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Soluble Iron/Gold Cluster Containing Carbosilane Dendrimers

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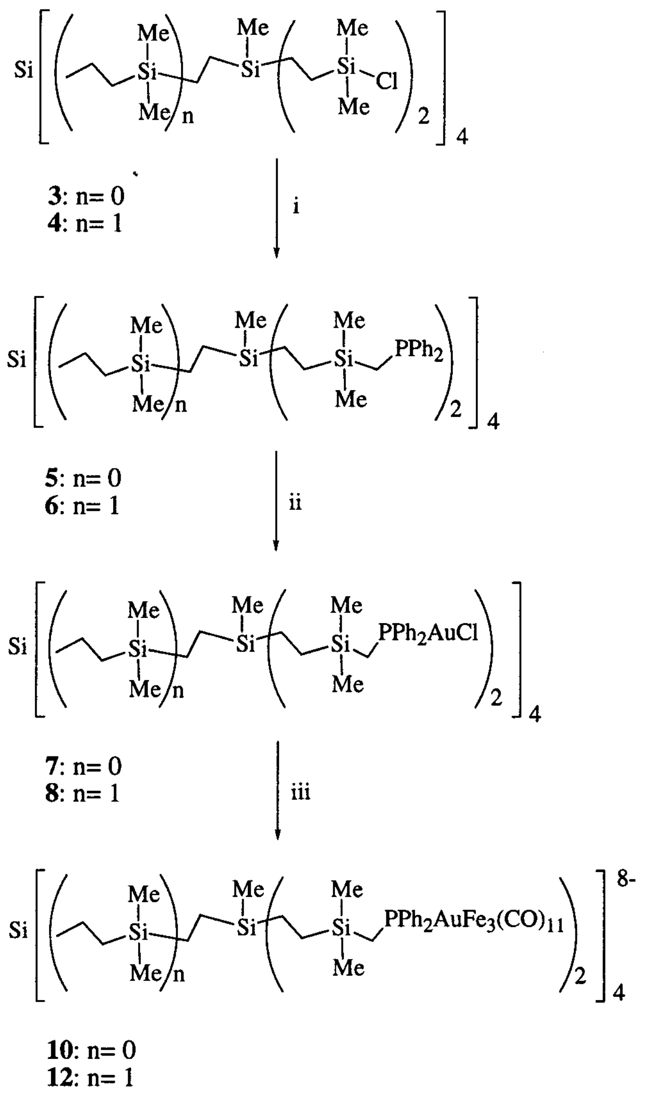
Summary: The synthesis of soluble carbosilane dendrimers terminated with $AuFe_2$ and $AuFe_3$ carbonyl cluster units is reported.

Metallodendrimers are expected to exhibit novel properties and features not found in classical systems. Dendrimers containing transition metal carbonyl clusters are known; two examples having molecular metal−metal-bonded systems have been obtained by reacting dendrimers containing peripheral ethynyl groups[1] or polyyne chains[2] with cobalt octacarbonyl to form $C_2[Co(CO)_3]_2$ tetrahedrane units. The cubane cage $[Fe_4S_4]^{2+}$ and, recently, the $[Re_6Se_8(MeCN)_6]^{2+}$ cluster were used as the core for dendrimers.[3] Dendrimers containing metal nanoclusters have also been described.[4]

In a recent paper,[5] we described a strategy to graft mixed transition-metal cluster units on the branch ends of a dendritic structure. This involves (i) the synthesis of carbosilane dendrimers following the method reported by van der Made and co-workers,[6] (ii) grafting of alkyldiphenylphosphino groups to the branch ends, by reaction with $LiCH_2PPh_2$,[7] (iii) attachment of AuCl units, taking advantage of the lability of the tetrahydrothiophene (THT) ligand in ClAu(THT),[8] and (iv) subsequent chloride displacement from Au by iron cluster anions to give carbosilane dendrimers containing mixed gold/iron clusters as terminal groups[9] (Scheme 1).

Scheme 1[a]



[a] Reagents and conditions: (i) $LiCH_2PPh_2 \cdot TMEDA$, THF, −10 °C; (ii) ClAu(THT), THF, 20 °C; (iii) $(PPh_4)_2[Fe_3(CO)_{11}]$, THF, 20 °C.

Some of the new products were shown to be extremely insoluble. Thus, while the ionic compound $[PPh_4]_4[Si(CH_2CH_2SiMe_2CH_2PPh_2\{AuFe_3(CO)_{11}\})_4]$ (**1**) is moderately soluble in THF and acetone, $[PPh_4]_8[Si(CH_2CH_2SiMe(CH_2PPh_2\{AuFe_3(CO)_{11}\})_2)_4]$ (**2**) is an intractable material (Chart 1).

To overcome these solubility problems for these and higher generations, we envisaged two methods: (i) using mononegative iron anions, such as $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}PPh_2)]^-$, which might afford more soluble species since they are then neutral, and (ii) enlarging the dendritic

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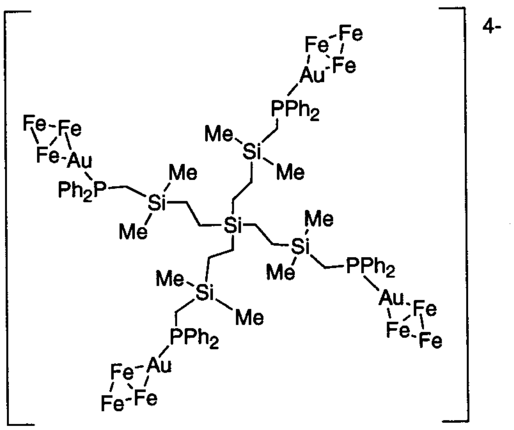
10.1021/om990343+ CCC: $18.00

Chart 1



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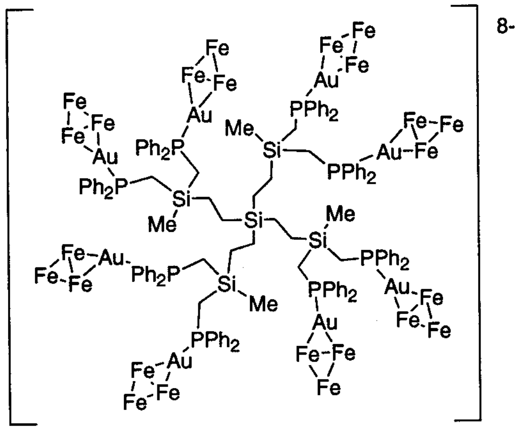

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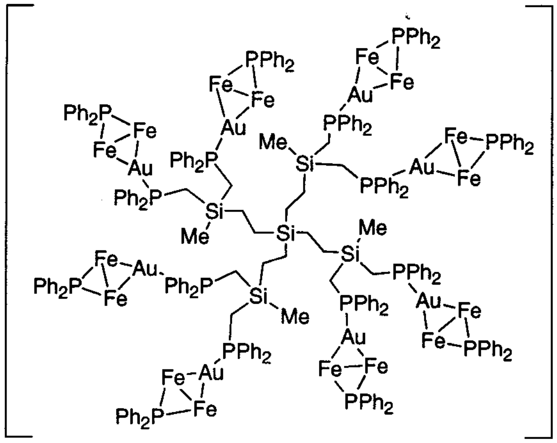
Chart 2



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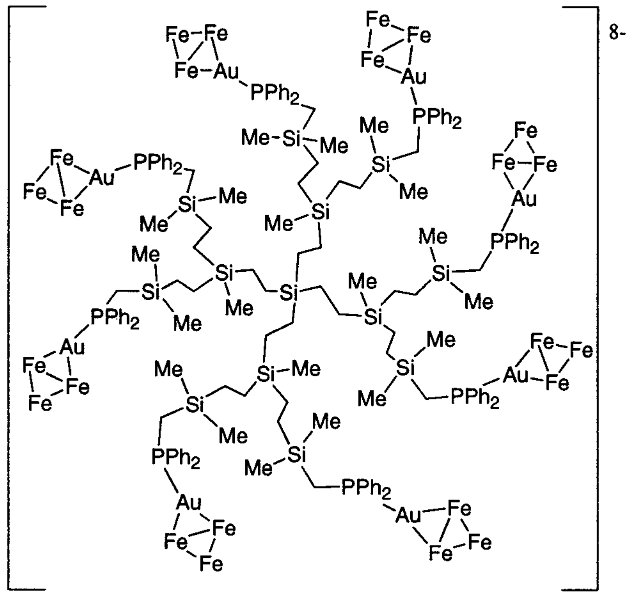

10

structure by introducing $CH_2CH_2SiMe_2$ units as spacers but keeping the same number of phosphino functions in order to decrease surface congestion and charge density. These expectations were confirmed, and thus, the reaction of $Si(CH_2CH_2SiMe(CH_2PPh_2AuCl)_2)_4$ with $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}PPh_2)]^-$ in THF gave the mixed-metal cluster dendrimer **9**, which was moderately soluble in common organic solvents (Chart 2). On the other hand, treatment of dendrimer **7** with $[Fe_3(CO)_{11}]^{2-}$ gave **10**, which, despite having eight "$[Fe_3(CO)_{11}(AuPPh_2)]$" fragments on the periphery like **2**, was soluble and could be analyzed spectroscopically.

Our study was extended to a carbosilane dendrimer with three layers of silicon atoms, in which the first was employed as a spacer without branching. Thus, **8** reacted with $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}PPh_2)]^-$ and $[Fe_3(CO)_{11}]^{2-}$ to give **11** and **12**, respectively, in moderate yield (Chart 3). The reaction proceeded readily to completion; it was monitored by ^{31}P NMR spectroscopy. Both compounds are soluble in acetone, THF, and dichloromethane. **11** is also soluble in chloroform.

All the new cluster compounds were characterized by elemental analyses and IR and multinuclear NMR spectroscopy. All of them are pure in the limit of NMR detection. Their IR spectra showed the expected absorptions in the carbonyl region, suggesting a metal core similar to that found in $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}PPh_2)\{\mu\text{-}AuPPh_3\}]$[10] or $[Fe_3(CO)_{11}\{\mu\text{-}AuPPh_3\}]^-$.[11] The $^{31}P\{^1H\}$ NMR spectrum of **9** and **11** showed one signal attributed to the PPh_2Au group and another for the bridging PPh_2 ligand ($^3J_{P-P} = 24$ Hz). The $^{29}Si\{^1H\}$ NMR spectrum showed the three different silicon environments expected for **10** and the four expected for **11** and **12**. Both the ^1H and ^{13}C NMR spectra were consistent with the structure proposed. No parent ion was observed in the MALDI-TOF spectrum in any case. However, molecular weights were measured by vapor pressure osmometry (see Experimental Section).

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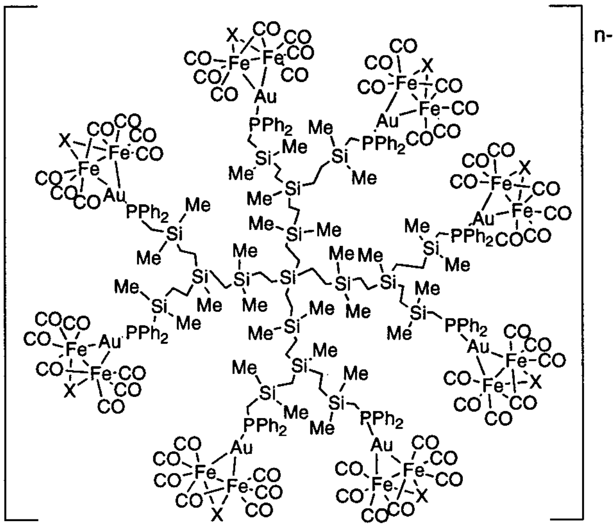
Chart 3



11; X= PPh_2; n=0

12; X= $Fe(CO)_4$; n= 8

In view of these results and the potential use of the Au−Cl fragments in the formation of clusters, our synthetic strategy is promising, since it would allow the surface of dendrimers to be covered with transition-metal clusters, which opens up new possibilities in catalytic processes.

Experimental Section

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 on a Varian 200 spectrometer. Elemental analyses of C and H were carried out at the Institut de Bio-Orgànica de Barcelona. MALDI-TOF mass spectra were recorded on a Bruker Biflex II. VPO measurements were carried out with a Knauer apparatus with benzil as standard. Compounds **3** and **4** were synthesized by hydrosilylation with $HSiMe_2Cl$ and $HSiMeCl_2$ following the method reported before.[6] The syntheses of **5**−**8** were very similar to those reported for related compounds.[5]

Synthesis of 9 and 11. Details of the synthesis of **9** also apply to **11**. A solution of $(PPh_4)[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}PPh_2)]$[12] (0.33 g, 0.53 mmol) in 10 mL of THF was added to a solution of $Si(CH_2CH_2SiMe(CH_2PPh_2AuCl)_2)_4$ (0.25 g, 0.066 mmol) and $TlBF_4$ (0.15 g, 0.51 mmol) in 15 mL of THF at 0 °C. The resulting solution first turned green and then dark red and was subsequently stirred for 1 h. It was evaporated to dryness, the residual solid was extracted with toluene (12 mL), the solution was filtered through Celite, and hexane (12 mL) was added. Yield: 45%. Anal. Calcd: C, 43.35; H, 2.77. Found: C, 43.15; H, 2.78. ^1H NMR (200 MHz, $CDCl_3$, δ (ppm)): 0.0 (s, 12H, CH_3); 0.16, 0.41 (m, 16H, CH_2); 1.8 (broad, 16H, CH_2P); 7.2−7.4 (m, 160H, C_6H_5). ^{31}P NMR (250 MHz, $CDCl_3$, δ (ppm)): 40.6 (d, $^3J_{P-P}$ = 23.7 Hz, CH_2PPh_2); 132.0 (d, $^3J_{P-P}$ = 23.7 Hz, Fe_2PPh_2). IR (THF, cm^{-1}): ν(CO) 2041 m, 2009 vs, 1966 s, 1775 m. VPO ($CHCl_3$, 42 °C): calcd., 7426; found, 7550.

11: yield 57%. Anal. Calcd: C, 44.86; H, 3.86. Found: C, 44.67; H, 3.86. ^1H NMR (200 MHz, $CDCl_3$, δ (ppm)): −0.20 (s, 12H, C^2H_3); −0.07 (s, 24H, C^1H_3); −0.04 (s, 48H, C^3H_3); 0.18−0.33 (m, 64H, CH_2); 1.94 (d, 16H, $^2J_{H-P}$ = 14.2, CH_2P), 7.3−7.6 (m, 160H, C_6H_5). ^{13}C NMR (200 MHz, $CDCl_3$, δ (ppm)): −6.9 (C^2H_3); −4.5 (C^1H_3); −2.5 (d, $^3J_{C-P}$ = 3.7 Hz, C^3H_3); 2.4 (C^1H_2); 4.0 (C^5H_2); 4.4 (C^4H_2); 6.5 (C^3H_2); 6.7 (C^2H_2); 8.7 (d, $^3J_{C-P}$ = 3.7 Hz, C^6H_2); 15.3 (d, J_{C-P} = 16.0 Hz, CH_2P); 125−138 (m, C_6H_5); 215 (broad, CO). ^{29}Si NMR (250 MHz, $CDCl_3$, δ (ppm)): 3.4 (Si_3); 5.9 (Si_1); 8.3 (Si_2); 9.5 (Si_0). ^{31}P NMR (250 MHz, $CDCl_3$, δ (ppm)): 42.0 (d, $^3J_{P-P}$ = 24.3 Hz, CH_2PPh_2); 129.9 (d, $^3J_{P-P}$ = 24.3 Hz, Fe_2PPh_2). IR (THF, cm^{-1}): ν(CO) 2041 m, 2007 vs, 1965 s, 1772 m. VPO ($CHCl_3$, 42 °C): calcd, 8460; found, 8870.

Synthesis of 10 and 12. Details of the synthesis of **10** also apply to **12**. Solid $(PPh_4)_2[Fe_3(CO)_{11}]$[13] (1.38 g, 1.20 mmol) was added to a solution of **7** (0.67 g, 0.15 mmol) in 15 mL of THF. The resulting solution turned dark purple and was stirred for 1 h. It was then filtered through Celite and concentrated *in vacuo* to half-volume, and 20 mL of cool 2-propanol was added. After the solution was cooled overnight, a dark purple solid was obtained in 63% yield. Anal. Calcd: C, 48.08; H, 3.43. Found: C, 47.86; H, 3.45. ^1H NMR (200 MHz, acetone-d_6, δ (ppm)): −0.19 (s, 12H, C^1H_3); −0.01 (s, 48H, C^2H_3); 0.33 (m, 48H, CH_2); 1.95 (d, 16H, $^2J_{H-P}$ = 12 Hz, CH_2P), 7.34−7.95 (m, 240H, C_6H_5 of PPh_2 and PPh_4^+). ^{13}C NMR (200 MHz, acetone-d_6, δ (ppm)): −6.1 (C^1H_3); −1.8 (C^2H_3); 3.3 (C^1H_2); 4.8 (C^3H_2); 5.5 (C^2H_2); 9.6 (C^4H_2); 15.4 (d, broad, J_{C-P} = 10 Hz, CH_2P); 117.8−137.9 (m, C_6H_5 of PPh_2 and PPh_4^+); 225.3 (br, CO). ^{29}Si NMR (250 MHz, THF, δ (ppm)): 2.6 (Si_2); 7.4 (Si_1). ^{31}P NMR (250 MHz, acetone-d_6, δ (ppm)): 23.0 (PPh_4^+); 45.9 (PPh_2). IR (THF, cm^{-1}): ν(CO) 2037 s, 1967 vs, 1935 sh, 1912 s, 1735 w. VPO (acetone, 42 °C): calcd for $[(PPh_4)_8M]$, 10 692; found, 9680.

12: yield 65%. Anal. Calcd: C, 48.32; H, 3.69. Found:[14] C, 46.74; H, 3.81. ^1H NMR (200 MHz, CD_2Cl_2, δ (ppm)): −0.23 (s, 12H, C^2H_3); −0.09 (s, 24H, C^1H_3); −0.03 (s, 48H, C^3H_3); 0.15−0.42 (m, 64H, CH_2); 1.87 (d, 16H, $^2J_{H-P}$ = 14.4 Hz, CH_2P); 7.3−8.0 (m, 240H, C_6H_5 of PPh_2 and PPh_4^+). ^{13}C NMR (200 MHz, acetone-d_6, δ (ppm)): −6.3 (C^2H_3); −4.0 (C^1H_3); −2.0 (broad, C^3H_3); 3.1 (C^1H_2); 4.6 (C^5H_2); 5.1 (C^4H_2); 7.1 (broad, $C^{3,2}H_2$); 9.4 (C^6H_2); 15.4 (broad, CH_2P); 117.7−137.8 (m, C_6H_5 of PPh_2 and PPh_4^+); 225.2 (broad, CO). ^{29}Si NMR (250 MHz, THF, δ (ppm)): 2.6 (d, $^2J_{Si-P}$ = 2 Hz, Si_3); 5.0 (Si_1); 7.4 (Si_2); 8.7 (broad, Si_0). ^{31}P NMR (250 MHz, THF, δ (ppm)): 22.3 (PPh_4^+); 44.9 (PPh_2). IR (THF, cm^{-1}): ν(CO) 2037 s, 1967 vs, 1935 sh, 1911 s, 1735 m. VPO (acetone, 42 °C): calcd for $(PPh_4)_8M$, 11 037; found, 11 654.

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[14] The elemental analysis for **12** was not satisfactory because the solvents were not removed even after several washings, recrystallizations, and high-vacuum drying, as seen by ^1H NMR. This behavior has been reported before: Slany, M.; Bardaji, M.; Caminade, A.-M.; Chaudret, B.; Majoral, J.−P. *Inorg. Chem.* **1997**, *36*, 1939.