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Chemistry in interphases. The solid-phase synthesis of well defined rhodium and iridium phosphine complexes†

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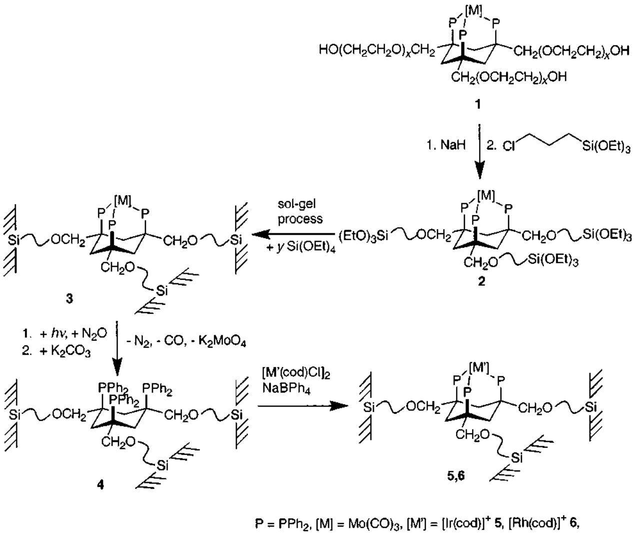
After polyethylene glycol functionalized metal complexes were supported by the sol–gel technique the organometallic protection group was eliminated in a combined photochemical/oxidative procedure and the immobilized non-coordinated ligand was treated with organometallic fragments to give new supported well defined rhodium and iridium complexes.

Transition metal catalysts anchored onto insoluble supports are of great interest since they are useful in industrial scale processes.[1–3] They allow easy purification as well as catalyst recycling and therefore play an important role with respect to ecological and economic aspects.[4,5] The main draw backs of catalysts which are bound to the surface of pre-formed supports are leaching of the active metal centre and reduced reactivity and selectivity compared to their homogeneous counterparts.[6] The simultaneous co-condensation of various types of alkoxysilanes with functionalized metal complexes under sol–gel process conditions lead to highly cross-linked polymers as stationary phases. If these stationary phases are penetrated by a mobile phase (solvent, reactant) particular regions exist in which the reactive centres become highly mobile.[6,7] Such interphases display reduced leaching and high reactivity and selectivity.[6] The synthesis of stationary phases is challenging as hydrolysable functional groups have to be attached to transition metal complex fragments. In addition the precursor complexes of the catalytically active species also have to withstand the sol–gel conditions which are considered as mild in terms of temperature but the chemical conditions (solvent, pH) are often not in favour of the reactive centre. Here, we present our preliminary findings on the support of well defined transition metal complexes using the $Mo(CO)_3$ fragment as the protecting group.[8]

The synthesis of the polyethylene glycol functionalized molybdenum complex **1** was carried out as described earlier.[9] The average chain length *x* was adjusted to 5–10, 50, 145 and 285, respectively. The properties of the PEG-functionalized molybdenum complexes **1** vary from amorphous powders with high decomposition points (x = 5–10) to waxy materials with low melting points (x = 145, 285). The solubility changes from CH_2Cl_2, acetone to THF and water with increasing chain length and the swelling abilities increase in the same order. The hydroxylic end groups of the homologous polymers of **1** react with $Cl(CH_2)_3Si(OEt)_3$ under Williamson ether synthesis conditions to the corresponding tris[(triethoxy)silyl] functionalized complexes **2**.‡ Simultaneous co-condensation of **2** with various amounts (y = 0, 6, 30 equivalents) of tetraethoxysilane (TEOS) allows generation of organic–inorganic hybrid polymers with different properties. When y is small (y = 0, 6) the PEG-functions dominate the character of the material (*vide supra*). Increasing the amount of TEOS (y = 30) leads to materials which are more like silica.§ As the polyethylene glycol spacers already offer a high flexibility, TEOS was used as co-condensing agent to achieve a high cross-linking of the polymer. To remove the $Mo(CO)_3$ protecting group from **3**, a suspension of the polymer in THF was irradiated with UV light in the presence of N_2O. After activation of the metal carbonyl bond with UV light the oxygen transferring agent N_2O is able to selectively oxidise the $Mo(CO)_3$ fragment to MoO_3 and generate **4** quantitatively.[8]¶ This was shown by a shift of the ^{31}P resonance to higher field (δ 29) in the ^{31}P CP MAS spectrum of **4** and confirmed by the absence of the ν(CO) absorptions due to the $Mo(CO)_3$ fragment in the IR spectrum. After conversion of MoO_3 into MoO_4^- with K_2CO_3 the molybdate was extracted by washing procedures. While a number of functionalized phosphine monomers were accessible in this manner in homogeneous solution[8] a partial oxidation of the supported phosphine ligand **4** is observed in the interphase. This was attributed to the high oxophilicity of the polyethylene glycol groups and is prevented by adding reducing agents like PBu^n_3 to the suspension. The quantitative replacement of the carbonyl fragment demonstrates the easy accessibility of the metal complex in the polymer material by small molecules like N_2O. When the supported tripodal phosphine ligand **4** is treated with Vaska's complex no reaction is observed. Obviously the $Ir(PPh_3)_2(CO)Cl$ complex is too large to enter the interphase and react with the tripodal phosphine. The dimers $[M(cod)Cl]_2$ (M = Rh, Ir) are readily split by **4** in the presence of $NaBPh_4$ to form the new anchored rhodium and iridium complexes **5**,**6**.‖ The characteristic ^{31}P NMR signals are shifted to δ 38.4 and -7, respectively.

All materials were characterised by multinuclear solid-state NMR spectroscopy. The ^{29}Si CP MAS NMR spectra confirm the presence of a polysiloxane network built up with different T (δ -56.0 to -66.3, T^1–T^3) and Q (δ -91.0 to -109.9, Q^2–Q^4) species. The ^{31}P CP MAS NMR spectra of the polymers **3**–**6** display single unique resonances characteristic for the complexes and ligand, respectively. The spectra are comparable



P = PPh_2, [M] = $Mo(CO)_3$, [M'] = $[Ir(cod)]^+$ **5**, $[Rh(cod)]^+$ **6**, cod = cyclooctadiene, ∿ = polyethylene glycol

Scheme 1

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† Dedicated to Professor Reinhard Schmutzler on the occasion of his 65th birthday.

with the corresponding monomer complexes in solution. This confirms the integrity of the reactive centres in the polymers and establishes that the method described above allows the support of well defined transition metal complexes. Interestingly the linewidth of the ^{31}P resonances strongly depend on the spacer lengths as well as the amount of co-condensate used and shows large differences between the ligand **4** and the complexes **3**, **5** and **6**, respectively. It was found that the flexibility of the supported complexes increases when the degree of polymerisation of the PEG spacer is expanded from 50 to 145. If the degree of polymerisation is enlarged to 285 the mobility is reduced which is caused by a stronger interaction among the polyethylene glycol chains. The strong increase of the linewidth from the ligand **4** to the complexes **5** and **6** is interpreted in terms of the larger chemical shift dispersion in metal complexes. This is caused by the hindered rotation of the phenyl groups of the sterically crowded transition metal complexes in the solid state.

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Notes and references

‡ *Standard procedure for* **2**: after a suspension of **1** (258 mg, 0.249 mmol) and NaH (54 mg, 2.241 mmol) in 70 ml of THF was stirred for 2 h at 80 °C, 357 µl (1.494 mmol) of $\mathrm{Cl(CH_2)_3Si(OEt)_3}$ were added dropwise at room temp. and stirred for 20 h at 60 °C. The reaction mixture was allowed to cool to room temp. and was neutralised and separated from precipitated salts by passing the suspension over a column of dry $\mathrm{NH_4Cl}$ (3 cm). The solvent was removed *in vacuo* and the oily residue treated with 30 ml of *n*-pentane. The yellow precipitate was separated and washed with *n*-pentane three times and dried *in vacuo*, Yield: 288 mg (70.0%). IR (KBr, $\mathrm{cm^{-1}}$): 1938, 1849 ν(CO). $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR ($\mathrm{CDCl_3}$): δ 46.7. ^{1}H NMR (acetone-d_6): δ 0.54–0.60 (m, $\mathrm{SiCH_2}$), 1.17 (t, $^3J_{\mathrm{HH}}$ 7.2 Hz, $\mathrm{OCH_2C}\mathit{H}_3$), 1.55–1.75 (m, $\mathrm{SiCH_2C}\mathit{H}_2$), 1.77–1.93 (m, $\mathrm{CH}\mathit{H}_\mathrm{e}$), 2.44–2.79 (m, $\mathrm{CH}\mathit{H}_\mathrm{a}$), 3.30–3.62 (m, $\mathrm{OCH_2CH_2OCH_2CH_2}$), 3.75 (q, $^3J_{\mathrm{HH}}$ 7.2 Hz, $\mathrm{OC}\mathit{H}_2\mathrm{CH_3}$), 7.05–7.39 (m, $\mathrm{C_6H_5}$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{CDCl_3}$): δ 7.1 (s, $\mathrm{SiCH_2}$), 17.5 (s, $\mathrm{OCH_2}\mathit{C}\mathrm{H_3}$), 23.3 (s, $\mathrm{SiCH_2}\mathit{C}\mathrm{H_2}$), 30.3 (m, $\mathrm{CH_2}$), 39.3 (br s, CP), 57.3 (s, $\mathrm{O}\mathit{C}\mathrm{H_2CH_3}$), 67.4–76.7 (m, $\mathrm{OCH_2CH_2OCH_2CH_2}$), 127.5 (s, *m*-$\mathrm{C_6H_5}$), 128.9 (s, *p*-$\mathrm{C_6H_5}$), 136.3 (m, *ipso*-, *o*-$\mathrm{C_6H_5}$).

§ *Standard procedure for* **3**: compound **2** (182 mg, 0.11 mmol), TEOS and $\mathrm{H_2O}$ were homogenised for 30 min at room temp. with a minimum amount of ethanol (0.5 ml). After one drop of $\mathrm{SnBu^n{}_2(OAc)_2}$ was added, the reaction mixture was warmed to 60 °C for 4 h and dried for another 4 h at 60 °C. The inhomogeneous gel particles were stirred in *n*-hexane (3 times for 3 h in 50 ml) and after drying *in vacuo* (1 h) washed with ethanol, acetone and *n*-hexane (each 3 × 10 ml) and again dried *in vacuo*. IR (KBr, $\mathrm{cm^{-1}}$): 1936, 1846 ν(CO). ^{31}P CP MAS NMR: δ 45.0 (s). ^{29}Si CP MAS NMR (Si-substructure): δ −59.7 (T^2), −67.2 (T^3), −92.1 (Q^2), −100.8 (Q^3), −109.2 (Q^4).

¶ *Standard procedure for* **4**: a suspension of **3** in 50 ml acetone placed in a double-walled Duran Schlenk tube was degassed and 5 ml of $\mathrm{PBu^n{}_3}$ added under $\mathrm{N_2O}$ atmosphere. The vigorously stirred suspension was cooled to 10 °C and $\mathrm{N_2O}$ was added (1.3–1.5 bar). The reaction mixture was irradiated for 30 min with the UV-light of a TQ 150W (Original Hanau) high-pressure mercury lamp, which was located 5 cm from the Schlenk tube. After complete conversion of the educt (monitored by ^{31}P CP MAS NMR spectroscopy) the red solution was filtered off and the yellow powder was washed twice with 5 ml of an aqueous solution of $\mathrm{K_2CO_3}$ (0.05 M) and three times each with 10 ml of acetone and *n*-pentane. The material was dried *in vacuo*. ^{31}P CP MAS NMR: δ 29.8 (s).

‖ *Standard procedure for* **5** *and* **6**: to 227 mg (0.035 mmol) of **4** suspended in 35 ml of $\mathrm{CH_2Cl_2}$ were added 21.9 mg (0.035 mmol) of $\mathrm{[Ir(cod)Cl]_2}$. The yellow suspension was stirred for 30 min and 24 mg (0.07 mmol) of $\mathrm{NaBPh_4}$ in 4 ml of $\mathrm{CH_2Cl_2}$ was added to the reaction mixture. After stirring for 20 h the product was separated from the solution, washed with acetone and *n*-hexane (each 3 × 5 ml) and dried *in vacuo*. IR (KBr, $\mathrm{cm^{-1}}$): 1415 ν(C=C). ^{31}P CP MAS NMR: δ 7.3 (br s). Material **6** was prepared according to the same procedure except that the suspension of **4** was added to the solution of $\mathrm{[Rh(cod)Cl]_2}$ in $\mathrm{CH_2Cl_2}$. IR (KBr, $\mathrm{cm^{-1}}$): 1462 ν(C=C). ^{31}P CP MAS NMR: δ 38.4 (br s).

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