeneous with those of the heterogeneous catalysis.[16,19]

In this article we wish to report on the synthesis of the monomeric and the polysiloxane- (T-) bound ether$-$phosphine complexes HRuCl(P$\sim$O)$_2$(P$^\frown$O) according to the sol$-$gel process and their solid-state spectroscopic characterization. By means of ^{31}P and ^{13}C CP-MAS NMR spectroscopic investigations an exchange process of the ether oxygen donors of the ruthenium complexes in the polysiloxane matrix is described for the first time. A further goal is to study the influence of the coordination of acetic acid and carbon monoxide toward the fluxional behavior of ether$-$phosphine complexes.

Results and Discussion

Preparation and Characterization of the Monomers 3a, 3c, 3b(T^0)$_3$, and 3d(T^0)$_3$.

Treatment of HRuCl(PPh$_3$)$_3$ (2) with three equiv of the O,P ligands 1a,c, 1b(T^0), 1d(T^0) [T^0 = Si-(OMe)$_3$, (T^n): T type silicon atoms (n = 1$-$3), the number of Si$-$O$-$Si bonds] (Chart 1, Table 1) at 100 °C in toluene affords the yellow monomeric ruthenium complexes HRuCl(P$\sim$O)$_2$-(P$^\frown$O) [3a,c, 3b(T^0)$_3$, 3d(T^0)$_3$] (Scheme 2). In the hydride region of the ^{1}H NMR spectra of 3a,c, 3b(T^0)$_3$, 3d(T^0)$_3$ at 30

(17) Lindner, E.; Bader, A.; Mayer, H. A. *Inorg. Chem.* **1991**, *30*, 3783–3785.

(18) Schubert, U.; Egger, C.; Rose, K.; Alt, C. *J. Mol. Catal.* **1989**, *55*, 330–339.

(19) Lindner, E.; Kemmler, M.; Mayer, H. A.; Wegner, P. *J. Am. Chem. Soc.* **1994**, *116*, 348–361.

(20) Fyfe, C. A.; Zhang, Y.; Aroca, P. *J. Am. Chem. Soc.* **1992**, *114*, 3252–3255.

(21) Liu. D. K.; Wrighton, M. S.; McKay, D. R.; Maciel, G. E. *Inorg. Chem.* **1984**, *23*, 212–220.

(22) Komoroski, R. A.; Magistro, A. J.; Nicholas, P. P. *Inorg. Chem.* **1986**, *25*, 3917–3925.

(23) Berni, L.; Clark, H. C.; Davies, J. A.; Fyfe, C. A.; Wasylishen, R. E. *J. Am. Chem. Soc.* **1982**, *104*, 438–445.

(24) Lindner, E.; Kemmler, M.; Mayer, H. A. *Chem. Ber.* **1992**, *125*, 2385–2390.

(25) Lindner, E.; Schreiber, R.; Kemmler, M.; Mayer, H. A.; Fawzi, R.; Steimann, M. *Z. Anorg. Allg. Chem.* **1993**, *619*, 202–208.

Scheme 2

(T^n):   T type silicon atom (T^0 = $-$Si(OMe)$_3$; n = 1$-$3, see Chart 1)
n =   number of Si$-$O$-$Si bonds
O,P: non$-$complexed ether$-$phosphine ligand
P$\sim$O: η^1-P$-$coordinated ether$-$phosphine ligand
P$^\frown$O: η^2-P$^\frown$O$-$chelated ether$-$phosphine ligand

Table 1. Labeling of the Compounds[a]

compound	monomers	polycondensated compound
Ph$_2$PCH$_2$CH$_2$OCH$_3$	1a	
R(Ph)PCH$_2$CH$_2$OCH$_3$[b]	1b(T^0)	1b'(T^n)
Ph$_2$PCH$_2$C$_4$H$_7$O	1c	
R(Ph)PCH$_2$C$_4$H$_8$O[b]	1d(T^0)	1d'(T^n)
HRuCl(P$\sim$O)$_2$(P$^\frown$O)	3a,c, 3b(T^0)$_3$, 3d(T^0)$_3$	3b'(T^n)$_3$, 3d'(T^n)$_3$
ClRu(O$_2$CCH$_3$)(P$\sim$O)$_3$		4b'(T^n)$_3$, 4d'(T^n)$_3$
HRuCl(CO)(P$\sim$O)$_3$		5b'(T^n)$_3$, 5d'(T^n)$_3$
HRuCl(CO)$_2$(P$\sim$O)$_2$		6b'(T^n)$_3$, 6d'(T^n)$_3$

[a] The label T characterizes the polymerization via the silicon atom (T type silicon atom: T^0 = $-$Si(OMe)$_3$, T^n: n = number of the Si$-$O$-$Si bonds in the polymer, n = 1$-$3). [b] R = CH$_2$CH$_2$CH$_2$Si(OMe)$_3$.

°C a quartet is observed caused by the coupling of the proton with three equivalent ^{31}P nuclei. The hydridic resonances (δ $-$17 to $-$19) show the typical chemical shifts of hydrogen ligands coordinated *trans* to Cl.[26] Since the oxygen donors of three ether$-$phosphine ligands in the complexes 3a,c, 3b(T^0)$_3$, 3d(T^0)$_3$ compete for one coordination site, fluxional behavior is observed in the ^{31}P{^{1}H} NMR spectra (32.39 MHz) measured in solution at various temperatures. At low temperature ($-$90 °C) the three phosphorus nuclei become distinguishable in the ^{31}P{^{1}H} NMR spectra which display typical ABX patterns (Table 2) indicating that the exchange process is frozen out. The coupling constants are consistent with the mutual *trans* positions of P^1 and P^2 and the *cis* position of P^3. As the temperature is raised ($-$35 °C), the lines of the AB signals (P^1, P^2) first broaden then coalesce while the X part (P^3) changes to a regular triplet. Upon further heating, the third O,P ligand (P^3) is involved in the exchange process as well, which is demonstrated by a single broad resonance at room temperature. Compound 3a reveals the *same spectroscopic data* and *dynamic behavior* as the "dihydride complex *trans*-H$_2$Ru(P$\sim$O)$_2$(P$^\frown$O)"

(26) Hoffman, P. R.; Caulton, K. G. *J. Am. Chem. Soc.* **1975**, *97*, 4221–4228.

Table 2. $^{31}P\{^1H\}$ (−30 °C, Toluene) and ^{31}P CP-MAS (24 °C) NMR Data of **3a,c**, **3b(T^0)$_3$**, **3d(T^0)$_3$**, **3b'(T^n)$_3$**, and **3d'(T^n)$_3$**

compound	$^{31}P\{^1H\}$ NMR (ppm)	compound	^{31}P CP-MAS NMR (ppm)
3a	58.5 (t, P^3), 32.0 (d, P^1, P^2) [^2J(PP) = 34 Hz] 57.8 (dd, P^3), 35.2 (dd, P^2), 27.0 (dd, P^1) [^2J(P^{1}P^2) = 284, ^2J(P^{1}P^3) = 29, ^2J(P^{2}P^3) = 35 Hz]^a	**3a**	60.1 (P^3), 33.0 (P^2), 24.1 (P^1) [^2J(P^{1}P^2) = 284 Hz]
3c	55.7 (dd, P^3), 47.4 (dd, P^2), 39.7 (dd, P^1) [^2J(P^{1}P^2) = 280, ^2J(P^{1}P^3) = 29, ^2J(P^{2}P^3) = 29 Hz]	**3c**	59.1 (P^3), 37.8 (P^2), 28.1 (P^1) [^2J(P^{1}P^2) = 280 Hz]
3b(T^0)$_3$	50.7 (dd, P^3), 38.5 (dd, P^2), 28.7 (dd, P^1) [^2J(P^{1}P^2) = 279, ^2J(P^{1}P^3) = 30, ^2J(P^{2}P^3) = 30 Hz]	**3b'(T^n)$_3$** **3b'(T^n)$_3$** + MeOH	52.0 (P^3), 37.8 (P^2), 28.1 (P^1) 41.8 (P^1, P^2, P^3)
3d(T^0)$_3$	52.4 (dd, P^3), 43.9 (dd, P^2), 25.1 (dd, P^1) [^2J(P^{1}P^2) = 279, ^2J(P^{1}P^3) = 30, ^2J(P^{2}P^3) = 30 Hz]	**3d'(T^n)$_3$**	52.8 (P^3), 35.1 (P^1, P^2)
3d'(T^n)$_3$ + MeOH	42.5 (P^1, P^2, P^3), 31.3 (P^1, P^2, P^3, see Scheme 3)^b	**3d'(T^n)$_3$** + MeOH	40.8 (P^1, P^2, P^3)

^{a} −80 °C. ^{b} Suspension.

which has been published earlier as a note.[7] The conclusive proof for the composition and geometry of complexes of the type **3** was supplied by a solution state ^{31}P NMR spectrum of **3a** with selectively decoupling of the protons of the phosphine ligands.[26] At −35 °C the X part (P^3) of the ^{31}P NMR spectrum is split into a doublet of triplets by the two mutually exchanging phosphines (P^1, P^2) and only *one hydride* bound to the metal. The elemental analyses of **3a,c**, **3b(T^0)$_3$**, **3d(T^0)$_3$**, in particular the values for the Cl ligand, confirm these results. Thus the "dihydride" for which detailed dynamic studies have been published elsewhere[7] is actually compound **3a**.

Sol−Gel Processing. The complexes HRuCl(P∼O)$_2$(P⌢O) [**3b(T^0)$_3$**, **3d(T^0)$_3$**] have been subjected to a basic polycondensation by treatment with NEt$_3$ and a 1.2 fold stoichiometric amount of water in ethanol (Scheme 2). The resulting yellow polymers **3b'(T^n)$_3$**, **3d'(T^n)$_3$** are air sensitive. In the case of the complex **3d'(T^n)$_3$** the polysiloxane matrix has been investigated by ^{29}Si solid state NMR spectroscopy. The ^{29}Si CP-MAS NMR spectrum displays signals of the T groups[27,28] with the relative intensities of T^1:T^2:T^3 = 0.6:3.8:5.6. The high degree of cross linkage of the T functions (degree of condensation[29] 83%) is traced back to the employment of NEt$_3$ as a Lewis base catalyst.

Comparison of the Monomers with the Polymers. The chemical shifts of the three P nuclei and the *trans* coupling constants between P^2 and P^1 can also be determined in the solid-state by the ^{31}P CP-MAS NMR spectra of the monomeric species **3a,c** at room temperature (Table 2). These results are in good agreement with those $^{31}P\{^1H\}$ NMR data obtained in solution at low temperatures. They show that the exchange process is slowed down in the solid state at room temperature. The ^{31}P signals in the $^{31}P\{^1H\}$ NMR spectra of the complexes **3b(T^0)$_3$**, **3d(T^0)$_3$** are shifted to higher field compared to the ^{31}P resonances of **3a,c** (Table 2). On going from the monomeric ruthenium complexes **3b(T^0)$_3$**, **3d(T^0)$_3$** to the polymers **3b'(T^n)$_3$**, **3d'(T^n)$_3$**, the geometry of the metal complexes remains preserved. This has been demonstrated by comparison of the ^{31}P chemical shifts of **3b(T^0)$_3$**, **3d(T^0)$_3$** in the $^{31}P\{^1H\}$ NMR spectra in solution and solid state with those of **3b'(T^n)$_3$**, **3d'(T^n)$_3$** in the ^{31}P CP-MAS NMR spectra in the solid state (Scheme 2 and Table 2). In both polymers the observation of two distinguishable signals with their corresponding side band patterns which do not change upon heating to 80 °C is in agreement with a rigid coordination sphere of the ruthenium complexes.
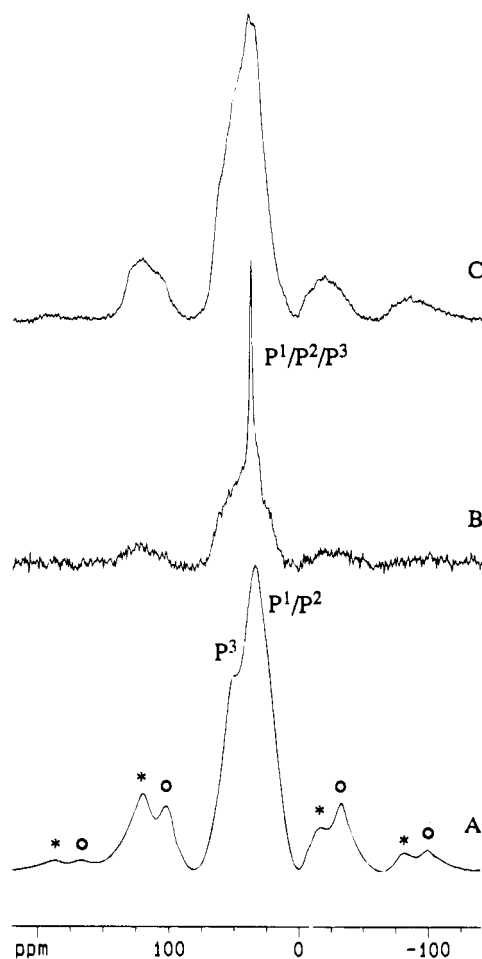
(27) Engelhardt, G.; Janeke, H.; Lippmaa, E.; Samoson, A. *J. Organomet. Chem.* **1981**, *210*, 295−301.
(28) Corriu, R. J. P.; Moreau, J. J. E.; Thepot, P.; Man, A. W. C. *Chem. Mater.* **1992**, *4*, 1217−1224.
(29) Degree of condensation of the T species = 100(T^1 + 2T^2 + 3T^3)/ [3(T^1 + T^2 + T^3)]; T^1, T^2, and T^3 are the relative peak areas of the simulated spectrum.

Figure 1. 1. Solid-state ^{31}P CP-MAS NMR spectra (121.49 MHz) of **3d'(T^n)$_3$** (A, 20°C, ν = 8 kHz), after treatment with MeOH (B, 20 °C, ν = 8 kHz), and at low temperature (C, −70 °C, ν = 8 kHz). Spinning side bands of P^1/P^2 are denoted as open circles; those of P^3, as asterisks.

Chemical Exchange in Interphases. In the concept of interphases it is assumed that particular regions exist in which a stationary and a mobile component penetrate one another in molecular dimensions although no homogeneous mixture is formed. In these regions the reaction center becomes highly mobile simulating the properties of a solution. If the polysiloxane- (T-) bound complex HRuCl(P∼O)$_2$(P⌢O) [**3d'(T^n)$_3$**] (stationary phase) is treated with methanol (mobile phase) a highly swollen gel is generated in which regions of high mobility exist (interphase). In the solid state ^{31}P CP-MAS NMR spectrum of this gel a signal with a very small line width at δ 40.8 is observed (Figures 1B, 2, and 3A). Its position corresponds to the weighted average of the signals of P^1/P^2 and P^3 in the ^{31}P CP-MAS NMR spectrum of "dry" **3d'(T^n)$_3$** (Figure 1A). This indicates that a chemical exchange process accounts
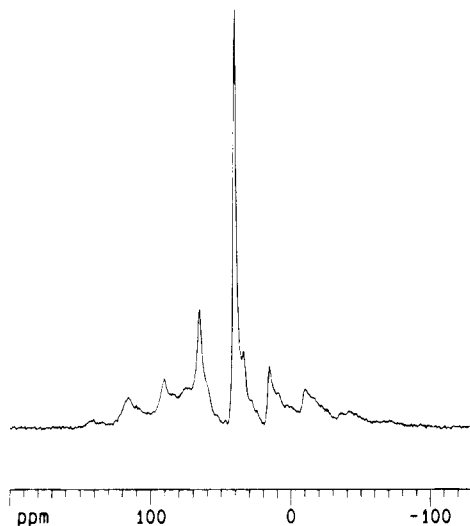
Figure 2. Solid-state, ^{31}P CP-MAS NMR spectra (121.49 MHz) of **3d'**(T^n)$_3$ (A, 20 °C, ν = 3 kHz) after treatment with MeOH.
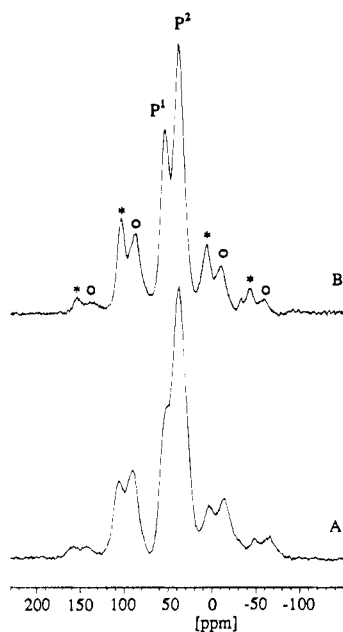

Figure 3. Solid-state ^{31}P CP-MAS NMR spectra (81 MHz) of **4b'**-(T^n)$_3$ (A, 20 °C, ν = 3.5 kHz) and after treatment with MeOH (B, 20 °C, ν = 3.5 kHz). Spinning side bands of P^1 are denoted as asterisks; those of P^2, as open circles.

for the equivalence of the three P atoms of the three ether—phosphine ligands (Scheme 3, **C**, **C'**, **C''**). As a consequence of the fluxional process the spinning side bands are strongly reduced. After removal of MeOH under vacuum the original ^{31}P CP-MAS NMR spectrum of **3d'**(T^n)$_3$ is obtained again. Figure 1C displays the low temperature (-70 °C) solid state ^{31}P CP-MAS NMR spectrum of the swollen gel which is comparable with the spectrum of "dry" **3d'**(T^n)$_3$ (Figure 1A). The isotropical signals of P^1/P^2 and P^3, respectively, are separated again and observed as broad peaks. Moreover the spinning side band patterns are compatible with those of "dry" **3d'**(T^n)$_3$ (Figure 1A). Hence the exchange of the ether—phosphine ligands in the interphase can be suppressed by lowering the temperature or by removal of the mobile phase (MeOH).

In addition to the exchange process discussed above, further contributions to the line broadening of the isotropical signal of P^1/P^2 and P^3 have to be considered. The flexibility of the matrix depends on the temperature and the degree of swelling. Upon cooling, the mobility of the matrix decreases, which will lower

the exchange rate of the three phosphorus sites and lead to a broadening of the signal. When the sample is rotated, the centrifugal forces are responsible for an inhomogeneous distribution of MeOH across the volume of the spinner. The result is a reduction of the regions with highly mobile (fluctuating) ether—phosphine complexes at higher spinning rates. This is displayed in the ^{31}P NMR spectra at different spinning speeds and at different field strengths (Figures 1B, 2, 4A). At a field strength of 4.7 T (81 MHz phosphorus resonance frequency) and spinning rates of 3 kHz (Figure 4A) the sharp signal is located on top of a broad peak which is due to less flexible anisotropic material. A higher field strength (7 T, 121.49 MHz, Figure 2) increases the spinning side bands which at rising spinning rates are strongly reduced, however, at the expense of the growth of less mobile regions (Figure 1B).

The ^{13}C NMR spectra of complex **3d'**(T^n)$_3$ are in agreement with a chemical exchange process as well. As a characteristic feature in the solid state ^{13}C CP-MAS NMR spectrum of "dry" **3d'**(T^n)$_3$ the resonance of the carbon atom C-6 of the P⌢O-chelated ligand is shifted downfield compared to the corresponding signal of the dangling ether—phosphine (P∼O) (form **A**, Scheme 3). After treatment of **3d'**(T^n)$_3$ with methanol, in particular the signal of C-8 is observed with reduced line width indicating a high mobility of the ether moieties of the ligands. In spite of the high mobility of this part of the ether functions the signal of the carbon atom 6 remains broad due to the exchange process of the chelated and nonchelated state of the ligands.

Reaction of 3b'(T^n)$_3$ and 3d'(T^n)$_3$ with Acetic Acid and Carbon Monoxide. To support the chemical exchange process which is active on the NMR time scale in the swollen polysiloxanes, the complexes **3b'**(T^n)$_3$, **3d'**(T^n)$_3$ have been treated with acetic acid and carbon monoxide (Scheme 2). The reaction of acetic acid with the fluxional metal complexes **3b'**-(T^n)$_3$, **3d'**(T^n)$_3$ liberates hydrogen to give the acetato complexes ClRu(O$_2$CMe)(P∼O)$_3$ [**4b'**(T^n)$_3$, **4d'**(T^n)$_3$]. The η^2-coordinated acetate function is recognized in the IR spectra of **4b'**(T^n)$_3$, **4d'**-(T^n)$_3$ by characteristic absorptions of the symmetric and antisymmetric CO$_2$ vibrations (Table 3). In the solid state ^{13}C CP-MAS NMR spectra the signal for the quaternary carbon atom of the η^2-coordinated acetato ligand is found at δ 196.8. The two chemically different phosphorus nuclei (P^1, P^2) give rise to two distinct resonances flanked by spinning side bands in the solid state ^{31}P CP-MAS NMR spectrum (Table 3 and Figure 3A). In contrast to **3b'**(T^n)$_3$, **3d'**(T^n)$_3$ the intensities of the spinning side bands in the ^{31}P CP-MAS NMR spectra of **4b'**-(T^n)$_3$, **4d'**(T^n)$_3$ remain unchanged after treatment of the polymers with methanol (Figure 3B). The fact that in the highly swollen gel of **4b'**(T^n)$_3$, **4d'**(T^n)$_3$ the two phosphorus sites and the chemical shift anisotropy are retained further supports the theory that the exchange process of η^1-P∼O and η^2-P⌢O is exclusively responsible for the line narrowing in the ^{31}P NMR spectra of the swollen gels **3b'**(T^n)$_3$, **3d'**(T^n)$_3$ while the higher mobility of the polymer matrix is not. Solely due to the swelling of the gel is a better resolution of the signals for P^1 and P^2 achieved. In a carbon monoxide atmosphere the Ru—O bond of the η^2-P⌢O chelated ligand in the polymers **3b'**(T^n)$_3$, **3d'**-(T^n)$_3$ is cleaved forming the corresponding carbonyl complexes **5b'**(T^n)$_3$, **5d'**(T^n)$_3$ (Scheme 2). This reaction has been monitored in the case of **3d'**(T^n)$_3$ by solid state ^{31}P CP-MAS NMR spectroscopy. In Figure 4, spectrum A displays the exchange signal of the highly swollen gel of the complex HRuCl(P∼O)$_2$-(P⌢O) [**3d'**(T^n)$_3$] which already has been discussed. Spectrum B was obtained within a few minutes after a partial reaction of **3d'**(T^n)$_3$ + MeOH with CO (2 bar) performed directly in the rotor. Besides the nonconverted, fluxional **3d'**(T^n)$_3$, the car-

Scheme 3

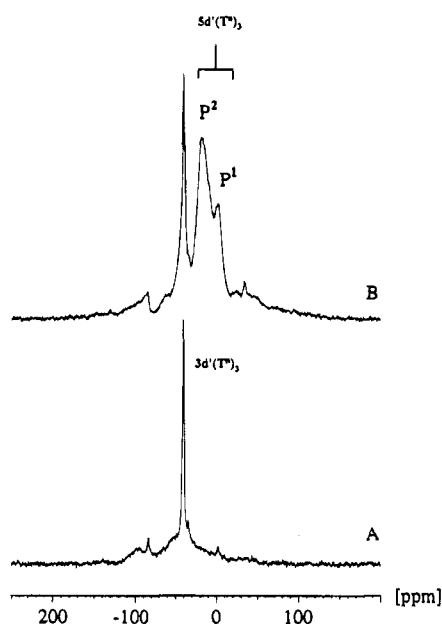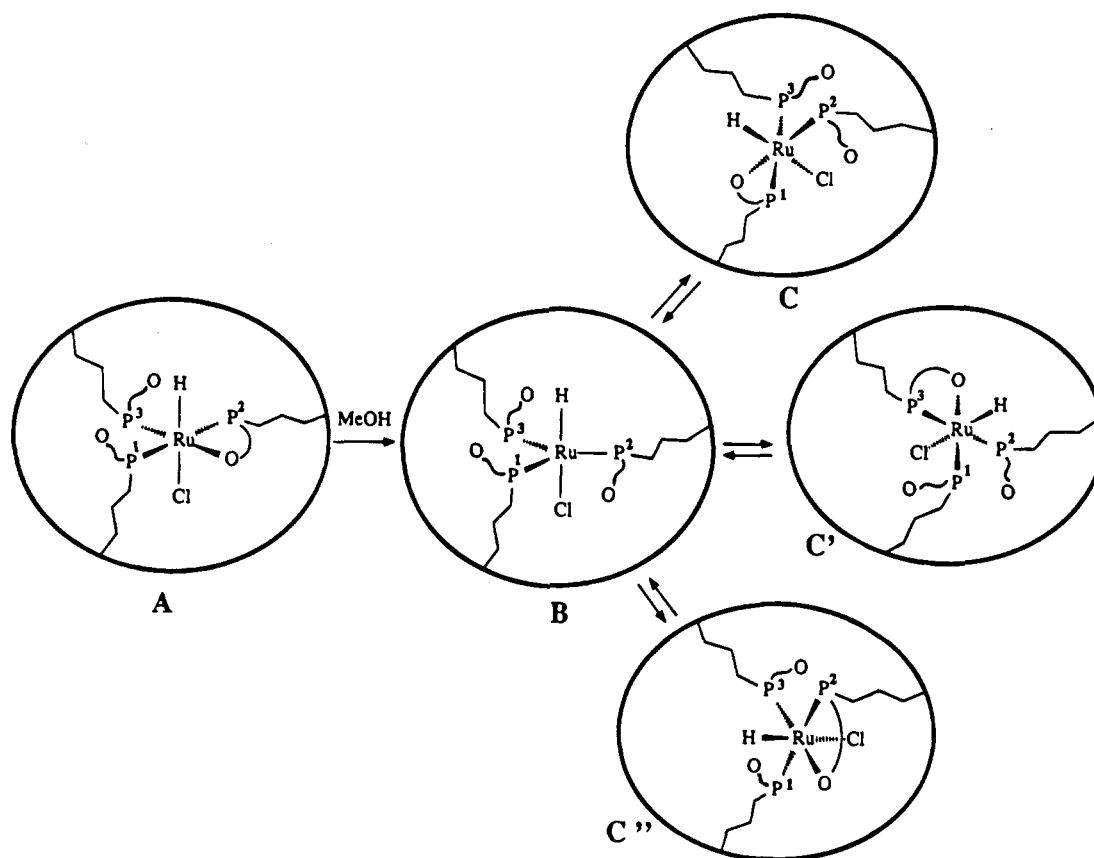Figure 4. Solid-state ^{31}P CP-MAS NMR spectra (81 MHz) of **3d'**-(T^n)$_3$ + MeOH (A, 20 °C, ν = 3.5 kHz) and after reaction with carbon monoxide (B, 20 °C, ν = 3.5 kHz).

bonyl complex HRuCl(CO)(P∼O)$_3$ [**5d'(T^n)$_3$**] is observed, generating two broad signals according to two different environments of the phosphorus sites (P^1, P^2) (Table 4). Because in the acetato complexes **4b'(T^n)$_3$**, **4d'(T^n)$_3$** and the carbonyl complexes **5b'(T^n)$_3$**, **5d'(T^n)$_3$** the weakly coordinated oxygen moiety is replaced by the stronger donating ligands O$_2$CMe and CO, respectively, the easy accessible coordination site is blocked preventing the O,P ligands to form chelates and thus suppress the exchange process (Schemes 2 and 3).

Table 3. ^{31}P CP-MAS NMR and IR Data of the Polysiloxane-Bound Compounds **4b'(T^n)$_3$**, **4d'(T^n)$_3$**, **5b'(T^n)$_3$**, **5d'(T^n)$_3$**, **6b'(T^n)$_2$**, **6d'(T^n)$_2$**

compound	$\delta(^{31}$P) (ppm)	ν(CO) (cm^{-1})^a
4b'(T^n)$_3$	55.2 (P^1), 40.1 (P^2)	1559,^{b} 1459^c
4d'(T^n)$_3$	57.0 (P^1), 41.6 (P^2)	1558,^{b} 1457^c
5b'(T^n)$_3$^{d}	17.0 (P^2), −0.5 (P^1)	1914
5d'(T^n)$_3$^{e}	18.7 (P^2), −0.9 (P^1)	1919
5d'(T^n)$_3$^{f}	18.9 (P^2), −0.7 (P^1)	1919
6b'(T^n)$_2$^{g}	20.6, −32.8 [**1b'(T^n)**]	2041, 1963
6d'(T^n)$_2$^{h}	20.9, −32.4 [**1d'(T^n)**]	2043, 1963
6d'(T^n)$_2$^{i}	21.0, −32.4 (**1d'(T^n)**]	2043, 1963

^{a} KBr. ^{b} ν_{as}(CO$_2$). ^{c} ν_s(CO$_2$). ^{d} From **5b(T^0)$_3$**. ^{e} From **5d(T^0)$_3$**. ^{f} From **3d'(T^n)$_3$**. ^{g} From **5b'(T^n)$_3$** via **5b(T^0)$_3$**. ^{h} From **5d'(T^n)$_3$** via **3d'(T^n)$_3$**. ^{i} From **5d'(T^n)$_3$** via **5d(T^0)$_3$**.

The polysiloxane-bound tris(ether−phosphine)ruthenium(II) complexes HRuCl(CO)(P∼O)$_3$ [**5b'(T^n)$_3$**, **5d'(T^n)$_3$**] reversibly replace one O,P ligand by carbon monoxide at 80 °C to give the complexes HRuCl(CO)$_2$(P∼O)$_2$ [**6b'(T^n)$_2$**, **6d'(T^n)$_2$**] (Scheme 2).^{24} After addition of CO the signal of the non-coordinated O,P ligand [**1b'(T^n)**, **1d'(T^n)**] is observed in the solid state ^{31}P CP-MAS NMR spectrum of **6b'(T^n)$_2$**, **6d'(T^n)$_2$** (Table 3).^{24}

Investigation of the Dynamic Parameters. If one is able to compare the relaxation parameters T_{1P} and $T_{1\rho H}$ and the cross polarization constant T_{PH} of similar systems, further insight into their dynamics can be obtained.$^{30-35}$ The dynamic parameters

(30) Voelkel, R. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1468.

(31) Harris R. K. *Analyst* **1985**, *110*, 649−655.

(32) Koenig, J. L.; Andreis, M. *Solid State NMR of Polymers;* Mathias, L. J., Ed.; Plenum Press: New York, 1991; 201−213.

(33) Komoroski, R. A. *High Resolution NMR Spectroscopy of Synthetic Polymers in Bulk;* VCH Publishers, Inc.: Deerfield Beach, FL, 1986; pp 63−226, 247−306.

(34) Pfleiderer, B.; Albert, K.; Bayer, E.; van den Ven, L.; de Haan, J.; Cramers, C. *J. Phys. Chem.* **1990**, *94*, 4189−4194.

Table 4. Dynamic and Chemical Behavior of Polysiloxane-Bound $3d'(T^n)_3$ Compared with $5d'(T^n)_3$

compound	$\delta(^{31}P)$(CP/MAS) (ppm)	T_{PH} (ms)[a]	$T_{1\rho H}$ (ms)[b]	T_{1P} (s)[c]
$5d'(T^n)_3{}^d$	18.7 (P²)	0.17	5.99	6.08
	-0.9 (P¹)	0.20	6.00	6.13
$3d'(T^n)_3$	35.1 (P¹, P²)	0.18	3.72	0.63
	52.8 (P³)	0.19	3.89	0.65
$3d'(T^n)_3$ + MeOH	40.8 (P¹, P², P³)	0.89	10.52	1.77
$3d'(T^n)_3$ + MeOH	40.8 (P¹, P², P³)	0.69	9.79	2.35
and	18.7 (P²)	0.34	4.12	3.75
$5d'(T^n)_3$ + MeOH	-0.7 (P¹)	0.35	4.19	3.94

(between the two MeOH groups: ↓ CO)

[a] Variation of the contact time. [b] According to Schaefer et al.[35] [c] According to Torchia. [d] From $5d(T^0)_3$.

T_{1P}, $T_{1\rho H}$, and T_{PH} of $3d'(T^n)_3$ and $5d'(T^n)_3$ are listed in Table 4. The P atoms of the η^1-coordinated ether–phosphine ligands in the complex $5d'(T^n)_3$ show the expected values.[19] Compared to the carbonyl complex $5d'(T^n)_3$, "dry" $3d'(T^n)_3$ reveals similar T_{PH} constants, however, the $T_{1\rho H}$ and in particular the T_{1P} values are smaller. This result indicates a chemical exchange of the ether–phosphine ligands in $3d'(T^n)_3$ already in the nonswollen state. After treatment with methanol the T_{PH}, $T_{1\rho H}$, and T_{1P} times of $3d'(T^n)_3$ + MeOH increase. The exchange of the highly mobile ether–phosphine ligands requires a longer contact time for the cross polarization of the posphorus nuclei.[22,30,32,36] The remarkable increase of the $T_{1\rho H}$ and T_{1P} relaxation times can be explained by the enhanced mobility of the P atoms as well. Due to the "liquid-like behavior" of the fluxional complex $3d'$-$(T^n)_3$ in its swollen gel matrix, even in the $^{31}P\{^1H\}$ NMR spectrum (suspension of $3d'(T^n)_3$ in MeOH at $-30\ °C$) the exchange signal of P¹, P², and P³ of the intermediates C, C', C'' [δ 42.5 ($\nu_{1/2}$ = 54 Hz), Scheme 3] can be observed. The ^{31}P CP-MAS NMR spectroscopic investigations performed on a sample of the "reaction mixture" which contains $3d'(T^n)_3$ + MeOH and $5d'(T^n)_3$ + MeOH are in agreement with these findings (Table 4). In this case the two complexes in the swollen gel matrix show different $T_{1\rho H}$ values compared to the separated complexes (Table 4). Thus, due to the mobility of $3d'(T^n)_3$ + MeOH, the dipolar coupling among the protons ("spin-diffusion process"[30–33]) is not efficient to average the $T_{1\rho H}$ values.

Conclusion. The chemical exchange of the ether oxygen donors in the ether–phosphine ligands of the polysiloxane-bound ruthenium complexes $HRuCl(P{\sim}O)_2(P{\frown}O)$ [$3b'(T^n)_3$, $3d'(T^n)_3$] is enabled by the swelling of the polymer which results in the higher mobility of the reaction centers. This affords a "conventional" $^{31}P\{^1H\}$ NMR spectrum in suspension by its "liquid-like" character even without a high power decoupling of the protons. The fluxional process is slowed down by decreasing the temperature and it is stopped by the addition of one donor molecule to the "vacant" coordination site at the ruthenium complexes. Thus the "classical" exchange of the ether–phosphine ligands in transition metal complexes in

solution is transferable to polymeric interphase systems. In spite of the high mobility in the interphases, the liquid phase is still not reached. This is demonstrated by the anisotropy of the fast exchange signal of the species C, C', C'' (spinning side bands Figure 4A), and by the fact that the interphases can be studied by cross polarization techniques (slow narrowing limit).

Experimental Section

Instrumentation. The elemental analyses were carried out on a Carlo Erba analyzer, Model 1106. IR data were obtained on a Bruker IFS 48 FT-IR spectrometer. The solution $^{31}P\{^1H\}$ and ^1H NMR spectra were recorded on a Bruker AC 80 spectrometer; the frequencies, standards, and temperatures were as follows. $^{31}P\{^1H\}$ NMR: 32.438 MHz, external 1% H_3PO_4 in acetone-d_6, 243 K. ^1H NMR: 80.13 MHz, residual protons of the solvents vs TMS, 300 K. The high-frequency-positive convention has been used in reporting all chemical shifts δ (ppm). Mass spectra (field desorption) were acquired on a Finnigan MAT 711A modified by "Mess- and Datensysteme" (8 kV, 60 °C) and are reported as mass/charge (m/z).

The solid-state NMR spectra were recorded on a Bruker MSL 200 and ASX 300 spectrometer with a wide-bore magnet (4.7 and 7.05 T) using samples of 200–400 mg in double-bearing rotors of ZrO_2. Magic-angle spinning was routinely performed at 4 and 8 kHz spinning rates at 297 K unless otherwise stated. All measurements were carried out under exclusion of molecular oxygen. Frequencies and standards: ^{31}P, 81.0 and 121.49 MHz ($NH_4H_2PO_4$); ^{13}C, 50.325 MHz [TMS, carbonyl resonance of glycine (δ = 170.09) as second standard]; ^{29}Si, 39.75 MHz (Q_8M_8).[37] Typically, the proton 90° pulse lengths for ^{31}P and ^{13}C CP-MAS NMR spectra were 5.0 and 7.5 μs for ^{29}Si. The spectra were recorded using spectral widths of 40 and 70 kHz (^{31}P), 20 kHz (^{13}C), and 10 kHz (^{29}Si). The repetition time was 2 s for CP-MAS NMR and 4 s for ^{31}P and ^{13}C MAS NMR spectra with ^1H high power decoupling (SPE). ^{13}C CP-MAS NMR spectra were recorded either with a ^1H FLIP-back pulse or by using the TOSS[38] technique. The cross polarization constants T_{PH} and T_{CH} were determined by variation of the contact time (20–25 suitable experiments).[36] The proton relaxation time in the rotating $T_{1\rho H}$ was measured by direct proton spin lock–τ–CP experiment as described by Schaefer and Stejskal.[35] The $T_{1\rho H}$ values were obtained by a single-exponential fit of the magnetization decays and were reproducible to ±5%. All the relaxation time data were obtained by using the Bruker software SIMFIT. For quantification of the silyl species T^1, T^2, and T^3 in the polysiloxane-bound complex $3d'(T^n)_3$, ^{29}Si CP-MAS NMR spectra at contact times of 3 and 5 ms were recorded. Both data sets were fitted by the Bruker deconvolution software GLINFIT (Gaussian lineshapes were used) . Due to similar T_{SiH} and $T_{1\rho H}$ data of the different silyl species in these polymers[19] the relative peak areas of the signals of the species in both fits showed a maximum discrepancy of 10% and were averaged.

Monomers, General Procedures. All manipulations were performed under argon by employing the usual Schlenk techniques. Methanol was dried with magnesium and distilled from $Mg(OMe)_2$. Acetone was distilled from $MgSO_4$. n-Hexane and toluene were distilled from sodium–benzophenone ketyl. H_2O was distilled under argon before use. The starting complex $HRuCl(CO)(PPh_3)_3$ (2)[39] and the ether–phosphines 1a,[40] 1c,[41] 1b,[42] and 1d[42] were synthesized as previously described.

General Procedure for the Synthesis of the Monomeric Complexes 3a–d. A suspension of 3 equiv of the ether–phosphine ligands 1a–d and 1 equiv of the ruthenium complex $HRuCl(PPh_3)_3$ (2) in

(35) Schaefer, J.; Stejskal, E. O.; Buchdahl, R. *Macromolecules* **1977**, *10*, 384–405.

(36) Mehring, M. *Principles of High Resolution NMR in Solids*, 2nd ed.; Springer-Verlag: Berlin, Heidelberg, Germany, New York, 1983; 143–155.

(37) Lippmaa, E.; Samoson, A. *Bruker Rep.* **1982**, *1*, 6.

(38) Dixon, W. T.; Schaefer, J.; Sefcik, M. D.; Stejskal, E. O.; McKay, R. A. *J. Magn. Reson.* **1982**, *49*, 341–345.

(39) Ahmad, N.; Levison, J. J.; Robinson, S. D.; Uttley, M. F. *Inorg. Synth.* **1974**, *15*, 48.

(40) Lindner, E.; Meyer, S.; Wegner, P.; Karle, B.; Sickinger, A.; Steger, B. *J. Organomet. Chem.* **1987**, *335*, 59–70.

(41) Lindner, E.; Mayer, H. A.; Wegner, P. *Chem. Ber.* **1986**, *119*, 2616–2630.

(42) Lindner, E.; Bader, A.; Glaser, E.; Pfleiderer, B.; Schumann, W.; Bayer, E. *J. Organomet. Chem.* **1988**, *355*, 45–53.

toluene was refluxed for 10 min. After removal of the solvent under vacuum, the light-yellow oils were dissolved in *n*-hexane (50 mL) at 60 °C. Separation of PPh$_3$ was achieved by allowing the mixture to stand overnight at −50 °C. For a quantative separation of PPh$_3$ this procedure was repeated.

Chlorohydridotris[diphenyl(2-methoxyethyl)phosphine-*P*;*P*′;-*O*″,*P*″]ruthenium(II) (3a). A suspension of 1a (576 mg, 2.36 mmol) and of 2 (727 mg, 0.787 mmol) in toluene (20 mL) was refluxed for 10 min. After treatment with *n*-hexane a yellow powder is formed which is sensitive to air and light (3a, 500 mg, 73%): ¹H NMR (C$_6$D$_6$) δ −17.7 [q, ²*J*(PH) = 25.3 Hz, RuH]; IR (KBr) 3072, 3051, 2983, 2919, 2872, 2819, 2801, ν(RuH) 2015, 1432, ν(C$_2$O) (P∼O) 1100, ν-(C$_2$O) (P⏜O) 1073, 980, 954, 829, 743, 695, 542, 502, 455 cm⁻¹; mass spectrum *m/z* 625.4 (M⁺ − 1a, 40), 660 (M⁺ − H − 1a + Cl, 100). Anal. Calcd for C$_{45}$H$_{52}$ClO$_3$P$_3$Ru: C, 62.10; H, 6.02; Cl, 4.07. Found: C, 62.21; H, 5.92; Cl, 4.71.

Chlorohydridotris[diphenyl(tetrahydrofuranyl-2-methyl)phosphine-*P*;*P*′;*O*″,*P*″]ruthenium(II) (3c). A suspension of 1c (554 mg, 2.05 mmol) and of 2 (632 mg, 0.683 mmol) in toluene (20 mL) was refluxed for 15 min and treated with *n*-hexane to form a yellow powder which is sensitive to air (3c, 544 mg, 84%): ¹H NMR (C$_6$D$_6$) δ −17.1 [q, ²*J*(PH) = 25.3 Hz, RuH]; IR (KBr) 3048, 2963, 2911, 2873, 2847, ν(RuH) 1975, 1432, ν(C$_2$O) (P∼O) 1091, ν(C$_2$O) (P⏜O) 1044/1022, 922, 892, 797, 743, 694, 539, 522, 492 cm⁻¹; mass spectrum *m/z* 678 (M⁺ − 1c, 20). Anal. Calcd for C$_{51}$H$_{58}$ClO$_3$P$_3$Ru: C, 64.58; H, 6.16; Cl, 3.74. Found: C, 63.91; H, 5.58; Cl, 4.37.

Chlorohydridotris[(2-methoxyethyl)phenyl(3-(trimethoxysilyl)-propyl)phosphine-*P*′;*P*′;*O*″,*P*″]ruthenium(II)(T⁰)$_3$ (3b). A suspension of 1b (845 mg, 2.558 mmol) and of 2 (788 mg, 0.853 mmol) in toluene (10 mL) was refluxed for 10 min. After treatment with *n*-hexane a yellow oil is obtained which is sensitive to air (3b, 520 mg, 70%): ¹H NMR (C$_6$D$_6$) δ −19.0 [q, ²*J*(PH) = 25.1 Hz, RuH]. Anal. Calcd for C$_{45}$H$_{82}$ClO$_{12}$P$_3$RuSi$_3$: C, 48.94; H, 7.32; Cl, 3.14. Found: C, 49.63; H, 7.50; Cl, 3.62.

Chlorohydridotris[phenyl(tetrahydrofuranyl-2-methyl)(3-(tri-methyloxysilyl)propyl)phosphine-*P*;*P*′;*O*″,*P*″]ruthenium(II)(T⁰)$_3$ (3d). A suspension of 1d (1.796 g, 5.04 mmol) and of 2 (1.553 g, 1.68 mmol) in toluene (20 mL) was refluxed for 10 min and treated with *n*-hexane to form a yellow resin which is sensitive to air (3d, 1.083 g, 58%): ¹H NMR (C$_6$D$_6$) δ −19.1 [q, ²*J*(PH) = 25.3 Hz, RuH]. Anal. Calcd for C$_{51}$H$_{88}$ClO$_{12}$P$_3$RuSi$_3$: C, 51.75; H, 7.35; Cl, 2.94. Found: C, 52.39; H, 7.57; Cl, 3.84.

Chlorohydridotris[(2-methoxyethyl)phenyl(polysiloxanylpropyl)-phosphine-*P*;*P*′;*O*″,*P*″]ruthenium(II)(Tⁿ)$_3$ [3b′(Tⁿ)$_3$]. A mixture of 3b (520 mg, 0.461 mmol), water (45 mg, 2.49 mmol), and catalytic amounts of NEt$_3$ (11.0 mg, 0.1 mmol) was polycondensated in ethanol (3 mL) within 8 h to a yellow, pyrophoric compound. After drying under vacuum the polymer was stirred for 8 h in *n*-hexane (two times in 100 mL). Then *n*-hexane was decanted and the product was dried for 4 h under vacuum [3b′(Tⁿ)$_3$, 438 mg, 103%]: IR (KBr) 3404, 3054, 2936, 2838, 1435, 1166, 1102, 953, 811, 744, 698, 542, 505, 462 cm⁻¹. Anal. Calcd for C$_{36}$H$_{55}$ClO$_{7.5}$P$_3$RuSi$_3$: C, 46.92; H, 5.55; Cl, 3.55; Ru, 10.97. Found: C, 44.66; H, 5.96; Cl, 3.81; Ru, 10.45.

Chlorohydridotris[phenyl(tetrahydrofuranyl-2-methyl)(polysi-loxanylpropyl)phosphine-*P*;*P*′;*O*″,*P*″]ruthenium(II)(Tⁿ)$_3$ [3d′(Tⁿ)$_3$]. A mixture of 3d (1.083 g, 0897 mmol), of water (87 mg, 4.85 mmol), and catalytic amounts of NEt$_3$ (21 mg, 0.2 mmol) was polycondensated in ethanol (6 mL) within 8 h to a yellow, relatively stable compound. After this was dried under vacuum, the polymer was then stirred for 8 h in *n*-hexane (two times in 100 mL). Then *n*-hexane was decanted and the product was dried for 4 h under vacuum [3d′(Tⁿ)$_3$, 906 mg, 101%]: ¹³C CP-MAS NMR (FLIP, 3.8 kHz) δ 129.1 (C-*i,o,m,p*), 80.3 (C-6, P⏜O), 74.6 (C-6, P∼O), 67.8 (C-8), 33.2 (C-3,5,10), 25.9 (C-9), 18.0 - 13.0 (C-1,2); 3d′(Tⁿ)$_3$ + MeOH: ¹³C CP-MAS NMR (FLIP, 3.8 kHz) δ 131.9 (C-*o*), 130.6 (C-*m*), 129.0 (C-*p*), 80.3 (very broad, C-6, P⏜O), 73.7 (very weak, C-6, P∼O), 67.6 (narrow signal, C-8), 49.4 (CH$_3$OH), 32.9 (C-3,5,10), 25.5 (C-9), 18.0 - 13.0 (C-1,2); ¹³C

MAS NMR (SPE, recycle delay 0.8 s, 3.9 kHz) δ 138.0 (C-*i*), 131.9 (C-*o*), 129.0 (C-*m,p*), 73.6 (C-6, P∼O), 67.5 (C-8), 49.4 (CH$_3$OH), 32.8 (C-3,5,10), 25.4 (C-9), 18.0 - 13.0 (C-1,2); ²⁹Si CP-MAS NMR δ −50.5 (T¹), −58.8 (T²), −66.2 (T³); IR (KBr) 3387, 3053, 2941, 2879, 1435, 1098, 937, 794, 744, 696, 506, 458 cm⁻¹. Anal. Calcd for C$_{42}$H$_{61}$ClO$_{7.5}$P$_3$RuSi$_3$: C, 50.46; H, 6.15; Cl, 3.55; Ru, 10.11. Found: C, 49.43; H, 5.47; Cl, 3.95; Ru, 9.95.

Synthesis of the Polymeric Acetato Complexes ClRu(O$_2$CMe)-(P∼O)$_3$ [4b′(Tⁿ)$_3$, 4d′(Tⁿ)$_3$] from 3b′(Tⁿ)$_3$ or 3d′(Tⁿ)$_3$ and Acetic Acid. To a suspension of 3b′(Tⁿ)$_3$ or 3d′(Tⁿ)$_3$ (in each case 300 mg, 0.325 and 0.300 mmol, respectively) in ethanol (10 mL) concentrated acetic acid (60 mg, 1.0 mmol) was added. After completion of the H$_2$ generation the reaction mixture was stirred for 4 h and 50 mL of *n*-hexane were added. After 15 min the supernatant solution was decanted and the residue was washed with water (three times with 8 mL), centrifuged, and dried under vacuum. The acetato complexes were characterized spectroscopically (Table 3 and Figure 4).

Carbonylchlorohydridotris[(2-methoxyethyl)phenyl(polysiloxa-nylpropyl)phosphine-*P*′,*P*′,*P*″]ruthenium(II)(Tⁿ)$_3$ [5b′(Tⁿ)$_3$]. A mixture of the monomeric complex HRuCl(CO)(P∼O)$_3$ (5b) (313 mg, 0.33 mmol), water (35 mg, 1.93 mmol), and (*n*-Bu)$_2$Sn(OAc)$_2$ (10 mg, 0.03 mmol) in 2 mL of EtOH was polycondensated according to method 1[19] to give a light gray polymer. The product was processed as described elsewhere.[24] [5b′(Tⁿ)$_3$, 281 mg, 89%]: ¹³C CP-MAS NMR (3.3 kHz) δ 138.5 (C-*i*), 129.5 (C-*o,m,p*), 68.4 (C-6), 57.9 (C-8), 50.4 (SiOCH$_3$), 26.6 (C-3,5), 17.5 (C-2), 13.9 (C-1); ²⁹Si CP-MAS NMR (FLIP, 3.9 kHz) δ −49.7 (T¹), −57.0 (T²), −66.5 (T³); IR (KBr) 3426, 3052, 2929, 2886, 2840, ν(CO) 1914, 1434, 1171, 1105, 1027, 955, 815, 744, 696, 668, 594, 501 cm⁻¹. Anal. Calcd for C$_{37}$H$_{55}$ClO$_{8.5}$P$_3$RuSi$_3$: C, 46.80; H, 5.84; Cl, 3.73; Ru, 10.65. Found: C, 44.81; H, 6.05; Cl, 3.38; Ru, 9.75.

Carbonylchlorohydridotris[phenyl(tetrahydrofuranyl-2-methyl)-(polysiloxanylpropyl)phosphine-*P*,*P*′,*P*″]ruthenium(II)(Tⁿ)$_3$ [5d′-(Tⁿ)$_3$]. A mixture of the monomeric complex HRuCl(CO)(P∼O)$_3$ [5d(T⁰)$_3$] (716 mg, 0.58 mmol), of water (71 mg, 3.92 mmol) and of (*n*-Bu)$_2$Sn(OAc)$_2$ (10 mg, 0.03 mmol) in 3 mL of EtOH was polycondensated according to method 1[19] to give a light gray polymer. The product was processed as described elsewhere.[24] [5d′(Tⁿ)$_3$, 590 mg, 99%]: IR (KBr) 3395, 3052, 2938, 2874, ν(CO) 1919, 1434, 1165, 1091, 934, 789, 743, 696, 668, 596, 501, 460 cm⁻¹. Anal. Calcd for C$_{43}$H$_{62}$ClO$_{7.5}$P$_3$RuSi$_3$: C, 50.25; H, 6.08; Cl, 3.45; Ru, 9.84. Found: C, 49.73; H, 6.19; Cl, 2.75; Ru, 9.70.

Carbonylchlorohydridotris[phenyl(tetrahydrofuranyl-2-methyl)-(polysiloxanylpropyl)phosphine-*P*,*P*′,*P*″]ruthenium(II)(Tⁿ)$_3$ [5d′-(Tⁿ)$_3$] from 3d′(Tⁿ)$_3$. Following a ³¹P solid state NMR spectroscopic investigation of 3d′(Tⁿ)$_3$, the polymer which was swollen in MeOH was subjected for 15 min to a CO pressure of 2 bar in a ZrO$_2$ spinner. The repeated measured solid-state NMR and IR spectra are in agreement with the formation of 5d′(Tⁿ)$_3$ (Table 4, Figure 4).

Behavior of the Polysiloxane-Bound Complexes 5b′(Tⁿ)$_3$, 5d′(Tⁿ)$_3$ toward Carbon Monoxide. Formation of the Complexes 6b′(Tⁿ)$_2$, 6d′(Tⁿ)$_2$. The carefully dried polymers 5b′(Tⁿ)$_3$, 5d′(Tⁿ)$_3$ (in each case 300 mg, 0.211 and 0.195 mmol, respectively) are heated to 70 °C under a CO pressure of 2 bar (pressure Schlenk tube). Within 1 h the complexes 6b′(Tⁿ)$_2$ and 6d′(Tⁿ)$_2$ and the liberated ether−phosphine ligands 1b′(Tⁿ) and 1d′(Tⁿ) are detected by ³¹P solid-state NMR and IR spectroscopy. When 6b′(Tⁿ)$_2$, 6d′(Tⁿ)$_2$ are flushed with argon at 70 °C, the starting polymers 5b′(Tⁿ)$_3$, 5d′(Tⁿ)$_3$ are formed again (Table 3).