Experimental Section

Measuring equipment: High-performance pH meter pMX 2000 (WTW, reading accuracy: 0.001 pH units) with temperature sensor, proportioning system ACCUSTEP (Tri-Continent Scientific), single-rod glass electrode 2GE1-DOKA (Jumo) with double-compartment system (salt bridge), cadmium-selective electrode Cd500 (WTW), titration cell with jacket for thermostatting. Chemicals: Analytically pure $HPC_2^+CF_3COO^-$ (C/H/F/N/S), $Cd(NO_3)_2 \times 4H_2O$ p. a., 0.1M aqueous solution of KOH (Aldrich, volumetric standard), 0.1M nitric acid (Aldrich, volumetric standard), KNO_3 (Fluka, MicroSelect, >99.5%). Measuring conditions: Aqueous solution, $T = 25.00 \pm 0.02\,°C$, ionic strength $I = 1.00\,M$ kept constant with KNO_3 as supporting electrolyte during the entire titration, humidified N_2 protective atmosphere. The pK_w value was determined to be 13.76. Calibration of pH meter and electrode system by strong acid/strong base titration.[13] Test system: Ni^{II}/glycine.[14] Titration example: $Cd(NO_3)_2$ (67.1 µmol) and $HPC_2^+CF_3COO^-$ (65.8 mg, 100.7 µmol) in supporting electrolyte solution (50.0 mL), adjusted to pH 2.5 with a known amount of nitric acid, titration with carbonate-free 0.1016M KOH solution (adjusted to $I = 1.00\,M$) up to pH 10.5. pK_a values: five titrations with a total of 336 experimental points ($\sigma_{fit} = 0.0039-0.0086$). Complex formation constants: seven titrations with different PC_2:Cd^{II} ratios and a total of 677 experimental points ($\sigma_{fit} = 0.0021-0.0086$). Program used: BEST.[5]

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[11] The partial occurrence of sulfide as a ligand complicates the situation (see for example the discussion in ref. [4c]).

[12] It has still to be studied in detail to which degree processes play a role that are coupled to the dissociation equilibrium, such as the complex formation of Cd^{II} with ligands of the vacuole.

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Colloid-Bound Catalysts for Ring-Opening Metathesis Polymerization: A Combination of Homogenous and Heterogeneous Properties[**]

Marcus Bartz, Jörg Küther, Ram Seshadri, and Wolfgang Tremel[*]

The advantages and disadvantages of molecular or homogenous versus surface-bound or heterogeneous catalysts are well known. The properties of the two kinds of catalyts have been combined by attaching catalytically active species to soluble polymers, which can be bound to highly branched macromolecules.[1] The use of transition metal ions as an intrinsic part (as "supramolecular glue") of highly branched systems also provides potential for the construction of hybrid catalytic systems.[2] Exploiting the fact that thiol-functionalized gold colloids behave like molecules (they are volatile, soluble, can be chromatographed) and possess a surface similar to the (111) surface of bulk gold, we have used a substituted, long-chain thiol to tether a Ru catalyst for ring-opening metathesis polymerization (ROMP) to gold colloids. The colloid-bound Ru species heterogeneously catalyzes the polymerization of norbornene in dichloromethane. At the same time, the catalyst system is readily soluble in and recoverable from acetone and therefore behaves like a molecular species. An interesting feature of the present catalytic system is the observation of much higher turnover frequencies (TOF) of the bound catalyst compared to the unbound molecular form.

Gold salts can be reduced in toluene in the presence of long-chain thiols [3] to give a material that almost perfectly bridges the world of molecular chemistry and the macroscopic world of extended solids and has opened up an exciting new area of nanomaterials.[4] The thiol-coated gold colloids (usually in the 2–10 nm size range) behave like molecules in that they can be dissolved, precipitated, redissolved, sublimed, crystallized, etc. This permits the use of characterization techniques such as solution NMR and time-of-flight MS that are not normally suitable for the study of solids. On the other hand, these colloids possess a distinct solid surface, not unlike the (111) surface of gold that has been the subject of many studies.[5,6]

We have been examining the binding of catalysts to gold (111) surfaces with ω-functionalized thiols with the intention of obtaining specific nanostructured materials, including functionalized atomic force microscopy (AFM) tips. One of the problems associated with multiple chemical modifications on a surface is the difficulty of characterizing the intermediates. This encouraged us to attempt the successive function-

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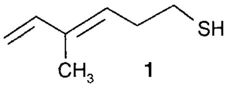
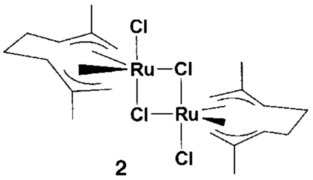
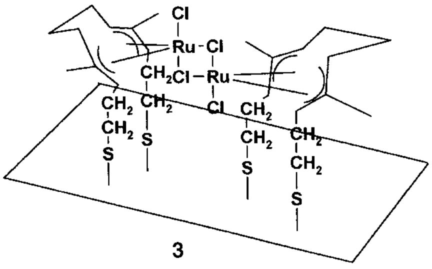
alization of gold colloids in solution. The advantages are that the reactions could be monitored very simply, for example, by FT-IR spectroscopy in the transmission mode or by NMR spectroscopy in solution. During these investigations, we prepared the thiol **1**, which has a terminal hexadiene functionality. This thiol binds to gold colloids in nonpolar solvents to give stable functionalized colloids that remain in solution unless precipitated with a polar solvent. The functionalized colloids coordinate to $\mathrm{RuCl_3}$ through the hexadiene functionality to yield a known catalytically active material[7, 8] that is acetone soluble with a high activity for the heterogeneous ROMP catalysis of norbornene in dichloromethane.[9] For further characterization of this surface-bound catalytic system, gold-coated glass slides were treated with **1** and then with $\mathrm{RuCl_3}$. This process, which also gives the active catalyst, was investigated by surface plasmon spectroscopy (SPS). Gold colloids were functionalized with **1** in toluene. The thiol-coated colloids were precipitated with methanol and dried for recording FT-IR spectra in pressed KBr pellets. The fact that the colloidal powder redissolves in toluene confirms that the colloids are thiol-passivated. The toluene solution was stirred with $\mathrm{RuCl_3 \cdot 5\,H_2O}$ for four days, during which time a precipitate formed. Washing the precipitate with methanol to remove excess $\mathrm{RuCl_3}$ gave a free-flowing powder that catalyzed the heterogeneous polymerisation of norbornene in dichloromethane. The powder was sufficiently soluble in [D$_6$]acetone for a ^{1}H NMR spectrum to be recorded. The FT-IR spectra were recorded on the powder in pressed KBr pellets. The spectra are consistent with the presence of the Cl-bridged dimeric catalytic species **2**[7] and suggest the formation of the colloid-bound catalyst **3**. The FT-IR spectra of the molecular catalyst and of the catalyst bound to gold colloids is shown in Figure 1. Blank experiments with $\mathrm{RuCl_3}$, with gold colloids, and with gold–glass substrates confirmed the specific catalytic activity of **3**.







The binding of the catalyst to the surface was monitored by recording SP spectra after successively exposing a gold-coated glass substrate to the thiol in toluene for 20 min at room temperature and then to $\mathrm{RuCl_3}$ in ethanol at 80 °C for 4–5 h. The spectra (Figure 2) are consistent with the accumulation of material on the gold surface. Exposure of this coated gold surface to norbornene in dichloromethane followed by work-up with methanol led to the formation of a white polymer film on the substrate. Because the SP spectra were recorded against water as the working medium, (necessary because of the refractive index), the solvent in the SP cell had to be changed after each reaction step. Thus much of the polymeric material was washed away. Hence curve 4 in Figure 2 can not be quantitatively evaluated and simply gives a qualitative indication of the increased surface thickness.

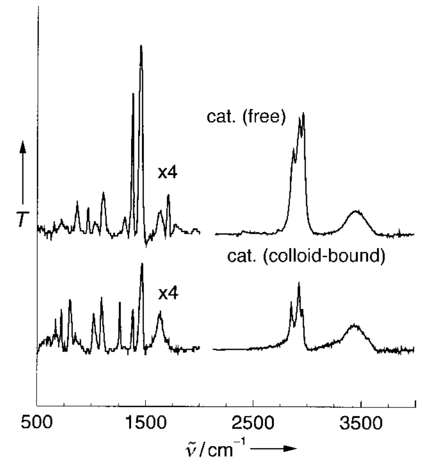


Figure 1. FT-IR spectra of the Ru ROMP catalyst unbound (A) and bound to gold colloids (B). T = transmission.

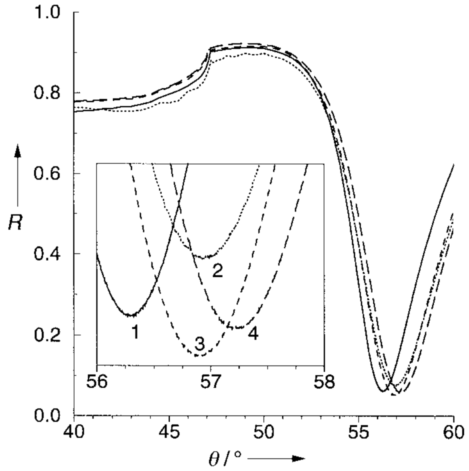


Figure 2. Surface plasmon resonance (SP) spectra of the clean gold surface (1), the surface after coverage with the thiol **1** (2), after exposure to $\mathrm{RuCl_3}$ in ethanol (3), and after polymerization of norbornene (4). All spectra were acquired in water.

Gel-permeation chromatographic analysis (polystyrene standard, Pl-Gel column combination 10^3–10^4 Å, trichloromethane solvent) of the polymeric material revealed that the polymer formed by catalysis on the modified gold-coated glass slides typically had a molecular weight of $M_w = 22\,000$ and a polydispersity index M_w/M_n of 2.2, whereas the colloid-bound catalyst yielded a polymer with $M_w = 17\,000$ and $M_w/M_n = 4.3$.

For the molecular (homogeneous) catalyst in dichloromethane, a TOF of 3000 h^{-1} was determined, similar to the TOFs of catalysts in earlier investigations.[8] For the catalyst bound to the colloid surface, the TOF was 16 000 h^{-1}, and for the catalyst on the flat gold surface, it was 80 000 h^{-1}. For calculating the TOF of the colloid- and surface-bound systems, the amount of catalyst was estimated by assuming full monolayer coverage in which each thiol molecule occupies an area of approximately 25 Å^2. Since full coverage is unlikely, the amount of catalyst is overestimated, and the TOFs of the bound catalysts represent lower limits of their activities. The dramatic increase in catalytic activity noted here is in keeping with a recent report of catalysts organized in Langmuir–Blodgett films[10] and is probably connected with the orientation of the catalyst on the surface in a manner that favors its interaction with the monomer and the growing polymer chain.

Experimental Section

6-Chloro-3-methyl-1-hexen-3-ol **A** was prepared by the method of Kise et al.[11] Vinyl bromide (50 g) was liquefied in a dry ice bath and was dissolved in THF (50 mL). Ethyl bromide (1 mL) and iodine (0.2 g) were added to magnesium (14.2 g) in THF (100 mL) under inert gas. The mixture was stirred at room temperature for 5 min. The solution of vinyl bromide in THF was then added slowly to the mixture. The mixture was stirred at room temperature overnight and then cooled to 10 °C. A solution of 5-chloropentanone (60 g) in THF (60 mL) was added at below 20 °C. The mixture was then allowed to warm to room temperature, stirred for an additional 2 h, and poured into 10 % HCl (300 mL). The organic layer was separated, and the aqueous layer was saturated with NaCl and extracted with ether. The organic phases were combined, dried over sodium sulfate, and the solvent evaporated. The remaining crude oily product was distilled under vacuum (3×10^{-2} mbar, b.p. 51 °C). Yield: 50 %. IR $\tilde{\nu} = 3450$ (OH), 3080 ($-CH{=}CH_2$), 2960–2870 (CH_2,CH_3) 1630 (C=C), 1470 (CH), 1311, 1105, 997, 918 cm^{-1} ($-CH{=}CH_2$); ^{1}H NMR: $\delta = 1.26$ (s, 3H, CH_3), 1.4–2.2 (m, 4H, $ClCH_2\mathit{CH_2CH_2}$), 3.50 (t, 2H, $ClCH_2$), 4.8–5.3 (m, 2H $=CH_2$), 5.68 (q, 1H $\mathit{CH}{=}CH_2$).

6-Chloro-3-methyl-1,3-hexadiene **B**: P_2O_5 (40 g) was added to a solution of **A** (30 g) in toluene (150 mL) at room temperature. The mixture was stirred for 1 h, and the white precipitate filtered off. The filtrate was washed with 5 % aqueous sodium hydrogencarbonate solution, saturated with NaCl, and dried over sodium sulfate. The toluene was removed under reduced pressure and the residual oil was distilled under vacuum (3×10^{-2} mbar, b.p. 60 °C). Yield: 55 %. IR: $\tilde{\nu} = 3090$, 2960 (CH_2, CH_3), 1606 (C=C), 1442, 1375, 1303, 1085, 997, 904 cm^{-1} ($-CH{=}CH_2$); ^{1}H NMR: $\delta = 1.70$, 1.79 (s, 3H, CH_3), 2.55 (q, 2H, $C\mathit{H_2}CH{=}$), 3.45 (t, 2H, $ClCH_2$), 4.92 (d, 1H *cis*-$CH{=}C\mathit{H_2}$), 5.06 (d, 1H, *trans*-$CH{=}C\mathit{H_2}$), 5.4 (t, 1H, $CH_2C\mathit{H}{=}$), 6.25, 6.65 (2q, 1H $C\mathit{H}{=}CH_2$).

3-Methyl-6-sulfanyl-1,3-hexadiene **C**: A solution of **B** (2 g) in ethanol (20 mL) was heated to reflux, and a solution of $Na_2S_2O_3$ (4 g) in water (20 mL) was added dropwise. The mixture was heated at reflux under inert gas for 4–5 h. The reaction mixture was added dropwise to deoxygenated 1N HCl (100 mL), and the mixture was heated to reflux for 4 h under argon atmosphere. It was then cooled to room temperature. The product was collected by shaking the solution with CH_2Cl_2. The organic layer was dried over sodium sulfate, and the solvent removed under reduced pressure. Yield: 60 %; m.p. 94 °C; IR: $\tilde{\nu} = 2960$–2870 (CH_2, CH_3), 2688 ($-SH$), 1440, 1375, 1309, 1163, 1053, 848 ($-CH{=}CH_2$); EI-MS: m/z (%): 128.22 (36.69) (monomer), 256.41 (54.37) (dimer).

Gold colloids **D** were prepared by the method of Brust et al.[3] by pouring 20 mL of an aqueous solution of $HAuCl_4$ (2 g in 100 mL H_2O) into a separating funnel. Toluene (80 mL) was added along with tetraoctylammonium bromide (0.12 g). Shaking the funnel transferred the $HAuCl_4$ from the aqueous into the toluene phase. Reduction at the water/toluene interface was performed with $NaBH_4$ (1.2 g) in water (25 mL). The organic layer became ruby red due to the formation of the colloid. Such colloids have been previously characterized by us.[12]

1. Synthesis of [dichlorobis(μ-chloro)bis[(3,4,5-η:8,9,10-η)-4,9-dimethyl-1,12-disulfanyldodecadienediyl]ruthenium(IV)] **E** on gold colloids: **C** (100 µL) was added to a solution of gold colloid **D** in toluene (80 mL) and the mixture stirred for 1 h. $RuCl_3 \cdot 5H_2O$ (0.1 g) was then added to the solution and the mixture was heated to reflux under argon for four days. The black precipitate was collected by filtration and washed with methanol to remove excess $RuCl_3$.

2. Synthesis of **E** on gold substrates: gold-coated glass slides were placed in a solution of **C** (100 µL) in toluene (50 mL) and stirred for 15 h. $RuCl_3$ was added and the mixture was heated under reflux until the solution became green. The gold-coated glass slide was removed, washed with ethanol, and stored under argon.

Polynorbornene **F**: 2-Norbornene (1.5 g) was dissolved in CH_2Cl_2 (12 mL), and 3 mL of a 10^{-2} M solution of ethyl diazoacetate in CH_2Cl_2 was added to the solution. Then 0.01 g of the colloid-bound catalyst or the catalyst-functionalized glass slide was added, and the liquid phase was stirred at 25 °C. The polymerization was stopped after different periods of time (Table 1) by adding methanol. The crude polymer was collected by filtration and purified by dissolving in toluene and reprecipitating with methanol.

Table 1. Ring-opening metathesis polymerization of norbornene with unbound and bound catalysts

Catalyst	Yield[a] [%]	t [min]	$c_{\text{cat.}}$ [M]	TOF[b] [h^{-1}]
unbound	30	5	8×10^{-6}	2990
colloid-bound	90	60	9.9×10^{-7}	15 000
bound on functionalized glass slide	30	15	2.55×10^{-7}	75 000

[a] Yield refers to isolated polymer. [b] TOF = turnover frequency in mol(polynorbornene)/[mol (catalyst) · h].

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