

Accessibility Studies of Sol-Gel Processed Phosphane-Substituted Iridium(I) Complexes in the Interphase^[‡]

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Dedicated to Professor Gottfried Huttner on the occasion of his 65th birthday

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The synthesis of the T-silyl functionalized, and therefore sol-gel processable, Vaska complex $[\text{IrCl}(\text{CO})\{(\text{C}_6\text{H}_5)_2\text{PC}_6\text{H}_4-(\text{CH}_2)_4\text{Si}(\text{OMe})_3\}_2]$ **[4(T⁰)]** succeeded by reaction of $[\text{Ir}(\mu\text{-Cl})(\text{COE})_2]_2$ (COE = cyclooctene; **1**) with the phosphane $(\text{C}_6\text{H}_5)_2\text{PC}_6\text{H}_4(\text{CH}_2)_4\text{Si}(\text{OMe})_3$ **[3(T⁰)]** in the presence of carbon monoxide. Subsequently, **4(T⁰)** was co-polycondensed with five equivalents of $(\text{MeO})_3\text{Si}(\text{CH}_2)_3\text{C}_6\text{H}_4(\text{CH}_2)_3\text{Si}(\text{OMe})_3$ **[5[Ph(1,4-C₃T⁰)₂]]** to give the polysiloxane-bound complex **X1**. For accessibility studies of the reactive centers, **X1** was

reacted in the interphase systems gas/solid and liquid/solid with HCl, Cl₂, CH₃I (¹³CH₃I), Cl₂HCCHCl₂, SO₂, O₂, and NCC≡CCN, in the course of which the xerogels **X2–X7** were formed. With the exception of the reversible species **X5** (SO₂) and **X6** (O₂) the reactions proceeded quantitatively. The composition of the polymers and the structures of the reactive centers were elucidated by means of multinuclear solid-state NMR (¹³C, ²⁹Si, ³¹P), IR, EDX, and EXAFS spectroscopy.

Introduction

In the last few years polymer-supported catalysts have evolved into an area of intensive research with the goal of combining the advantages of homogeneous and heterogeneous catalysis.^[1–10] The catalysts are easily separable from the reaction products and they can be used for several runs, although frequently with some loss of activity due to metal leaching. In addition the reactive centers are very often not well defined, which also causes a decrease of the activity and selectivity. So far these drawbacks have prevented a commercial application of heterogenized catalysts. A versatile approach to reduce or even eliminate these problems is

the introduction of the concept of an interphase.^[11–14] Interphases are systems in which a stationary phase (comprised of a polymer, space, and reactive centers) and a mobile component (gas, liquid, or dissolved reactants) penetrate each other on a molecular scale without forming a homogeneous phase. Stationary phases are usually generated by simultaneous co-condensation of T-silyl-functionalized transition metal complexes with various bifunctionalized alkoxy-silanes.^[15–20] This procedure affords the possibility of modifying materials by controlling the mobility of the entire polymer, the density, and the distance of the reactive centers as well as swelling capabilities.

A major problem intrinsic to interphases is that of low diffusion, which adversely influences the activity of the catalysts as not all reactive centers are readily accessible for the substrates. Excellent model systems for accessibility studies are iridium complexes, which are much more stable than their corresponding rhodium congeners.

The objective of this work was to study the performance of organometallic model reactions in interphases. Therefore the reactive behavior of an iridium(I) complex incorporated into a stationary phase towards a series of molecules with different shapes and sizes like oxygen, sulfur dioxide, dicyanoethyne, and different halogenated substrates was examined. The resulting products were characterized by several spectroscopic methods as well as by EXAFS and EDX.

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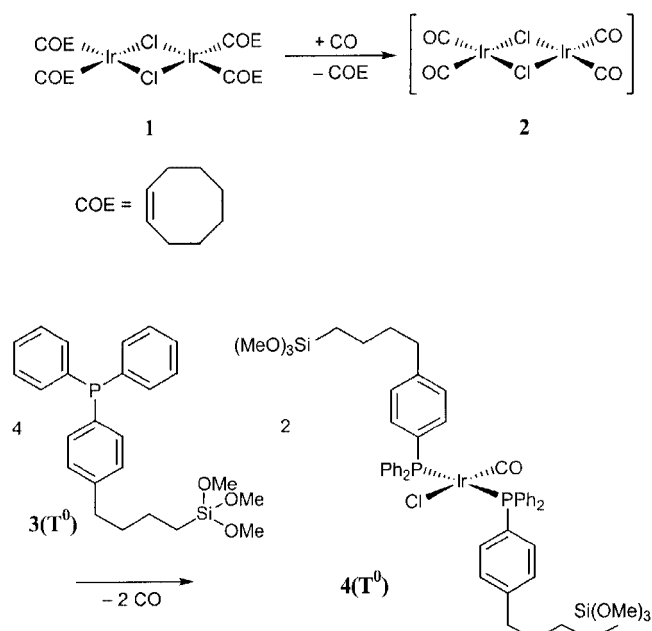
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Results and Discussion

Sol-Gel Processing of the Monomeric Iridium(I) Precursor Complex 4(T⁰)

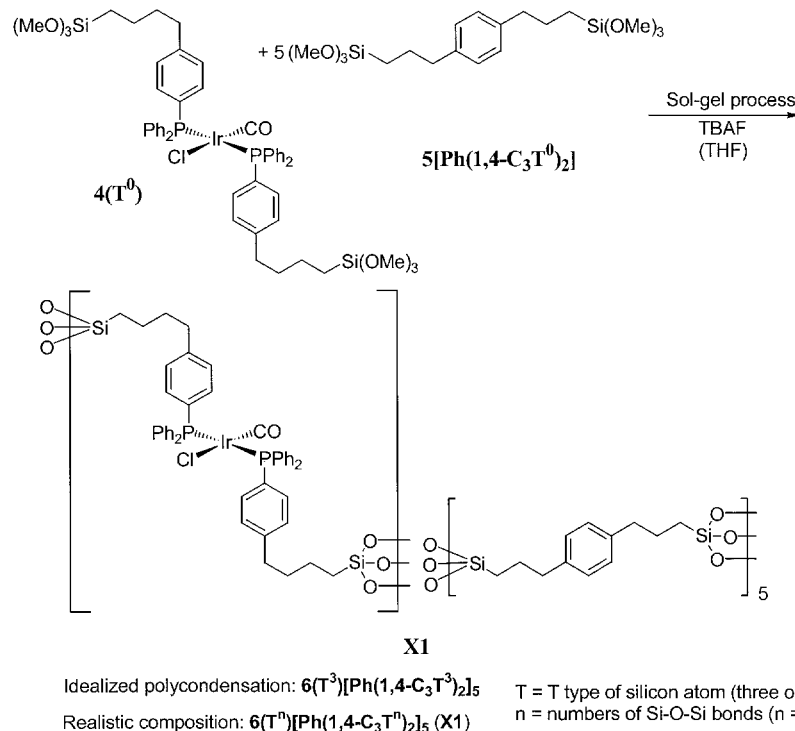
The iridium(I) complex 4(T⁰) was obtained by a modification of the synthetic pathway of Roberto et al. (Scheme 1).^[21] A stoichiometric amount of the T-silyl-func-



Scheme 1

tionalized phosphane ligand 3(T⁰)^[22] was added to an acetonitrile solution of [Ir(μ-Cl)(CO)₂]₂ (2) to give a light brown solution of 4(T⁰) which was subjected to the sol-gel process directly. A single peak in the ³¹P{¹H} NMR spectrum of 4(T⁰) at δ = 24.7 ppm and one ν(CO) absorption in the IR spectrum at 1966 cm⁻¹ indicated the completeness of the reaction.^[23,24]

A 1:5 mixture of the iridium complex 4(T⁰) and of the co-condensation agent 5[Ph(1,4-C₃T⁰)₂]^[18] was hydrolyzed and polycondensed in water/THF in the presence of tetrabutylammonium fluoride (TBAF) as catalyst at room temperature (Scheme 2). The resulting xerogel X1 was isolated as a pale yellow powder which is rather air stable. Only one signal, with a chemical shift of δ = 24.4 ppm, is observed in the ³¹P CP/MAS NMR spectrum of the polysiloxane-bound iridium(I) complex X1, in agreement with the spectrum of the monomeric complex 4(T⁰) measured in solution (Figure 1). To decide whether the phosphanes in X1 are *cis* or *trans* oriented to each other a *J*-resolved 2D ³¹P CP/MAS NMR spectrum according to a phase-cycled spin-echo-experiment was recorded (Figure 2).^[25] The observed ²J_{P,P} coupling constant of approximately 400 Hz is consistent with a *trans* configuration. In the ¹³C CP/MAS NMR spectrum of X1 all main signals stem from the co-condensing moiety. The missing signal for the Si-OMe function indicates a high degree of hydrolysis. All silicon atoms in the polysiloxane matrix are in the direct proximity of protons, therefore silyl species are detectable by cross polarization (CP). The signals in the ²⁹Si CP/MAS NMR spectrum of the copolymer X1 are located in the typical range for T-silyl functions and their substructures T² and T³ [δ = -57.3



Scheme 2

(T²), -65.7 ppm (T³)). The degree of condensation, which was determined by commonly used methods,^[26,27] is 87%. Spin-lattice relaxation times of the protons in the rotating frame ($T_{1\rho H}$) were determined by a direct spin lock- τ -CP experiment^[28] via the ²⁹Si and ³¹P nuclei. In all cases the observed decays of the magnetization were monoexponential. Thus the relaxation mechanism is spin-diffusion controlled and the material can be considered as homogenous. The formation of domains larger than 1–2 nm in diameter is excluded.

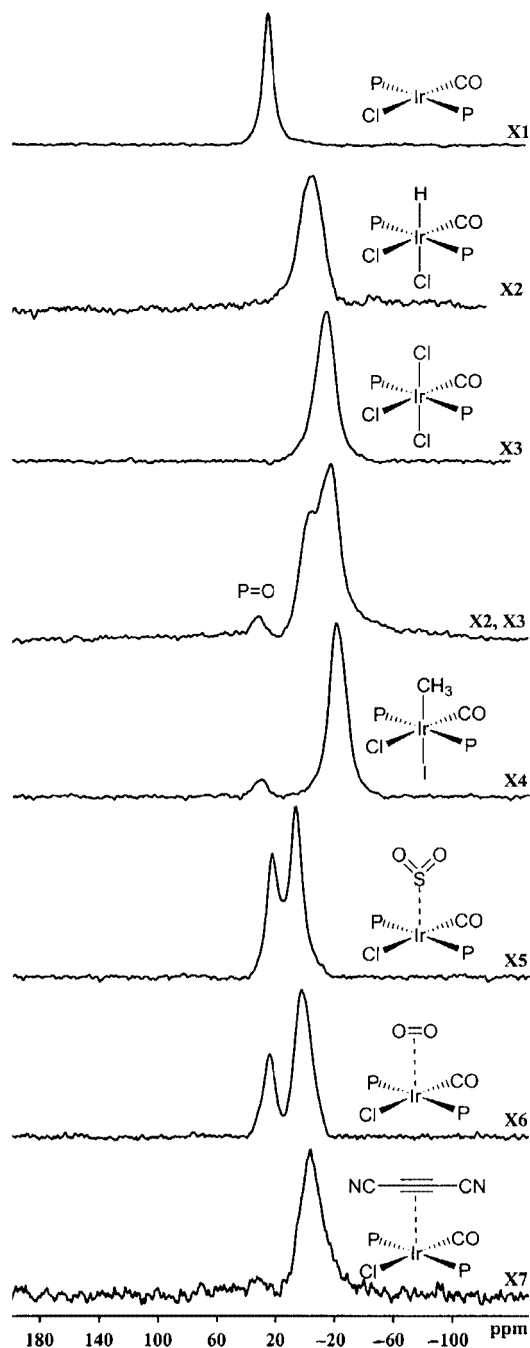


Figure 1. ³¹P CP/MAS NMR spectra of the stationary phases X1–X7

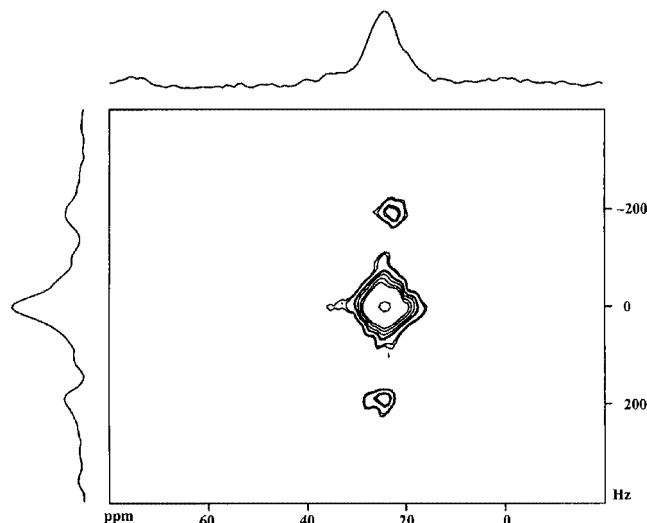


Figure 2. *J*-resolved 2D ³¹P CP/MAS NMR spectrum of X1

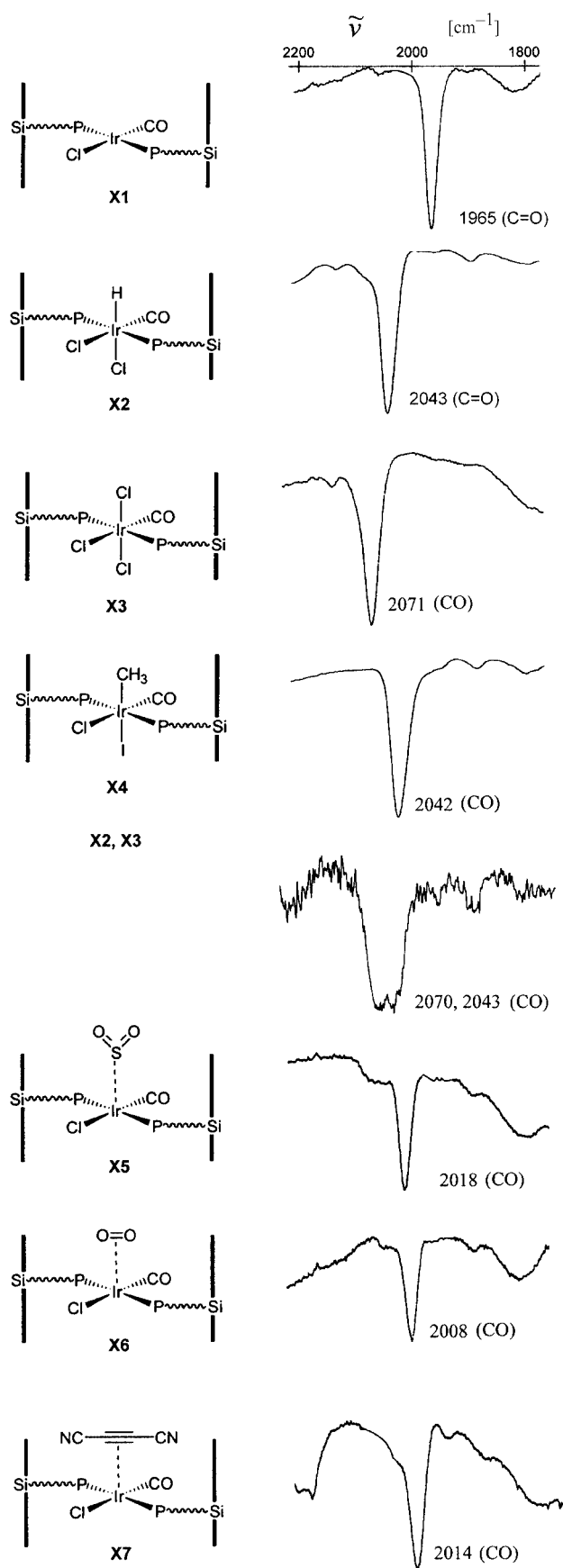
The $\nu(\text{CO})$ vibration (1965 cm^{-1}) in the IR spectrum of X1 is similar to that of 4(T⁰) in solution (Figure 3). The elemental composition of the stationary phase X1 was determined by EDX (Table 1).

Oxidative Addition Reactions on the Stationary Phase X1 with Hydrogen Chloride, Chlorine, Tetrachloroethane, and Methyl iodide (¹³C-Methyl Iodide)

Treatment of the solid X1 with hydrogen chloride or chlorine (interphase system: solid/gas) led to a color change from yellow to white and the polymer-anchored iridium complexes X2 and X3, respectively, were formed quantitatively. The ³¹P CP/MAS NMR and IR spectra are in full agreement with the data recorded for the corresponding monomeric complexes in solution (see Exp. Sect. and Figure 1 and 3).^[29]

In the case of the reaction between X1 and tetrachloroethane in benzene (interphase system: solid/liquid) a mixture of two different products was obtained. One component proved to be the meridional trichloroiridium(III) complex X3, the monomeric congener of which was described in earlier work by Al-Najjar.^[30] Interestingly the second species turned out to be complex X2, already isolated from the reaction between hydrogen chloride and X1. Obviously after initial oxidative addition of the C–Cl bond both a $\beta\text{-C-Cl}$ and a $\beta\text{-C-H}$ elimination take place at room temperature in a competitive reaction path. The ³¹P CP/MAS NMR spectrum reveals two resonances at $\delta = -3.0$ (X2) and -18.2 ppm (X3) (Figure 1).^[31] An unresolved broad absorption in the C≡O region between 2030 and 2080 cm^{-1} was found in the IR spectrum of this mixture (Figure 3). A direct comparison of these results with those of the known monomeric iridium(III) complexes^[29] confirms the adopted structures depicted in Scheme 3.

Methyl iodide could also be oxidatively added in benzene to the iridium complex in X1 in the interphase (solid/liquid) to give the air-stable light brown polymer X4 (Scheme 3). The carbonyl ligand gives rise to a strong absorption band at 2042 cm^{-1} , which is in accordance with literature values

Figure 3. IR spectra of the stationary phases **X1**–**X7**

for the corresponding monomeric complex in solution.^[32] Only one resonance is observed in the ^{31}P CP/MAS NMR of **X4** (Figure 1), indicating a complete conversion in the reaction. If ^{13}C -labeled methyl iodide was used an additional intense signal was observed in the ^{13}C CP/MAS NMR spectrum, which is consistent with an iridium-bound methyl group (Figure 4).

Reactions of the Stationary Phase **X1** with Sulfur Dioxide, Oxygen, and Dicyanoethyne

In the solid/gas and solid/liquid interphase systems the polysiloxane-bound iridium(I) complex **X1** was reacted with sulfur dioxide, oxygen, and dicyanoethyne to give the polymeric products **X5**, **X6**, and **X7**, respectively (Scheme 3). The C=O stretching vibration in the IR spectra of these materials confirmed a complete conversion. Absorptions at 1818, 2008, and 2014 cm^{-1} (Figure 3) were observed, which are shifted to higher wave numbers relative to **X1** (1966 cm^{-1}). These spectra were recorded under a sulfur dioxide (**X5**) or oxygen (**X6**) atmosphere. If these gases are removed, the spectrum of the starting compound **X1** appears again. However, the ^{31}P CP/MAS NMR spectra of **X5** and **X6** reveal two ^{31}P resonances (Figure 1). Since the rotors could not be packed under an oxygen or sulfur dioxide atmosphere a reversible reaction took place resulting in partial formation of the starting material **X1**. In contrast to this observation the dicyanoethyneiridium(I) complex **X7** shows only one ^{31}P signal at $\delta = -3.3$ ppm (Figure 1). These findings are in agreement with literature data^[33] for the monomeric congeners in which oxygen, dicyanoethyne, and sulfur dioxide are η^2 -, η^2 -, and η^1 -coordinated, respectively.

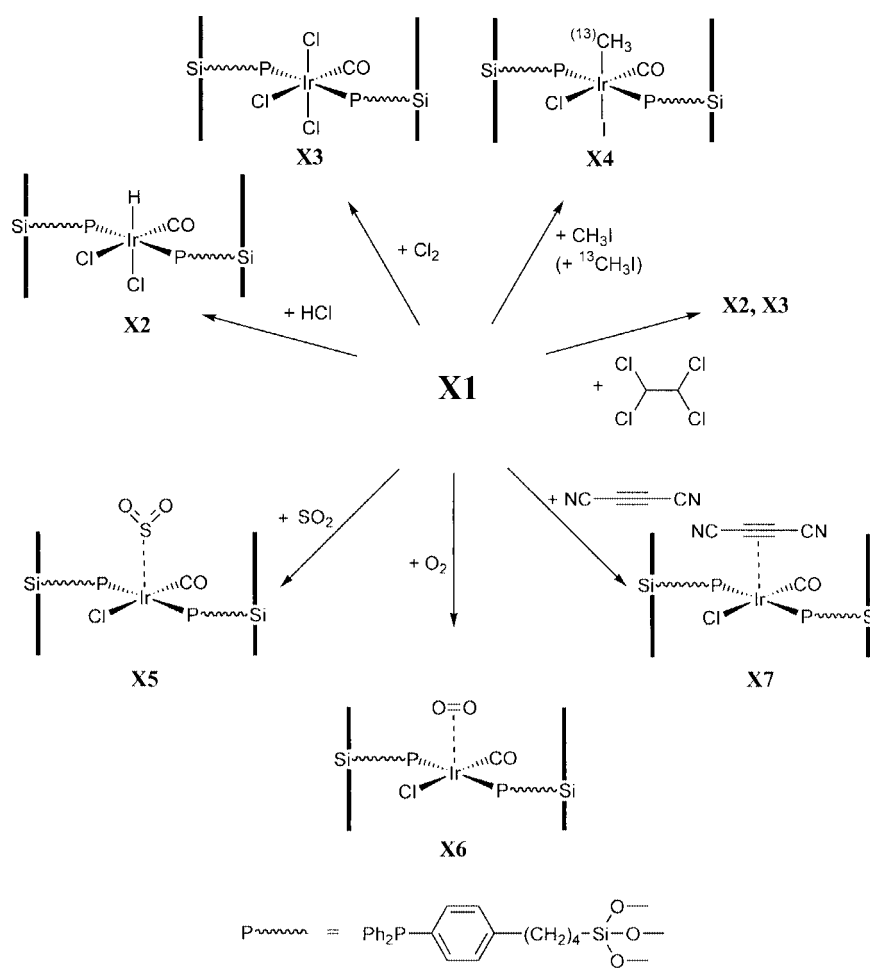
EXAFS and EDX Measurements of Selected Stationary Phases

One of the most powerful methods to obtain interatomic distances of amorphous materials is extended X-ray absorption fine structure spectroscopy (EXAFS). The xerogel **X4** was chosen as an example to determine the bond lengths between the metal center and the coordinating atoms of the ligand. The k^3 -weighted EXAFS function (see a in Figure 5) of **X4** can be described best by six different atom shells. The first intensive peak in the corresponding Fourier transform (see b in Figure 5) is mainly due to the carbon atoms. Chlorine and phosphorus atoms were found in the case of the most intense peak, and the third intense peak belongs to the iodine and oxygen atoms. For the most intense peak of the Fourier transform (see b in Figure 5), two equivalent phosphorus atoms and one chlorine atom, with Ir–P and Ir–Cl bond lengths of 2.40 and 2.46 Å, were found. These results reveal a good agreement between the experimental and the calculated functions. A significant improvement in the fit of the first intense peak was obtained if two carbon atoms with Ir–C1 (Ir–CO bond) and Ir–C2 (Ir–CH₃) bond lengths of 1.86 and 2.19 Å, respectively, are considered (see b in Figure 5). Additionally, one iodine and one oxygen atom, with an Ir–I bond length of 2.63 Å and

Table 1. Elemental analysis of compounds **X1**–**X4** by EDX; hydrogen cannot be measured by X-ray emission spectroscopy therefore the reference data have been renormalized to exclude hydrogen

Xerogel			Reference data ^[a] Composition [%]					EDX ^[b] Composition [%]						
	C	O	Si	P	Cl	Ir	I	C	O	Si	P	Cl	Ir	I
X1	57.54	13.87	15.38	2.83	1.62	8.77	–	59.33	15.54	13.87	2.60	1.19	7.47	–
X2	56.62	13.65	15.13	2.78	3.18	8.63	–	56.59	11.16	17.77	3.51	2.89	8.08	–
X3	55.74	13.43	14.89	2.74	4.70	8.50	–	58.78	14.58	13.14	3.18	4.76	5.56	–
X4	54.63	13.04	14.46	2.66	1.52	8.25	5.44	54.55	13.37	14.89	2.97	1.14	8.57	4.50

^[a] Calculated from theory. Complete condensation was assumed. ^[b] Quantified by the ZAF correction procedure.



Scheme 3

an Ir–O bond length of 3.08 Å, were detected, leading to an improvement of 7.4 and 18.9% in the fit, respectively. The interatomic distances of **X4** are similar to those in similar iridium(III) complexes such as $[\text{IrCl}_3(\text{CO})(\text{PPh}_3)_2]$,^[34] $[\text{IrCl}(\text{H})(\text{SH})\text{CO}(\text{PPh}_3)_2]$,^[35] and $[\text{Ir}(\text{OCIO}_3)(\text{CH}_3)(\text{H}_2\text{O})-(\text{CO})(\text{PPh}_3)_2]\text{ClO}_4$ ^[36] (Table 2).

The EDX spectra of compounds **X3** and **X4** are displayed in Figure 6. The K_α lines of carbon, oxygen, silicon, phosphorus, and chlorine and the L_α line of iridium are clearly visible. The M_α and M_β lines of iridium are overlapped by the K_α peak of phosphorus. In the case of **X4**, the L line series of iodine also appears in the spectrum. The increasing

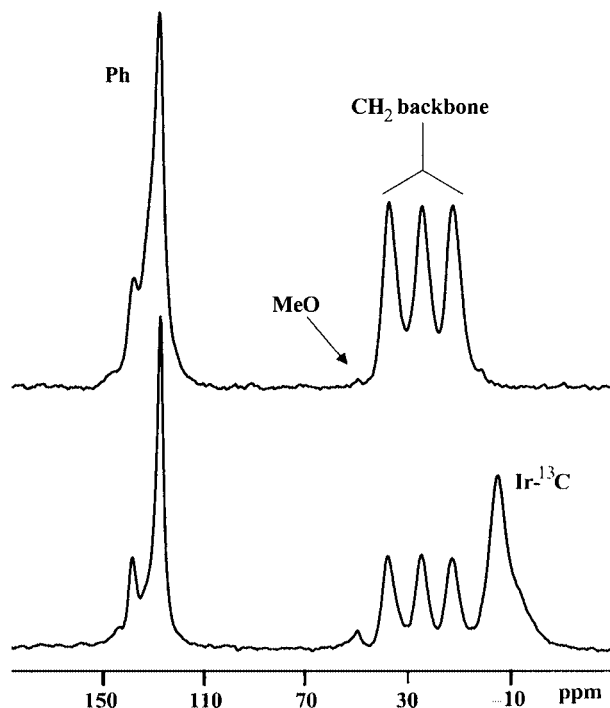


Figure 4. ^{13}C CP/MAS NMR spectra of the stationary phase **X4** (top: without ^{13}C labeling of the methyl iridium group; bottom: with ^{13}C labeling of the methyl iridium group)

content of chlorine in the xerogels **X1–X3** is evident as the intensity of the chlorine K line emission increases in the same direction.

Table 2. EXAFS-determined structural data of **X4**

	$N^{[a]}$	$r \text{ [Å]}^{[b]}$	$\sigma \text{ [Å]}^{[c]}$
Ir–C1 (CO) ^[d]	1	1.86 ± 0.02	0.050 ± 0.005
Ir–C2 (CH ₃) ^[d]	1	2.19 ± 0.02	0.095 ± 0.010
Ir–P ^[d]	2	2.40 ± 0.02	0.067 ± 0.010
Ir–C ^[d]	1	2.46 ± 0.03	0.097 ± 0.010
Ir–I ^[d]	1	2.63 ± 0.03	0.118 ± 0.012
Ir–O ^[d]	1	3.08 ± 0.03	0.050 ± 0.005

[a] Coordination number N . [b] Interatomic distance r . [c] Debye–Waller factor σ . [d] Absorber backscatterer.

Quantification of the EDX spectra was carried out using the ZAF correction procedure. However, as this correction procedure is valid only for flat specimens, and as the xerogels exhibit a pronounced morphology (Figure 7), special care had to be taken to find a locally flat specimen area larger than the expected electron range, which is certainly below 10 μm under the present conditions. Other sources of error, especially in light element analysis, are uncertainties in fundamental parameters and spectrometer calibration at X-ray energies below 1 keV. Spectral interference occurring between iridium and phosphorus can be corrected by peak deconvolution. Due to its high fluorescence yield, the Au-M_α line also appears under the K_β emission of phosphorus. However, the gold coating can be neglected with respect to quantification as, owing to its thickness of only 20 nm, additional absorption effects are not introduced.

Despite the numerous sources of error simultaneous quantification of all the elements present was carried out successfully. The elemental analyses by EDX are summarized in Table 1 and compared to data obtained from theory. These have been renormalized to exclude hydrogen as a

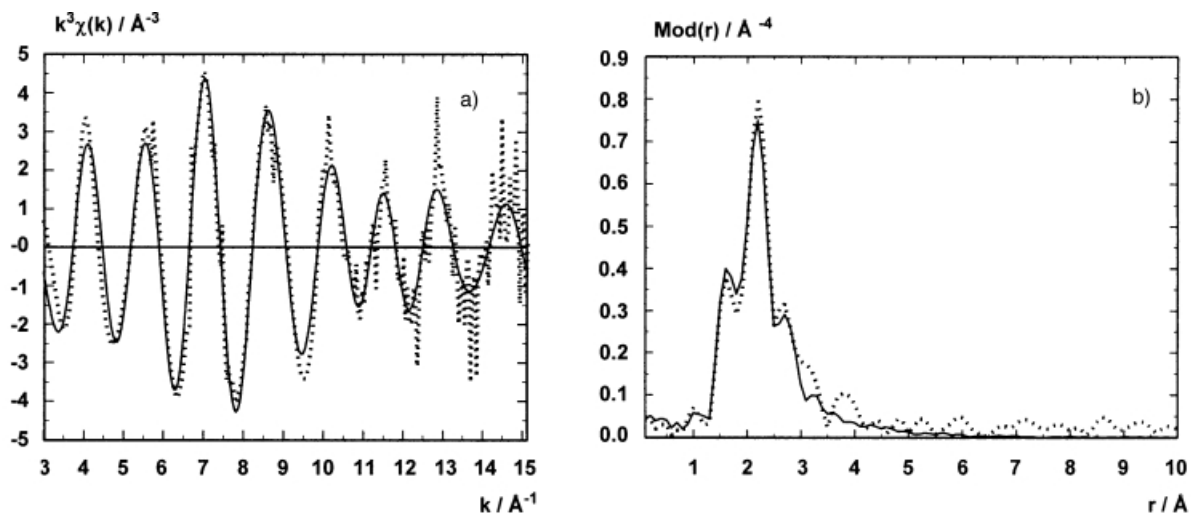


Figure 5. Experimental (dotted line) and calculated (solid line) $k^3\chi(k)$ (a) (k range: 2.99–15.14 $\text{\AA}^{-1}$) and their Fourier transforms (b) for **X4** (Ir- L_3 -edge) (see Table 2 for fit parameter)

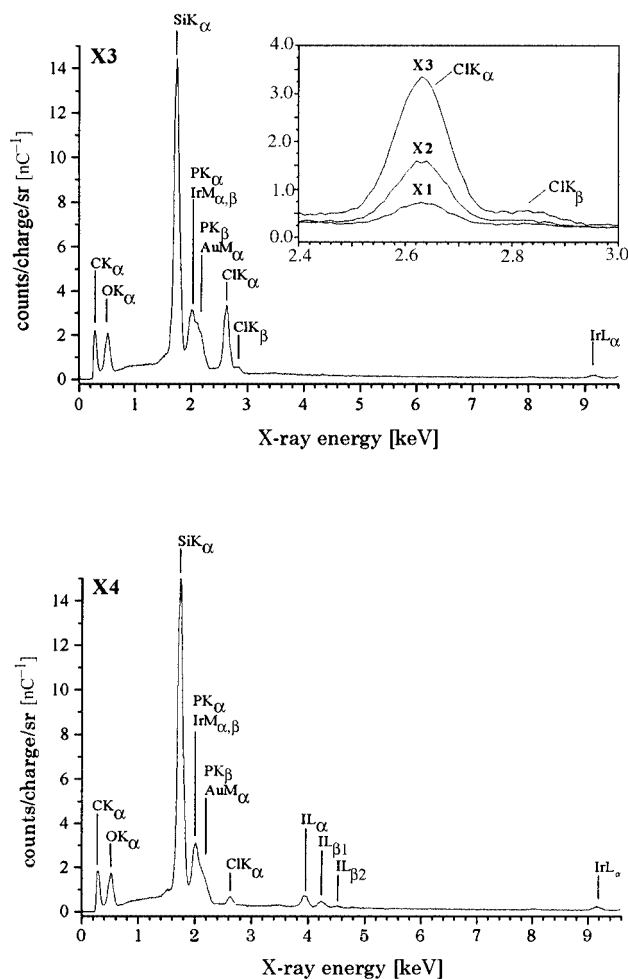


Figure 6. Energy-dispersive X-ray spectra of compounds **X3** (top) and **X4** (bottom); as shown by comparison of the Cl- K_{α} emission line intensities in the inlay, the chlorine content clearly increases from **X1**–**X3**; quantification results are summarized in Table 1

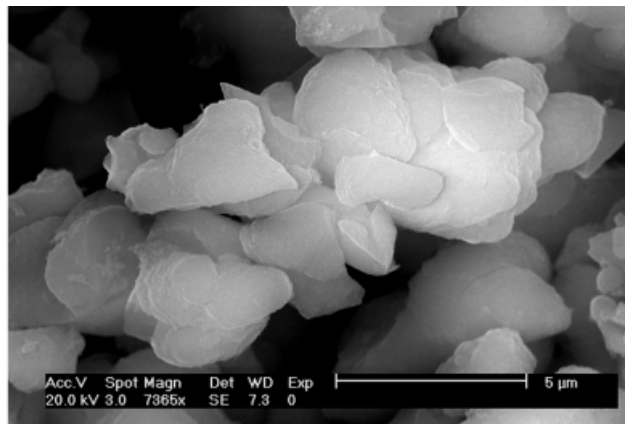


Figure 7. Scanning electron micrograph of **X1**

single-electron atom does not emit characteristic X-rays. Except for the iridium content in xerogel **X3** the elemental analyses support the reference data within the limits of error with the given samples.

Conclusion

For successful catalytic processes in interphases the polysiloxane-bound reactive centers should be completely accessible for substrate molecules. Therefore catalytic model reactions, for example the activation of small and larger molecules, are of great importance for the better understanding of catalytic reactions in interphases. To introduce reactive centers a phosphaneiridium(I) complex has been chosen because such a system is suitable for the envisaged model reactions. For the construction of a mobile stationary phase the T-silyl functionalized iridium complex **4(T⁰)** was co-polycondensed with the bifunctionalized co-condensation agent $(\text{MeO})_3\text{Si}(\text{CH}_2)_3\text{C}_6\text{H}_4(\text{CH}_2)_3\text{Si}(\text{OMe})_3$ [**5[Ph(1,4-C₃T⁰)₂]**] which has already been successfully employed in the rhodium-catalyzed hydroformylation of 1-hexene. The iridium-containing xerogel **X1** was then subjected to various oxidative additions and to the coordination of an alkyne. It could be unequivocally demonstrated that the iridium centers in **X1** were completely accessible for a variety of substrates with different shapes and sizes. The higher cross linkage of the T-silyl bifunctionalized co-condensation agent in the hybrid polymer matrix does not exert a disadvantageous effect on the accessibility of the metal centers. This fact presents a necessary precondition for a successful catalytic process. With the examples of the reactions with sulfur dioxide and dioxygen it could be shown that substrate molecules are also able to leave the polysiloxane matrix reversibly without any interference.

Most of these model reactions were also carried out with the corresponding rhodium(I) interphase system. However, the formed complexes proved to be unstable and partially decomposed.

Experimental Section

General: IR data were obtained on a Bruker IFS 48 FT-IR spectrometer. CP/MAS solid state NMR spectra were recorded on a Bruker DSX 200 multinuclear spectrometer equipped with a wide-bore magnet (field strength 4.7 T). Magic angle spinning was applied up to 10 kHz (4 mm ZrO_2 rotors) and 3–4 kHz (7 mm ZrO_2 rotors). Frequencies and standards: ^{31}P : 81.961 MHz (4.7 T) [85% H_3PO_4 , $\text{NH}_4\text{H}_2\text{PO}_4$ ($\delta = 0.8$ ppm) as second standard]; ^{13}C : 50.228 MHz (4.7 T), [TMS, carbonyl resonance of glycine ($\delta = 176.05$ ppm) as second standard]; ^{29}Si : 39.73 MHz (4.7 T), (Q_8M_8 as second standard). All samples were packed with exclusion of molecular oxygen. The J -resolved 2D phase-cycled spin-echo-experiment was carried out according to ref.^[25] [90° proton pulse length 3.8 μs , 180° proton pulse length 7.6 μs , contact time T_c 1 ms, recycle delay 1.5 s, time domain (F1) 64, time domain (F2) 2048, number of scans 512]. The cross polarization constants T_{XH} were determined by variation of the contact time T_c (14–16 experiments). The proton relaxation times in the rotating frame $T_{1\rho\text{H}}$ were measured by direct proton spin lock- τ -CP experiments^[28] via ^{31}P . The relaxation parameters were obtained using Bruker software SIMFIT and WINFIT following the procedure described in ref.^[15]

The EXAFS measurements were performed at the Ir- L_3 -edge at 11215 eV on the beamline X1.1 at the Hamburger Synchrotron-

strahlungslabor (HASYLAB) at DESY, Hamburg at 20 °C, with a Si(111) double crystal monochromator under ambient conditions (5.46 GeV, beam current 120 mA). Data were collected in transmission mode with ion chambers. Energy calibration was monitored with 20 µm thick platinum metal foil at the L₃-edge at 11564 eV. All measurements were performed under an inert gas atmosphere. The samples were prepared from a mixture of **X4** and polyethylene. Data were analyzed with a program package specially developed for the requirements of amorphous samples.^[37] The program AUTOBK of the University of Washington^[38] was used for background removal, and the program EXCURV92^[39] was used for the evaluation of the XAFS function. The resulting EXAFS function was weighted with k^3 . Data analysis in k space was performed according to the curved-wave multiple-scattering formalism of the program EXCURV92. The mean free path of the scattered electrons was calculated from the imaginary part of the potential (VPI was set to -4.00), the amplitude reduction factor AFAC was fixed at 0.8, and an overall energy shift ΔE_0 was introduced to fit the data. In the fitting procedure the intermolecular coordination numbers were varied and the intramolecular coordination numbers were fixed according to the known values of the ligands around the iridium atom of **X4**.

Scanning electron microscopy^[40] was performed on an XL 30 scanning electron microscope from Philips equipped with an DX-4 energy dispersive X-ray detection system by EDAX. This consists of a liquid-nitrogen-cooled lithium-drifted silicon detector with an active area of 10 mm² and the eDXi 2.11 software package. The detector resolution is 149 eV at Mn-K_α (5.984 keV) and the sample-detector distance is 50 mm in the present system. The sample powder was placed on a commercial specimen stub covered with an adhesive tab and subsequently covered with a sputtered 20 nm gold layer to ensure conductivity. The primary beam energy was 20 keV during all investigations. A probe current of 192 pA was applied for recording electron micrographs, whereas X-ray emission spectra were acquired under spot illumination applying a probe current of 569 pA for 400 live seconds (dead time approx. 33%). Measurements were repeated several times at various specimen positions to ensure reproducibility. Quantification of the X-ray spectra was carried out employing the ZAF correction procedure^[41–43] after subtraction of the Bremsstrahlung background.

All reactions and manipulations were carried out under argon with usual Schlenk techniques. All solvents were distilled from sodium benzophenone or calcium hydride. H₂O was distilled under inert gas prior to use. All solvents and reagents were stored under argon. [IrCl(COE)₂]₂ was purchased from Aldrich, all other chemicals were bought from Fluka. The T-silyl functionalized triphenylphosphine **3(T⁰)** and dicyanoethyne were prepared according to literature methods.^[22,44]

Carbonylchlorobis[diphenyl{4-[4-(trimethoxysilyl)butyl]-phenyl}phosphane-κP]iridium(I) [4(T⁰)]: In a three-necked flask [IrCl(COE)₂]₂ (350.0 mg, 0.390 mmol) was suspended in 10 mL of acetonitrile. After 10 min the argon was replaced by carbon monoxide. Undissolved [IrCl(COE)₂]₂ disappeared immediately, and a yellow solution was obtained, which indicated the formation of [IrCl(CO)₂]₂. After 10 min under an atmosphere of CO the T-silyl functionalized triphenylphosphane **3(T⁰)** (684.3 mg, 156 mmol) was added. The color of the solution changed to brown yellow. According to the ³¹P{¹H} NMR and IR spectra the reaction was finished after 20 min. The complex **4(T⁰)** was sol-gel processed without further purification. ³¹P{¹H} NMR (C₆D₆): δ = 24.7 (s) ppm. IR (KBr): $\tilde{\nu}$ = 1966 (C≡O) cm⁻¹.

Xerogel X1: In a 100 mL Schlenk-tube 5 mL of the crude solution of **4(T⁰)** in acetonitrile (441.7 mg, 0.39 mmol) was added to 4 mL of THF. Subsequently, the co-condensation agent **5[Ph(1,4-C₃T⁰)₂]** (784.9 mg, 195 mmol) was reacted with the above-mentioned mixture in the presence of 1 mL of water and 0.1 mL of a 0.1 M solution of tetrabutylammonium fluoride (TBAF) in THF as the catalyst. Stirring overnight afforded a light yellow gel. The liquid constituents were separated from the crude gel by filtration (P3) and the product was washed three times each with 10 mL of THF and 10 mL of *n*-hexane. Finally the xerogel was dried under vacuum for 4 h to give a yellow powder. Yield: 895.1 mg. ¹³C CP/MAS NMR: δ = 139.3, 128.3 (C-phenyl, backbone and ligand), 37.9, 25.2, 12.9 (CH₂, backbone and spacer) ppm. ²⁹Si CP/MAS NMR: δ = -56.6 (T²), -65.7 (T³) ppm. ³¹P CP/MAS NMR: δ = 24.4 ppm. IR (KBr): $\tilde{\nu}$ = 1965 (C≡O) cm⁻¹.

General Procedure for the Synthesis of the Xerogels X2, X3, X5, and X6 (Gas/Solid Interphases): **X1** (100.0 mg) was placed in a 100 mL Schlenk tube with a magnetic stirring bar. Subsequently argon was replaced by the respective gaseous reactants at room temperature. After removal of excess reactant by argon the xerogels **X2**, **X3**, **X5**, and **X6** were obtained. In the case of the polymers **X2** and **X3** the yields were quantitative.

X2: X1 was treated with hydrogen chloride. Yield: 101.2 mg. ³¹P CP/MAS NMR: δ = -3.2 ppm. IR (KBr): $\tilde{\nu}$ = 2043 (C≡O) cm⁻¹.

X3: X1 was treated with chlorine. Yield: 102.1 mg. ³¹P CP/MAS NMR: δ = -20.4 ppm. IR (KBr): $\tilde{\nu}$ = 2071 (C≡O) cm⁻¹.

X5: X1 was treated with sulfur dioxide. Yield: 101.6 mg. ³¹P CP/MAS NMR: δ = 23.9 (**X1**), 7.8 (**X5**) ppm. IR (KBr): $\tilde{\nu}$ = 2018 (C≡O) cm⁻¹.

X6: X1 was treated with oxygen. Yield: 101.6 mg. ³¹P CP/MAS NMR: δ = 24.1 (**X1**), 3.0 (**X6**) ppm. IR (KBr): $\tilde{\nu}$ = 2008 (C≡O) cm⁻¹.

General Procedure for the Synthesis of the Xerogels X4 and X7 and Treatment of X1 with Tetrachloroethane (Liquid/Solid Interphases): A suspension of **X1** (100.0 mg) in 5 mL of benzene was treated with 0.5 mL of methyl iodide, ¹³CH₃I, dicyanoethyne, or tetrachloroethane, and the mixture stirred for 24 h at ambient temperature. The liquid constituents were removed by filtration (P3) and, after drying under vacuum, the respective xerogels were obtained.

X4: X1 was reacted with CH₃I or ¹³CH₃I. Yield: 96.4 mg (96.3 mg for ¹³CH₃I). ¹³C CP/MAS NMR: δ = 139.1 (139.4*), 128.6 (128.3*) (C-phenyl, backbone and ligand), 50.1 (50.1*) (OCH₃), 37.6 (38.2*), 24.5 (24.9*), 12.5 (12.7*) (CH₂, backbone and spacer), -5.1 (¹³CH₃-Ir) ppm. The asterisk indicates data for the ¹³C labeled compound. ³¹P CP/MAS NMR: δ = -20.2 ppm. IR (KBr): $\tilde{\nu}$ = 2042 (C≡O) cm⁻¹.

X6: X1 was reacted with dicyanoethyne. Yield: 95.8 mg. ³¹P CP/MAS NMR: δ = -3.3 ppm. IR (KBr): $\tilde{\nu}$ = 2192 (C≡N), 2014 (C≡O) cm⁻¹.

Behavior of X1 Toward Tetrachloroethane: **X1** was reacted with tetrachloroethane. Yield: 96.7. ³¹P CP/MAS NMR: δ = -3.5 (**X2**), -18.3 (**X3**) ppm. IR (KBr): $\tilde{\nu}$ = 2070, 2043 (C≡O) cm⁻¹.

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