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Transition metal clusters containing carbosilane dendrimers

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Abstract

The reaction of a series of AuCl-terminated carbosilane dendrimers with THF solutions of the anions $[Mo(CO)_3Cp]^-$, $[Mo_2(\mu\text{-}H)(\mu\text{-dppm})(CO)_8]^-$ and $[Mn_3(\mu\text{-}H)(CO)_{12}]^{2-}$ enabled new mixed gold/transition metal clusters containing carbosilane dendrimers to be isolated. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Gold; Molybdenum; Manganese; Cluster; Dendrimer

1. Introduction

Metallodendrimers are seen as very promising materials in areas such as catalysis, given that the combination of their nanoscopic dimensions and the ease with which they are dissolved in organic solvents makes them suited to closing the gap between homo- and heterogeneous catalysis [1].

The metal center can be placed at the core, as a part of backbone dendritic connectivity, or on the surface [2]. In the latter case, the dendritic cores are first prepared by traditional dendrimer synthesis in which ligands or functional groups capable of coordinating metal ions or reacting with metal complexes are introduced at the final step of the synthesis. For example, the excellent coordinating ability of phosphines has been utilized to prepare new organometallic dendrimers [3]. In addition, starting from ClAuP-terminated dendrimers we were able to obtain the first dendrimers with metal carbonyl clusters grafted onto their periphery [4]. The strategy followed for these derivatives involves chloride displacement from the gold fragment by iron cluster anions, such as $[Fe_2(CO)_7(PPh_2)]^-$ or $[Fe_3(CO)_{11}]^{2-}$. Very recently, the introduction of the cluster fragments $[Ru_3(CO)_{11}]$ [5], and $[Ru_5C(CO)_{12}]$ or $[Au_2Ru_6C(CO)_{16}]$ [6] at the periphery of dendrimers has been described.

In order to extend this reaction to other metal systems and corroborate the applicability of our method, here we report the synthesis of new Mo/Au and Mn/Au clusters containing carbosilane dendrimers.

2. Results and discussion

Carbosilane dendrimers were chosen for study because of their chemical and thermal stability. Details of the synthesis of the phosphine functionalized dendrimers and the ClAu-terminated dendrimers have been reported elsewhere [4a].

Fig. 1 shows the dendrimers used in this research. It should be noted that 3G-8Au is not strictly the third generation dendrimer because its second layer of silicon atoms acts only as a spacer without branching and its role is to increase the solubility of the compounds [4b].

2.1. Dendrimers containing $AuMoCp(CO)_3$ as terminal group

These were formed by adding solid $Na[MoCp(CO)_3]$ diglyme to a previously cooled CH_2Cl_2 solution of the dendrimers 1G-4Au, 1G-8Au, 2G-8Au, 2G-16Au and 3G-8Au. After half an hour, the corresponding work-up of the resulting solution gave yellow microcrystals of **1**–**5** in moderate amounts (Scheme 1). An alternative method involves the use of a THF solution of $Na[MoCp(CO)_3]$ obtained by sodium amalgam reduction of the dimer $[MoCp(CO)_3]_2$. The reactions were

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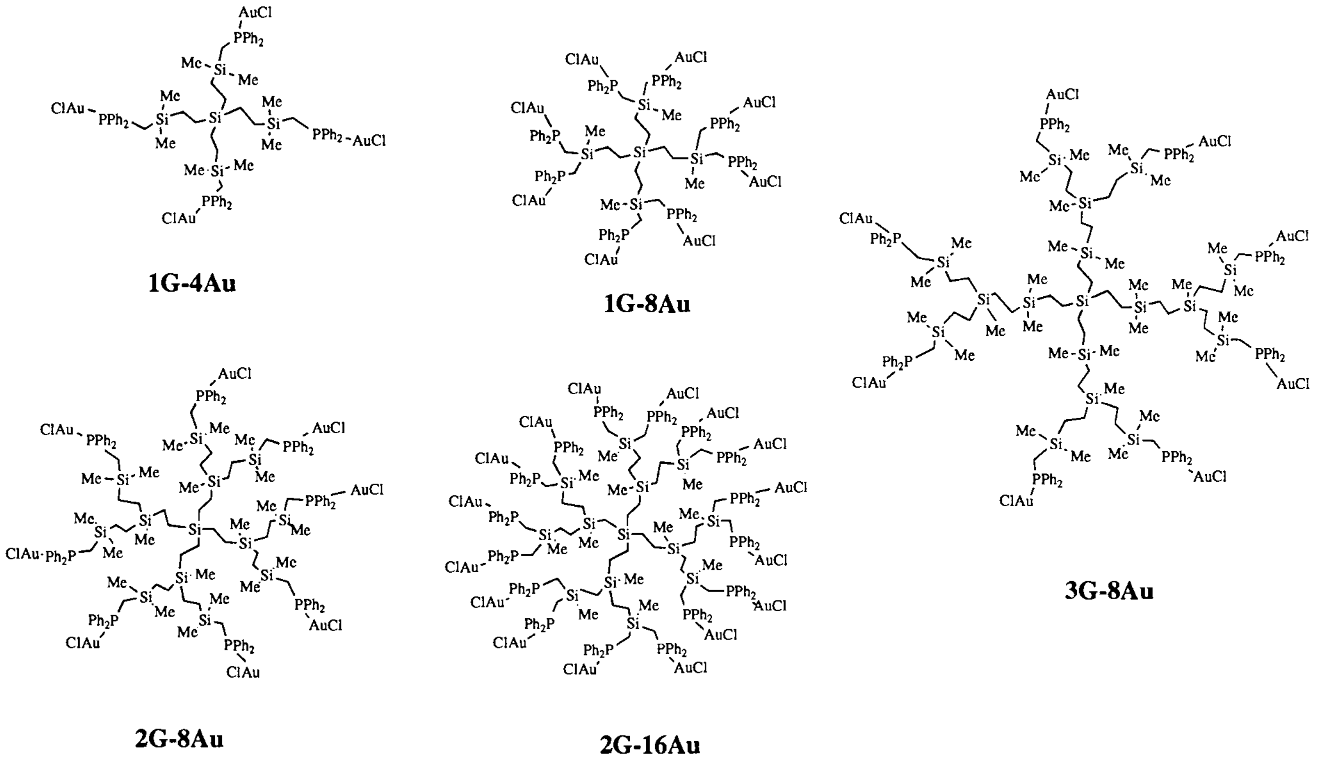


1G-4Au

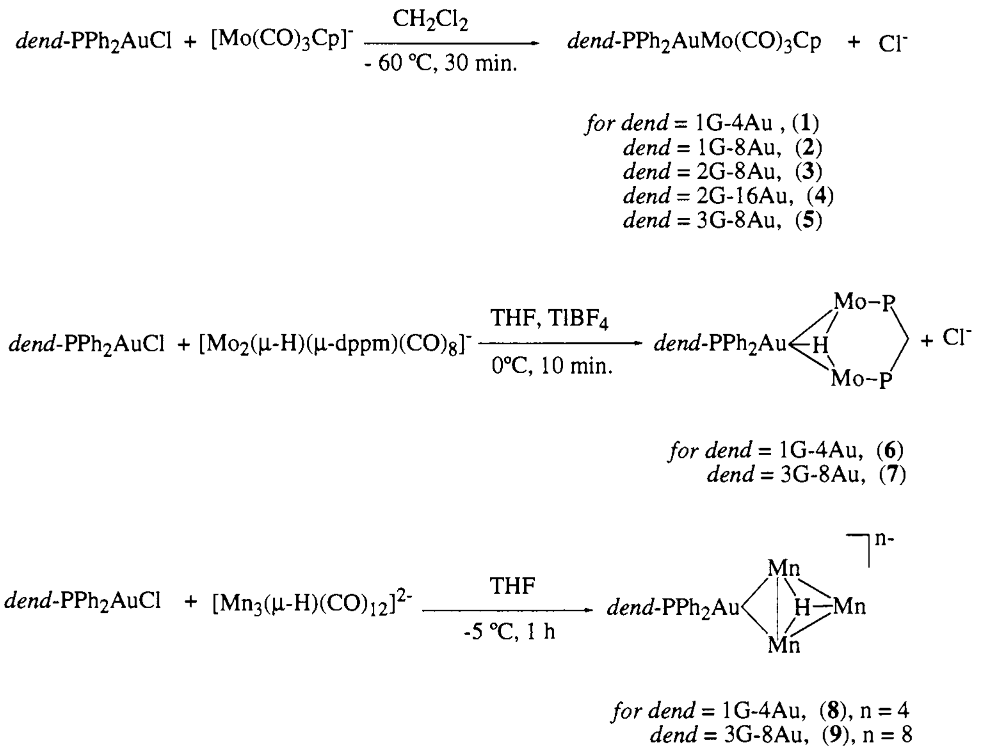
1G-8Au

3G-8Au

2G-8Au

2G-16Au

Fig. 1. Carbosilane dendrimers used in this work.



$dend\text{-}PPh_2AuCl + [Mo(CO)_3Cp]^- \xrightarrow[-60\ °C,\ 30\ min.]{CH_2Cl_2} dend\text{-}PPh_2AuMo(CO)_3Cp + Cl^-$

for dend = 1G-4Au , (**1**)
dend = 1G-8Au, (**2**)
dend = 2G-8Au, (**3**)
dend = 2G-16Au, (**4**)
dend = 3G-8Au, (**5**)

$dend\text{-}PPh_2AuCl + [Mo_2(\mu\text{-}H)(\mu\text{-}dppm)(CO)_8]^- \xrightarrow[0°C,\ 10\ min.]{THF,\ TlBF_4} dend\text{-}PPh_2Au$ + Cl^-

for dend = 1G-4Au, (**6**)
dend = 3G-8Au, (**7**)

$dend\text{-}PPh_2AuCl + [Mn_3(\mu\text{-}H)(CO)_{12}]^{2-} \xrightarrow[-5\ °C,\ 1\ h]{THF} dend\text{-}PPh_2Au$

for dend = 1G-4Au, (**8**), n = 4
dend = 3G-8Au, (**9**), n = 8

Scheme 1. Synthesis of dendrimers **1**–**9**.

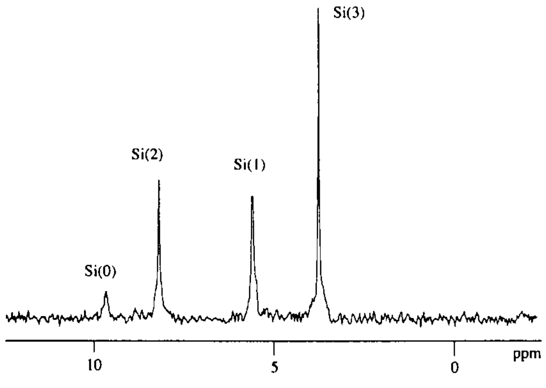


Fig. 2. $^{29}Si(^{1}H)$-NMR spectrum of 7.

monitored by IR and ^{31}P-NMR spectra. The IR spectrum for **1**–**5** showed a ν(CO) pattern for all of them which was very similar to that found for $PPh_3AuMoCp(CO)_3$ [7], with shifting of the bands to higher frequencies than those displayed for the starting molybdenum anion. In all cases, a unique signal at about 38–39 ppm on the ^{31}P-NMR spectrum confirmed that the reactions completed. ^{1}H- and ^{13}C-NMR spectra show the presence of the $-CH_3$, $-CH_2-$ and Cp groups and the $^{29}Si\{^{1}H\}$-NMR spectrum confirmed the presence of different silicon atoms in the molecule. Unfortunately, no parent ion was observed in the MALDI-TOF spectrum in any case, which confirmed our results for the iron/gold cluster dendrimers [4]. For this series of compounds, $[PPh_4]_4[Si[CH_2CH_2SiMe_2(Fe_3(CO)_{11})]_4$ was the only compound that displayed a molecular peak in the MALDI-TOF spectrum. Although the addition of ionizing species such as Ag^+ or MeO^- has been successfully used to detect neutral carbonyl metal clusters by electrospray spectroscopy [8], the molecular peak for the simplest dendrimer **1** was not observed. The use of MeOH did not improve our results because of the fragmentation of the dendrimer to give only one peak of $[Au\{MoCp_2(CO)_3\}]$, which is easily identified by its isotopic distribution. The addition of NaMeO also gave $[Au_2\{MoCp(CO)_3\}_3]$.

All the new cluster compounds were soluble in acetone, THF and dichloromethane and characterized by elemental analyses.

2.2. Dendrimers containing $AuMo_2$ clusters as terminal group

Compounds **6** and **7** were obtained in reasonable yields by treating 1G-4Au and 3G-8Au with a THF solution of $[NH_4][Mo_2(\mu\text{-}H)(\mu\text{-dppm})(CO)_8]$ (dppm = diphenylphosphinomethane) in the presence of $TlBF_4$ as a halide abstractor. The reaction was instantaneous and the products were obtained as air-stable yellow solids after the work-up of the solution (Scheme 1). However, their solutions decomposed slowly when allowed to warm to room temperature. Compounds **6** and **7** were characterized by elemental analyses and spectroscopic techniques. Their IR spectra showed an identical pattern to that found for the cluster $[Mo_2(CO)_8(\mu_3\text{-}H)(\mu\text{-dppm})(\mu\text{-}AuPPh_3)]$ [9], which showed that the cluster fragments were grafted onto the surface of the dendrimers. This is corroborated by the ^{31}P-NMR spectra which show a triplet for the $AuPPh_2$ signal while the MoP peaks appear as a doublet, and confirms that the bridging nature of diphosphine is retained in **6** and **7**. On the other hand, the total disappearance of the signal at 21 ppm due to the starting AuCl dendrimer reveals that complete chloride replacement of gold has taken place. The most interesting feature of the ^{1}H-NMR spectra is found in the hydride region, since the signal of the hydride appears as a doublet of triplets due to coupling with AuP and the Mo_2P_2 phosphorus. The $^{29}Si\{^{1}H\}$-NMR spectrum shows the four silicon atoms expected for **7** (Fig. 2). No parent ion was observed in the MALDI-TOF or FAB spectra.

2.3. Dendrimers containing $AuMn_3$ as terminal group

The reaction of $[PPh_4]_2[Mn_3(\mu\text{-}H)(CO)_{12}]$ with THF solutions of 1G-4Au or 3G-8Au in a 4:1 or 8:1 molar ratio, respectively, at 268 K was monitored by ^{31}P-NMR spectroscopy. After 1 h, the signal at about 21 ppm due to the starting dendrimers completely disappeared. A new signal emerged at 58 ppm, which was attributed to anions **8** and **9**, accompanied by the signal corresponding to the $PPh4^+$ cation at 23 ppm. Work-up of THF solutions containing $[PPh4^+]_8$ and $[PPh4^+]_9$ gave good yields of dark-green compounds which were characterized analytically and spectroscopically (Scheme 1). In spite of supporting high electron density, both compounds are air-stable solids, although their THF solutions decompose slowly under nitrogen at room temperature. The ν(CO) IR pattern can be almost superimposed on the pattern found for the cluster anion $[Mn_3(\mu\text{-}H)(CO)_{12}(\mu\text{-}AuPPh_3)]^-$ [10]. The ^{1}H-NMR spectra showed the hydride ligand at about -22 ppm as well as the CH_3- and $-CH_2-$ groups of the carbosilane backbone. The $^{29}Si\{^{1}H\}$-NMR spectra showed the two different silicon environments expected for **8** and the four expected for **9**. The ^{13}C-NMR spectra are consistent with the structure proposed, but in no case was any parent ion observed in the MALDI-TOF spectrum.

2.4. Attempts to synthesize the dendrimer 3G-32P

In order to increase the number of functional groups on the periphery of the dendrimers, we attempted the formation of the third generation dendrimer 3G-32P

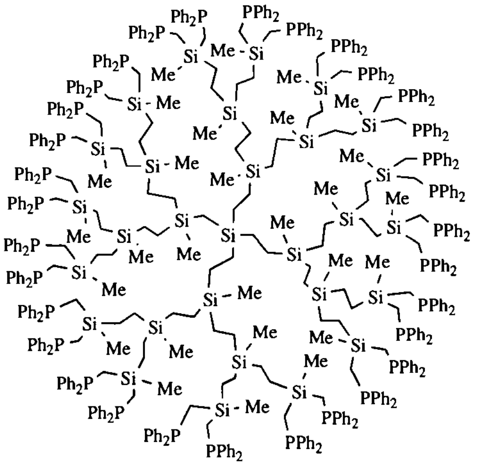


Fig. 3. Dendrimer 3G-32P.

(Fig. 3), by reacting Si[$CH_2CH_2SiMe(CH_2CH_2SiMe(CH_2CH_2SiMeCl_2)_2)_2]_4$ with the salt $LiCH_2PPh_2$ in THF for several hours at − 10°C. In contrast with the rest of phosphino-terminated dendrimers prepared by us, the 3G-32P gave a complex ^{31}P-NMR spectrum, suggesting the presence of more than one species. This was interpreted on the basis of the strong congestion on the dendrimer surface due to the presence of a great number of phosphine groups (Fig. 4). In order to corroborate this, molecular modeling calculations were carried out on the different phosphorus containing dendrimers used in this study. The results are listed in Table 1. From the parameter 'mean surface area per terminal group' we could determine the different surface compactness of the molecules and concluded that 3G-8P is clearly, as expected, the more open dendrimer given the presence of the spacers $CH_2CH_2SiMe_2$. 1G-8P, 2G-16P and 3G-32P have similar surface congestion, although 3G-32P shows the lowest value, which explains its difficulty in being formed. 3G-8P has a globular or disk-like structure, whereas the others are more spherical.

In conclusion, we have shown in this paper that the route to cluster/dendrimer species based on the grafting of metal clusters on the periphery of AuCl-containing dendrimers is suitable for transition metals other than iron.

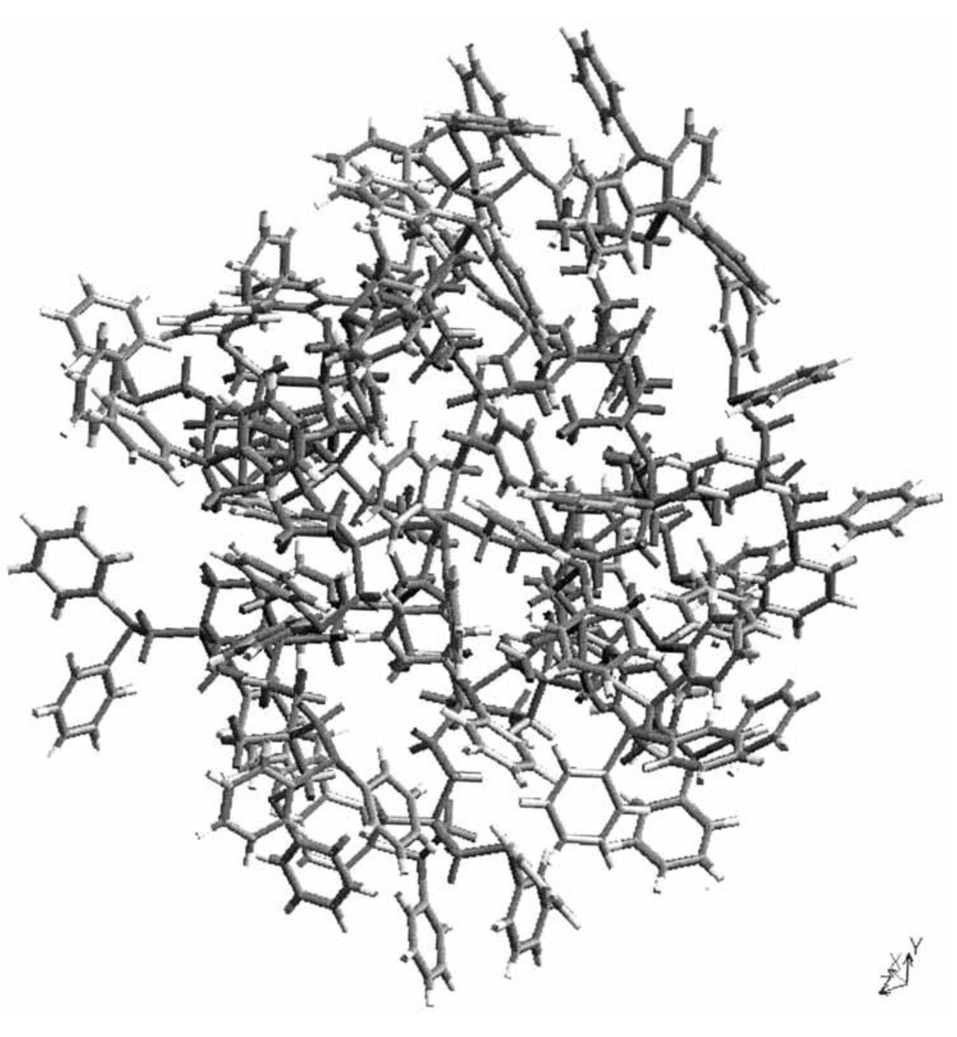


Fig. 4. Energy-minimized structure of dendrimer 3G-32P (Molecular Simulations CERIUS^2 software).

Table 1
Mean surface area per terminal group of the phosphorus terminated dendrimers 1G-4P, 1G-8P, 2G-8P, 2G-16P and 3G-32P

Dendrimer	1G-4P	1G-8P	2G-8P	2G-16P	3G-8P	3G-32P
Mean radius	7.03	6.39	8.70	8.73	11.23	11.62
Room [a]	77.6	32.1	59.5	29.9	99.0	26.5

[a] Mean surface area per terminal group (see Section 3).

3. Experimental

3.1. General comments

All manipulations were performed under an atmosphere of prepurified N_2 with standard Schlenk techniques, and all solvents were distilled from appropriate drying agents. Infrared spectra were recorded on a Nicolet FT-IR 520 spectrophotometer. $^{31}P\{^1H\}$- and $^{29}Si\{^1H\}$-NMR spectra were obtained on a Bruker DXR 250 and $^{13}C\{^1H\}$- and ^1H-NMR on a Varian 200 spectrometer. Elemental analyses of C and H were carried out at the Institut de Bio-Orgànica in Barcelona. The compounds $Na[MoCp(CO)_3]$ diglyme [11], $[NEt_4][Mo_2(\mu\text{-}H)(\mu\text{-dppm})(CO)_8]$ [12] and $[PPh_4]_2[Mn_3(\mu\text{-}H)(CO)_{12}]$ [13] were prepared as previously described.

Molecular Models of compounds 1G-4P, 1G-8P, 2G-8P, 2G-16P, 3G-8P and 3G-32P were constructed with the CERIUS^2 program [14] using the Universal Force Field [15] with the charge-equilibration approximation. The central fragment $Si(CH_2CH_2SiMe_2\text{–})_4$ was obtained from the crystal structure of $Si[(CH_2CH_2SiMe_2(C_2Co_2(CO)_6)]_4$ [16] taken from the Cambridge Structural Database [17]. The $\text{–}CH_2CH_2SiMe_2\text{–}$ fragment for further generations was also taken from this structure while the $\text{–}CH_2PPh_2$ fragment was obtained from reference [18]. As a large number of conformations are possible for these compounds, a conformer search was also carried out by the Random-Sampling method for different angle averages. Although, in general, no more stable conformers were obtained, their existence could not be discarded. But comparison of different conformers seems to indicate that no gross structural changes can be expected. Moreover, rotation of some groups or branches along different bonds produces similar conformers after minimization.

In order to quantify the surface congestion of these compounds or their ability to incorporate new fragments, we used the following simple method. A mean radius R was calculated for each model, with the radius defined as the distance between the central silicon atom and each of the phosphorus atoms. The surface of a sphere of radius R was calculated and then divided by the number of phosphine groups. Although this available area for group incorporation has no actual meaning, it is still useful to compare a family of compounds.

3.2. Preparation of the compounds

3.2.1. Synthesis of compounds containing $AuMoCp(CO)_3$ (**1**–**5**)

Details of the synthesis of **1** also apply to **2**–**5**. Solid $Na[MoCp(CO)_3]\cdot$(diglyme (0.35 g, 0.87 mmol) was added to a solution of 1G-4Au (0.46 g, 0.22 mmol) in 10 ml of CH_2Cl_2 at −60°C. The solution was stirred for 30 min and then concentrated to dryness. The residue was extracted with toluene (3 ml), filtered through celite, and hexane (5 ml) was added. A yellow solid was obtained in 72% yield.

Characterization data (**1**): ^1H-NMR (200 MHz, $CDCl_3$, δ(ppm)): 0.07 (s, 24 H, $\text{–}CH_3$); 0.16–0.19 (m, 16 H, $\text{–}CH_2\text{–}$); 1.77 (d, $^2J(H\text{–}P) = 14.6$ Hz, 8 H, CH_2P); 5.20 (s, 20 H, C_5H_5); 7.4–7.8 (m, 40 H, C_6H_5). $^{13}C\{^1H\}$-NMR (200 MHz, $CDCl_3$, δ(ppm)): −2.2 (s, $\text{–}CH_3$); 2.4 (s, $\text{–}C^1H_2\text{–}$); 8.6 (s, $\text{–}C^2H_2\text{–}$); 14.4 (d, $^1J(C\text{–}P) = 14.2$ Hz, CH_2P); 87.6 (s, C_5H_5); 128.1–132.8 (m, C_6H_5); 230.8 (s, CO). $^{29}Si\{^1H\}$-NMR (250 MHz, acetone-d_6, δ(ppm)): 3.8 (d, $^2J(Si\text{–}P) = 1.7$ Hz, Si_1); 9.7 (s, Si_0). $^{31}P\{^1H\}$-NMR (250 MHz, $CDCl_3$, δ(ppm)): 39.7 (PPh_2). IR (THF, cm^{-1}): ν(CO) 1950 vs, 1862 m, 1840 vs. Anal. Found: C, 40.69; H, 3.55. Calc. for $C_{100}H_{108}Au_4Mo_4O_{12}P_4Si_5$: C, 40.88; H, 3.71%.

(**2**) 30% yield: ^1H-NMR (200 MHz, $CDCl_3$, δ(ppm)): −0.30 (m, 12 H, $\text{–}CH_3$); 0.06–0.18 (m, 16 H, $\text{–}CH_2\text{–}$); 1.8 (br, 16 H, $\text{–}CH_2P$); 5.1 (s, 40 H, C_5H_5); 6.8–8.0 (m, 80 H, C_6H_5). $^{13}C\{^1H\}$-NMR (200 MHz, $CDCl_3$, δ(ppm)): −2.5 (s, $\text{–}CH_3$); 2.5 (br, C^1H_2) 7.5 (br, $\text{–}C^{1,2}H_2\text{–}$); 13.2 (sbr, CH_2P); 87.8 (s, C_5H_5); 129.2–132.8 (m, C_6H_5); 231.1 (s, CO). $^{29}Si\{^1H\}$-NMR (250 MHz, $CDCl_3$, δ(ppm)): 3.9 (sbr, Si_1); 12.1 (s, Si_0). $^{31}P\{^1H\}$-NMR (250 MHz, $CDCl_3$, δ(ppm)): 38.2 (PPh_2). IR (THF, cm^{-1}): ν(CO) 1948 vs, 1862 m, 1837 vs. Anal. Found: C, 39.72; H, 3.17. Calc. for $C_{186}H_{164}Au_8Mo_8O_{24}P_8Si_5$: C, 39.71; H, 3.04%.

(**3**) 72% yield: ^1H-NMR (200 MHz, $CDCl_3$, δ(ppm)): −0.17 (s, 12 H, $\text{–}C_1H_3$); 0.03 (s, 48 H, $\text{–}C_2H_3$); 0.40–0.47 (m, 48 H, $\text{–}CH_2\text{–}$); 1.82 (d, $^2J(H\text{–}P) = 14.6$ Hz, 16 H, CH_2P); 5.27 (s, 40 H, C_5H_5); 7.4–7.8 (m, 80 H, C_6H_5). $^{13}C\{^1H\}$-NMR (200 MHz, $CDCl_3$, δ(ppm)): −6.6 (s, $\text{–}C^1H_3$); −2.1 (s, $\text{–}C^2H_3$); 4.3 (s, $\text{–}C^3H_2\text{–}$); 8.7 (s, $\text{–}C^4H_2\text{–}$); 14.4 (d, $^1J(C\text{–}P) = 14.2$ Hz, CH_2P); 87.6 (s, C_5H_5); 128.8–134.8 (m, C_6H_5); 230.8 (s, CO). $^{29}Si\{^1H\}$-NMR (250 MHz, $CDCl_3$, δ(ppm)): 3.7 (d, $^2J(Si\text{–}P) = 2.1$ Hz, Si_2); 8.3 (s, Si_1). $^{31}P\{^1H\}$-NMR (250 MHz,

$CDCl_3$, δ(ppm)): 39.4 (PPh_2). IR (THF, cm^{-1}): ν(CO) 1950 vs, 1862 m, 1840 vs. Anal. Found: C, 39.30; H, 3.93. Calc. for $C_{212}H_{244}Au_8Mo_8O_{24}P_8Si_{13}$: C, 41.52; H, 4.01%.

(**4**) 90% yield: ^1H-NMR (200 MHz, $CDCl_3$, δ(ppm)): − 0.25 (sbr, 12 H, C^1H_3); − 0.02 (sbr, 24 H, C^2H_3); 0.26 (br, 48 H, –CH_2–); 2.05 (sbr, 32 H, CH_2P); 5.10 (s, 80 H, C_5H_5); 7.1–7.8 (m, 160 H, C_6H_5); $^{13}C\{^1H\}$-NMR (200 MHz, $CDCl_3$, δ(ppm)): − 6.8 (s, C^1H_3); − 2.6 (s, C^2H_3); 4.4 (sbr, –C^3H_2–); 8.1 (s, –C^4H_2–); 13.2 (br, CH_2P); 87.7 (s, C_5H_5); 127.9–131.8 (m, C_6H_5); 231.1 (s, CO); $^{29}Si\{^1H\}$-NMR (250 MHz, THF, δ(ppm)): 1.8 (d, ^2J(Si–P) = 9.6 Hz, Si_2), 7.0 (s, Si_1); not observed (Si_0); $^{31}P\{^1H\}$-NMR (250 MHz, $CDCl_3$, δ(ppm)): 38.0 (PPh_2). IR (THF, cm^{-1}): ν(CO) 1949 vs, 1862 m, 1837 vs. Anal. Found: C, 39.98; H, 3.20. Calc. for $C_{372}H_{356}Au_{16}Mo_{16}O_{48}P_{16}Si_{13}$: C, 40.10; H, 3.22%.

(**5**) 70% yield: ^1H-NMR (200 MHz, $CDCl_3$, δ(ppm)): − 0.17 (s, 12 H, C^2H_3); − 0.07 (s, 24 H, C^1H_3); 0.08 (s, 48 H, C^3H_3); 0.26–0.32 (m, 64 H, –CH_2–); 1.84 (d, ^2J(H–P) = 14.1 Hz, 16 H, –CH_2P); 5.28 (s, 40 H, C_5H_5); 7.4–7.8 (m, 80 H, C_6H_5). $^{13}C\{^1H\}$-NMR (200 MHz, $CDCl_3$, δ(ppm)): − 6.6 (s, –C^2H_3); − 4.3 (s, –C^1H_3); − 2.1 (s, –C^3H_3); 2.6 (s, –CH_2–); 4.3 (sbr, –C^5H_2–); 4.6 (s, –C^4H_2–); 6.7 (s, –C^3H_2–); 6.9 (s, –C^2H_2–); 8.7 (s, –C^6H_2–); 14.4 (d, ^1J(C–P) = 14.5 Hz, CH_2P); 87.6 (s, C_5H_5); 128.1–134.8 (m, C_6H_5); 230.7 (s, CO). $^{29}Si\{^1H\}$-NMR (250 MHz, $CDCl_3$, δ(ppm)): 3.8 (d, ^2J(Si–P) = 2.1 Hz, Si_3); 5.9 (s, Si_1); 8.3 (s, Si_2); 9.5 (s, Si_0). $^{31}P\{^1H\}$-NMR (250 MHz, $CDCl_3$, δ(ppm)): 39.6 (PPh_2). IR (THF, cm^{-1}): ν(CO) 1949 vs, 1863 m, 1840 vs. Anal. Found: C, 42.01; H, 4.35. Calc. for $C_{228}H_{284}Au_8Mo_8O_{24}P_8Si_{17}$: C, 42.28; H, 4.42%.

*3.2.2. Synthesis of compounds containing $AuMo_2$ clusters (**6**–**7**)*

Details of the synthesis of **6** also apply to **7**. A previously cooled (− 20°C) tetrahydrofuran (THF) 10 ml solution of $(NEt_4)[Mo_2(\mu\text{-}H)(\mu\text{-dppm})(CO)_8]$ (0.27 g, 0.29 mmol) was added to a solution of 1G-4Au (0.15 g, 0.07 mmol) and $TlBF_4$ (0.08 g, 0.29 mmol) in 15 ml of THF. After 10 min stirring at 0°C, the mixture was filtered through celite to eliminate NEt_4BF_4 and TlCl salts and the yellow solution was concentrated to dryness. The residue was extracted with pre-cooled toluene (5 ml) and hexane (10 ml) was added. A yellow solid was obtained in 43% yield.

Characterization data (**6**): ^1H-NMR (200 MHz, acetone-d_6, δ(ppm)): − 10.99 (dt, ^2J(PAu–H) = 86.3 Hz, ^2J(PMo–H) = 9.3 Hz, 4 H, μ_3-H); 0.09 (s, 24 H, CH_3); 0.18 (br, 16 H, –CH_2–); 2.20 (d, ^2J(H–P) = 15.1 Hz, 8 H, CH_2P); 3.71 (t, ^2J(P–H) = 9.5 Hz, 8 H, PCH_2P); 7.1–7.9 (m, 120 H, C_6H_5). $^{13}C\{^1H\}$-NMR (200 MHz, acetone-d_6): − 2.1 (s, CH_3); 2.7 (s, –C^1H_2–); 9.2 (s, –C^2H_2–); 13.8 (d, ^1J(C–P) = 18.3 Hz, CH_2P); 39.3 (t, ^1J(C–P) = 14.4 Hz, PCH_2P); 125.9–137.3 (m, C_6H_5); 213.5 (s, CO). $^{31}P\{^1H\}$-NMR (250 MHz, acetone-d_6, δ(ppm)): 28.6 (d, ^3J(PP) = 5.7 Hz, dppm); 39.1 (t, ^3J(PP) = 5.7 Hz, PPh_2Au). $^{29}Si\{^1H\}$-NMR (250 MHz, acetone-d_6, δ(ppm)): 3.7 (s, Si_1); 9.7 (s, Si_0). IR (THF, cm^{-1}): ν(CO): 2026 m, 2008 m, 1968 s, 1933 vs, 1909 vs, 1891 vs. Anal. Found: C, 46.32; H, 3.41. Calc. for $C_{200}H_{180}Au_4Mo_8O_{32}P_{12}Si_5$: C, 46.53; H, 3.51%.

(**7**) 60% yield: ^1H-NMR (200 MHz, acetone-d_6, δ(ppm)): − 11.00 (dt, ^2J(PAu–H) = 86.5 Hz, ^2J(PMo–H) = 8.6 Hz, 8 H, μ_3-H); − 0.18 (s, 48 H, C^2H_3); − 0.03 (s, 24 H, C^1H_3); 0.14 (s, 12 H, C^3H_3); 0.33–0.46 (m, 64 H, –CH_2–); 2.22 (d, ^2J(H–P) = 14.7 Hz, 16 H, CH_2P); 3.70 (t, ^2J(P–H) = 8.4 Hz, 16 H, PCH_2P); 7.1–8.0 (m, 240 H, C_6H_5). $^{13}C\{^1H\}$-NMR (200 MHz, acetone-d_6): − 6.1 (s, C^2H_3); − 3.9 (s, C^1H_3); − 2.0 (s, C^3H_3); 3.3 (s, –C^1H_2–); 4.7 (s, –C^5H_2–); 5.3 (s, –C^4H_2–); 7.1 (s, –C^3H_2–); 7.3 (s, –C^2H_2–); 9.2 (s, –C^6H_2–); 13.8 (d, ^1J(C–P) = 17.4 Hz, CH_2P); 39.3 (t, ^1J(C–P) = 13.8 Hz, PCH_2P); 125.9–137.3 (m, C_6H_5); 213.6 (s, CO). $^{31}P\{^1H\}$-NMR (250 MHz, acetone-d_6, δ(ppm)): 28.6 (d, ^3J(PP) = 5.5 Hz, dppm); 39.1 (t, ^3J(PP) = 5.5 Hz, PPh_2Au). $^{29}Si\{^1H\}$-NMR (250 MHz, acetone-d_6, δ(ppm)): 3.7 (s, Si_3); 5.6 (s, Si_1); 8.2 (s, Si_2); 9.7 (s, Si_0). IR (THF, cm^{-1}): ν(CO): 2026 m, 2009 m, 1967 s, 1933 vs, 1908 vs, 1892 vs. Anal. Found: C, 47.43; H, 4.34. Calc. for $C_{428}H_{428}Au_8Mo_{16}O_{64}P_{24}Si_{17}$: C, 47.04; H, 3.95%.

*3.2.3. Synthesis of compounds containing $AuMn_3$ clusters (**8**–**9**)*

Details of the synthesis of **8** also apply to **9**. A solution of $(PPh_4)_2[Mn_3(\mu\text{-}H)(CO)_{12}]$ (0.58 g, 0.49 mmol) in 15 ml was added to a solution of the compound 1G-4Au (0.26 g, 0.12 mmol) in 20 ml of THF at − 5°C. The resulting solution turned dark green and was stirred for 1 h, then filtered through celite and concentrated to dryness. The residue was extracted with pre-cooled acetone (5 ml), concentrated and methanol (10 ml) was added. A green solid was obtained in 43% yield.

Characterization data (**8**): ^1H-NMR (200 MHz, acetone-d_6, δ(ppm)): − 22.2 (s, 4 H, μ_3-H); 0.09 (s, 16 H, CH_3); 0.26 (m, 24 H, –CH_2–); 2.1 (sbr, 8 H, CH_2P); 7.0–8.5 (m, 120 H, C_6H_5). $^{13}C\{^1H\}$-NMR (200 MHz, acetone-d_6, δ(ppm)): − 2.3 (s, CH_3); 2.6 (s, –C^1H_2–); not found (s, –C^2H_2–); 9.2 (br, CH_2P); 117.8–136.1 (s, C_6H_5); 224.8 (br, CO). $^{29}Si\{^1H\}$-NMR (250 MHz, acetone-d_6, δ(ppm)): 3.5 (s, Si_1), 9.2 (s, Si_0). $^{31}P\{^1H\}$-NMR (250 MHz, acetone-d_6, δ(ppm)): 23.0 (PPh_4); 58.1 (PPh_2). IR (THF, cm^{-1}): ν(CO): 2050 w; 1990 m; 1981 m; 1965 s; 1942 w; 1925 m; 1881 w. Anal. Found: C, 47.75; H, 3.17. Calc. for $C_{212}H_{172}Au_4Mn_{12}O_{48}P_8Si_5$: C, 47.84; H, 3.26%.

(**9**) 83% yield: ^1H-NMR (200 MHz, acetone-d_6, δ(ppm)): − 22.0 (s, 8 H, μ_3-H); − 0.15 (s, 12 H, C^2H_3); − 0.02 (s, 24 H, C^1H_3); 0.15 (s, 48 H, C^3H_3); 0.36–0.48

(m, 64 H, –CH_2–); 2.3 (d, ^2J(H–P) = 12.8 Hz, 16 H, CH_2P); 7.4–8.0 (m, 240 H, C^6H_5). $^{13}C\{^1H\}$-NMR (200 MHz, acetone-d_6): not observed (s, C^2H_3); −3.6 (s, C^1H_3); −1.8 (s, C^3H_3); 4.8 (s, –C^3H_2–); 7.2 (s, –C^4H_2–); 9.4 (sbr, CH_2P); 117.8–136.2 (m, C^6H_5); not observed (s, *C*O). $^{31}P\{^1H\}$-NMR (250 MHz, acetone-d_6, δ(ppm)): 23.0 (s, *P*Ph_4); 58.2 (s, *P*Ph_2). $^{29}Si\{^1H\}$-NMR (250 MHz, acetone-d_6, δ(ppm)): 3.6 (s, Si_3); 5.6 (s, Si_1); 8.1 (s, Si_2); 9.6 (s, Si_0). IR (THF, cm^{-1}): ν(CO): 2050 w; 1990 m; 1981 m; 1965 s; 1942 w; 1925 m; 1882 w. Anal. Found: C, 48.46; H, 3.89. Calc. for $C_{452}H_{412}Au_8Mn_{24}P_{16}O_{96}Si_{17}$: C, 48.27; H, 3.69%.

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