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[9] A drop of metallic Hg (2–3 g) was added to a solution of $[Mo_3S_4(H_2O)_9]^{4+}$ (2 mmol) in 4 M HCl (20 mL) under nitrogen. As the reaction proceeded, the color changed to royal blue. The resulting solution (10 ml) was added to cucurbituril (20 mg) in 4 M HCl (20 ml). After 4 d at room temperature, dark blue well-formed crystals of **1** appeared (yield 66 %). Elemental analysis (%): calcd for $[Mo_6S_8Hg(H_2O)_{14}Cl_4](C_{36}H_{36}N_{24}O_{12})Cl_4 \cdot 14H_2O$: C 15.35, H 3.29, N 11.93, S 9.10, Cl 10.07; found: C 15.44, H 3.33, N 12.01, S 9.12, Cl 9.93.

[10] The Se analogues **2** and **3** were prepared similarly. Satisfactory analytical data (C, H, N, Cl) were obtained.

[11] Crystal data for **1**:[18] Crystal dimensions $0.12 \times 0.10 \times 0.06$mm^3, monoclinic, space group $C2/m$, $a = 16.775(1)$, $b = 18.298(1)$, $c = 15.268(1)$ Å, $\beta = 102.128(1)^\circ$, $V = 4581.9(5)$ Å^3, $\rho_{calcd} = 2.042$g cm^{-3}, $\lambda(Mo_{K\alpha}) = 0.71073$ Å, $T = 160$ K, total/unique reflections 18445/5645 collected with Bruker SMART CCD diffractometer, $R_{int} = 0.0644$. Final refinement converged with $R_1 = 0.0450$ for 3399 reflections with $F_o \geq 4\sigma(F_o)$ and $wR_2 = 0.1197$ for all reflections.

[12] Crystal data for **2**:[18] Crystal dimensions $0.14 \times 0.08 \times 0.04$mm^3, monoclinic, space group $C2/m$, $a = 16.832(2)$, $b = 18.340(2)$, $c = 15.287(2)$ Å, $\beta = 101.842(2)^\circ$, $V = 4619(1)$ Å^3, $\rho_{calcd} = 2.296$g cm^{-3}, $\lambda(Mo_{K\alpha}) = 0.71073$ Å, $T = 160$ K, total/unique reflections 14341/5631 collected with Bruker SMART CCD diffractometer, $R_{int} = 0.0646$. Final refinement converged with $R_1 = 0.0476$ for 3226 reflections with $F_o \geq 4\sigma(F_o)$ and $wR_2 = 0.1218$ for all reflections.

[13] Due to insufficient size of the crystals only cell parameters could be determined for **3**: $a = 16.705(7)$, $b = 18.382(9)$, $c = 15.268(9)$ Å, $\beta = 101.93(4)^\circ$, $V = 4578(6)$ Å^3.

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[15] a) Preparation of **4**: To a saturated (about 5 mM) solution of cucurbituril in 2.5 M HCl (3 ml), a 10 mM solution of $[W_3Se_4(H_2O)_9]^{4+}$ in 2.5 M HCl (3 ml) was added. The mixture was stirred and left for 4 d at room temperature. Dark green crystals suitable for X-ray analysis were obtained (yield 72 %). Elemental analysis (%): calcd for $[\{W_3Se_4(H_2O)_8Cl\}_2](C_{36}H_{36}N_{24}O_{12})Cl_6 \cdot 12H_2O$: C 12.29, H 2.63, N 9.55, Cl 8.06; found: C 12.18, H 2.75, N 9.30, Cl 8.10. b) Crystal data for **4**:[18] Crystal dimensions $0.12 \times 0.05 \times 0.03$mm^3, monoclinic, space group $C2/m$, $a = 16.825(1)$, $b = 8.558(2)$, $c = 15.167(1)$ Å, $\beta = 105.364(2)^\circ$, $V = 4566.5(6)$ Å^3, $\rho_{calcd} = 2.560$g cm^{-3}, $\lambda(Mo_{K\alpha}) = 0.71073$ Å, $T = 160(1)$ K, total/unique reflections 20050/5663 collected with Bruker SMART CCD diffractometer, $R_{int} = 0.0697$. Final refinement converged with $R_1 = 0.0635$ for 3558 reflections with $F_o \geq 4\sigma(F_o)$ and $wR_2 = 0.1909$ for all reflections.

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[18] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-134604 (**1**), -134605 (**2**), and CCDC-134606 (**4**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Nanoscale Super Clusters of Clusters Assembled around a Dendritic Core**

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The construction of nanoscale molecular architectures is of considerable current interest.[1–4] The development of dendrimer-based clusters of clusters as quantum dots should provide unique advantages, for example, in the preparation of monodispersed particles with well-defined molecular structures and surface functionalities. In the course of our studies on synthesis, deposition, and ordering of platinum group clusters,[5, 6] we have prepared novel dendrimers based on an “inside-out” approach.

Here we describe the synthesis and characterization of nanoscale super clusters of clusters assembled around a dendritic core. High-resolution transmission electron microscopy (HRTEM) in conjunction with molecular modeling using force-field calculations have been employed to establish the morphology of these nanoparticles. In contrast to the “magic-number” synthesis[7] of colloids wherein metal particles are stabilized by a “passivating” external layer of organic ligands, we have used a large internal organic scaffold, $[\text{DAB-dendr-}\{N(CH_2PPh_2)_2\}_{16}]$,[8] to construct an array of sixteen clusters, thereby forming a nanoscale self-ordering molecule (DAB = diaminobutane).

Compounds **1** and **2** (Figure 1) were prepared by binding the 16[P-N-P] tridentate terminal functionalities of the organic third-generation dendritic core to cluster units $[Ru_5C(CO)_{12}]$ or $[Au_2Ru_6C(CO)_{16}]$. Both **1** and **2** show a molecular multiple-layer structure (Figure 2). They may be viewed as a sphere consisting of a nonconducting organic core with a sheath of conducting metal particles over the surface, which in turn is covered by a further outer layer of insulating carbonyl ligands. For conduction to occur, an electron introduced into the molecule would first have to tunnel through the carbonyl sheath to the “metallic layer”, move through the metallic layer to an exit point, and then tunnel again out of the molecule.

$[\text{DAB-dendr-}\{N(CH_2PPh_2)_2\}_{16}(\mu_3{:}\eta^1\eta^1\eta^1\text{-}Ru_5C(CO)_{12})_{16}]$ **1**

$[\text{DAB-dendr-}\{N(CH_2PPh_2)_2\}_{16}(\mu{:}\eta^1\eta^1\text{-}Au_2Ru_6C(CO)_{16})_{16}]$ **2**

In addition to compounds **1** and **2**, we have also prepared and characterized the respective dimeric componds **3** and **4** as

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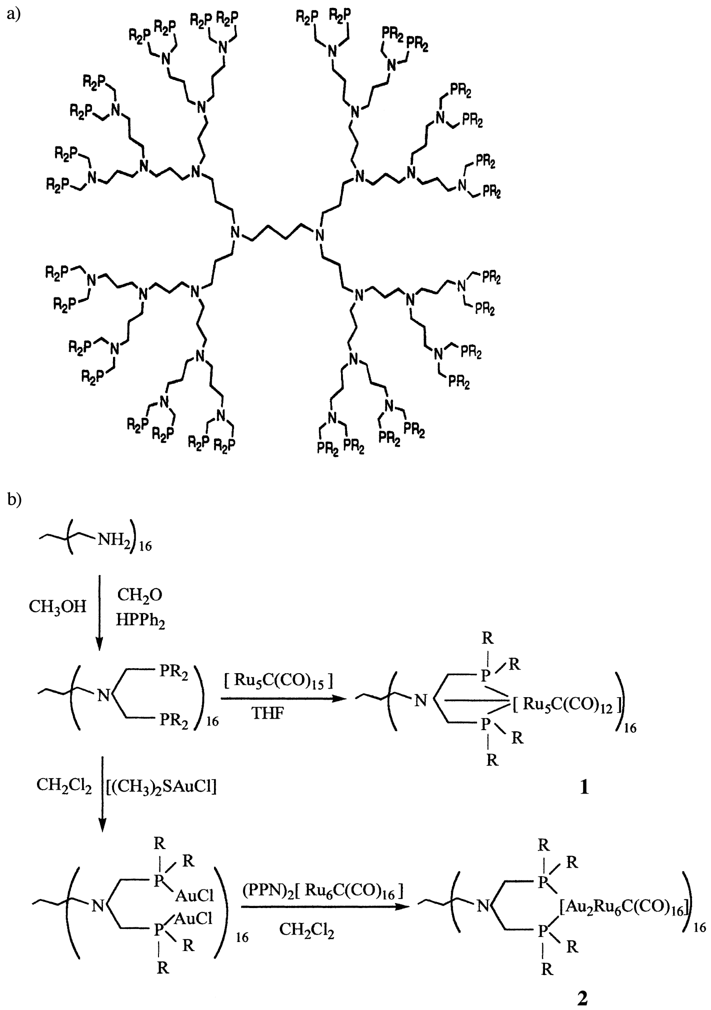

Figure 1. a) Chemical formula of the dendrimer molecule used for assembling the super clusters of clusters. b) The synthetic route to compounds **1** and **2**. R = C_6H_5 (Ph); PPN = $[PPh_3NPPh_3]^+$.

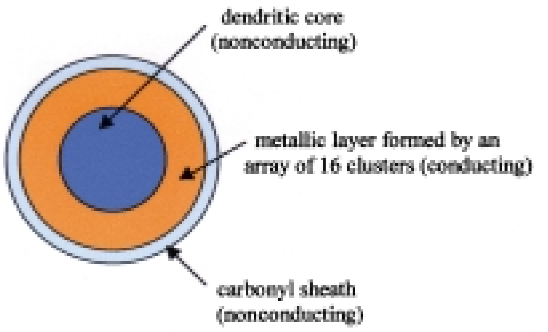

Figure 2. Representation of the molecular "multilayer" structure of compounds **1** and **2**.

$[\{(CH_2)_4N(CH_2PPh_2)_2[Ru_5C(CO)_{12}]\}_2]$ **3**

$[\{(CH_2)_4N(CH_2PPh_2)_2[Au_2Ru_6C(CO)_{16}]\}_2]$ **4**

$[PhCH_2N(CH_2PPh_2)_2\{Au_2Ru_6C(CO)_{16}\}]$ **5**

well as the model compound **5**. Crystals of **3** suitable for single-crystal X-ray crystallography were grown from a chloroform solution by slow evaporation. The determined molecular structure is shown in Figure 3a. Two pentaruthenium clusters, related by a center of inversion, are linked by the bis-tridentate ligand. The amino nitrogen and the two phosphorus atoms of each terminal unit coordinate to three basal ruthenium atoms of the cluster, displacing three axial carbonyl ligands from the parent cluster. The pyramidal geometry of the pentaruthenium carbido cluster is retained. Single crystals of **5** were obtained from dichloromethane by addition of hexane. The resulting X-ray structure (Figure 3b) shows precisely how the P-N-P chelating ligand binds and organizes the Au_2Ru_6 cluster core. The same bonding mode is therefore anticipated in the dendritic compound.

Compounds **1** and **3** display almost identical IR spectra in the CO region, strongly suggesting the coordinated clusters adopt a similar bonding mode. Evidence for the coordination of all the tridentate P atoms to clusters was provided by the observed single peak in the ^{31}P NMR spectrum.[9] Elemental analyses for both **1** and **2** as well as TGA measurement for **1** are in good agreement with those calculated for each dendrimer molecule containing sixteen $[Ru_5C(CO)_{12}]$ or $[Au_2Ru_6C(CO)_{16}]$ cluster units.

Initial attempts to record HRTEM images of **1** deposited on a carbon film revealed that the material was highly perturbed by the electron beam, probably because of CO ejection causing movement. Despite this, good HRTEM images (Figures 4a and 4b) were recorded by careful control of the beam current and exposure time. In Figure 4a a single approximately cubic molecule of dimensions 46 × 46 Å is shown on the carbon surface. A second image taken some 10 s later (Figure 4) shows the molecule to have collapsed inwardly to give a smaller, denser particle. This may be explained by decarbonylation and agglomeration of the carbonyl clusters covering the perimeter of the dendrimer as we have observed previously. In direct contrast, Figure 5 shows an essentially spherical single molecule (ca. 8 nm in diameter) of **2** supported on the carbon film. The large contrast observed is consistent with the large metal content and may be compared to the molecular model (Figure 6) generated with Chem 3D based on modified MM2 parameters. These giant molecules of **2** show no further change to the electron beam even after several minutes of intense irradiation.

In conclusion, we have developed a route to a new family of giant molecules which display self-ordering and which may be used in the production of nanoscale metal particles. The assembly of different, as well as similar, clusters onto successive generations of dendrimers should also be possible. Their properties suggest that they may be of use in gas delivery/storage systems (CO, NO, ethene, etc.) switched thermally or electrochemically,[10] delivering metal particles of precise nuclearity to surfaces for nanoelectronics, and catalysis.

Experimental Section

Syntheses: Compunds **1** and **3** were synthesized by the addition of stoichiometric amounts of $[Ru_5C(CO)_{15}]$ to a solution of [DAB-dendr-$\{N(CH_2PPh_2)_2\}_{16}$] (48 h) or $[(CH_2)_4N(CH_2PPh_2)_2]_2$ (10 h), respectively, in THF. Products **1** and **3** may be isolated in good yield (90% and 40%) by

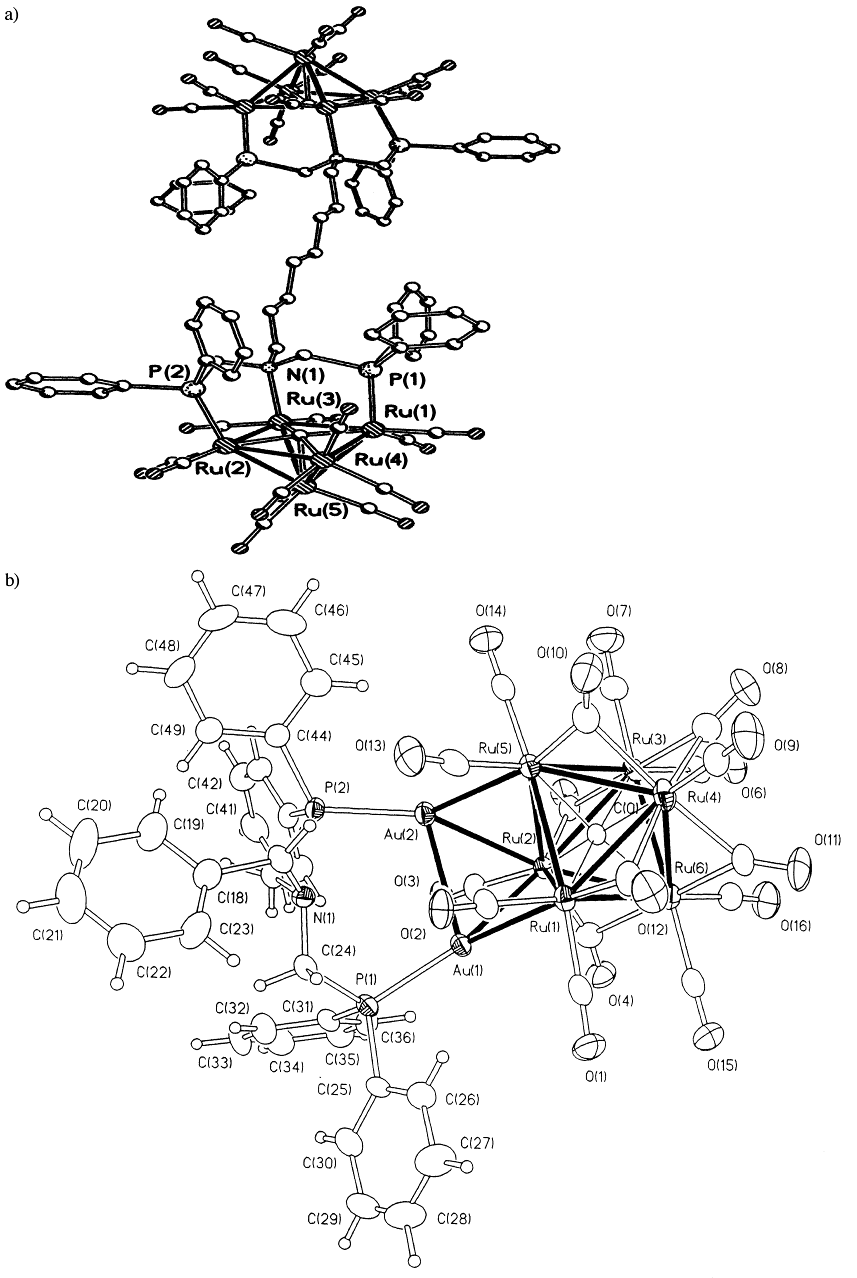

Figure 3. a) Solid-state molecular structure of **3**.[11] Selected bond lengths [Å]: P(1)–Ru(5) 2.294(2), N(2)–Ru(1) 2.211(5), P(2)–Ru(2) 2.301(2), Ru(5)–Ru(1) 2.8218(8), Ru(1)–Ru(2) 2.8127(7), Ru(2)–Ru(4) 2.8966(8), Ru(4)–Ru(5) 2.8617(7). b) Solid-state molecular structure of **5**.[11] Selected bond lengths [Å]: Au(1)–Au(2) 2.9362(6), P(1)–Au(1) 2.301(2), P(2)–Au(2) 2.314(2), Au(1)–Ru(1) 2.8213(6), Au(1)–Ru(2) 2.7451(6), Au(2)–Ru(2) 2.8200(6), Au(2)–Ru(5) 2.7725(6).

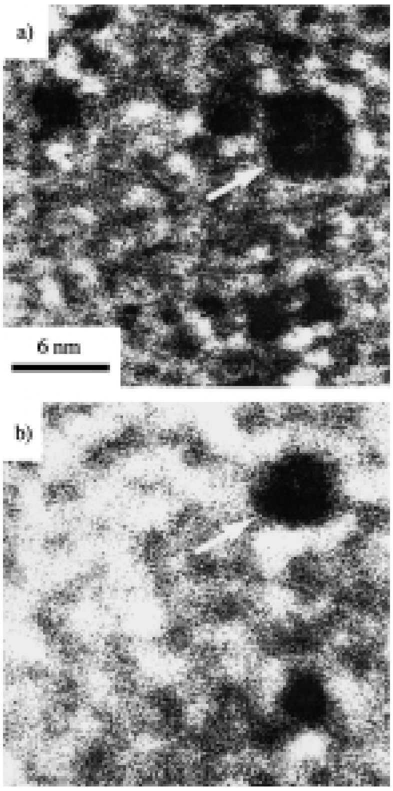

Figure 4. HRTEM images of **1** deposited on a holey carbon film: a) An intact molecule (indicated by an arrow) at $t \approx 0$. b) The same molecule (indicated by an arrow) 10 s later after decarbonylation and collapse.

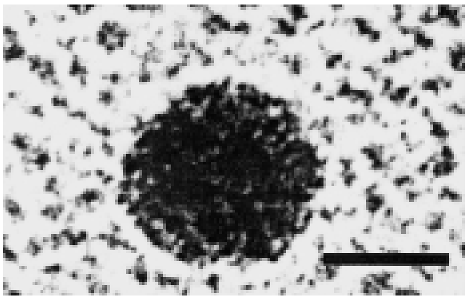

Figure 5. HRTEM image of a single molecule of **2** deposited on a holey carbon film. The length of the bar is 5 nm.

precipitation (hexane) and thin layer chromatography on silica gel. To obtain **2**, **4**, and **5**, we firstly synthesized intermediate compounds [DAB-dendr-{N(CH_2PPh_2AuCl)$_2$}$_{16}$], [{(CH_2)$_4$N(CH_2PPh_2AuCl)$_2$}$_2$], and [$PhCH_2N(CH_2PPh_2AuCl)_2$] by the addition of [$(CH_3)_2SAuCl$] to a solution of [DAB-dendr-{N(CH_2PPh_2)$_2$}$_{16}$] (2 h), [(CH_2)$_4$N(CH_2PPh_2)$_2$]$_2$ (2 h) or [$PhCH_2N(CH_2PPh_2)_2$] (1 h), respectively, in dichloromethane. Further reactions with $(PPN)_2[Ru_6C(CO)_{16}]$ for about 48 h in freshly distilled CH_2Cl_2 produced compounds **2**, **4**, and **5** (yield: 60, 70, and 80%, respectively), which were then purified by recrystallization.

IR absorption measurements (CH_2Cl_2): $\tilde{\nu}$(C≡O) [cm^{-1}] for **1**: 2055.4(s), 2014.4(s), 2003.0(sh), 1985.4(sh), 1968.8(sh); **2**: 2065.0(w), 2025.7(vs), 1998.0(m); **3**: 2056.2(s), 2014.3(s), 2003.6(sh), 1983.3(sh), 1970.3(sh); **4**: 2065.6(m), 2025.1(vs), 1987.2(m); **5**: 2066.4(m), 2026.3(vs).

Elemetal analysis (%): **1**: found: C 39.18, H 2.80, N 1.89, P 4.77; calcd: C 39.43, H 2.58, N 1.94, P 4.58; **2**: found: C 31.32, H 2.09, N 1.18; calcd: C 29.67, H 1.78, N 1.34; **4**: found: C 30.10, H 1.98, N 0.45; calcd: C 29.24, H 1.66, N 0.73.

^{31}P NMR measurements: single, sharp peak for **1**: $\delta = 30.0$, **3**: $\delta = 30.5$ in $CDCl_3$; **2**: $\delta = 21.6$, **4**: $\delta = 17.4$, **5**: $\delta = 21.6$ in CD_2Cl_2.

TGA analysis for **1** (298–600 K) under argon gas gave a residual mass corresponding to the calculated Ru content of the sample.

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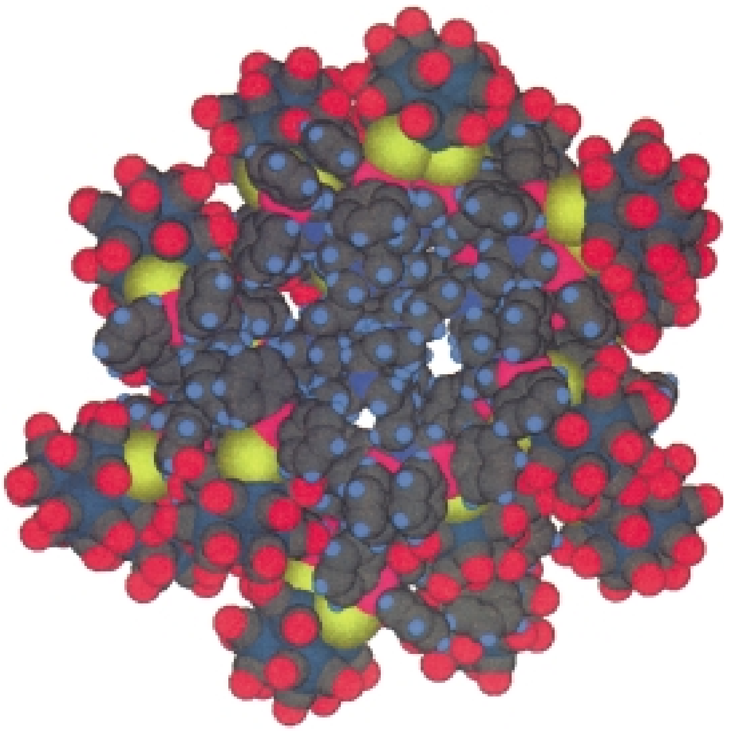

Figure 6. Chem 3D model of **2** (minimized by using modified MM2 parameters and molecular dynamics). Color code: Oxygen (red), hydrogen (light blue), ruthenium (dark green), carbon (black), phosphorus (violet), nitrogen (dark blue), gold (yellow).

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[9] A second peak in the ^{31}P NMR spectra for **2**, **4**, and **5** was also observed at $\delta \approx 55$. This is believed to arise from a slow fluctional process involving Au/cluster rearrangement.

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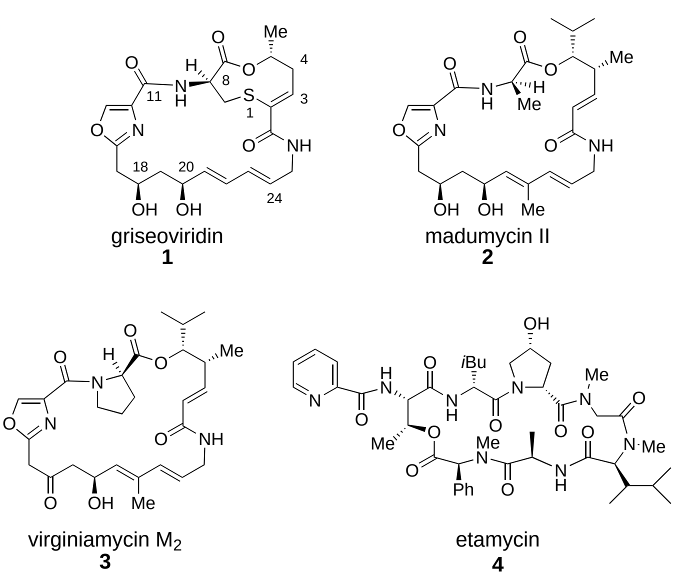
[11] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-136888 and -136889. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

The Synthesis of Streptogramin Antibiotics: (−)-Griseoviridin and Its C-8 Epimer**

Curt A. Dvorak, William D. Schmitz, Daniel J. Poon, David C. Pryde, Jon P. Lawson, Richard A. Amos, and Albert I. Meyers*

The streptogramin antibiotics are a family of compounds that were isolated from a variety of soil organisms belonging to the genus *Streptomyces.*[1] On isolation they can be separated into two distinct groups, one of which is termed Group A containing a 23-membered unsaturated ring such as that found in griseoviridin (**1**),[1] madumycin II (**2**),[2] and virginiamycin M_2 (**3**).[3] Also isolated from this family of mold metabolites are macrocyclic depsipeptides (e.g. etamycin (**4**)[4]), known as Group B, which usually contain five to seven amino acids in a cyclic array (Figure 1). The antibiotics in Group A (**1**–**3**) exhibit a strong synergism when combined with those in Group B with respect to their activity toward Gram-positive bacteria. Recently, the Food and Drug Administration (FDA) (USA) has approved a combination of Group A and Group B to be used against bacteria which have already shown resistance toward vancomycin.[5]


griseoviridin **1**

madumycin II **2**

virginiamycin M_2 **3**

etamycin **4**

Figure 1. Streptogramin antibiotics.

In 1996 we described[2] the synthesis of madumycin II (**2**) and Schlessinger and Li[3] simultaneously reported the total synthesis of virginiamycin M_2 (**3**). Pattenden et al. subsequently reported the synthesis of 14,15-anhydropristinamy-

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