Towards Main-Chain-Polyoxometalate-Containing Hybrid Polymers: A Highly Efficient Approach to Bifunctionalized Organoimido Derivatives of Hexamolybdates**

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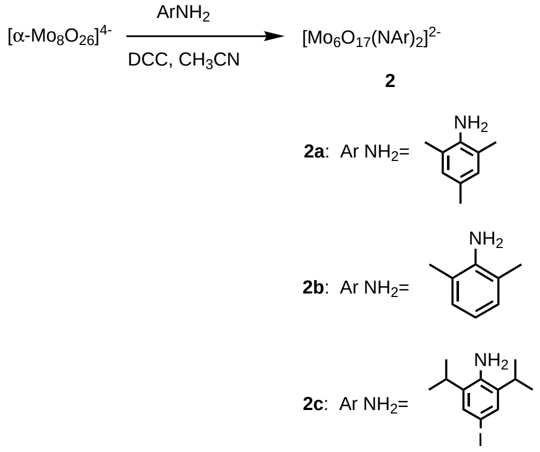
There have been increasing efforts towards making multifunctional hybrid materials by using covalently linked polyoxometalates (POMs) and organic polymers.[1–5] The motivation lies not only in the combination of the so-called value-adding properties,[6,7] but also in the exploration of possible synergistic effects.[8,9] For example, the covalent grafting of electron-accepting POMs into an organic conjugated polymer may result in highly photoconductive materials with photochromic effects. Judeinstein reported the first POM–polymer hybrid ten years ago where a lacunary Keggin POM cluster was covalently linked to a polystyrene or polymethacrylate backbone through Si–O bonds.[1] This approach has been expanded recently by Lalot and co-workers to prepare polymer–POM cross-linked networks[2] and by Stein and co-workers to generate macroporous silica materials functionalized with POM clusters.[3,4] A polymer–POM hybrid has also been reported recently by Maatta and co-workers.[5] While these works are exemplary, they all involve insulating non-conjugated polymers and the POMs are all introduced as polymer pendants. To our knowledge, there has been no report of covalently embedding POMs in the main chain of a conjugated polymer or any organic polymer. This might be because of the critical challenges associated with preparing pure bifunctionalized POMs in sufficient quantity (that is, in gram amounts). Although the bifunctionalization of hexamolybdates with organoimido ligands has been demonstrated,[10] the reaction always results in a mixture of various multiple functionalized products, which makes the isolation of large amounts of the desired bifunctionalized product tedious and impractical, if not impossible. This situation is expected since POMs usually have numerous equally reactive sites. Selective functionalization other than mono or exhaustive functionalization is thus hard to achieve.[11] Herein we report an unusual transformation which allows the selective synthesis of bifunctionalized hexamolybdates in high yields. The reaction is clean and the purification is simple, which paves the way for the synthesis of main-chain-POM-containing polymers. A bifunctionalized cluster (compound **2c**, see scheme 1) with two iodo functional groups has been synthesized and successfully applied as a monomer for the synthesis of the first POM–conjugated-polymer hybrid.



Scheme 1. Synthesis of bifunctionalized hexamolybdates.

We have previously reported an efficient method for the direct functionalization of the hexamolybdate ion [Eq. (1), where DCC = *N,N'*-dicyclohexyl methanediimine].[12] Attempting to use the same approach but with higher amine loading ratios failed to generate the bifunctionalized product in high yields. Instead, a mixture of various polyfunctionalized products are formed and thus repeated recrystallization is needed for product purification. When the tetrabutylammonium salt of the α-octamolybdate ion, $[\alpha\text{-Mo}_8O_{26}]^{4-}$, is subjected to the same reaction conditions, however, bifunctionalized hexamolymbdate products are selectively synthesized (Scheme 1). Yields of over 60% are readily obtained.

$$[\mathrm{Mo_6O_{19}}]^{2-} + \mathrm{ArNH_2} \xrightarrow[\mathrm{CH_3CN}]{\mathrm{DCC}} [\mathrm{Mo_6O_{18}(NAr)}]^{2-} \qquad (1)$$

We carried out the reaction of the $[\alpha\text{-Mo}_8O_{26}]^{4-}$ ion with TMA in deuterated acetonitrile and monitored the reaction mixture directly by ^{1}H NMR spectroscopy. The same reaction but with the $[Mo_6O_{19}]^{2-}$ cluster was also carried out for comparison. TMA has one single resonance signal for the aromatic protons in its ^{1}H NMR spectrum, as do the functionalized products, which makes monitoring of the reaction convenient. It is found that with an POM:amine:DCC ratio of 1:2:2, both reactions are completed in 12 h. As shown by the NMR spectra in Figure 1, the $[Mo_8O_{26}]^{4-}$ cluster gives overwhelmingly the bifunctionalized products, whereas $[Mo_6O_{19}]^{2-}$ gives mixtures of both mono- and bifunctionalized products. The resonance signal at 6.88 ppm corresponds to the monofunctionalized product, while the one at 6.86 ppm corresponds to the *cis* bifunctionalized product. Notice that there is another signal at 6.87 ppm, which is attributable to the bifunctionalized product in a *trans* conformation.

To shed some light on the possible reaction mechanism, we studied the effect of the reactant ratios on product distributions. With the $[\alpha\text{-Mo}_8O_{26}]^{4-}$ ion as the reactant, the dominant

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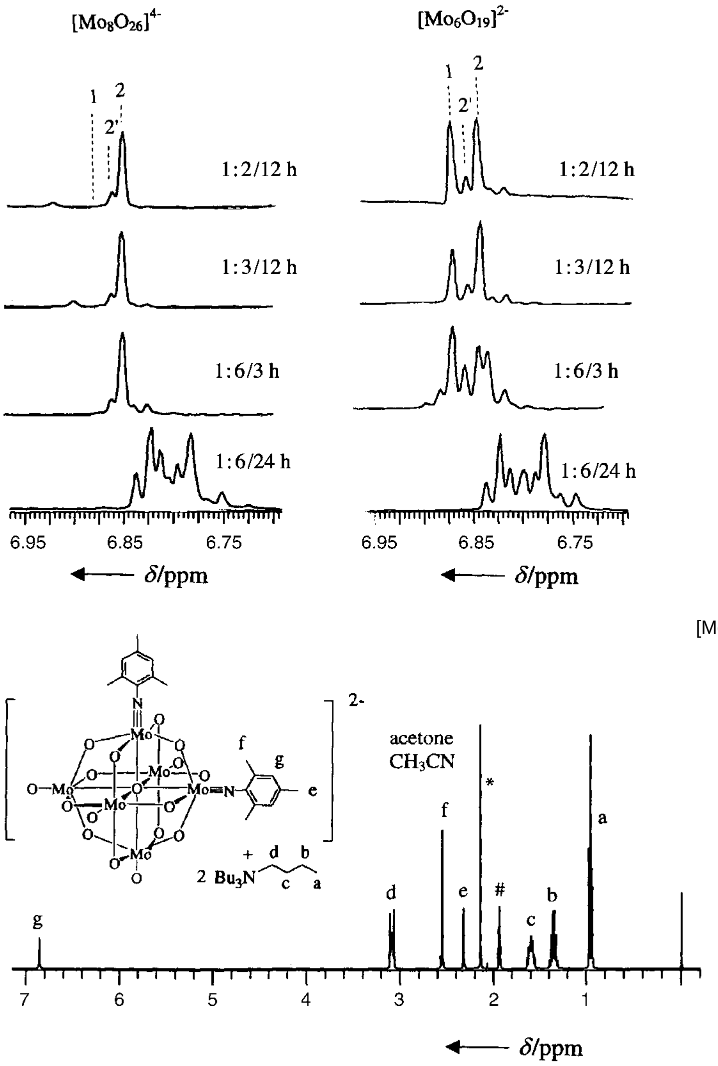

Figure 1. ^{1}H NMR spectra of the reaction mixtures of $[\alpha\text{-}Mo_8O_{26}]^{4-}$ (left) or $[Mo_6O_{19}]^{2-}$ (right) with 2,4,6-trimethylaniline (TMA) and DCC in [D$_3$]MeCN. The POM:amine ratios and reaction times are shown next to the spectra; 1 = monofunctionalized product, 2 = *cis* bifunctionalized product, 2′ = *trans* bifunctionalized product. The bottom spectrum is the ^{1}H NMR spectrum of the purified product **2a**.

product after 12 h of reaction is the bifunctionalized cluster, whether the cluster:amine ratio is 2:1, 1:1, 1:2, or 1:3. Longer reaction time does not change the product distribution. Even with a cluster:amine ratio of 1:6, the bifunctionalized cluster is still the major product after 3 h of reaction, although unlike the reactions with lower amine:POM ratios, letting the reaction go longer results in a mixture of products (Figure 1). This result is because of further reactions of the bifunctionalized product with excess amine. In contrast, direction functionalization of the $[Mo_6O_{19}]^{2-}$ ion with two or more equivalents of amine always led to a mixture of products. Similar product distributions are obtained for the two reactions when excess amine is used and the reaction time is sufficiently long.

While more studies, including reaction kinetics and spectroscopic studies, are needed to elucidate the detailed reaction mechanism, our results did provide some clues for the transition from the $[\alpha\text{-}Mo_8O_{26}]^{4-}$ cluster to the functionalized hexamolybdate product. Since the cluster skeleton has changed during the reaction, cluster disassembly and reassembly must be involved in the reaction process. It is known that the $[Mo_8O_{26}]^{4-}$ cluster can disassemble to the $[Mo_2O_7]^{2-}$ cluster in the presence of base.[13,14] It is likely that the octamolybdate ion is first decomposed to the dimolybdate ion. This proposal is further supported by our observation that the reaction of the dimolybdate ion with two equivalents of TMA gives similar product distributions to that of the octamolybdate ion with TMA. Since the bifunctionalized product is predominantly formed, it is possible that the dimolybdate ion forms an intermediate complex with two equivalents of amine, which then assembles with two other dimolybdate ions to form the bifunctionalized hexamolybdate product (solid-line path in Figure 2). The majority of the functionalization (imido formation) appears to occur before the hexamolybdate cluster formation, although further functionalization on hexamolybdate ions are possible, particularly when the amine is in excess (dashed-line path in Figure 2).

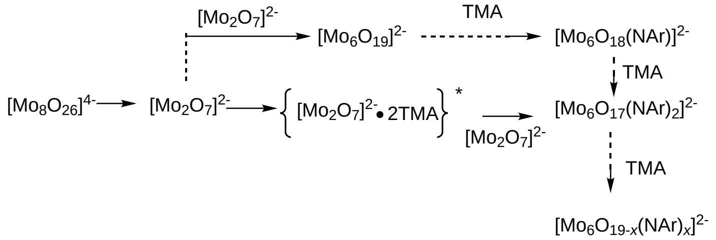

Figure 2. Proposed reaction mechanism for the formation of bi- and polyfunctionalized clusters. For details see the main text.

We have synthesized three bifunctionalized hexamolybdates (Scheme 1). Compounds **2a**–**2c** are all soluble in common organic solvents, their ^{1}H NMR spectra (see Experimental Section and Figure 1) show clearly resolved signals, which can all be unambiguously assigned. The structures of Compounds **2b** and **2c** are also characterized by single-crystal X-ray diffraction.[15] Both Compounds **2b** and **2c** crystallize in the triclinic space group $P\bar{1}$. Consistent with previous reports, the two organoimido ligands occupy two terminal positions in a *cis* conformation.[10] While compounds **2b** and **2c** show very similar molecular structures, their crystal-packing motifs are rather different. Within the lattice of $(Bu_4N)_2$**2c**, the cluster ions are organized into dimers where the iodine atom of one cluster is brought into close proximity to a μ_2-oxygen atom of another cluster (Figure 3). The I–O separation observed is 3.20 Å, which is 0.3 Å shorter than the sum of their van der Waals radius, which indicates the presence of a weak van der Waals interaction between them. It is known that among all the oxygen atoms in a $[Mo_6O_{19}]^{2-}$ ion, the μ_2 oxygen atoms have the highest negative charge density.[16] The charge density on the μ_2 oxygen atom can be further increased by the electron-donating effect of the two organoimido ligands,[8] which should facilitate the interaction of the μ_2 oxygen atom with the highly polarizable iodine atom. The "dimerization" is also boosted by the π–π stacking of the two near parallel phenyl rings. The existence of the π–π interactions is

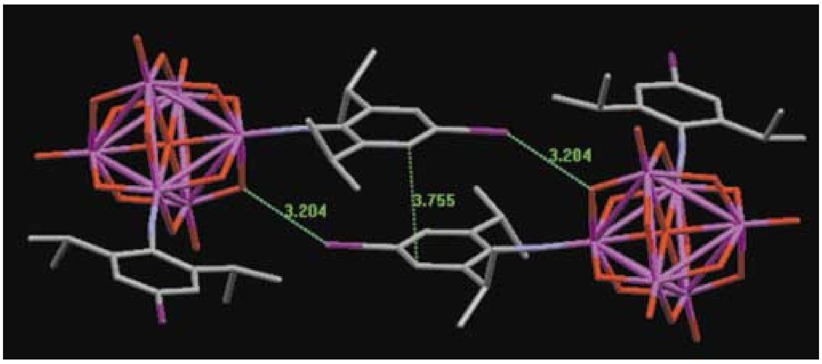

Figure 3. Dimer formation of the anions **2c** in the lattice of $(Bu_4N)_2$**2c**. Highlighted numbers indicate the interatomic distances [Å].

clearly indicated by their short vertical separation of 3.755 Å. The "dimerization" is not observed in the crystal structure of **2b**.

Compound **2c** has two iodo groups, which makes it an excellent monomer from which a main-chain-POM-containing conjugated polymer (or oligomer) can be synthesized through Palladium-catalyzed coupling reactions.[17] As shown in Scheme 2, we have carried out the Pd-catalyzed coupling of **2c** with 2,5-di(2,2-dimethylpropoxy-1,4-diethynylbenzene). The reaction went smoothly in DMF at room temperature and the polymer can be readily separated by pouring the reaction mixture into methanol. The ^1H NMR spectra of the polymer are consistent with the proposed structure.[18] Based on the end group analysis, the number of repeating units in the polymer is estimated to be about 18.[19] While the molecular weights of the polymer appear not to be very high,[19] nonetheless, good quality films can be readily prepared by spin-coating or casting, which allows the physical properties of the polymers to be studied. The detailed structural and physical property characterizations of this unique main-chain-POM-containing hybrid polymer are in progress and will be reported in a separate paper shortly.

In conclusion, we have discovered an unusual and highly efficient approach for the selective synthesis of bifunctionalized organoimido hexamolybdates. This approach allows the facile introduction of two functional groups to a hexamolybdate cluster, and thus paves the way for the synthesis of main-chain-POM-containing hybrid polymers.

Experimental Section

$(Bu_4N)_2[Mo_6O_{19}]$ and $(Bu_4N)_2[Mo_2O_7]$ were prepared by literature methods.[13] $(Bu_4N)_4[\alpha\text{-}Mo_8O_{26}]$ was conveniently prepared by the addition of NBu_4Br to an aqueous solution of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (purchased from Acros), from which the product immediately precipitates. The structure of $(Bu_4N)_4[\alpha\text{-}Mo_8O_{26}]$ was confirmed by elemental analysis and X-ray single-crystal structure determination.[20]

A typical synthesis for compounds **2a**–**2c** is exemplified by the synthesis of **2a**: A mixture of TMA (0.14 g, 1.0 mmol), *N,N'*-dicyclohexylcarbodiimide (0.21 g, 1.0 mmol), and $(Bu_4N)_4[Mo_8O_{26}]$ (1.08 g, 0.46 mmol) was refluxed in anhydrous acetonitrile (8 mL) under nitrogen for about 24 h. After being cooled to room temperature, filtration of the resulting dark-red solution removed the white precipitates. The product precipitates from the filtrate as orange crystals. The product was collected by filtration, washed successively with EtOH and Et_2O several times, and then recrystallized twice from acetone to yield 0.52 g of **2a** (yield based on Mo: 65 %). Elemental analysis (%) calcd for $C_{50}H_{94}N_4O_{17}Mo_6$: C 37.56, H 5.92, N 3.50; found: C 37.18, H 5.74, N 3.54; ^1H NMR (400 MHz, $[D_3]$MeCN, 25 °C, TMS): $\delta = 6.86$ (m, ArH, 4 H), 3.10 (t, $J = 8.50$ Hz, NCH_2, 16 H), 2.56 (s, (Ar-)Me_2, 12 H), 2.33 (s, (Ar-)Me, 6 H), 1.60 (q, $J = 8.50$ Hz, CH_2, 16 H), 1.35 (H, $J = 8.50$ Hz, CH_2, 16 H), 0.96 ppm (t, $J = 7.25$ Hz, CH_3, 24 H). UV/Vis (MeCN): λ (ε) = 206 (8.9×10^{-4}), 242 (6.3×10^{-4}), 360 nm (3.2×10^{-4}).

2b (yield, 62 %): Elemental analysis (%) calcd for $C_{48}H_{88}N_4O_{17}Mo_6$: C 36.70, H 5.77, N 3.57; found: C 36.56, H 5.74, N 3.53; ^1H NMR (400 MHz, $[D_3]$MeCN, 25 °C, TMS):$\delta = 7.03$ (m, ArH, 4 H), 6.88 (m, ArH, 2 H), 3.10 (t, $J = 8.50$ Hz, NCH_2, 16 H), 2.60 (s, (Ar-)Me_2, 12 H), 1.60 (q, $J = 8.50$ Hz, CH_2 , 16 H), 1.35 (H, $J = 8.50$ Hz, CH_2, 16 H), 0.96 ppm (t, $J = 7.25$ Hz, CH_3, 24 H). UV/Vis (MeCN): λ (ε) = 208 (6.5×10^{-4}), 244 (5.1×10^{-4}), 356 ppm (2.8×10^{-4}). Crystals suitable for single-crystal X-ray analysis were grown by diffusion of Et_2O into an acetonitrile solution at room temperature.

2c (yield, 63 %): Elemental analysis (%) calcd for $C_{56}H_{104}N_4O_{17}Mo_6I_2$: C 34.76, H 5.42, N 2.90; found: C 34.60, H 4.61, N 2.83; ^1H NMR (400 MHz, $[D_3]$MeCN, 25 °C, TMS):$\delta = 7.47$ (s, ArH, 4 H), 3.81 (m, $J = 7.50$ Hz, CH, 4 H), 3.10 (t, $J = 8.50$ Hz, NCH_2, 16 H), 1.60 (q, $J = 8.50$ Hz, CH_2, 16 H), 1.35(H, $J = 8.50$ Hz, CH_2, 16 H), 1.25 (d, $J = 6.25$ Hz, (Ar-)CH*Me*$_2$, 24 H), 0.96 (t, $J = 7.25$ Hz, CH_3, 24 H). UV/Vis (MeCN): λ (ε) = 206 (8.7×10^{-4}), 250 (7.2×10^{-4}), 366 (6.2×10^{-4}). Crystals suitable for single-crystal X-ray analysis were grown from acetonitrile at room temperature.

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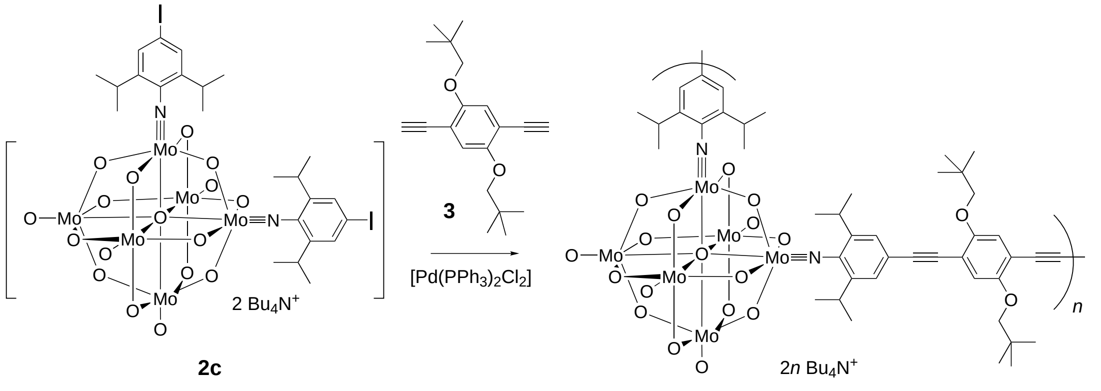

Scheme 2. Synthesis of main-chain-POM-containing conjugated polymers.

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[15] Crystal structure data for **2b**: $C_{48}H_{90}Mo_6N_4O_{17}$, $M_r = 1570.88$, triclinic, $P\bar{1}$, $a = 12.4970(5)$, $b = 12.6163(5)$, $c = 20.5340(9)$ Å, $\alpha = 81.523(2)$, $\beta = 76.693(2)$, $\gamma = 76.237(2)°$, $V = 3045.4(2)$ Å^3, $Z = 2$, $Z' = 1$, $\rho_{calcd} = 1.713\ g\,cm^{-3}$, $T = 100(2)$ K, $R1 = 0.0395$, and $wR2 = 0.1083$. GOF $(F^2) = 1.062$. Crystal structure data for **2c**: $C_{56}H_{104}I_2Mo_6N_4O_{17}$, $M_r = 1394.87$, triclinic, $P\bar{1}$, $a = 16.3470(6)$, $b = 19.4509(7)$, $c = 22.6548(8)$ Å, $\alpha = 98.023(2)$, $\beta = 96.859(2)$, $\gamma = 90.465(2)°$, $V = 7079.6(4)$ Å^3, $Z = 4$, $Z' = 2$, $\rho_{calcd} = 1.815\ g\,cm^{-3}$, $T = 100(2)$ K, $R1 = 0.0369$, and $wR2 = 0.0964$. GOF $(F^2) = 1.027$. CCDC-187412 and -187413 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit @ccdc.cam.ac.uk).

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[18] ^1H NMR spectrum of the polymer: (400 MHz, [D$_6$]acetone, 25 °C): $\delta = 7.32$ (b, ArH, 4H), 7.10 (b, ArH, 2H), 4.04 (b, CH, 4H), 3.79 (b, OCH_2, 4H), 3.45 (t, $J = 6.25$ Hz, NCH_2, 16H), 1.81 (b, CH_2, 16H), 1.44 (m, CH_2, 16H), 1.34 (d, $J = 7.50$ Hz, (Ar-)CH*Me*$_2$, 24H), 1.17 (s, 18H, CH_3 in alkoxy chains), 0.97 ppm (t, $J = 7.37$ Hz, CH_3, 24H). UV/Vis (MeCN): $\lambda_{max} = 440$ nm.

[19] A small peak at 7.47 ppm in the ^1H NMR spectrum of the polymer is identified as arising from the end-group protons associated with the aromatic terminus. The integration of the peak at 7.47 ppm versus that at 7.32 ppm is 1:18. Assuming both ends of the polymer are capped by the iodo end group (as no acetylene proton resonance is observed in the NMR spectrum), this integration ratio gives the number of repeating units at 18.

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A Three-Phase Emulsion/Solid-Heterogenization Method for Transport and Catalysis**

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We describe a method for the heterogenization of (catalytic) reactions, which eliminates the need for organic solvents. The method relies on a novel multiphase transport concept, namely on the transport of hydrophobic substrates to an entrapped catalyst, and the transport of the resulting product from the catalyst-entrapping environment back into the bulk. The general idea is as follows: A catalyst is entrapped inside a hydrophobically modified porous sol-gel matrix; the hydrophobic substrate for that catalyst forms an emulsion in water in the presence of a suitable surfactant; and the powdered catalytic sol-gel material is dispersed in that emulsion. Upon contact of the surfactant with the hydrophobic interface of the sol-gel matrix, it reorients and spills the substrate into the pores of the matrix, where the catalyst is entrapped. The catalytic process takes place there, and the product is extracted out by the same transport vehicle, namely by the emulsifying surfactant; then the emulsion is broken, and the product separated.

We term this whole process the EST (emulsion–solid transport) process, and have demonstrated it (following a detailed search for optimal conditions) with the $[CH_3(C_8H_{17})_3N]^+[RhCl_4]^-$ catalyzed hydrogenation of chalcone and *cis*-stilbene, in which the solid is a partially alkylated SiO_2 sol-gel matrix within which the catalyst is entrapped, and where the emulsifying surfactant is cetyl(trimethylammonium) *p*-toluenesulfonate.

Heterogenization of homogeneous catalytic procedures has been of central interest in the field of catalysis. Several heterogenization methods have been developed[1] which can be classified into the following categories: Covalent-bond immobilization of the catalyst on supports such as inorganic matrices,[2] organic-polymer solids,[3] organic–inorganic composites,[4] and recently also on dendrimers[5] and liquid–liquid biphasic systems[6] in which the catalyst is in one phase and the product is in the other. Recent examples of such systems are fluorinated biphasic catalytic systems[7] and ionic liquids.[8] Other methods include supported liquid-phase catalysis (SLPC), which is based on immobilizing the catalyst within a thin liquid film on a high surface area support[9] and physical immobilization of the catalysts within porous supports, which requires no covalent bonding and which retains the homogeneous catalyst in its native structure. Sol-gel catalysis has been

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