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Reversible Switching of the Sol−Gel Transition with Ultrasound in Rhodium(I) and Iridium(I) Coordination Networks

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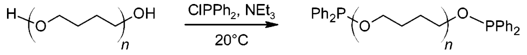
Abstract: Reversible coordination networks were prepared by combining diphenylphosphinite telechelic polytetrahydrofuran (**2**) with $[RhCl(COD)]_2$ or $[IrCl(COD)]_2$ in chloroform. Both systems resulted in stable gels at concentrations above 50 and 30 g/L for the rhodium(I) and iridium(I) networks, respectively. The rheological properties of the two coordination networks (100 g/L) were determined with oscillatory shear experiments, which showed that the elastic moduli are constant over a wide frequency range, indicating gel-like behavior; the iridium(I) gel has an elastic modulus distinctly higher (2.8×10^3 Pa) than that of the rhodium(I) gel (1.0×10^3 Pa). Ultrasonication of the rhodium(I) gel caused liquefaction after 3 min; regelation occurred 1 min after sonication was stopped. The iridium(I) gel was also liquefied after 3 min of sonication, but regelation took 1.5 h at room temperature and more than 10 days at −20 °C. ^{31}P NMR measurements on model complexes showed that the large differences in gelation times are in agreement with the ligand exchange kinetics of the rhodium(I) and iridium(I) complexes. We propose that sonication of the gels results in ligand exchange, which changes the network topology without changing the coordination chemistry. Upon sonication, the fraction of metal centers in active cross-links decreases and thereby reduces the gel fraction to zero. The system is not at equilibrium, and upon standing the gel fraction increases at a rate that is determined by the exchange kinetics of the metal complex. The observed effects offer opportunities to use ultrasound in the activation of dormant transition metal catalysts.

Introduction

Reversibly controlling the rheological properties of fluids may fully alter the way everyday appliances such as clutches, brakes, and vibration damping equipment operate. Whereas electrorheological[1−4] and magnetorheological materials[5,6] are based on macroscopic phenomena, more recently several molecular approaches[7] have been developed where use is made of temperature, pH,[8−10] and light[11,12] as external stimuli. The ultrasound-induced reversible gelation of solutions of dinuclear palladium(II) salicylidene complexes reported by Naota and Koori is certainly one of the most intriguing examples.[13]

Scheme 1. Synthesis of Diphenylphosphinite Telechelic Polytetrahydrofuran **2**



2, $M_n = 1.8 \times 10^3$ g/mol

Recently, we reported on the development of high molecular weight linear coordination polymers by combining diphenylphosphine telechelic polytetrahydrofuran with palladium(II) dichloride.[14] Sonication of solutions of these polymers in toluene led to a reversible decrease in molecular weight and viscosity. The alkyldiphenylphosphine-based coordination polymers were shown to reach equilibrium 1 day after sonication, whereas equilibration of alkyldicyclohexylphosphine-based coordination polymers took approximately 60 days.[15] These results show that ultrasonication of linear coordination polymers can be used to change rheological properties.

However, much more dramatic changes in rheological properties may be expected near the critical point of physical gels which can be obtained by increasing the functionality of a coordination polymer above 2.[16] Such coordination networks,

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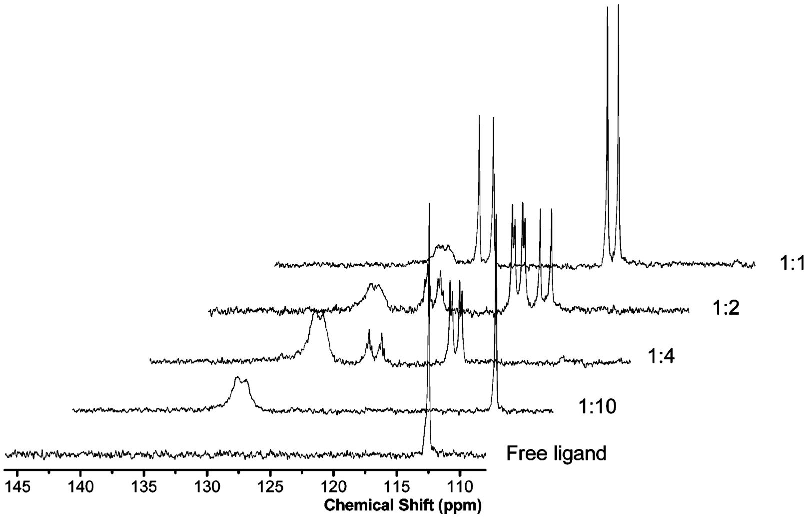

Figure 1. ^{31}P NMR spectra of rhodium(I) chloride complexes of ligand **1** at different rhodium-to-phosphinite ratios.

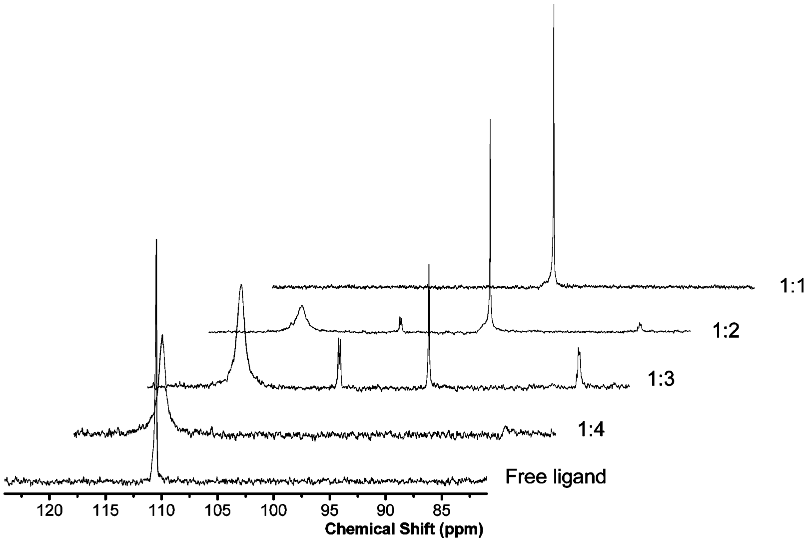

Figure 2. ^{31}P NMR spectra of iridium(I) chloride complexes of ligand **1** at different iridium-to-phosphinite ratios.

Table 1. ^{31}P NMR Chemical Shifts (ppm) of Rhodium(I) Complexes of **1** in CD_2Cl_2

species	shift (ppm)[a]	J_{Rh-P} (Hz)	J_{P-P} (Hz)
1, free ligand	113.0 s		
[Rh(**1**)$_4$]Cl	130.7 d	155.6	
[RhCl(**1**)$_3$]	119.5 dd	162.1	40.1
	126.1 dt	208.2	
[RhCl(**1**)$_2$]$_2$	117.3 d	175.4	
[Rh(COD)(**1**)]	127.3 d	223.4	

[a] s = singlet, d = doublet, t = triplet.

containing reversible cross-links, allow the material to respond to changes in its environment, such as temperature and concentration. Rowan et al. reported on mechanoresponsive coordination networks.[17,18] Reversible linear coordination polymers based on bifunctional pyridine bis(imidazolyl) ligands and Zn^{2+} or Co^{2+} were extended with lanthanoid ions (3% of Eu^{3+} or La^{3+}), which act as reversible cross-links between the polymer chains and led to the formation of thixotropic gels.

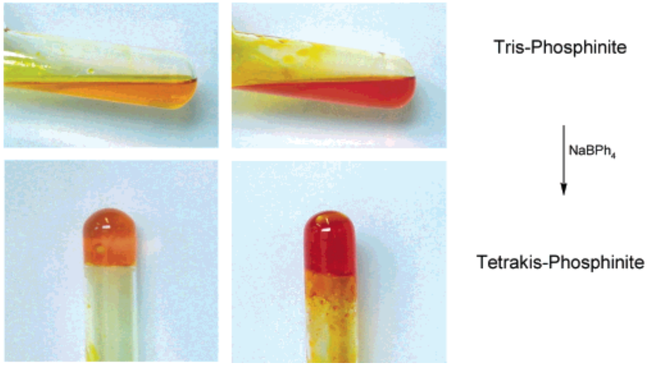

Figure 3. Enforced formation of [Rh(**2**)$_4$]BPh$_4$ (left) and [Ir(**2**)$_4$]BPh$_4$ (right) in THF causing gelation.

Lanthanoid ions were also used by Sudhölter and co-workers to prepare water soluble reversible coordination networks.[19,20] Bifunctional pyridine bis(carboxylate) ligands were combined with neodymium(III) and lanthanum(III) metal centers. These

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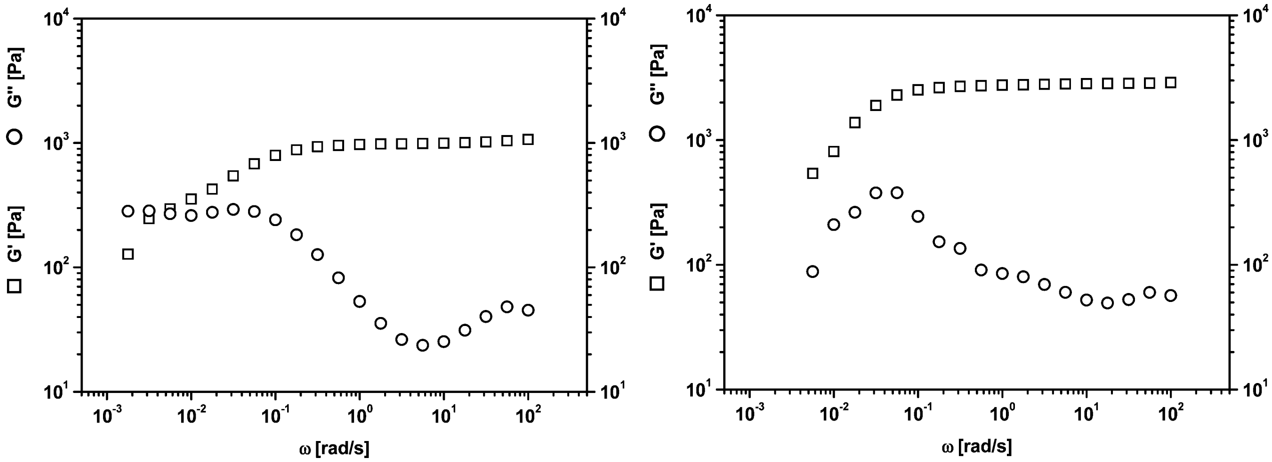


Figure 4. Oscillatory shear measurements of coordination networks in $CHCl_3$. Frequency-dependent storage (□) and loss (○) moduli of rhodium(I) gel (left) and iridium(I) gel (right) in chloroform (c = 100 g/L, T = 0 °C).

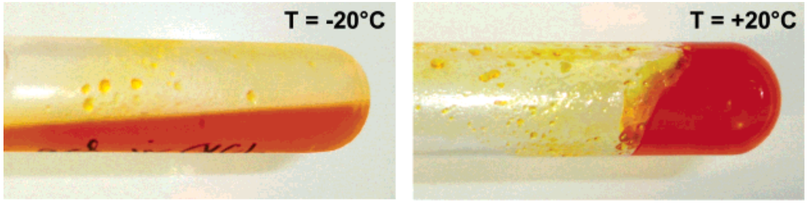
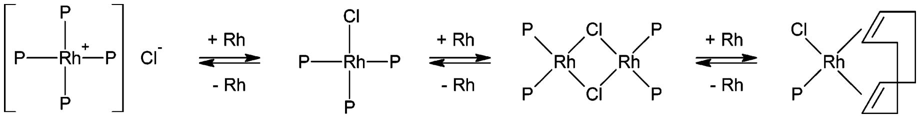


Figure 5. Iridium(I)-based gel 3 days after sonication, kept at −20 °C (left) and after 1 h at 20 °C (right).

Scheme 2. Equilibria between the Different Rhodium(I) Phosphinite Complexes



Scheme 3. Equilibria between the Different Iridium(I) Phosphinite Complexes

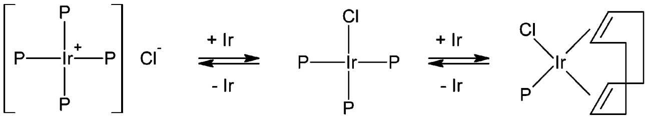


Table 2. ^{31}P NMR Chemical Shifts (ppm) of Iridium(I) Complexes of **1** in $CDCl_3$

species	shift (ppm)[a]	J_{P-P} (Hz)
1, free ligand	111.3 s	
[Ir(**1**)$_4$]Cl	115.6 s	
[IrCl(**1**)$_3$]	106.9 d 85.6 t	31.4
[IrCl(COD)(**1**)]	98.9 s	

[a] s = singlet, d = doublet, t = triplet.

lanthanoid metals can accept up to three of these ligands and may lead to cross-linked systems. The viscoelastic behavior of the neodymium based system, however, indicated that the system did not form a gelated network, because the average functionality was reduced by cyclization.

Poly(4-vinylpyridine) can be regarded as a polyfunctional ligand, and in combination with bifunctional palladium(II) and platinum(II) pincer complexes this polymer has been used to form a highly cross-linked system.[21] Using small variations in the pincer ligand, Craig et al. were able to study the influence of the thermodynamics and kinetics of ligand exchange on rheological properties of the coordination network.[22,23]

Here, we report on the reversible mechanochemistry of coordination networks containing rhodium(I) and iridium(I). These metal ions were selected for the development of reversible coordination networks, because they readily coordinate four phosphorus ligands. The two metals have similar coordination chemistry, although their ligand exchange kinetics are very different.[24] Rhodium features fast exchange kinetics and is applied in many different catalytic reactions.[25] Iridium is also used in many catalytic reactions, but due to its higher stability it has, for example, also been used to isolate analogues of unstable rhodium intermediate species in hydroformylation.[26] The preparation and characterization of rhodium(I) and iridium(I) coordination networks are described, and ultrasonic switching of their rheological properties is reported.

Results

Ligand Synthesis. Initial attempts to form complexes of rhodium(I) chloride with 1-dodecyldiphenylphosphine[27] were

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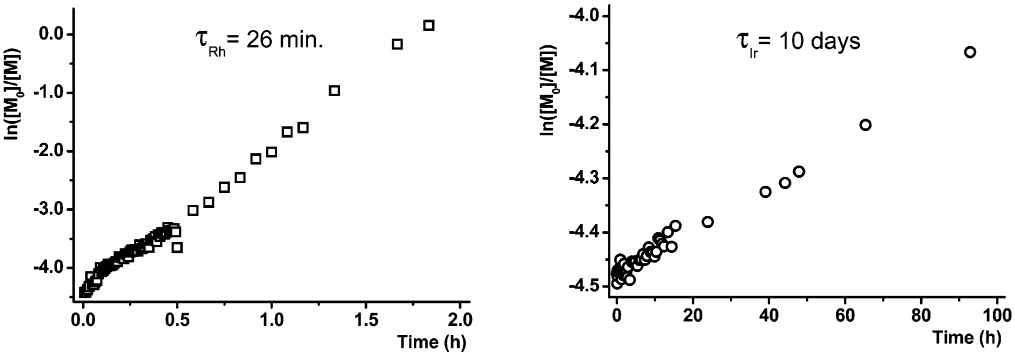

Figure 6. Kinetics plots of rhodium(I) tetrakisphosphinite (left) and iridium(I) tetrakisphosphinite complexes (right) reacting with their corresponding metal precursors (ln(M_0/M) vs time; M_0 and M are, respectively, the initial concentrations and the concentrations at time t of the tetrakisphosphinite complexes; 0.4 M of **1** in $CDCl_3$; $T = 20$ °C).

successful, but the complexes were found to be very labile and to decompose rapidly in the presence of oxygen. Strong coordination is easily achieved when π-acceptor ligands are employed.[28] Alkyldiphenylphosphinite ligands were selected so as to obtain a kinetically stable system to facilitate characterization. The small monofunctional 1-dodecyldiphenylphosphinite **1** was used as a reference. For the development of reversible coordination networks, a polymeric diphenylphosphinite ligand was synthesized by functionalization of hydroxyl telechelic polytetrahydrofuran (Scheme 1). The diol was reacted with chlorodiphenylphosphine in the presence of triethylamine, and polymeric ligand **2** was obtained as an oil that slowly crystallized out ($M_n = 1.8 \times 10^3$ g/mol, $M_w/M_n = 1.9$). ^1H, ^{13}C, and ^{31}P NMR analysis established complete conversion of the alcohol into the phosphinite.

Complexation Stoichiometry. To obtain a coordination network, each metal center must connect on average more than two bifunctional ligands. To determine the number of ligands that is bound in rhodium and iridium complexes, their complexation stoichiometry was investigated. Solutions of **1** (0.10 M in $CDCl_3$) were mixed with $[RhCl(COD)]_2$ and $[IrCl(COD)]_2$, and the samples were analyzed with ^{31}P NMR spectroscopy. The ^{31}P NMR spectra and chemical shifts corresponding to the rhodium(I) complexes are depicted in Figure 1 and summarized in Table 1; those for the iridium(I) complexes are presented in Figure 2 and Table 2.

Rhodium. Upon addition of 0.1 equiv of $[RhCl(COD)]_2$ to a solution of **1**, a broad doublet appeared at $\delta = 130.7$ ppm which sharpened upon cooling to 0 °C ($J_{Rh-P} = 155.6$ Hz), while free ligand **1** ($\delta = 113.0$ ppm) was also still present. The doublet was assigned to a cationic tetrakisphosphinite species $[Rh(\mathbf{1})_4]Cl$.[29] Further addition of $[RhCl(COD)]_2$ (0.25 equiv in total) led to an increase in the tetrakisphosphinite species and appearance of a new set of signals. The observation of a doublet of doublets ($\delta = 119.5$ ppm, $J_{Rh-P} = 162.1$ Hz, $J_{P-P} = 40.1$ Hz) and a doublet of triplets ($\delta = 126.1$ ppm, $J_{Rh-P} = 208.2$ Hz, $J_{P-P} = 40.1$ Hz) is consistent with the presence of a square planar trisphosphinite complex $RhCl(\mathbf{1})_3$, in which the two phosphorus atoms cis-coordinated to the chloride couple with the single phosphorus trans-coordinated to the chloride atom.[30−32] Increasing the metal quantity to 0.5 equiv caused a decrease in both the tetrakis- and the trisphosphinite species, and a doublet emerged at $\delta = 117.3$ ppm ($J_{Rh-P} = 175.4$ Hz). This species corresponds most likely to a chloride-bridged dinuclear rhodium(I) species: $[RhCl(\mathbf{1})_2]_2$. At a stoichiometric metal-to-ligand ratio, another species appears at $\delta = 127.3$ ppm ($J_{Rh-P} = 223.4$ Hz), which we tentatively assign to the mononuclear $RhCl(COD)(\mathbf{1})$. Scheme 2 shows the equilibria between the different rhodium(I) phosphinite complexes.

Iridium. The complexation of phosphinite **1** with $[IrCl(COD)]_2$ is similar to that with the rhodium(I) dimer. Adding the iridium(I) dimer to a solution of **1** in deuterated chloroform first gave the orange-red tetrakis phosphinite complex $[Ir(\mathbf{1})_4]Cl$ with a signal at $\delta = 115.7$ ppm.[33] In contrast to the rhodium(I) complexes, this was the sole species observed at 1:4 metal-to-ligand stochiometry. Addition of iridium(I) to give a 1:3 metal-to-ligand ratio led to the formation of two additional complexes, a trisphosphinite species $[IrCl(\mathbf{1})_3]$, which is observed at $\delta = 106.9$ ppm (doublet, $J_{P-P} = 31$ Hz) and 85.6 ppm (triplet), and the mononuclear $[IrCl(COD)(\mathbf{1})]$ complex, observed at $\delta = 98.9$ ppm. Mixing the metal precursor in a 1:2 stoichiometry with **1** resulted in exclusive formation of the mononuclear species. Whereas the rhodium(I) system gave rise to a chloride-bridged dinuclear complex at a 1:2 metal-to-ligand ratio, no such species was observed for the iridium(I) system. Although mention is made in literature of iridium(I) pentakisphosphinite complexes,[34] no pentakis complex was observed here, not even when a 10-fold excess of the ligand was used, probably because the phosphinite ligand is too bulky.[33] Scheme 3 shows the equilibria between the different iridium(I) phosphinite complexes.

Preparation of Rhodium(I) Coordination Networks. With the knowledge that rhodium(I) can coordinate up to four alkyldiphenylphosphinite ligands, we employed polymeric phosphinite ligand **2** to obtain a reversible coordination network. Ligand **2** was complexed with $[RhCl(COD)]_2$ in a rhodium-to-phosphorus stoichiometry of 1:4. Several solvents were used, but stable gels were only obtained in chloroform and dichloromethane at concentrations of 50 g/L or higher. The gels prepared in dichloromethane and chloroform were diluted to

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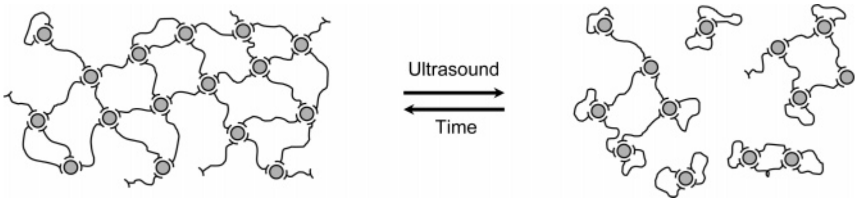
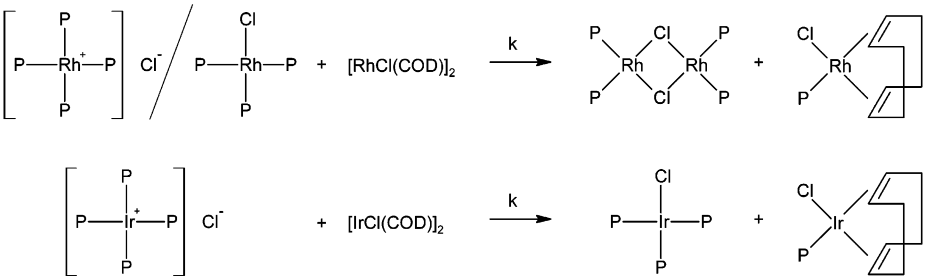


Figure 7. Proposed effects of sonication on the coordination networks, resulting in loss of the gel fraction.

Scheme 4. Reaction of Tetrakis- and Trisphosphinite Complexes with the Corresponding Metal Precursors To Assess the Ligand Exchange Rates (P = Ligand **1**)



25 g/L, to break up the gels, and analyzed with ^{31}P NMR spectroscopy. Nearly identical chemical shifts and coupling constants were observed for the rhodium(I) complexes measured in chloroform, suggesting the presence of the same complexes. ^{31}P NMR spectroscopy indicated the presence of the rhodium(I) tetrakisphosphinite species together with the rhodium(I) trisphosphinite species in approximately equal amounts. The solutions in THF, toluene, tetrachloroethylene, dioxane, diethyl ether, and tetrachloromethane, which did not gelate, were also analyzed with ^{31}P NMR, which revealed that in these solvents only the rhodium(I) trisphosphinite species and free ligand **2** were present. Formation of a gel or infinite network requires that polymer chains be connected to each other via active cross-links. Due to the lower functionality of the trisphosphinite species ($f = 3$), a substantially higher degree of conversion has to be achieved to reach the gel point.[16] In addition, at this stoichiometry, a larger fraction of free ligand ($f = 1$) is present, further lowering the overall functionality. The importance of the tetrakisphosphinite complex ($f = 4$) was validated by its enforced formation through replacement of the chloride counterion by a noncoordinating counterion (Figure 3). To a solution of **2** and $[RhCl(COD)]_2$ (1:4 rhodium-to-phosphorus stoichiometry) in THF (100 g/L), sodium tetraphenylborate in a drop of methanol was added. Immediately after addition, the solution gelated. ^{31}P NMR analysis confirmed the formation of the tetrakisphosphinite complex.

Preparation of Iridium(I) Coordination Networks. The stoichiometry studies with **1** showed that exclusive formation of the iridium(I) tetrakisphosphinite complex is readily achieved at an iridium-to-phosphorus ratio of 1:4. Upon complexation of the polymeric phosphinite ligand **2** with $[IrCl(COD)]_2$, stable gels were formed in chloroform at concentrations as low as 30 g/L. In contrast to the rhodium(I)-based gels, where gelation is almost instantaneous, the formation of the iridium(I) gels took approximately 30 min.

Preparation of an iridium(I) gel in THF was not successful. ^{31}P NMR analysis showed that only the iridium(I) trisphosphinite complex and free ligand **2** were present. Just as for the rhodium(I)-based system in THF, abstraction of the chloride anion with sodium tetraphenylborate led to the formation of $[Ir(\mathbf{2})_4]BPh_4$ ($f = 4$) and a stable gel formed instantaneously (Figure 3).

Oscillatory Shear Experiments. Oscillatory shear experiments were performed on the chloroform-based rhodium(I) and iridium(I) gels to investigate their shear rate-dependent mechanical properties (Figure 4). The gels were measured under a nitrogen atmosphere and at 0 °C to prevent solvent evaporation.

The curves of the rhodium(I) gel (open symbols) indicate gel-like behavior as the storage modulus (G') is independent of shear rate down to a frequency of 0.2 rad/s and significantly larger than the loss modulus (G''). A value of 1×10^3 Pa was found for the storage modulus in the frequency range of 100−0.1 rad/s; at lower frequencies the storage modulus decreases rapidly. The loss modulus displays low values at high frequencies (<100 Pa), while increasing at low frequencies to 300 Pa at 0.002 rad/s. At a frequency of 0.004 rad/s, the storage and loss moduli for the rhodium gel cross and the system starts displaying liquidlike behavior.

The behavior of the iridium(I) gel (closed symbols) resembles that of the rhodium(I) gel, with a plateau value of the storage modulus (2.8×10^3 Pa) that is approximately three times higher than the storage modulus found for the rhodium(I) gel. The loss modulus of this material shows a maximum at 0.4 rad/s and is lower than the storage modulus over the entire frequency range.

Both materials exhibit gel-like behavior, but the iridium(I) gel has a considerably higher storage modulus. Employing iridium(I) chloride instead of rhodium(I) chloride to build up a coordination network thus results in a stiffer gel.

Ultrasonication of Rhodium(I) Coordination Networks. A gel was prepared by mixing $[RhCl(COD)]_2$ and polymeric ligand **2** in chloroform (75 g/L). This gel was loaded into a water-cooled reaction vessel, and the sonication probe was positioned in the gel together with a digital thermometer. During sonication, the material around the probe rapidly became liquid and a cloud of bubbles appeared. After 3 min, the gel had completely liquefied. When sonication was stopped, a stable gel was reestablished within 1 min. During the first 3 min of sonication, the temperature rose to 43 °C, although the sample was cooled with 15 °C water. The gel functions as an insulator, and cooling is therefore poor until complete liquefaction. After liquefaction, the temperature stabilizes at 33 °C, considerably lower than the melting temperature of the gel (51 °C). Liquefaction can therefore not be explained by thermal effects alone. It is proposed that reversible scission of coordinative bonds plays a major role and enables the formation of a metastable state. Experiments with gels prepared in dichloromethane were troublesome, because of solvent evaporation. Sonication of chloroform-based gels at a concentration of 100 g/L resulted only in liquefaction of a small portion of the gel.

Ultrasonication of Iridium(I) Coordination Networks. Iridium(I)-based gel was prepared in chloroform at a concentration of 50 g/L by mixing the $[IrCl(COD)]_2$ with polymeric ligand **2** (Ir/P = 0.25). This gel, which has a gel dissociation temperature of 50 °C, was sonicated in the same manner as the rhodium gel, and after approximately 3 min, the gel had completely liquefied. During this time, the temperature rose from 12 to 30 °C (temperature of cooling water 12 °C). After liquefaction, the temperature remained constant at approximately 28 °C. When sonication was stopped, the gel remained liquid for a considerably longer time than in the experiment with the rhodium(I)-based gel. Gelation occurred after approximately 1.5 h. When a solution obtained by heating the gel above its melting point was cooled in a water bath (15 °C), gelation occurred within minutes, showing a gelation mechanism different than that for the gel liquefied through sonication. This was confirmed by placing a freshly sonicated iridium(I) sol at −20 °C. At this temperature, the liquid did not gelate even after 10 days, but a sample taken from this liquid and kept at room temperature (20 °C) gelated within 1 h (Figure 5).

Ligand Exchange Rates. The very different behavior of the sonicated gels prompted us to investigate the rate of ligand exchange of the rhodium(I) and iridium(I) complexes. These rates were determined by adding the metal precursors to the trisphosphinite and tetrakisphosphinite complexes (Scheme 4).[35] Formation of new complexes can only occur by dissociation of the phosphinite ligands, which is therefore representative for the ligand exchange rate.

^{31}P NMR analysis showed that conversion of the rhodium(I) tetrakisphosphinite complex to the trisphosphinite and bisphosphinite complexes followed first-order kinetics ($\tau \approx 26$ min, Figure 6, left) Similarly, when $[IrCl(COD)]_2$ was added to a solution of tetrakisphosphinite iridium(I) chloride, the formation of iridium(I) trisphosphinite and monophosphinite complexes was observed. This reaction also followed first-order kinetics, but with $\tau \approx 10$ days (Figure 6, right). This shows that the combination of alkyldiphenylphosphinite ligands with iridium(I) chloride leads to a system in which the ligand exchange processes are very slow.

Discussion and Conclusions

Combining diphenylphosphinite telechelic polytetrahydrofuran with either rhodium(I) or iridium(I) chloride leads to coordination networks, which both form stable gels in chloroform. The coordination chemistry of the two metals is similar as shown with ^{31}P NMR. In both systems, the presence of tetrakisphosphinite complexes was essential to obtaining stable gels. One explanation for this observation is the requirement for sufficiently high degrees of functionality in the systems, which are not reached with only trisphosphinite complexes present. An alternative explanation is the presence of additional interactions between the cationic tetrakisphosphinite complexes, further increasing the number of active cross-links. Such interactions have been observed earlier by Rowan et al.[18] However, ^{1}H DOSY NMR spectroscopy on the $[Ir(\mathbf{1})_4]Cl$ model system showed the absence of aggregation of this complex in $CDCl_3$; we therefore do not expect the tetrakisphosphinite complexes in the network to give rise to aggregation.[36]

Sonication of the gels caused liquefaction of the gels within 3 min. Whereas the rhodium(I)-based system forms a gel almost immediately after sonication is stopped, the iridium(I)-based system requires 1.5 h at room temperature to reconstitute the gel. ^{31}P NMR analysis directly after the sonication experiments did not show the presence of any free ligand.

We conclude that sonication induces ligand exchange but does not change coordination stoichiometry. Instead, the action of mechanical forces on the network leads to a change in topology and decreases the fraction of metal centers engaged in active cross-links. The gel fraction is thereby converted into sol (Figure 7). After liquefaction, the system is not at equilibrium, and upon standing the gel fraction increases again at a rate that is determined by the exchange kinetics of the metal complex. In the absence of free ligand, the rate-limiting step is the dissociation of phosphinite ligands. Reconstitution of the gel is therefore expected to correspond to the kinetics of the process depicted in Scheme 4.

Ultrasound induces stronger rheological effects on gels than on linear polymer solutions,[14,15] and ultrasonication of gels is also expected to result in more effective bond scission, because gels are infinitely large molecules on which the mechanical forces of ultrasound act more strongly.[37] Quantification of bond scission requires kinetically stable systems, and the iridium(I) phosphinite coordination networks studied here are promising systems for further quantification studies. The stability of the coordination networks may be increased even further by employing better π-acceptor ligands such as phosphites, which lead to even stronger coordinative bonds.[28]

The use of ultrasound as a rheology switch for reversible gels is not limited to the coordination networks reported here. Many physical networks with slow exchange kinetics are known.[38] Sonication of such gels may lead to even slower reconstitution of the gels than for the experiments described here. Investigating the mechanochemistry of reversible networks based on different cross-linking interactions is therefore of great interest and may lead to practical applications in stimuli-responsive materials or may facilitate the processing of highly viscous materials.

Finally, one of the most significant effects of reversibly breaking coordinative bonds in the rhodium(I) and iridium(I) coordination networks is the transient formation of coordinatively unsaturated metal complexes. Such species are known to be excellent catalysts in a multitude of reactions. The current coordination networks are promising systems to probe the influence of mechanical forces on catalytic activity and selectivity.

Supporting Information Available: Experimental procedures, ^{1}H, ^{13}C, and ^{31}P NMR of polymeric ligand **2**, and diffusion-ordered NMR spectroscopy of complex $[Ir(\mathbf{2})_4]Cl$. This material is available free of charge via the Internet at http://pubs.acs.org.

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[35] Experiments were performed in $CDCl_3$ at 20 °C, at a concentration of 0.4 M with respect to ligand **1**. A stoichiometric excess of metal precursor was added to the solution, and spectra were gathered during regular intervals.

[36] Details on the ^{1}H DOSY NMR measurements can be found in the Supporting Information.

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