Immobilization, Characterization, and Preliminary Reactivity Studies of Halfsandwich Ruthenium Complexes on Silica

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Summary. The complexes $[RuCp(CH_3CN)_2(Ph_2PCH_2CH_2Si(OMe)_3)]PF_6$ and $[RuCp(CH_3CN)$ $(Ph_2PCH_2CH_2Si(OMe)_3)_2]PF_6$ were obtained in good yields by treatment of $[RuCp(CH_3CN)_3]PF_6$ with 1 and 2 equivs of $Ph_2PCH_2CH_2Si(OMe)_3$. Both free $Ph_2PCH_2CH_2Si(OMe)_3$ and the two complexes were grafted onto the surface of powdered silica. The surface coverage was determined independently by ³¹P solid state NMR and IR spectroscopy. IR data revealed that for $Ph_2PCH_2CH_2Si(OMe)_3$ and the complexes 52, 52, and 18 molecules, respectively, were immobilized per 100 nm² of SiO₂ surface. Similar values were obtained from ³¹P MAS NMR measurements. With the immobilized first complex the catalytic redox isomerization of allyl alcohol to propanal has been studied by means of IR spectroscopy and ¹H NMR spectroscopy showing the quantitative formation of aldehyde. While in the first cycle satisfactory turnover numbers were achieved, the subsequent cycles showed only low conversions to aldehyde presumably due to decomposition of the complex. The immobilized second complex was catalytically inactive.

Keywords. Ruthenium complexes; Immobilization; Alkylsiloxane monolayers; Surface confined catalysts.

Introduction

Immobilization of organometallic compounds on solid substrate surfaces offers a number of interesting and useful applications and has been the subject of numerous

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studies [1]. Apart from the fundamental interest in the structure and properties of surface-confined metal complexes and their reactivity in this 'frozen' state compared to the conventional environment of a homogeneous solution, several technological applications such as nonlinear optical materials [2], nanolithographic masks of organic-organometallic block copolymers [3], or covalently bonded, supported transition metal catalysts [4] have been discovered and have urged combined efforts of classical organometallic research with surface chemistry and surface analysis.

The ultimate goal of immobilizing a reactant on a solid support is to gain control over the local concentration, the geometric orientation, and the molecular structure of a reactive species and to be able to tune its reactivity to specific, practical demands. One of the most successful strategies to anchor molecules on surfaces in a controlled and uniform orientation is based on the self-assembly process [5], where bifunctional, α, ω -disubstituted hydrocarbons $X - (CH_2)_n - Y$ are adsorbed from dilute solutions via a surface anchor group -X and form highly ordered, monomolecular films, whose outer surfaces are exclusively comprised of the second functionality -Y [6]. The present study is part of an ongoing effort in our group to exploit these favorable features of self-assembled adsorption for a controlled immobilization of transition metal complexes on solid supports. We have previously investigated a model reaction [7] of the cationic 18-electron Ru complex $[\operatorname{Ru}Cp(\eta^4 - C_5H_4O)(L)]^+$, tethered to a silica surface via a link ligand $L = Cl_3Si - (CH_2)_{16} - Y (Y = C_5H_4N, CN)$, with several tertiary phosphines and have found that in this surface-bound configuration, even strong bases react only with the diene ligand, whereas the metal center, which is the primary target in homogeneous solution, appears to be inaccessible on the surface due to the rigid, densely-packed molecular environment. In the present study, we have chosen a catalytically active model complex $[RuCp(CH_3CN)_2(PR_3)]^+$ which has been shown to catalyze the redox isomerization of allyl alcohols to aldehydes in homogeneous solution with high efficiency and high yields [8]. Both the basicity and the size of the phosphine ligand PR_3 were found to strongly influence the reaction pattern. Immobilization of this complex on silica via a ω -trialkoxysilyl-ligand $Ph_{2}PCH_{2}CH_{2}Si(OMe)_{3}$ was therefore expected to have a similar strong effect on the reaction rates and product distributions. Using a combination of FT-IR and NMR techniques for solid and liquid samples, we have attempted to a) elucidate the structure and packing density of the adsorbed catalyst, b) characterize the rate of the allyl alcohol isomerization, and c) assess the possibility of recycling and reusing the immobilized catalyst.

Results and Discussion

Synthesis and Immobilization of Ph₂PCH₂CH₂Si(OMe)₃ and Phosphine RuCp Complexes

The complexes $[RuCp(CH_3CN)_2(Ph_2PCH_2CH_2Si(OMe)_3)]PF_6$ (1) and $[RuCp(CH_3CN)(Ph_2PCH_2CH_2Si(OMe)_3)_2]PF_6$ (2) were obtained in 68 and 73% isolated yields by treatment of $[RuCp(CH_3CN)_3]PF_6$ with 1 and 2 equivs of $Ph_2PCH_2CH_2Si(OMe)_3$. Characterization was accomplished by a combination of

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Scheme 1

¹H, ¹³C{¹H} NMR, IR spectroscopy, and elemental analyses. The NMR spectra of these compounds bear no unusual features and it is sufficient to point out that in the ³¹P{¹H} NMR spectrum of **1** and **2** signals at $\delta = 47.5$ and 44.8 ppm are observed.

The ligand $Ph_2PCH_2CH_2Si(OMe)_3$ and complexes **1** and **2** were all grafted onto the silica surface according to the simplified reaction Scheme 1.

The surface coverage was determined independently by ³¹P MAS NMR and IR spectroscopy utilizing internal standards. FT-IR spectroscopy was used to examine the adsorption of the metal complexes on silica (Fig. 1). Characteristic peaks of the non-adsorbed compound are at $\bar{\nu} = 2840 \text{ cm}^{-1}$ (symmetric C–H stretch of the Si–OMe groups) and at 2280 and 2271 cm⁻¹ assignable to $\bar{\nu}$ (CN) of **1** and **2**. A further sharp band occurs at 1438 cm⁻¹ which may be assigned either to one of the two $\bar{\nu}(C-C)$ of the phenyl substituents or the $\delta(C_6H_5)$ -vibration of the phosphine moiety of the complexes [9]. These vibrations can be also detected in the spectra of the loaded silica providing evidence for the successful anchoring of 1 and 2 on the support material. The CH-region of the loaded silica shows no absorbance of the SiOMe groups indicating a high extent of hydrolysis of the methoxygroups. Values for the surface coverage of $Ph_2PCH_2CH_2Si(OMe)_3$, complexes 1 and 2 are 52 (8.63 $\cdot 10^{-4}$ mmol/m²), 52 (8.63 $\cdot 10^{-4}$ mmol/m²), and 18 molecules $(2.99 \cdot 10^{-4} \text{ mmol/m}^2)$ per 100 nm^2 of SiO₂ surface. Comparable values were obtained from single pulse ³¹P solid state NMR spectroscopy revealing that 39, 66, and 13 molecules of $Ph_2PCH_2CH_2Si(OMe)_3$ and complexes 1 and 2 were immobilized per 100 nm^2 of SiO₂ surface. The ³¹P-CP/MAS NMR spectra of free and immobilized 1 and 2 are shown in Fig. 2. These data correspond well to the solution chemical shifts (see Exp.).



Fig. 1. IR spectra of 1 and 2 in the solid reference state (bottom) and adsorbed on silica (top); the hatched bands represent SiO₂ vibrations

The following conclusions can be drawn from these results: a) The surface coverage is determined primarily by the size of the phosphine ligand, as indicated by the fact that the coverages of the isolated ligand $Ph_2PCH_2CH_2Si(OMe)_3$ and **1** are essentially the same. Complex **2**, on the other hand, yields a coverage of only about 30% of complex **1**. b) The surface coverage of unsubstituted, long-chain hydrocarbon films obtained by adsorption of octadecyltrimethoxysilane $CH_3(CH_2)_{17}Si(OMe)_3$, for example, is on the order of 500 molecules per 100 nm² of silica surface [10], which is about one order of magnitude higher than the phosphine-substituted compounds in this study. Thus, the larger cone angle of the phosphine group in diphenylalkylphosphines Ph_2PR appears to prevent a dense packing and interlocking of the alkyl groups as in unsubstituted hydrocarbon films. However, the coverages achieved here are still about a factor of 5–10 higher than literature results with comparable complexes such as $Ph_2PCH_2CH_2Si(OMe)_3$ Ru(CO)₄ [9] or $Ph_2PCH_2CH_2Si(OEt)_3Rh(CO)Cl$ [4c].

Redoxisomerization of Allyl Alcohol to Propanal Catalyzed by Immobilized **1**

Recently *Kulawiec* and *Trost* have shown [11] that the isomerization of allyl alcohols to the corresponding aldehyde is catalyzed by $RuCp(PPh_3)_2Cl$ in the presence



Fig. 2. ³¹P-CP/MAS NMR spectra of **1** and **2** in the solid reference state (bottom) and adsorbed on silica (top)

of NH₄PF₆. Since the catalyst is substitutionally inert, high temperatures (typically 100°C in dioxane as the solvent) and high concentrations of both a chloride scavenger (10 mol%) as well as the catalyst (5 mol%) have been used. We have improved this process by utilizing the cationic complex $[\text{Ru}Cp(\text{PR}_3)(\text{CH}_3\text{CN})_2]^+$ (R = Me, Ph, Cy) [8]. Here we investigate the isomerization of allyl alcohol to propanal catalyzed by immobilized **1** and **2** by means of IR spectroscopy and ¹H NMR spectroscopy.

Treatment of immobilized 1 (2 mg, 2.05 mol% of pre-catalyst) with allyl alcohol in fluorobenzene at 60°C affords quantitatively propanal as monitored *in situ* by IR spectroscopy (Fig. 3). The decreasing OH-peak of the allyl alcohol and the increasing peak at $\bar{\nu} = 2714 \text{ cm}^{-1}$ (one of the two CH-peaks of the CHO-group of the emerging aldehyde) were periodically monitored by IR spectroscopy. The $\bar{\nu}$ (CO) stretching frequency of propanal could not be used for monitoring the isomerization process since this signal was superimposed by the intensive Si–O stretching frequencies of SiO₂ (see Fig. 1, hatched bands). After each reaction cycle, the reactant solution was removed by syringe. The catalyst was dried and recovered by purging N₂ through the cell for 15 minutes. As shown in Fig. 3, only the first cycle exhibits satisfactory turnover numbers of allyl alcohol. The second and third cycles show only low conversions to aldehyde while a decrease of the



Fig. 3. Band intensities of $\bar{\nu}(OH)$ at 3620 cm⁻¹ (bottom) and of $\bar{\nu}(CH)$ at 2714 cm⁻¹ (top) for the isomerization of allyl alcohol to propanal as a function of reaction time; the labels 1, 2, and 3 represent three consecutive reaction cycles with freshly prepared reactant solution in contact with the recovered catalyst

OH-band of allyl alcohol is still observed. A side reaction of allyl alcohol with the substrate SiO₂ could be excluded from measurements of pure SiO₂ (without catalyst) in contact with allyl alcohol in fluorobenzene, which did not show any spectral changes with time. The adsorbed catalyst after 3 reaction cycles showed the same intensity for the $\bar{\nu}$ (C–C)/ δ (C₆H₅)-vibration at $\bar{\nu}$ = 1438 cm⁻¹ as the initial, freshly adsorbed catalyst. Likewise, the ³¹P-CP/MAS NMR spectrum of the recycled catalyst was identical with that of freshly immobilized **1**. Thus, leaching of the catalyst appears to be unlikely but cannot be conclusively ruled out. The $\bar{\nu}$ (CN) peak at $\bar{\nu}$ = 2280 cm⁻¹, however, disappeared after the first reaction cycle suggesting that the catalyst may be converted into another species, which no longer catalyzes the reduction of allyl alcohol to propanal, but still converts allyl alcohol to some unknown product concomitant with loss of the hydroxyl group. The reason for this behavior, however, remains unclear.

The same reaction has been also performed with immobilized 1 (80 mg, 0.15 mol% of pre-catalyst) in neat allyl alcohol (1 cm^3) at 70°C for 24 h. The formation of propanal was monitored by ¹H NMR spectroscopy revealing that after 30 min, 3, 6, and 24 h approximately 2, 18, 46, and 100% of propanal were formed. There was no evidence for other side products. The catalyst was recovered by removal of the solvent, drying under vacuum, and washing with *n*-pentane and the next catalytic cycle was performed under the same reaction conditions. However, ¹H NMR spectroscopy showed that only 8% of allyl alcohol was converted to propanal. In subsequent cycles the solid sample exhibited no longer any catalytic activity.

Finally, it has to be noted that immobilized **2** was inactive for the redoxisomerization of allyl alcohol and no propanal could be detected.

Conclusion

In the present contribution mono- and bisphosphine complexes of the types $[RuCp(CH_3CN)_2(Ph_2PCH_2CH_2Si(OMe)_3)]PF_6$ (1) and $[RuCp(CH_3CN)(Ph_2PCH_2CH_2Si(OMe)_3)_2]PF_6$ (2) were prepared and subsequently immobilized on SiO₂. This was achieved under mild conditions with a high surface coverage. The structure and packing density of the adsorbed complexes could be determined by two independent methods *viz* ³¹P MAS NMR and IR spectroscopy. Immobilized 1 and 2 and were tested as catalysts for the redoxisomerization of allyl alcohol to propanal. Whereas with 1 quantitative conversion was achieved in the first run, decomposition of the catalyst occurred in subsequent reaction cycles with concomitant loss of catalytic activity. In contrast to immobilized 1, complex 2 was catalytically inactive.

Experimental

General

All manipulations were performed under an inert atmosphere of N₂ or Ar by using Schlenk techniques and a glove box. All chemicals were standard reagent grade and used without further purification. The solvents were purified according to standard procedures [12]. The deuterated solvents were dried over 4 Å molecular sieves. [Ru*Cp*(CH₃CN)₃]PF₆ and *Ph*₂PCH₂CH₂Si(*OMe*)₃ were prepared according to Refs. [13, 14]. All experiments were carried out with Merck silica (specific surface area $388 \pm 2 \text{ m}^2/\text{g}$). The silica was treated in an UV-cleaning chamber prior to use to remove adsorbed organic impurities but was not dried at elevated temperatures. The complexes gave satisfactory C and H elemental analyses.

Liquid-State NMR and IR Spectroscopy

¹H, ¹³C{¹H}, and ³¹P{¹H} NMR spectra were recorded on a Bruker Avance-250 spectrometer operating at 250.13, 62.86, and 101.26 MHz and were referenced to $SiMe_4$ and H_3PO_4 (85%). Infrared spectra were recorded on Mattson RS-10000 and Perkin-Elmer 16PC FT-IR spectrometers.

Solid-State NMR Spectroscopy

All ³¹P NMR spectra were recorded on a Bruker Avance 300 spectrometer (standard bore), equipped with a 4 mm broad-band MAS probehead and ZrO₂ rotors. The rotational speed for all experiments was 12 kHz. Phosphorous spectra were referenced with respect to 85% H₃PO₄ (aq) by setting the ³¹P NMR peak of solid PPh₃ to -7.0 ppm. ³¹P-CP/MAS spectra (cross polarization with magic angle spinning) were measured with a contact time of 3 ms and a relaxation delay of 6 s. Quantitative measurements were done by ³¹P single pulse experiments with a relaxation delay time of 120 s.

Synthesis of $[RuCp(CH_3CN)_2(Ph_2PCH_2CH_2Si(OMe)_3)]PF_6$ (1)

A solution of $[RuCp(CH_3CN)_3]PF_6$ (0.100 g, 0.230 mmol) and 1 equiv of $Ph_2PCH_2CH_2Si(OMe)_3$ (0.077 g, 0.230 mmol) in 5 cm³ of CH₂Cl₂ was stirred for 2 h at room temperature. Upon removal of the solvent under reduced pressure, a yellow compound was obtained which was collected on a glass frit, washed with petroleum ether, and dried under vacuum. Yield 0.109 g (68%); ¹H NMR (acetone-d₆,

20°C): $\delta = 7.66-7.40$ (m, 10H, PPh₂), 4.53 (s, 5H, Cp), 3.53 (s, 9H, Si(OMe)₃), 2.70–2.55 (m, 2H, PCH₂CH₂), 2.38 (d, $J_{PH} = 1.42$ Hz, 6H, NC–CH₃), 0.71–0.53 (m, 2H, PCH₂CH₂); ¹³C{¹H} NMR (acetone-d₆, 20°C): $\delta = 132.2$ (d, $J_{PC} = 40.4$ Hz, Ph¹), 132.9 (d, $J_{PC} = 10.1$ Hz, Ph^{2. 6}), 130.4 (d, $J_{PC} = 2.8$ Hz, Ph⁴), 128.9 (d, $J_{PC} = 9.7$ Hz, Ph^{3. 5}), 128.6 (s, NC–CH₃), 22.9 (d, ¹ $J_{PC} = 22.9$ Hz, PCH₂CH₂), 76.5 (d, $J_{CP} = 1.84$ Hz, Cp), 50.4 (d, $J_{PC} = 1.8$ Hz, Si(OMe)₃), 4.00 (d, ² $J_{PC} = 2.76$ Hz, PCH₂CH₂), 3.2 (d, $J_{PC} = 0.9$ Hz, NC–CH₃); ³¹P{¹H} NMR (acetone-d₆, 20°C): $\delta = 47.5$ (PPh₂), -146.5 (¹ $J_{PF} = 707.9$ Hz, PF₆); IR (KBr): $\bar{\nu} = 2280$ cm⁻¹ (CN).

Synthesis of $[RuCp(CH_3CN)(Ph_2PCH_2CH_2Si(OMe)_3)_2]PF_6$ (2)

This complex has been obtained analogously to **1** utilizing 0.1 g of $[\text{Ru}Cp(\text{CH}_3\text{CN})_3]\text{PF}_6$ (0.230 mmol) and 0.154 g of $Ph_2\text{PCH}_2\text{CH}_2\text{Si}(OMe)_3$ (0.460 mmol). Yield 0.173 g (73%); ¹H NMR (acetone-d₆, 20°C): $\delta = 7.61-7.21$ (m, 20H, PPh₂), 4.76 (s, 5H, Cp), 3.47 (s, 18H, Si(OMe)_3), 2.53 (s, 3H, NC-CH₃), 2.28-2.09, 1.86-1.76 (m, 4H, PCH₂CH₂), 0.45-0.26 (m, 4H, PCH₂CH₂); ¹³C{¹H} NMR (acetone-d₆, 20°C): $\delta = 137.1$ (m, Ph), 134.5 (m, Ph), 132.8 (m, Ph), 130.6 (s, Ph), 130.2 (s, Ph), 129.6 (s, NC-CH₃), 128.9 (m, Ph), 82.3 (d, $J_{PC} = 0.5 \text{Hz}$, Cp), 50.4 (s, Si(OMe)_3), 21.9 (t, ¹J_{PC} = 11.3 \text{Hz}, PCH₂CH₂), 4.6 (t, ²J_{PC} = 3.2 \text{Hz}, PCH₂CH₂), 3.8 (s, NC-CH₃); ³¹P{¹H} NMR (acetone-d₆, 20°C): $\delta = 44.8$ (PPh₂), -143.0 (¹J_{PE} = 707.7 Hz, PF₆); IR (KBr): $\bar{\nu} = 2271$ cm⁻¹ (CN).

Immobilization of Ph₂PCH₂CH₂Si(OMe)₃, 1, and 2

The phosphine ligand $Ph_2PCH_2CH_2Si(OMe)_3$ as well as complexes **1** and **2** were immobilized by rigorously stirring a suspension of SiO₂ and an appropriate amount of ligand or complex (typically 280 mmol of substrate per 250 mg of SiO₂) in 20 cm³ of toluene under dry N₂ for 24 h at room temperature. The solid was separated by centrifuging. Upon removal of the supernatant, the silica was washed several times with dry CH₂Cl₂ and again centrifuged. The samples were dried under vacuum at room temperature for 24 h and characterized by means of ³¹P-CP/MAS NMR: signals at -14.7, 49.1, and 39.9 ppm for immobilized $Ph_2PCH_2CH_2Si(OMe)_3$, **1**, and **2**.

The surface coverage was determined by two independent methods. *Method A*. An IR-calibration curve was generated by mixing weighted amounts of the respective complex and silica in order to simulate silica with different surface coverages. IR-spectra were then obtained by mixing these powders with KBr and pressing them into disks containig 5.6 w/w% of the calibration mixture. The $\delta(C_6H_5)$ -vibration of the phosphine group of the complex was integrated and the peak area as a function of surface coverage was determined. The liquid phosphine ligand $Ph_2PCH_2CH_2Si(OMe)_3$ was polymerised in 5 w/w% HCl, filtered off, and dried *in vacuo* prior to use. Values for the surface coverage for $Ph_2PCH_2CH_2Si(OMe)_3$, **1**, and **2** are 52 molecules/100 nm² (8.63 · 10⁻⁴ mmol/m²), 52 molecules/100 nm² (8.63 · 10⁻⁴ mmol/m²), and 18 molecules/100 nm² (2.99 · 10⁻⁴ mmol/m²).

Method B. The surface coverage was determined by means of ³¹P MAS NMR spectroscopy integrating the ³¹P signals of mixtures of the surface-immobilized compounds together with a weighted amount of $[NBu_4^n]PF_6$ for the free ligand and $Ph_3P = O$ for complexes **1** and **2** as a standard utilizing single pulse experiments with a pulse delay of 120 s. The integral of the ³¹P signal of PF₆⁻ counterion in **1** and **2** has been set to unity. Values for the surface coverage for $Ph_2PCH_2CH_2Si(OMe)_3$, **1**, and **2** are 39 molecules/100 nm² ($6.43 \cdot 10^{-4} \text{ mmol/m}^2$), 66 molecules/100 nm² ($11.00 \cdot 10^{-4} \text{ mmol/m}^2$), and 13 molecules/100 nm² ($2.18 \cdot 10^{-4} \text{ mmol/m}^2$).

Redoxisomerization of Allyl Alcohol to Propanal Catalyzed by Immobilized 1

Method A. Allyl alcohol was dissolved in fluorobenzene (1 v/v% solution) to provide IR-transmittance of the sample. The reaction was monitored between CaF₂-plates separated by a 0.2 mm teflon spacer. Upon addition of 2 mg of immobilized **1** (corresponds to *ca.* 2.05 mol% of pre-catalyst) and 180 mm³ of allyl alcohol in fluorobenzene a start spectrum was recorded. The reactant solution was heated to

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 60° C and additional spectra were recorded after defined intervals. All spectra were referenced against neat fluorobenzene. The changes in the IR spectra were used to monitor the conversion of allyl alcohol to propanal by integration of the decreasing OH-peak of allyl alcohol and the increasing peak at $\bar{\nu} = 2714 \text{ cm}^{-1}$ (one of the two CH-peaks of the CHO-group of the emerging aldehyde). After each reaction cycle, the reactant solution was removed by syringe. The catalyst was dried and recovered by purging N₂ through the cell for 15 minutes. The cell was refilled with fresh dilute solution of allyl alcohol and the next catalytic cycle was performed.

Method B. A suspension of 80 mg of immobilized **1** (corresponds to *ca*. 0.15 mol% of pre-catalyst) in 1 cm³ of neat allyl alcohol was stirred in a *Schlenk* tube at 70°C for 24 h. After that a ¹H NMR spectrum was recorded revealing the quantitative formation of propanal. The catalyst was recovered by removal of the solvent, drying under vacuum, and washing with *n*-pentane and the next catalytic cycle was performed. ¹H NMR spectroscopy showed that only 8% of allyl alcohol had been converted to propanal. In subsequent cycles the solid sample exhibited no longer catalytic activity. Under the same reaction conditions, immobilized **2** was catalytically inactive and no propanal could be detected even after prolonged reaction times.

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