naturally occurring glycopeptide antibiotics and sets the stage for the design and synthesis of combinatorial libraries of these important structures for chemical biology studies. Particularly rewarding in this venture were the development and utilization of the triazene-based synthetic technology for the construction of complex biaryl ethers[16] and the adoption of the Suzuki coupling reaction in the strategy[1] for the synthesis of the AB ring system of the target molecule.[17,19]

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[14] Authentic compound **12** was obtained from natural vancomycin hydrochloride by the following sequence: 1) introduction of the benzyloxycarbonyl (Cbz) group at the N atom (Cbz-Cl, NaOH, MeOH/H_2O); 2) methylation of the three phenolic hydroxy groups and the carboxyl moiety (Cs_2CO_3, MeI, DMF); 3) sugar hydrolysis (TFA, CH_2Cl_2[12]); 4) methylation of the newly liberated phenolic hydroxy group (Cs_2CO_3, MeI, DMF); 5) silylation of the benzylic hydroxy group (TBSOTf, 2,6-lutidine); 6) protection of the primary amide with a Ddm groups (Ddm-OH, AcOH, H_2SO_4 cat.); and 7) Cbz → Boc exchange (H_2, 10 % $Pd(OH)_2$/C; then Boc_2O, Et_3N). (TBSOTf = *tert*-butyldimethylsilyltrifluoromethanesulfonate).
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Site-Directed Surface Derivatization of MCM-41: Use of High-Resolution Transmission Electron Microscopy and Molecular Recognition for Determining the Position of Functionality within Mesoporous Materials**

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Thomas Maschmeyer, Justin M. Matters,
Caroline L. Roper, Simon Parsons,
Brian F. G. Johnson, and Melinda J. Duer

Dedicated to Professor Sir John M. Thomas on the occasion of his 65th birthday

There is considerable commercial interest in the immobilization of catalysts on solid oxide supports, since the active materials thus prepared are considerably easier to handle, retrieve, and recycle than their homogeneous counterparts.[1] They may also exhibit improved activities and selectivities over those found for the homogeneous analogues. An approach used frequently in the heterogenization of homogeneous catalysts onto siliceous materials is the covalent linking of the active moiety to the surface through a surface-bound tether containing a functional group (for example $(MeO)_3Si$-$CH_2CH_2CH_2NH_2$).[2, 3] This methodology has been employed successfully in the functionalization of various traditional types of silica support, and with the advent of mesoporous silicas, in particular MCM-41,[4] it has been utilized extensively in the development of the surface chemistry of these materials.

The two key features of mesoporous silicas are their highly regular structure composed of channels in a hexagonal arrangement with diameters of 20 to 100 Å and their large surface areas ($\geq 750\ m^2 g^{-1}$). The large pore sizes offer the possibility to tether sizeable and complex catalytically active sites within the silica framework. The topological restraints produced by the confinement of solvent, substrate, and reactant may be expected to give a greater efficiency and selectivity in the catalytic process (Figure 1 a).

MCM-41 is composed of particles that usually range in size from 0.5 to 5 μm. Both the internal and external surfaces terminate in a layer of silanol groups (Si – OH), which are the reactive handle by which any derivatization/anchoring of catalytic centers may take place. Hence, derivatization of the surface of freshly calcined MCM-41 with an appropriately functionalized tether for anchoring a given catalyst will take

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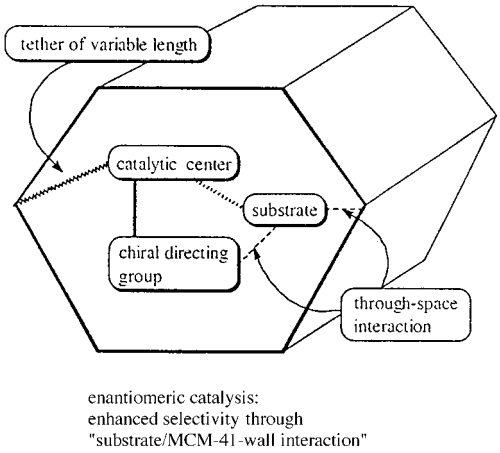

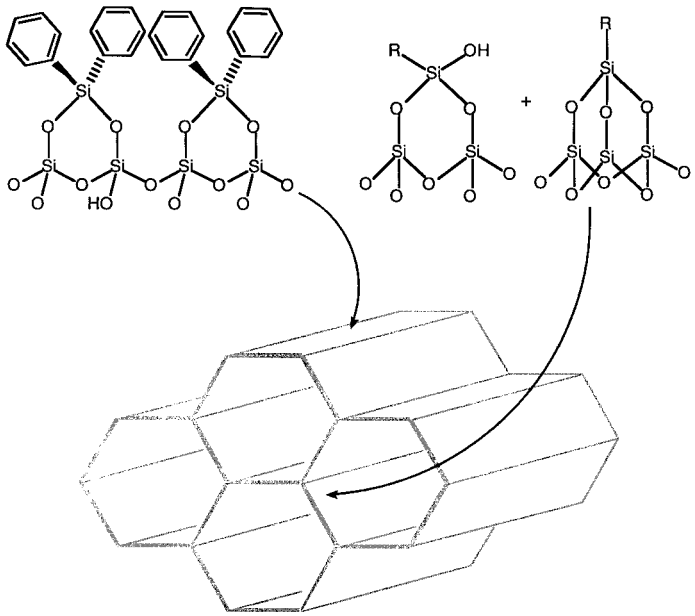

Figure 1. a) Conceptual representation of a catalyst encapsulated within a single MCM-41 pore to illustrate the substrate–wall interactions. b) A schematic representation of the passivation of the external surface with R_2SiCl_2 and the subsequent derivatization of the internal surface. R = $(CH_2)_3NH_2$.

place predominantly on the external surfaces of the particles because of their greater accessibility. Subsequent coupling of the catalytically active species to the support will hence take place at the most accessible tethers, thus giving heterogenized catalysts covering predominantly the outer surface of the MCM-41 particles. Furthermore, it should be possible to increase the dispersion and maximize performance per active site by using low loadings of the catalyst, so that the catalytic entities will bond almost exclusively to the external surface. This situation would be similar to that when amorphous silica is used as the support.

As part of our ongoing program to construct enantioselective catalysts[4] that are located within the channels of MCM-41 (so as to elucidate confinement effects on their turnover frequency (TOF) and selectivity) we have developed the first technique to determine directly the position of tethers bearing functional groups within a mesoporous matrix. Herein we report: 1) a method for the synthesis and characterization of selectively functionalized mesoporous silica (MCM-41) from a combination of Ph_2SiCl_2 and $(MeO)_3SiCH_2CH_2CH_2NH_2$ (Figure 1b); b) the synthesis and structural characterization of a model compound $[Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_4C_{10}H_{20}O_6)\cdot NH_4PF_6]$ (**2**), which exhibits the ammonium–cluster-crown interaction that must correspond to the binding interaction between $[Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_4C_{10}H_{20}O_6]$ (**1**) and a mesoporous silica surface derivatized with the ammonium functionality; 3) the host–guest-type binding of **1** onto the walls of mesoporous silica (MCM-41)[5] functionalized with $(-O)_3SiCH_2CH_2CH_2NH_3^+BF_4^-$ (Figure 2), and with a pore

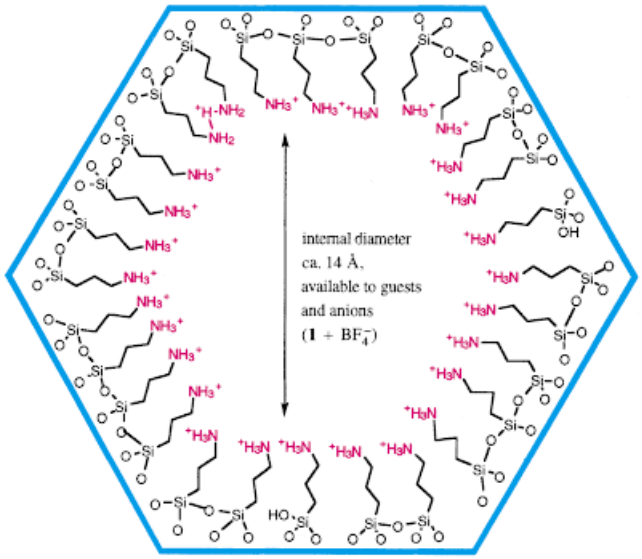

Figure 2. An MCM-41 pore fully derivatized with $(-O)_3SiCH_2CH_2CH_2NH_3^+BF_4^-$.

diameter of approximately 30 Å, together with spectroscopic proof of the retention of the integrity of the cluster probe (FT-IR spectroscopy and ^{13}C magic-angle spinning (MAS) NMR spectroscopy); and 4) determination of the positions of the cluster–tether ensemble inside and outside the siliceous mesopores by bright-field high-resolution transmission electron microscopy.

The surface of the mesoporous silica (MCM-41) was derivatized by the well-established method of condensation of one or several Si–OMe bonds with the surface silanol groups.[6] The first sample A was treated with $(MeO)_3SiCH_2CH_2CH_2NH_2$ (twofold excess) in THF for 12 h at ambient temperature. The second sample B was first treated with Ph_2SiCl_2 (0.01 equiv) on the assumption that the most kinetically available Si–OH groups were those on the outside surfaces of the silica particles (ca. 1 μm in diameter) and hence, these would be silylated and deactivated to further reaction. By this method the amine tether is expected to be located predominantly inside the channels.[7] The sample was then treated with $(MeO)_3SiCH_2CH_2CH_2NH_2$ as for A. Both samples were washed with copious amounts of THF and dried under vacuum (10^{-3} mmHg) at 348 K. Acidification by the

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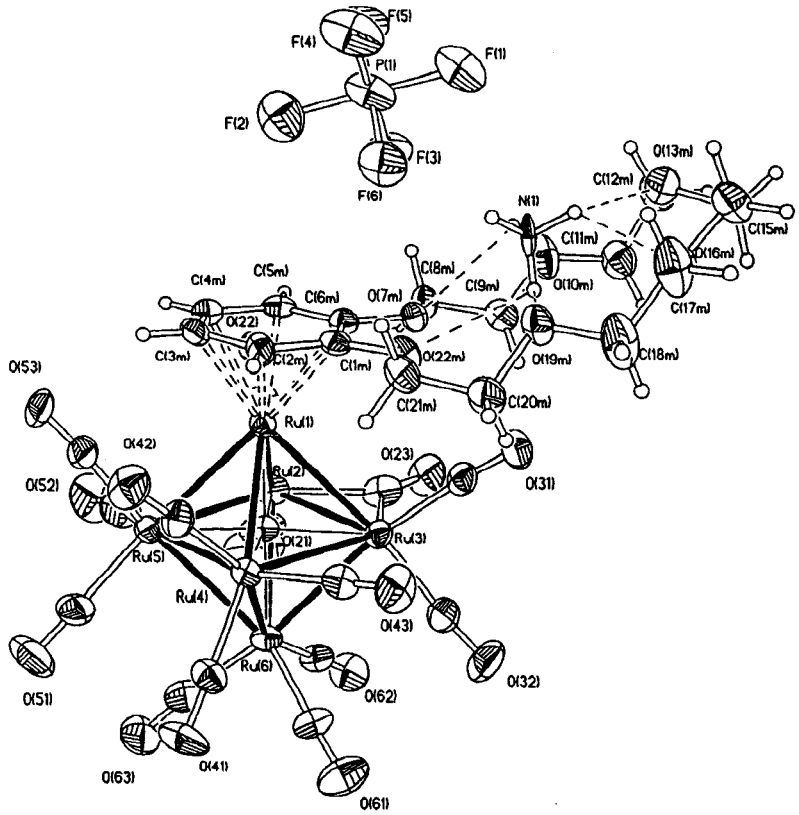

Figure 3. The crystal structure of **2**. Bond lengths [Å]: Ru(1)–C(1m) 2.288(9), O(7m)–N(1) 2.94(2), Ru(1)–C(2m) 2.246(9), O(10m)–N(1) 2.84(2), Ru(1)–C(3m) 2.216(10), O(13m)–N(1) 2.80(2), Ru(1)–C(4m) 2.203(10), O(16m)–N(1) 2.79(2), Ru(1)–C(5m) 2.255(9), O(19m)–N(1) 2.87(2), Ru(1)–C(6m) 2.291(9), O(22m)–N(1) 3.02(2), C(1m)–C(2m) 1.397(13), N(1)–F(1) 3.05(2), C(2m)–C(3m) 1.420(12), N(1)–F(3) 3.07(2), C(3m)–C(4m) 1.416(14), N(1)–F(6) 2.96(2), C(4m)–C(5m) 1.388(14), C(5m)–C(6m) 1.390(14), C(6m)–C(1m) 1.417(13).

addition of about one equivalent of HBF_4 (with respect to NH_2 groups) in diethyl ether/THF (1/1) yielded the ammonium head groups. Again the samples were washed, dried, and stored under an inert atmosphere.

As part of the continued development of the chemistry of the areneruthenium clusters based on the Ru_6C unit,[8] we have examined ways to incorporate these redox active units[9] into supramolecular assemblies. Given the wealth of host–guest chemistry of crown compounds[10] we concentrated our initial investigations in this area with a view to examine the molecular recognition behavior of the new receptor clusters. The cluster compound **1** was synthesized by direct reaction of the arylcrown ether with the hexaruthenium carbido cluster $[Ru_6C(CO)_{17}]$, and displays host–guest type behavior with Na^+ and NH_4^+ ions (shown both spectroscopically and electrochemically).[11] Furthermore, incorporation of such recognition characteristics (e.g for RNH_3^+) in the cluster unit has led to several possible applications, wherein these metal-rich domains may, with appropriate functionality, be directed onto surfaces or large (nanoscale) biomolecules (see Figure 4). This paper describes one such application. To verify the host–guest interaction between **1** and ammonium guests, the model host–guest complex **2** was crystallized from a stochiometric mixture of **1** and NH_4PF_6 in CH_2Cl_2/toluene by layering with diethyl ether.

The crystal structure of **2**, a model for the surface binding, shows the arene ring is η^6-coordinated to a single ruthenium atom (Figure 3). The oxygen atoms in the macrocyclic ring remain approximately planar, with a mean deviation of 0.186 Å. This plane lies at an angle of 27.2° to the arene ring that bonds the macrocycle to the cluster. The ammonium ion can be clearly seen to act as a guest within the macrocyclic cavity. The nitrogen atom lies 0.805(16) Å above the average plane of the oxygen atoms, with three of the hydrogen atoms[12] interacting with two oxygen atoms each, and with the remaining hydrogen atom directed towards the counterion.

Binding, and hence staining, of the the ammonium-functionalized surface to the cluster–crown compound **1** was achieved by the addition of the functionalized MCM-41 samples A and B to a solution of the cluster–crown compound **1** in dichloromethane to form a slurry**.** The dark red solutions grew paler whilst the previously white MCM-41 became brown/black, which indicated the uptake of **1.** After several hours the solution was filtered off, and the now dark solid was washed thoroughly with dichloromethane and dried under vacuum. When this methodology is employed with non-functionalized MCM-41 no detectable loading of the "staining" cluster **1** could be observed. The ^{13}C MAS NMR spectra for samples A and B further established the presence of the cluster–tether ensemble (Figure 4), with the chemical

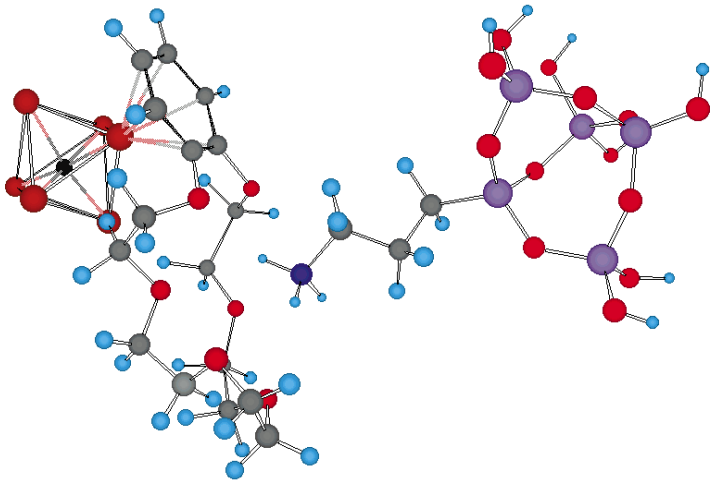

Figure 4. A Chem 3D model of the interaction of **1** with $H_3N^+CH_2CH_2CH_2Si{\equiv}$MCM-41. Modified MM2 parameters (less metal carbonyl groups) have been used.

shifts observed being consistent with those of their solution analogues.[10] The CO absorption band in the IR spectra (Nujol mull) showed that **1** was present in both samples, although the main absorptions were shifted by about 10 cm^{-1} to lower energy, which possibly indicates the existence a

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secondary C=O ··· H–X-type interaction (where X is N^+ or to a lesser extent OSi). The main absorption in sample A was shifted the most. This may arise from a greater contribution from the secondary interaction (see above) and possibly indicates how a greater surface density of functionalized tethers may be produced on the outer surface of MCM-41. The spectral profiles for both samples were essentially identical.

Both samples and also a calcined sample of MCM-41 were then imaged by high-resolution transmission electron microscopy (HR-TEM) (Figure 5a–c). The micrographs show representative examples of the materials produced, with all being essentially homogeneous. Figure 5a reveals the regular nature of the mesopores of the MCM-41 silica (the inset shows a Fourier transform with spots in the 100 direction); the absence of 001 spots in the Fourier transform shows that there is no crystallographic order in the direction of the pore axis. Inspection of the micrographs of A·**1** and B·**1** (Figures 5b and c, respectively) revealed dramatic differences were produced by the two different synthetic procedures. The dark surfaces of MCM-41 in A indicate that **1** is present predominantly at the external surfaces of this sample, adhered by the host–guest interaction (Figure 4). This indicates that the majority of the ammonium tethers are bound to the outer surface of MCM-41. In stark contrast, the electron micrograph of B has essentially "clean" exterior surfaces but retains strong image contrast of the clusters inside the mesopores (compare with Figure 5a). Thus, in sample B the tethers have been forced to bind almost entirely to the internal surface of MCM-41. Since the available internal volume[13] of the siliceous host is several orders of magnitude greater than that occupied by the introduced "staining agent" **1** (taking into account the reduction in pore volume because of the internally bound tethers) the distribution of **1** across the internal surface will be dictated by the position of the grafted ammonium tethers. The distribution of "staining agent" within the pores, as indicated by Figure 5c, is uniform and reflects an even circumfusion of the alkylammonium tethers.

We have presented the first method for directly imaging the position of functional tethers grafted onto the surface of a mesoporous material and, at the same time, have validated a simple method by which one may direct the location of the grafted functionality within mesoporous solids. This has been made possible by a strong partnership between supramolecular, organometallic, and solid-state chemistry. The results presented herein provide a foundation for the future examination of the effects of mesopore confinement on catalysis.

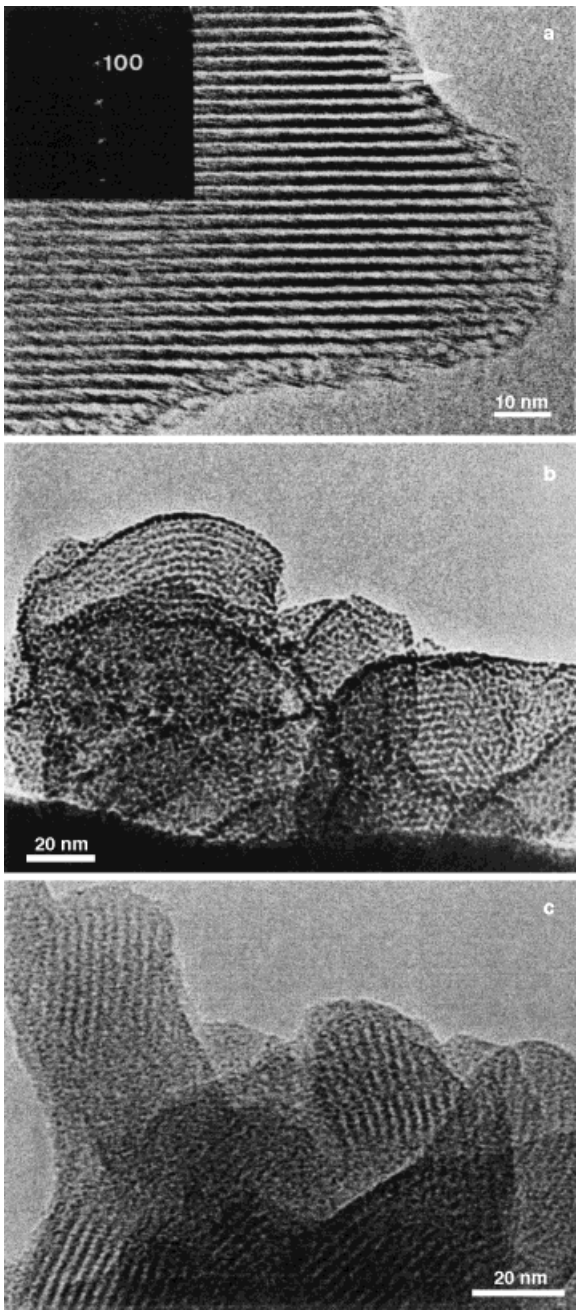

Figure 5. a) A HR-TEM micrograph of calcined MCM-41. The inset shows the Fourier transform with data in the 100 direction. b) A HR-TEM micrograph of sample A "stained" with **1** that shows strong contrast on the surface of the particles, which indicates the clusters are bound predominently to the outer surface of the derivatized MCM-41 particles. c) A HR-TEM micrograph of sample B "stained" with **1** that shows the presence of clusters within the MCM-41 channels (dark spots) and little or no contrast at the surface of the particles over and above that of calcined MCM-41.

Experimental Section

All reactions were carried out with the exclusion of air and with solvents freshly distilled in an atmosphere of nitrogen. FT-IR spectra were recorded on a Perkin-Elmer 1600 series FT-IR spectrometer in CH_2Cl_2 with NaCl cells or a Nujol mull. Positive-ion fast atom bombardment (FAB) mass spectra were obtained on a Kratos MS50TC spectrometer, with CsI as a calibrant. Separation of products was accomplished by thin layer chromatography on plates supplied by Merck (Kieselgel-60 F_{254}, 0.25 mm).

Preparation of propylammonium-functionalized MCM-41 samples A and B: MCM-41 (1 g) was dehydrated under vacuum at 200 °C for 2 h and was then slurried in THF (30 mL). Ph_2SiCl_2 (0.02 mL) was added, and the suspension was stired for one hour. The reaction mixture was cooled to 195 K, and $(MeO)_3Si(CH_2)_3NH_2$ (1.0 mL) added. The slurry was stirred for 3 h, slowly warmed to ambient temperature, and then left for a further 20 h at 50 °C. After this time the mixture was filtered and washed with copious amounts of THF (100 mL) and diethyl ether (50 mL), and dried under high vacuum. The ammonium functionality was obtained through acidification by the addition of a solution of $HBF_4 \cdot OEt_2$ (85%) in diethyl ether diluted in diethyl ether (30 mL) to the now dry white solid and stirred for 30 min. The resulting slurry was then filtered and washed with diethyl ether (100 mL), and dried under vacuum.

1: In a typical reaction $[Ru_6C(CO)_{17}]$ (200 mg, 0.18 mmol) and benzo[18]-crown-6 (130 mg, 0.42 mmol) were dissolved in dibutyl ether (25 ml) and

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refluxed under N_2 for 16 h. The resulting products were eluted on a silica column, first with pure dichloromethane, to yield $[Ru_6C(CO)_{17}]$ starting material (ca. 20 mg). Further elution with dichloromethane/methanol (99/1) gave a brown solution of **1**. This was recrystallized from dichloromethane by layering with hexane to give pure **1** (107 mg, 44 %). IR (cm^{-1}): 2074m, 2023vs, 1980w, 1967sh, 1808vw; positive-ion MS (FAB): *m/z*: 1324, 1294, 1267, 1237, 1209, 1182, 1153, 1125, 1096, 1067, 1039, 1011, 981, 952, 925 (calcd for $[M^+]$: 1324); ^{1}H NMR: $\delta = 6.14$ (dd, $J = 3$, 5 Hz, 2H), 5.47 (dd, $J = 3$, 5 Hz, 2H), 4.33 (m, 2H), 4.04 (m, 2H), 3.85 (m, 4H), 3.59 (m, 12H); ^{13}C NMR: $\delta = 197.6$, 126.5, 83.7, 77.7, 71.1, 70.7 (overlapped), 70.5, 68.9; elemental analysis: found: C 27.9, H 1.9, N 0.0; calcd: C 28.1, H 1.8, N 0.0. A crystal structure of this compound has been obtained.[14]

Cocrystallization of **1** with NH_4PF_6: A solution of **1** was stirred with a slight excess (1.1 equiv) of NH_4PF_6 in methanol (30 mL) for an hour. The product $\mathbf{1}\cdot NH_4^+PF_6^-$ was crystallized by layering a solution in CH_2Cl_2/toluene with diethyl ether (94 % yield). IR: $\tilde{\nu}_{co} = 2074$m, 2023vs, 1984w, 1964w, 1805vw (cm^{-1}); ^{1}H NMR: $\delta = 7.04$ (s, 4H), 5.70 (dd, $J = 3$, 6 Hz, 2H), 5.09 (dd, $J = 3$, 6 Hz, 2H), 4.21 (m, 2H), 3.90 (m, 2H), 3.70 (m, 16H); positive-ion MS (FAB): *m/z*: 1340 (calcd: 1338).

Crystal structure of **2:** $C_{34.5}H_{32}F_6NO_{20}Ru_6$, $M_r = 1532.00$, monoclinic, space group $P2_1/c$, a = 9.6080(16), $b = 17.071(2)$, c = 28.633(4) Å, $\beta = 95.806(14)^\circ$, $V = 4672.2(12)$ Å^3, $\rho = 2.178$ g cm^{-3}, $Z = 4$, $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, $\mu = 2.024$ mm^{-1}, $T = 220(2)$ K. The data were collected on a Stoe Stadi four-circle diffractometer equipped with a cooling device (Oxford Cryosystems) from a rapidly cooled crystal (red needle, mounted axially, dimensions: $0.58 \times 0.12 \times 0.12$ mm^3), over the range $5.20 < 2\theta < 50.06^\circ$. Absorption correction was achieved by ψ scans (max./min. transmission 0.322/0.286). Of a total of 10316 reflections collected, 8243 were independent ($R_{int} = 0.0872$). The structure was solved by Patterson methods (DIRDIF program)[15] and refined against F^2 with the SHELXTL program[16] with $R_1 = 0.0545$ (for 5460 data with $F > 4\sigma(F)$) and $wR_2 = 0.1223$ (all data). Hydrogen atoms were placed in calculated positions and allowed to refine riding on their carbon atoms. The lattice contains a disordered toluene solvate molecule centered about an inversion center (one half per asymmetric unit in two orientations with equal occupancy). Max./min. residual electron density 1.484/ − 0.813 e Å^{-3}.

A · **1** and B · **1:** A solution of **1** (0.04 g) in CH_2Cl_2 (20 mL) was added to a slurry composed of A or B (0.2 g) in diethyl ether (10 mL), and the mixture stirred for 20 h under ambient conditions. The brown solid was then filtered off and washed with CH_2Cl_2 (20 mL) and diethyl ether (50 mL), and dried under high vacuum (0.5 h).

MASNMR spectroscopy: The spectra were recorded on a Chemagnetics CMX 400 NMR spectrometer at a spectral frequency of 100.56 MHz. Pulses at 399.98 MHz for ^{1}H were used for the cross polarization (CP) and decoupling experiments. ^{13}C excitation pulse (90°) = 3.6 μs. The ^{1}H 90° pulse length was 3.6 μs, and a contact time of 2 ms was used for the proton CP experiments. Recycle delays of 5 s were left between scans for the CP experiments, and for the proton decoupling experiments. A decoupling field strength of 62.5 kHz was used during the acquisition. All spectra are referenced to TMS at $\delta = 0$, with the alkyl resonance of hexamethylbenzene at $\delta = 17.35$ used as a secondary external reference. The temperature used in the experiments was 298 ± 0.5 K. The sample spinning speed was 6 MHz and was controlled to within ± 5 Hz. Of the order of 5000 scans and 1024 data points per scan were collected.

HR-TEM of activated A · **1** and B · **1**: The sample was ground in air. The dry powder was then deposited on a copper grid with a holey carbon film, transferred to a Jeol TEM-200CX electron microscope (operating at 200 kV), and kept in the microscope vacuum overnight. The images were recorded at magnifications of 49 000 ×.

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