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Very large neutral and polyanionic Fe/Au cluster-containing dendrimers

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Abstract

Treatment of tetrahydrofuran solutions of a series of ClAu-terminated dendrimers with the iron anions $[Fe_2(CO)_7(PPh_2)]^-$ and $[Fe_3(CO)_{11}]^{2-}$ has allowed the new dendrimer species decorated on the surface by Fe_2Au or Fe_3Au units to be isolated, including one having up to 192 Fe_2Au clusters. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Iron; Gold; Phosphorus; Dendrimer; Cluster

1. Introduction

The incorporation of metals in dendrimers, either on the surface, within the branches, or at the core, may provide an opportunity to generate new materials with specific functions [1]. In general, the grafting of metal centers into the dendrimer has been achieved by using organometallic species [2]. Recently, several groups have described the alternative use of metal cluster to form exotic metal cluster/dendrimer systems. Thus, the cubane cage $[Fe_4S_4]^{2+}$ [3] and the octahedral clusters $[Re_6Se_8(MeCN)_6]^{2+}$ [4a] and $[Mo_6Cl_8]$ [4b] were used as the core of dendrimeric systems whereas the $C_2[Co(CO)_3]_2$ tetrahedrane cluster was used as a part of the backbone dendritic connectivity as well as peripheral groups of polyalkyne systems [5]. However, the grafting of hetero-polynuclear metal clusters on the surface of dendrimers was reported in our pioneering work in which up to eight $[Fe_2Au(CO)_7(PPh_2)]$, or $[Fe_3Au(CO)_{11}]$ fragments were attached onto the surface of the second generation of a phosphorous terminated carbosilane dendrimer [6]. Very recently, the introduction of the cluster fragments $Ru_3(CO)_{11}$ [7], and $[Ru_5C(CO)_{12}]$ or $[Au_2Ru_6C(CO)_{16}]$ [8] at the periphery of dendrimers has been described. We now report an extension of our previous work to synthesize more complex clusters-containing dendritic systems.

2. Results and discussion

The gold-terminated dendrimers described by some of us [9] were chosen because of their solubility, no-surface congestion and the well known reactivity of the AuCl unit towards metal cluster fragments. Thus, the third generation dendrimer $(ClAu)_{24}[G_3]$ was reacted with a stoichiometric amount of $(NEt_4)[Fe_2(CO)_7(PPh_2)]$ in THF at 0°C in the presence of $TlBF_4$ as a halide abstractor to give $(Fe_2Au)_{24}[G_3]$ as a brown solid in moderate yield (Scheme 1). The IR spectrum showed the expected absorptions in the carbonyl region, analogous to those found in $[Fe_2Au(CO)_7(PPh_2)(PPh_3)]$ [10]. The completion of the reaction has been proven by ^{31}P-NMR spectroscopy which showed the total disappearance of the signal at 21.2 ppm due to the PAuCl fragments of the starting dendrimer. Thus, the ^{31}P-NMR spectrum of the product shows one singlet at 62.5 ppm for the phosphorus atoms located within the

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cascade structure, a doublet at 42.2 ppm (^3J(P–P) = 24.9 Hz) for the peripheral phosphorous atoms, and a doublet at 129.2 ppm for the phosphido bridging groups. Both the ^{1}H- and ^{13}C-NMR spectra were consistent with the proposed structure. Compound $(Fe_2Au)_{24}[G_3]$ which exhibits 24 Fe/Au cluster fragments on the surface (Fig. 1) is soluble in the most common organic solvents and it can be manipulated in the air for a few minutes without appreciable decomposition. In view of these results, we extended this reaction to higher generation dendrimers. Thus, the action of the iron carbonylate to solutions of $(ClAu)_{48}[G_4]$ and $(ClAu)_{96}[G_5]$ [9] allowed us to obtain the dendrimers $(Fe_2Au)_{48}[G_4]$ and $(Fe_2Au)_{96}[G_5]$, respectively. Finally, the use of the sixth generation has permitted to obtain the new species $(Fe_2Au)_{192}[G_6]$, which is, by far, the molecule with the highest number of trimetallic units described up to now. These reactions were monitored by ^{31}P-NMR spectroscopy and in all cases the total disappearance of the signal corresponding to the Au*P*Ph$_2$ fragment, which is shifted 21 ppm downfield, indicates full substitution of the chloride. The new species were characterized by elemental analyses and IR and NMR (^{1}H-, ^{13}C- and ^{31}P-) spectroscopy. They are pure in the limit of NMR detection. Unfortunately, no parent ion was observed in the MALDI-TOF spectrum in any case which agree with the results reported for the starting gold dendrimers [9]. This is not surprising since all MALDI-TOF experiments show that fragmentations involving the internal P–O–C_6H_4–CH=N–NMe linkages easily occur, even if molecular peaks can be detected for the uncomplexed dendrimers [11]. The use of electrospray MS did not allow to obtain either the parent molecular peaks.

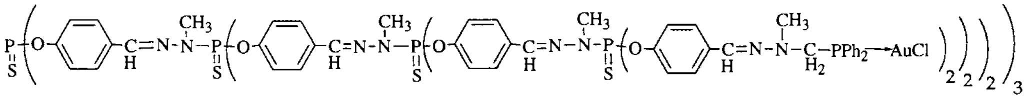
The presence of such a high number of metal atoms on the surface of $(Fe_2Au)_{192}[G_6]$ prompted us to try to visualize this molecule by high-resolution electron microscopy. Samples were prepared by slow evaporation of a tetrahydrofuran solution on a carbon-coated cooper grid. Unfortunately, the compound proved to be unstable and the micrographs show the presence of spherical structures of gold, indicating that decomposition has occurred during the deposition process.

It seemed interesting to attempt the synthesis of similar species by using the dianion $[Fe_3(CO)_{11}]^{2-}$ instead of the monoanion $[Fe_2(CO)_7(PPh_2)]^-$ in order to examine the solubility and stability of the resulting anionic cluster-containing dendrimers. In fact, the reaction of the salt $(PPh_4)_2[Fe_3(CO)_{11}]$ with $(ClAu)_{24}[G_3]$ gave the compound $(Fe_3Au^-)_{24}[G_3]$ (Fig. 1). This compound is soluble in THF, acetone and dichloromethane in spite of the presence of 24 negative charges. However, its stability in THF solution was reduced (^{31}P-NMR monitoring) so the use of the triiron anion as starting block for the synthesis of other cluster-containing dendrimers was not investigated yet.

We are currently extending these studies to higher generations and to higher cluster nuclearities.

3. Experimental

All manipulations were performed under an atmosphere of pre-purified N_2 with use of standard Schlenk techniques, and all solvents were distilled from appropriate drying agents. Infrared spectra were recorded in THF solutions on an FT IR 520 Nicolet spectrophotometer. $^{31}P\{^1H\}$- and $^{29}Si\{^1H\}$-NMR spectra were obtained on a Bruker DXR 250 and $^{13}C\{^1H\}$- and ^{1}H-NMR spectra were recorded on a Varian 200 spectrometer. Elemental analyses of C and H were carried out at the Institut de Bio-Orgànica de Barcelona. The



$(ClAu)_{24}[G_3]$

$$(ClAu)_{24}[G_3] + 24\,(NEt_4)[Fe_2(\mu\text{-}PPh_2)(\mu\text{-}CO)(CO)_6] \xrightarrow[0\,°C,\ THF]{TlBF_4} (Fe_2Au)_{24}[G_3] + 24\,Et_4NCl$$

$$(ClAu)_{192}[G_6] + 192\,(NEt_4)[Fe_2(\mu\text{-}PPh_2)(\mu\text{-}CO)(CO)_6] \xrightarrow[0\,°C,\ CH_2Cl_2]{TlBF_4} (Fe_2Au)_{192}[G_6] + 192\,Et_4NCl$$

$$(ClAu)_{24}[G_3] + 24\,(PPh_4)_2[Fe_3(CO)_{11}] \xrightarrow[-10\,°C]{THF} [PPh_4]_{24}\{(Fe_3Au)_{24}[G_3]\} + 24\,PPh_4Cl$$

Scheme 1.

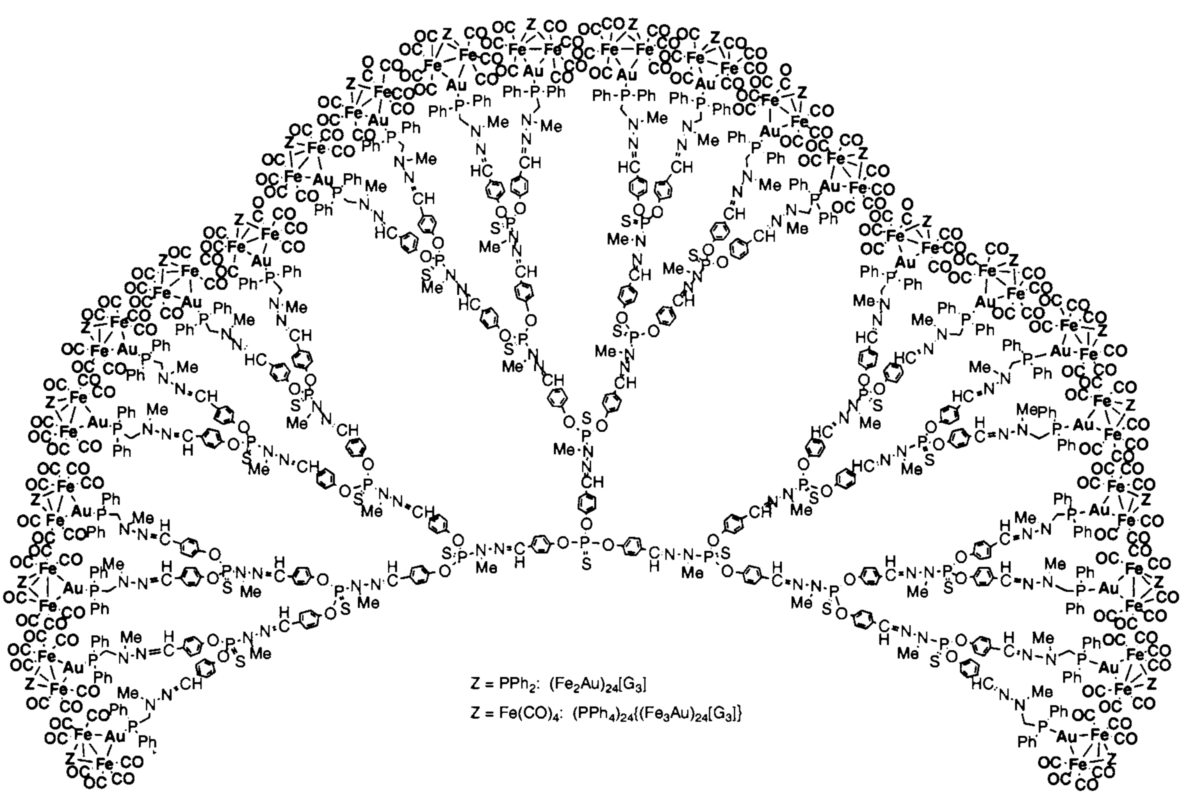


Fig. 1.

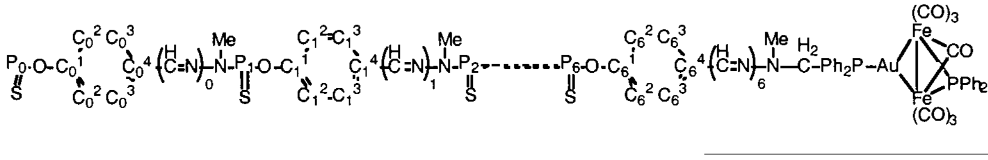
compounds (NEt$_4$)[Fe$_2$(CO)$_7$(PPh$_2$)] [12], (PPh$_4$)$_2$[Fe$_3$(CO)$_{11}$] [13] were prepared as previously described.

3.1. Synthesis of (Fe$_2$Au)$_{192}$[G$_6$]

Details of the synthesis of the six generation compound also apply to other generation species.

A solution of (NEt$_4$)[Fe$_2$(μ-PPh$_2$)(μ-CO)(CO)$_6$] (79 mg, 0.127 mmol) in 15 ml of CH$_2$Cl$_2$ was added to a solution of (ClAu)$_{192}$[G$_6$] (100 mg, 6.61 10^{-4} mmol) and TlBF$_4$ (37 mg, 0.127 mmol) in 15 ml of CH$_2$Cl$_2$ 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, the solution was filtered through Celite, and hexane was added.

The numbering used for ^{13}C- and ^{31}P-NMR is as follows:



Selected data for (Fe$_2$Au)$_{192}$[G$_6$]: red powder; 73% yield; ^{1}H-NMR (200 MHz, CDCl$_3$) δ 2.83 (br s, 576H, CH$_2$N(C*H*$_3$)); 3.21 (br s, 567H, P$_{1,2,3,4,5,6}$NC*H*$_3$); 4.47 (br, 384H, C*H*$_2$P); 6.9–7.8 (m, 5745H, C$_6$*H*$_4$, C$_6$*H*$_5$ and C*H*=N). ^{13}C{^{1}H}-NMR (200 MHz, CDCl$_3$) δ 33.0 (d, ^2J(C–P$_{1-6}$) = 15.5 Hz, P$_{1-6}$NCH$_3$); 38.6 (s, N(*C*H$_3$)-CH$_2$PPh$_2$); 60.9 (d, ^1J(C–P) = 36.5 Hz, CH$_2$PPh$_2$); 121.1 (C$_6^2$); 121.8 (C$_{0-5}^2$); 126.7 (C$_6^3$); 128.1 (d, ^3J(C–P) = 10.6 Hz, *m*-C$_6$H$_5$ (Fe$_2$)); 129.0 (d, ^3J(C–P) = 10.2 Hz, *m*-C$_6$H$_5$ (Au)); 129.6 (br, *p*-C$_6$H$_5$ (Fe$_2$)); 131.0; 130.9 (br, *p*-C$_6$H$_5$ (Au) and C$_6^4$); 132.0/131.6 (C$_{0-5}^4$); 132.8 (d, ^2J(C–P) = 8.9 Hz, *o*-C$_6$H$_5$ (Fe$_2$)); 133.2 (d, ^2J(C–P) = 13.5 Hz, *o*-C$_6$H$_5$ (Au)); 138.5 (d, ^1J(C–P) = 33.1 Hz, CH=N, *i*-C$_6$H$_5$); 149.7 (d br, O–C$_6^1$); 151.3 (br, O–C$_{0-5}^1$); 213.0 (CO). ^{31}P{^{1}H}-NMR (250 MHz, CDCl$_3$, δ(ppm)): 42.4 (d, ^3J(P–P) = 24.0 Hz, PAu); 62.5 (br s, P$_{1-6}$); 129.4 (d, ^3J(P–P) = 24.0 Hz, PFe$_2$). IR (CH$_2$Cl$_2$, cm^{-1}) ν_{CO} 2043m, 2011vs, 1970s, 1774m. Anal. Found: C, 45.72; H, 3.19; N, 4.42. Calc. for C$_{9192}$H$_{7272}$Au$_{192}$Fe$_{384}$N$_{762}$P$_{574}$O$_{1725}$S$_{190}$: C, 46.16; H, 3.06; N, 4.46%.

3.2. (Fe$_2$Au)$_{24}$[G$_3$]

Red powder; 24% yield; ^{1}H-NMR (200 MHz, CDCl$_3$) δ 2.87 (72H, CH$_2$N(C*H*$_3$)); 3.24 (br, 63H, P$_{1,2,3}$NC*H*$_3$);

4.49 (48H, $C\mathit{H}_2P$); 6.9–7.6 (m, 705H, $C_6\mathit{H}_4$, $C_6\mathit{H}_5$ and $C\mathit{H}$=N). ^{13}C{^{1}H}-NMR (200 MHz, $CDCl_3$) δ 33.0 (d, $^{2}J(C–P_{1-3}) = 13.3$ Hz, $P_{1-3}NCH_3$); 38.6 (d, $^{3}J(C–P) = 5.1$ Hz, $N(\mathit{C}H_3)CH_2PPh_2$); 61.0 (d, $^{1}J(C–P) = 29.4$ Hz, $\mathit{C}H_2PPh_2$); 121.2 (C_3^2); 121.9 (C_{0-2}^2); 126.8 (C_3^3); 128.2 (d, $^{3}J(C–P) = 10.6$ Hz, m-(C_6H_5) (Fe_2)); 129.0 (d, $^{3}J(C–P) = 10.6$ Hz, m-(C_6H_5) (Au)); 129.6 (br, p-(C_6H_5) (Fe_2)); 131.1 (br, p-(C_6H_5) (Au) and C_3^4); 132 (C_{0-2}^4); 132.8 (d, $^{2}J(C–P) = 9.5$ Hz, o-(C_6H_5) (Fe_2)); 133.2 (d, $^{2}J(C–P) = 13.5$ Hz, o-(C_6H_5) (Au)); 138.9 (d, $^{1}J(C–P) = 33.4$ Hz, CH=N, i-C_6H_5); 149.8 (d, $^{2}J(C–P) = 6.9$ Hz, O–C_3^1); 151.4 (m, O–C_{0-2}^1). ^{31}P{^{1}H}-NMR (250 MHz, $CDCl_3$) δ 42.2 (d, $^{3}J(P–P) = 24.9$ Hz, PAu); 62.5 (br s, P_{1-3}); 129.2 (d, $^{3}J(P–P) = 24.9$ Hz, PFe_2). IR (THF, cm^{-1}) ν_{CO} 2042m, 2010vs, 1970s, 1778m. Anal. Found: C, 45.89; H, 2.99; N, 4.24. Calc for $C_{1128}H_{888}Au_{24}Fe_{48}N_{90}O_{213}P_{70}S_{22}$: C, 46.09; H, 3.05; N, 4.29%.

3.3. *($Fe_3Au)_{24}[G_3]$*

Red powder; 50% yield; ^{1}H-NMR (200 MHz, CD_2Cl_2) δ 3.10 (72H, $CH_2N(C\mathit{H}_3)$); 3.29 (br, 63H, $P_{1,2,3}NC\mathit{H}_3$); 4.61 (48H, $C\mathit{H}_2P$); 7.0–7.8 (m, 945H, $C_6\mathit{H}_4$, $C_6\mathit{H}_5$ and $C\mathit{H}$=N). ^{13}C{^{1}H}-NMR (200 MHz, CD_2Cl_2) δ 33.3 (d, $^{2}J(C–P_{1,2,3}) = 11.4$ Hz, $P_{1,2,3}NCH_3$); 38.7 (d, $^{3}J(C–P) = 2.9$ Hz, $N(\mathit{C}H_3)CH_2PPh_2$); 61.6 (d, $^{1}J(C–P) = 2.9$ Hz, $\mathit{C}H_2PPh_2$); 121.4 (C_3^2); 122.1 (C_{0-2}^2); 126.8 (C_3^3); 128.8 (d, $^{3}J(C–P) = 10.3$ Hz, m-(C_6H_5) (Au)); 129.8 (br, p-(C_6H_5) (Au) and C_3^4); 132.3 (C_{0-2}^4); 134.1 (d, $^{2}J(C–P) = 14.2$ Hz, o-(C_6H_5) (Au)); 139.5 (br, CH=N, i-(C_6H_5)); 149.8 (br, O–C_3^1); 151.6 (br, O–C_{0-2}^1). ^{31}P{^{1}H}-NMR (250 MHz, CD_2Cl_2) δ 23.2 (PPh_4^+); 43.5 (PAu); 62.7 (br s, P_{1-3}). IR (THF, cm^{-1}) ν_{CO} 2039m, 1968vs, 1936sh, 1916sh, 1736m. Anal. Found: C, 48.84; H, 3.34; N, 3.21. Calc. for $C_{1512}H_{1128}Au_{24}Fe_{72}N_{90}P_{70}O_{309}S_{22}$: C, 48.91; H, 3.04; N, 3.40%.

3.4. *($Fe_2Au)_{48}[G_4]$*

Red powder; 53% yield; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 2.85 (144H, $CH_2N(C\mathit{H}_3)$); 3.22 (br, 135H, $P_{1,2,3,4}NC\mathit{H}_3$); 4.49 (96H, $C\mathit{H}_2P$); 6.9–7.6 (m, 1425H, $C_6\mathit{H}_4$, C_6H_5 and CH=N). ^{13}C{^{1}H}-NMR (200 MHz, $CDCl_3$, δ(ppm)): 32.9 (d, $^{2}J(C–P_{1,2,3,4}) = 12.1$ Hz, $P_{1,2,3,4}NCH_3$); 38.6 (d, $^{3}J(C–P) = 4.7$ Hz, $N(\mathit{C}H_3)CH_2PPh_2$); 60.9 (d, $^{1}J(C–P) = 27.9$ Hz, $\mathit{C}H_2PPh_2$); 121.2 (C_4^2); 121.9 (C_{0-3}^2); 126.7 (C_4^3); 128.1 (d, $^{3}J(C–P) = 10.6$ Hz, m-(C_6H_5) (Fe_2)); 129.0 (d, $^{3}J(C–P) = 10.4$ Hz, m-(C_6H_5) (Au)); 129.6 (br, p-(C_6H_5) (Fe_2)); 131.0; 130.9 (br, p-(C_6H_5) (Au and C_4^4); 132.0/131.6 (C_{0-3}^4); 132.8 (d, $^{2}J(C–P) = 9.3$ Hz, o-(C_6H_5) (Fe_2)); 133.2 (d, $^{2}J(C–P) = 13.5$ Hz, o-(C_6H_5) (Au)); 138.6 (d, $^{1}J(C–P) = 33.5$ Hz, CH=N, i-(C_6H_5); 149.7 (d, $^{2}J(C–P) = 7.3$ Hz, O–C_4^1); 151.2 (m, O–C_{0-3}^1); 225.3 (CO). ^{31}P{^{1}H}-NMR (250 MHz, $CDCl_3$) δ 42.4 (d, $^{3}J(P–P) = 24.7$ Hz, PAu); 62.5 (br s, P_{1-4}); 129.4 (d, $^{3}J(P–P) = 24.7$ Hz, PFe_2). IR (THF, cm^{-1}) ν_{CO} 2041m, 2007vs, 1960s, 1764m. Anal. Found: C, 45.98; H, 3.37; N, 4.31. Calc. for $C_{2280}H_{1800}Au_{48}Fe_{96}N_{186}P_{142}O_{429}S_{46}$: C, 46.14; H, 3.06; N, 4.39%.

3.5. *($Fe_2Au)_{96}[G_5]$*

Red powder; 47% yield; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 2.87 (288H, $CH_2N(C\mathit{H}_3)$); 3.25 (br, 279H, $P_{1,2,3,4,5}NC\mathit{H}_3$); 4.51 (br, 192H, $C\mathit{H}_2P$); 7.0–7.6 (m, 2865H, $C_6\mathit{H}_4$, $C_6\mathit{H}_5$ and $C\mathit{H}$=N). ^{13}C{^{1}H}-NMR (200 MHz, $CDCl_3$) δ 32.9 (d, $^{2}J(C–P_{1,2,3,4,5}) = 11.7$ Hz, $P_{1,2,3,4,5}NCH_3$); 38.6 (d, $^{3}J(C–P) = 4.7$ Hz, $N(\mathit{C}H_3)CH_2PPh_2$); 60.9 (d, $^{1}J(C–P) = 32.5$ Hz, CH_2PPh_2); 121.1 (C_5^2); 121.9 (C_{0-4}^2); 126.8 (C_5^3); 128.1 (d, $^{3}J(C–P) = 10.6$ Hz, m-C_6H_5 (Fe_2)); 129.0 (d, $^{3}J(C–P) = 10.6$ Hz, m-C_6H_5 (Au)); 129.6 (br, p-C_6H_5 (Fe_2)); 131.0; 130.9 (br, p-C_6H_5 (Au and C_5^4); 132.0/131.6 (C_{0-4}^4); 132.8 (d, $^{2}J(C–P) = 9.4$ Hz, o-C_6H_5 (Fe_2)); 133.2 (d, $^{2}J(C–P) = 13,7$ Hz, o-C_6H_5 (Au)); 138.6 (d, $^{1}J(C–P) = 33.0$ Hz, $\mathit{C}H$=N, i-C_6H_5); 149.7 (d br, O–C_5^1); 151.2 (m br, O–C_{0-4}^1); 212.4 (CO). ^{31}P{^{1}H}-NMR (250 MHz, $CDCl_3$) δ 42.4 (d, $^{3}J(P–P) = 23.7$ Hz, PAu); 62.5 (br s, P_{1-5}); 129.4 (d, $^{3}J(P–P) = 23.7$ Hz, PFe_2). IR (CH_2Cl_2, cm^{-1}) ν_{CO} 2040m, 2009vs, 1970s, 1777m. Anal. Found: C, 46.07; H, 2.99; N, 4.28. Calc. for $C_{4584}H_{3624}Au_{96}Fe_{192}N_{378}O_{861}P_{286}S_{94}$: C, 46.16; H, 3.06; N, 4.44%.

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