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Branched and dendritic metallo-carbosiloxanes with $OCH_2PPh_2ML_n$ end-grafted units

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Abstract

A straightforward method for the preparation of metallo carbosiloxanes of type $Si(OCH_2CH_2CH_2SiMe_2[OCH_2PPh_2M(CO)_n])_4$ ($n = 3$, M = Ni, **7a**; $n = 4$, M = Fe, **7b**; $n = 5$: M = Mo, **7c**; M = W, **7d**), $Si(OCH_2CH_2CH_2SiMe[OCH_2PPh_2Ni(CO)_3]_2)_4$ (**8**) and $Me_2Si(OCH_2CH_2CH_2SiMe[OCH_2PPh_2Ni(CO)_3]_2)_2$ (**11**) is described. The reaction of $Si(OCH_2CH_2CH_2SiMeXCl)_4$ (**1**: X = Me, **2**: X = Cl) or $Me_2Si(OCH_2CH_2CH_2SiMeCl_2)_2$ (**9**) with $HOCH_2PPh_2$ (**3**) produces $Si(OCH_2CH_2CH_2SiMe_2(OCH_2PPh_2))_4$ (**4**), $Si(OCH_2CH_2CH_2SiMe(OCH_2PPh_2)_2)_4$ (**5**) or $Me_2Si(OCH_2CH_2CH_2SiMe(OCH_2PPh_2)_2)_2$ (**10**) in presence of DABCO. Treatment of the latter molecules with $Ni(CO)_4$ (**6a**), $Fe_2(CO)_9$ (**6b**), $M(CO)_5(Thf)$ (**6c**: M = Mo; **6d**: M = W), respectively, gives the title compounds **7a**–**7d**, **8** and **11** in which the PPh_2 groups are datively bound to a 16-valence-electron metal carbonyl fragment.

The formation of analytical pure and uniform branched and dendritic metallo-carbosiloxanes is based on elemental analysis, and IR, ^1H, $^{13}C\{^1H\}$, $^{29}Si\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectroscopic studies. In addition, ESI-TOF mass spectrometric studies were carried out.

Keywords: Metallo dendrimer; Carbosiloxane; Phosphane; Metal carbonyl; Nickel; Iron; Molybdenum; Tungsten

1. Introduction

There is a wide interest in the synthesis of metallo dendrimers, since such three-dimensional and highly branched molecules successfully can be used as, for example, interface between homogenous and heterogeneous catalysis [1]. One possible entry into such catalytic active materials is given by the fixation of catalytical active sites at the periphery of soluble macromolecular supports, for example, carbosilane dendrimers functionalized with arylnickel(II) moieties [2]. Another approach to synthesise metallo dendrimers is given by the introduction of terminal-bound R_2P groups (R = singly bound organic ligand), which can later be used for the complexation of the organometallic part [3].

We here report on the synthesis of Ph_2PCH_2O-functionalised carbosiloxanes and carbosiloxane dendrimers which on their reaction with diverse transition metal carbonyls give the respective metallo compounds.

2. Results and discussion

The target of this study is the synthesis of organometallic carbosiloxanes and respective dendrimers featuring $M(CO)_n$ fragments ($n = 3$, M = Ni; $n = 4$, M = Fe; $n = 5$: M = Mo, W) as end-grafted units. They are accessible in a two-step synthesis procedure. Exhaustive alcoholysis of $Si(OCH_2CH_2CH_2SiMeXCl)_4$ (**1**: X = Me, **2**: X = Cl) [4] with $HOCH_2PPh_2$ (**3**) in presence of DABCO (DABCO = *d*i*aza*b*i*cyclo*o*ctane) in toluene at 25 °C produces $Si(OCH_2CH_2CH_2SiMe_2(OCH_2PPh_2))_4$ (**4**) and $Si(OCH_2CH_2CH_2SiMe(OCH_2PPh_2)_2)_4$ (**5**).

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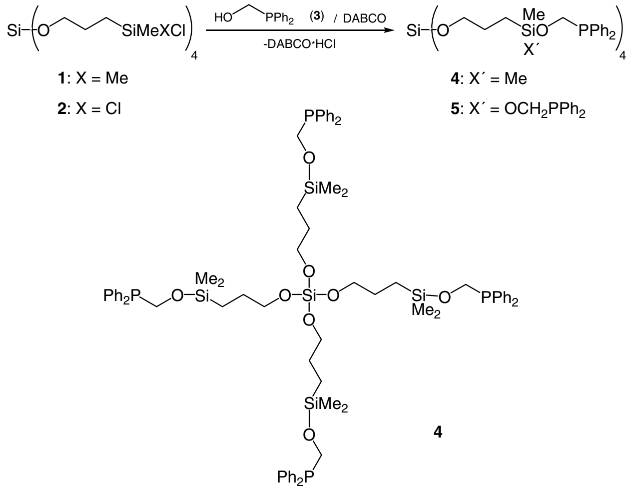
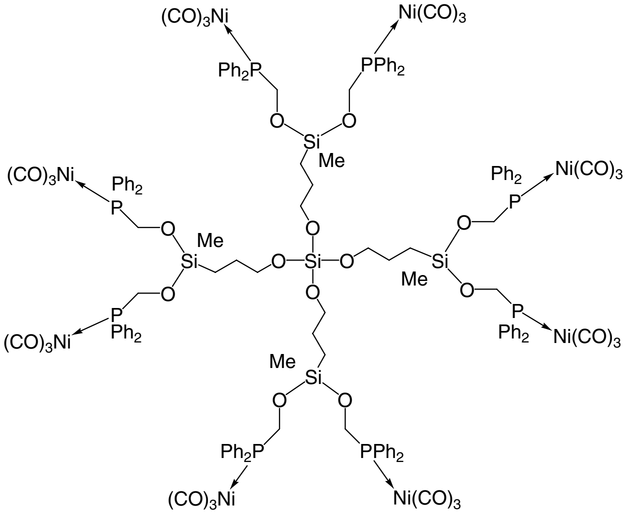


(1)

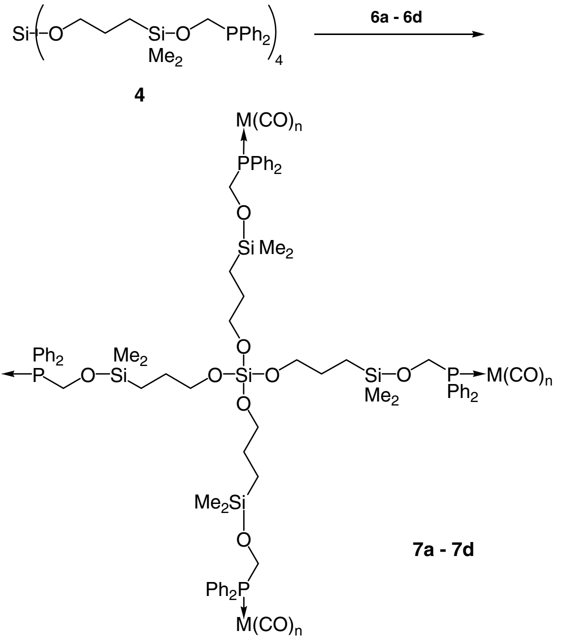
Molecules **4** and **5** can be isolated in analytical pure form by filtration through a pad of Celite and evaporation of all volatile materials in oil-pump vacuum.

Compounds **4** and **5** contain Ph_2P ligated units, which allow the coordination of transition metal fragments. In this respect, **4** and **5** were reacted with $Ni(CO)_4$ (**6a**), $Fe_2(CO)_9$ (**6b**) or $M(CO)_5(Thf)$ (**6c**: M = Mo, **6d**: M = W) in a 1:4 (reaction of **4** with **6**) or 1:8 (reaction of **5** with **6**) molar ratio in tetrahydrofuran at 25 °C. Upon loss of CO (from **6a**), $Fe(CO)_5$ (from **6b**) or Thf (from **6c**, **6d**) the metallo carbosiloxanes $Si(OCH_2CH_2CH_2SiMe_2[OCH_2PPh_2M(CO)_n])_4$ ($n = 3$, M = Ni, **7a**; $n = 4$, M = Fe, **7b**; $n = 5$: M = Mo, **7c**; M = W, **7d**) and dendrimer $Si(OCH_2CH_2CH_2SiMe[OCH_2PPh_2Ni(CO)_3]_2)_4$ (**8**) (Fig. 1) are formed in excellent yield (Eq. (2)) (Table 1)



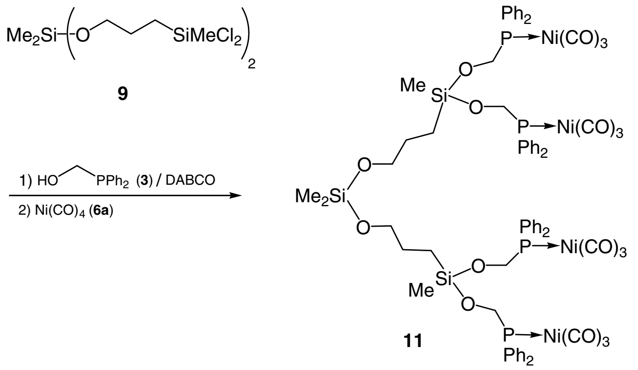
8

Fig. 1. Schematic view of dendrimer **8**.



(2)

The basic outline for the preparation of **4**, **5**, **7** and **8** with a SiO_4 core (vide supra) can also be applied for the synthesis of the cauliflower-type dendritic molecule $Me_2Si(OCH_2CH_2CH_2SiMe[OCH_2PPh_2Ni(CO)_3]_2)_2$ (**11**).



(3)

Dendritic **11** can be synthesised in the same way as **7** and **8** by alcoholysis of $Me_2Si(OCH_2CH_2CH_2SiMeCl_2)_2$- (**9**) with $HOPPh_2$ (**3**). The thus obtained $Me_2Si(OCH_2CH_2CH_2SiMe(OCH_2PPh_2)_2)_2$ (**10**) species reacts with four equivalents of $Ni(CO)_4$ (**6a**) to produce **11** by loss of carbon monoxide.

Table 1
Synthesis of **7a**–**7d**

Compound	M	*n*	Yield[a] (%)
7a	Ni	3	99
7b	Fe	4	94
7c	Mo	5	76
7d	W	5	79

[a] Based on **4**.

Like the Ph_2PCH_2O-modified systems **4**, **5** and **10** also their metal-containing derivatives **7a–7d**, **8** and **11** are viscous oils. After appropriate work-up they can be isolated as colourless (**4**), pale yellow (**5, 7a**, **7c**, **7d**, **8**, **11**) or orange (**7b**) oils in 75–99% yield and are soluble in most common organic solvents.

Compounds **4**, **5**, **7**, **8**, **10** and **11** are fully characterised by IR, ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectroscopy. Additionally, $^{29}Si\{^1H\}$ NMR spectroscopic studies were carried out with **4**, **5**, **7b** and **10**.

Representative absorptions for all new synthesised species are observed for the SiO units between 1070 and 1095 cm^{-1} and for the CO building blocks in the range of 1930–2070 cm^{-1}. The absorption pattern and location of the ν_{CO} vibrations are in accordance with similar literature-known $(R_3P)M(CO)_n$ compounds ($M(CO)_n = Ni(CO)_3$, $Fe(CO)_4$, Mo/ $W(CO)_5$; R = singly bound organic ligand) [5]. Further distinct vibrations are observed at ca. 1255 cm^{-1} for the Si–C bonds.

Besides IR spectroscopy, $^{31}P\{^1H\}$ NMR studies are best suitable to monitor the progress of the alcoholysis and complexation steps. The Ph_2PCH_2O groups in **4**, **5** and **10** give rise to a $^{31}P\{^1H\}$ NMR resonance signal at −12.2 (**4**, **5**) or −11.9 ppm (**10**). Complexation of the latter units by $M(CO)_n$ leads to a shift to lower field depending on the respective metal carbonyls used (**7a**, **8** and **11**: ca. 30.0, **7b**: 77.9, **7c**: 35.5, **7d**: 17.3 ppm). These data are in agreement with similar $R_3PM(CO)_n$ species [5,6].

In addition to $^{31}P\{^1H\}$ NMR spectroscopy the corresponding transformation from $SiMe_2Cl$- or $SiMeCl_2$-functionalised carbosiloxanes to Ph_2PCH_2O-modified branched and dendritic molecules is nicely confirmed by ^1H and $^{13}C\{^1H\}$ NMR studies. New resonance patterns, due to the Ph_2PCH_2O fragments appear in the ^1H NMR spectra between 7.2 and 7.6 ppm (Ph) and at ca. 4.3 ppm (OCH_2P). In the $^{13}C\{^1H\}$ NMR spectra characteristic resonance signals are observed between 128.0 and 137.5 ppm (Ph) and at approximately 65 ppm (OCH_2P). For the CH_2 unit of the OCH_2PPh_2 fragments typical PH (^1H NMR) and PC ($^{13}C\{^1H\}$ NMR) coupling constants are observed. Specific for the $M(CO)_n$-functionalised molecules is that in the $^{13}C\{^1H\}$ NMR spectra the CO resonance signals are observed between 196 and 214 ppm, depending on the corresponding metal carbonyl building block present.

ESI-TOF mass spectrometric studies of selected examples (**4**, **5** and **7**) were carried out. It appeared that for the $Ni(CO)_3$-modified molecules no spectra could be obtained, while for **7b** the ions $M^+ - 4CO$ and $M^+ - 4(PPh_2Fe(CO)_4)$ could be detected. For **4** it was necessary to dope with AgSCN for a better ionisation. As result thereof, $[M + Ag]^+$ as molecular ion and $[M + Ag - 2(Ph_2PCH_2OMe)]^+$ are found.

In this study it could be shown that Ph_2PCH_2O entities allow the successful introduction of metal carbonyls $M(CO)_n$ ($n = 3$, M = Ni; $n = 4$, M = Fe; $n = 5$, M = Mo, W) in carbosiloxane molecules by the formation of dative phosphorus–metal bonds. The respective metallo carbosiloxanes and metallo dendrimers are obtained in excellent yield and resemble the first examples in carbosiloxane dendrimer chemistry, featuring transition metal carbonyl moieties as end-grafted units.

3. Experimental

3.1. General methods

All manipulations were performed in dry solvents under an atmosphere of purified nitrogen (O_2 traces: copper catalyst, BASF AG, Ludwigshafen; H_2O: molecular sieve 4 Å, Roth) using standard Schlenk techniques. Solvents were freshly purified and dried by distillation. Diethyl ether and tetrahydrofuran: sodium/ benzophenone. Toluene: sodium. Celite (Errg. B6, Riedel de Häen), degassed at 10^{-2} mbar and 25 °C, was used for filtration procedures. IR spectra were recorded with a Perkin–Elmer FT-IR 1000 spectrometer as films between NaCl plates or as solutions in CaF_2 cells, respectively. The NMR spectra were measured in $CDCl_3$ or CD_3CN (dried over 4 Å molecular sieve) with a Bruker Avance 250 spectrometer at 298 K: ^1H NMR (250.130 MHz), internal standard $CDCl_3$, $\delta = 7.26$; CD_3CN, $\delta = 1.94$; $^{13}C\{^1H\}$ NMR: (62.902 MHz), internal standard $CDCl_3$, $\delta = 77.2$; CD_3CN, $\delta = 1.24, 118.10$; $^{29}Si\{^1H\}$ NMR (49.662 MHz) external standard, relative to $SiMe_4$, $\delta = 0.0$; $^{31}P\{^1H\}$ NMR (101.202 MHz) external standard H_3PO_4 ($\delta = 0.0$), relative to $P(OCH_3)_3$, $\delta = 139.0$. Elemental analyses were performed by the Organic Department of Chemnitz, Technical University with a Vario EL C,H,N-analyser (Heraeus). The ESI-TOF mass spectra were measured with a Mariner mass spectrometer (Applied Biosystems) operating in the positive ion mode in the range of 3.0–6.0 kV. As solvent acetonitrile or tetrahydrofuran was used. For doping AgSCN was added.

3.2. Starting materials

Compounds **1**, **2**, **4** and **9** were prepared according to well established literature procedures [4,7]. All other chemicals were obtained commercially and were used without further purification.

3.3. Synthesis of $Si(OCH_2CH_2CH_2SiMe_2(OCH_2PPh_2))_4$ (4)

1.73 g (8.00 mmol) of $HOCH_2PPh_2$ (**3**) are dissolved in 50 mL of toluene and 0.45 g (4.00 mmol) of DABCO are added in one portion. Afterwards 1.26 g (2.00 mmol) of **1**, dissolved in 2 mL of toluene, are added to the latter reaction mixture. Immediately DABCO*HCl starts to precipitate. After 15 h of stirring at 25 °C the reaction mixture is filtrated through a pad of Celite and all volatiles are evaporated in oil-pump vacuum at 55 °C. Compound **4** is obtained as a colourless, air sensitive, viscous oil. Yield: 2.35 g (1.7 mmol, 87% based on **1**).

IR (NaCl) ν [cm^{-1}]: 1252 (vs) [$\delta_{\mathrm{Si-C}}$], 1074 (vs) [$\nu_{\mathrm{Si-O}}$]. ^{1}H NMR (CDCl$_3$): δ 0.00 (s, 24 H, SiMe), 0.3–0.6 (m, 8 H, $\mathrm{SiOCH_2CH_2C}H_2\mathrm{SiO}$), 1.4–1.7 (m, 8 H, $\mathrm{SiOCH_2C}H_2\mathrm{CH_2SiO}$), 3.5–3.7 (m, 8 H, $\mathrm{SiOC}H_2\mathrm{CH_2CH_2SiO}$), 4.30 (d, 8 H, J_{PH} = 5.8 Hz, $\mathrm{SiOCH_2P}$), 7.0–7.5 (m, 40 H, Ph). ^{13}C{^{1}H} NMR (CDCl$_3$): δ −2.2 (SiMe), 11.8 ($\mathrm{SiOCH_2CH_2}C\mathrm{H_2SiO}$), 26.0 ($\mathrm{SiOCH_2}C\mathrm{H_2CH_2SiO}$), 66.1 (d, J_{PC} = 5.3 Hz, $\mathrm{SiOCH_2P}$), 68.3 ($\mathrm{SiO}C\mathrm{H_2CH_2CH_2SiO}$), 128.2 (d, J_{PC} = 6.7 Hz, ^{m}C/Ph), 128.5 (^{p}C/Ph), 132.9 (d, J_{PC} = 17.7 Hz, ^{o}C/Ph), 137.2 (d, J_{PC} = 11.5 Hz, ^{i}C/Ph). ^{29}Si{^{1}H} NMR (CDCl$_3$): δ −81.8 (SiO$_4$), 20.6 (SiO). ^{31}P{^{1}H} NMR (CDCl$_3$): δ −12.2. ESI-TOF [*m/z*] (rel. int.): [M + Ag]$^+$ 1461(12), [M + Ag − $\mathrm{Me_2OCH_2PPh_2}$]$^+$ 1188 (100). Anal. Calc. for $\mathrm{C_{72}H_{96}O_8P_4Si_5}$ (1353.81); C, 63.87, H, 7.15. Found: C, 63.94, H, 7.11%.

3.4. *Synthesis of $\mathrm{Si(OCH_2CH_2CH_2SiMe(OCH_2PPh_2)_2)_4}$ (**5**)*

Molecule **5** can be prepared by the procedure described for **4**. In this respect, 2.59 g (12.0 mmol) of $\mathrm{HOCH_2PPh_2}$ (**3**) and 0.67 g (6.0 mmol) of DABCO are dissolved in 70 mL of toluene and 1.07 g (1.5 mmol) of **2** are added in one portion. After appropriate work-up, **5** can be obtained as a pale yellow oil of high viscosity. Yield: 2.85 g (1.3 mmol, 88% based on **2**).

IR (NaCl) ν [cm^{-1}]: 1258 (vs) [$\delta_{\mathrm{Si-C}}$], 1079 (vs) [$\nu_{\mathrm{Si-O}}$]. ^{1}H NMR (CDCl$_3$): δ 0.00 (s, 12 H, SiMe), 0.4–0.6 (m, 8 H, $\mathrm{SiOCH_2CH_2C}H_2\mathrm{SiO}$), 1.4–1.7 (m, 8 H, $\mathrm{SiOCH_2C}H_2\mathrm{CH_2SiO}$), 3.6–3.8 (m, 8 H, $\mathrm{SiOC}H_2\mathrm{CH_2CH_2SiO}$), 4.34 (d, 16 H, J_{PH} = 5.8 Hz, $\mathrm{SiOCH_2P}$), 7.2–7.6 (m, 80 H, Ph). ^{13}C{^{1}H} NMR (CDCl$_3$): δ −4.6 (SiMe), 9.9 ($\mathrm{SiOCH_2CH_2}C\mathrm{H_2SiO}$), 26.0 ($\mathrm{SiOCH_2}C\mathrm{H_2CH_2SiO}$), 63.7 (d, J_{PC} = 7.2 Hz, $\mathrm{SiOCH_2P}$), 66.5 ($\mathrm{SiO}C\mathrm{H_2CH_2CH_2SiO}$), 128.7 (d, J_{PC} = 6.7 Hz, ^{m}C/Ph), 129.2 (^{p}C/Ph), 132.9 (d, J_{PC} = 17.7 Hz, ^{o}C/Ph), 137.0 (d, J_{PC} = 12.4 Hz, ^{i}C/Ph). ^{29}Si{^{1}H} NMR (CDCl$_3$): δ −81.8 (SiO$_4$), −1.0 (SiO$_2$). ^{31}P{^{1}H} NMR (CDCl$_3$): δ −12.2. Anal. Calc. for $\mathrm{C_{120}H_{132}O_{12}P_8Si_5}$ (2154.48); C, 66.89, H, 6.18. Found: C, 66.76, H, 6.25%.

3.5. *Synthesis of $\mathrm{Si(OCH_2CH_2CH_2SiMe_2[OCH_2PPh_2Ni(CO)_3])_4}$ (**7a**)*

0.27 g (0.20 mmol) of **4** are dissolved in 20 mL of diethyl ether and 0.21 g (1.20 mmol) of Ni(CO)$_4$ (**6a**) are added in one portion. After 90 min of stirring at 25 °C all volatile materials are removed in oil-pump vacuum leaving **7a** as an orange, viscous oil. Yield: 0.38 g (0.19 mmol, 99% based on **4**).

IR (CaF$_2$) ν [cm^{-1}]: 2069 (s), 1997 (vs) [$\nu_{\mathrm{C\equiv O}}$], 1256 (vs) [$\delta_{\mathrm{Si-C}}$], 1093 (vs) [$\nu_{\mathrm{Si-O}}$]. ^{1}H NMR (CDCl$_3$): δ 0.04 (s, 24 H, SiMe), 0.4–0.7 (m, 8 H, $\mathrm{SiOCH_2CH_2C}H_2\mathrm{SiO}$), 1.3–1.8 (m, 8 H, $\mathrm{SiOCH_2C}H_2\mathrm{CH_2SiO}$), 3.5–3.9 (m, 8 H, $\mathrm{SiOC}H_2\mathrm{CH_2CH_2SiO}$), 4.4 (bs, 8 H, $\mathrm{SiOCH_2P}$), 7.2–7.8 (m, 40 H, Ph). ^{13}C{^{1}H} NMR (CDCl$_3$): δ −2.8 (SiMe), 11.6 ($\mathrm{SiOCH_2CH_2}C\mathrm{H_2SiO}$), 25.8 ($\mathrm{SiOCH_2}C\mathrm{H_2CH_2SiO}$), 64.4 (d, J_{PC} = 29.4 Hz, $\mathrm{SiOCH_2P}$), 66.4 ($\mathrm{SiO}C\mathrm{H_2CH_2CH_2SiO}$), 128.9 (d, J_{PC} = 9.6 Hz, ^{m}C/Ph), 130.3 (^{p}C/Ph), 133.2 (d, J_{PC} = 14.0 Hz, ^{o}C/Ph), 134.8 (d, J_{PC} = 32.5 Hz, ^{i}C/Ph), 196.6 (CO). ^{29}Si{^{1}H} NMR (CDCl$_3$): δ −81.9 (SiO$_4$), 21.7 (d, J_{SiP} = 7.3 Hz, SiO). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 29.5. Anal. Calc. for $\mathrm{C_{84}H_{96}Ni_4O_{20}P_4Si_5}$ (1353.81); C, 52.42, H, 5.03. Found: C, 52.27, H, 5.25%.

3.6. *Synthesis of $\mathrm{Si(OCH_2CH_2CH_2SiMe_2[OCH_2PPh_2Fe(CO)_4])_4}$ (**7b**)*

0.29 g (0.80 mmol) of Fe$_2$(CO)$_9$ (**6b**) are added in one portion to a solution originated of 0.27 g (0.20 mmol) of **4** in 30 mL of toluene. The orange suspension is stirred for 15 h at 25 °C. Afterwards the almost clear solution is filtrated through a pad of Celite and all volatiles are removed from the eluate in oil-pump vacuum. Compound **7b** is obtained as a orange-red oil of high viscosity in 0.38 g (0.18 mmol, 94% based on **4**) yield.

IR (CaF$_2$) ν [cm^{-1}]: 2049, 1974, 1933 (vs) [$\nu_{\mathrm{C\equiv O}}$]; 1254 (vs) [$\delta_{\mathrm{Si-C}}$]; 1096 (vs) [$\nu_{\mathrm{Si-O}}$]. ^{1}H NMR (CDCl$_3$): δ 0.08 (s, 24 H, SiMe), 0.3–0.8 (m, 8 H, $\mathrm{SiOCH_2CH_2C}H_2\mathrm{\text{-}SiO}$), 1.3–1.8 (m, 8 H, $\mathrm{SiOCH_2C}H_2\mathrm{CH_2SiO}$), 3.5–3.9 (m, 8 H, $\mathrm{SiOC}H_2\mathrm{CH_2CH_2SiO}$), 4.45 (d, 8 H, J_{PH} = 13.5 Hz, $\mathrm{SiOCH_2P}$), 7.3–7.8 (m, 40 H, Ph). ^{13}C{^{1}H} NMR (CDCl$_3$): δ −2.7 (SiMe), 11.5 ($\mathrm{SiOCH_2CH_2}C\mathrm{H_2SiO}$), 25.7 ($\mathrm{SiOCH_2}C\mathrm{H_2CH_2SiO}$), 64.8 (d, J_{PC} = 25.7 Hz, $\mathrm{SiOCH_2P}$), 65.9 ($\mathrm{SiO}C\mathrm{H_2CH_2CH_2SiO}$), 128.4 (d, J_{PC} = 10.1 Hz, ^{m}C/Ph), 129.0 (^{p}C/Ph), 130.8 (d, J_{PC} = 17.7 Hz, ^{o}C/Ph), 132.8 (d, J_{PC} = 11.5 Hz, ^{i}C/Ph), 213.2 (d, $^2J_{\mathrm{PC}}$ = 19.2 Hz, CO). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 77.9. ESI-TOF [*m/z*] (rel. int.): [M$^+$ − 4CO] 1913 (1), [M$^+$ − 4PPh$_2$Fe(CO)$_4$] 1761 (20). Anal. Calc. for $\mathrm{C_{88}H_{96}Fe_4O_{24}P_4Si_5}$ (2025.334); C, 52.18, H, 4.77. Found: C, 51.73, H, 4.98%.

3.7. *Synthesis of $\mathrm{Si(OCH_2CH_2CH_2SiMe_2[OCH_2PPh_2Mo(CO)_5])_4}$ (**7c**)*

0.26 g (1.00 mmol) of Mo(CO)$_6$ are dissolved in 100 mL of tetrahydrofuran and the solution is irritiated with a high pressure mercury lamp for 5 h in a photolysis reactor. A slow continuous stream of N$_2$ is bubbled through the reaction mixture to remove the CO. To the thus obtained Mo(CO)$_5$(Thf) (**6c**) species, 0.24 g (0.18 mmol) of **4**, dissolved in 20 mL of tetrahydrofuran, are added in one portion. After 15 h of stirring at 25 °C the reaction mixture is filtrated through a pad of Celite and all volatiles are removed in oil-pump vacuum. Excess of $\mathrm{Mo(CO)_6}$ is sublimed off in oil-pump vacuum by using a cooling finger. **7c** remains as analytical pure, dark yellow oil of high viscosity. Yield 0.31 g (0.14 mmol, 76% based on **4**).

IR ($\mathrm{CaF_2}$) ν [$\mathrm{cm^{-1}}$] 2072 (w), 1988 (w), 1945 (vs) [$\nu_{\mathrm{C\equiv O}}$]; 1252 (vs) [$\delta_{\mathrm{Si–C}}$]; 1074 (vs) [$\nu_{\mathrm{Si–O}}$]. ^{1}H NMR ($\mathrm{CDCl_3}$): δ −0.08 (s, 24 H, SiMe), 0.5–0.7 (m, 8 H, $\mathrm{SiOCH_2CH_2C}\mathit{H}_2\mathrm{SiO}$), 1.4–1.7 (m, 8 H, $\mathrm{SiOCH_2C}\mathit{H}_2\mathrm{CH_2SiO}$), 3.6–3.9 (m, 8 H, $\mathrm{SiOC}\mathit{H}_2\mathrm{CH_2CH_2SiO}$), 4.25 (d, 8 H, J_{PH} = 60 Hz, $\mathrm{SiOCH_2P}$), 7.4–7.7 (m, 40 H, Ph). ^{13}C{^{1}H} NMR ($\mathrm{CDCl_3}$): δ −2.9 (SiMe), 10.7 ($\mathrm{SiOCH_2CH_2}\mathit{C}\mathrm{H_2SiO}$), 25.7 ($\mathrm{SiOCH_2}\mathit{C}\mathrm{H_2CH_2SiO}$), 65.0 (d, J_{PC} = 33.5 Hz, $\mathrm{SiOCH_2P}$), 65.9 ($\mathrm{SiO}\mathit{C}\mathrm{H_2CH_2CH_2SiO}$), 128.5 (d, J_{PC} = 9.1 Hz, ^{m}C/Ph), 129.0 (^{p}C/Ph), 130.1 (d, J_{PC} = 11.5 Hz, ^{o}C/Ph), 132.3 (d, J_{PC} = 34.5 Hz, ^{i}C/Ph), 205.7 (d, J_{PC} = 9.1 Hz, *cis*-CO), 210.1 (d, J_{PC} = 12.5 Hz, *trans*-CO). ^{31}P{^{1}H} NMR ($\mathrm{CDCl_3}$): δ 35.5. Anal. Calc. for $\mathrm{C_{92}H_{96}Mo_4O_{28}P_4Si_5}$ (2297.74); C, 48.09, H, 4.21. Found: C, 48.27, H, 4.57%.

3.8. *Synthesis of* $\mathit{Si(OCH_2CH_2CH_2SiMe_2[OCH_2PPh_2W(CO)_5])_4}$ *(**7d**)*

0.35 g (1.00 mmol) of $\mathrm{W(CO)_6}$ and 0.24 g (0.18 mmol) of **4** are reacted as described for the preparation of **7c**. Appropriate work-up gives a yellow oil of high viscosity. Yield: 0.38 g (0.14 mmol, 79% based on **4**).

IR ($\mathrm{CaF_2}$) ν [$\mathrm{cm^{-1}}$]: 2071 (w), 1979 (w), 1943 (vs) [$\nu_{\mathrm{C\equiv O}}$]; 1252 (vs) [$\delta_{\mathrm{Si–C}}$]; 1074 (vs) [$\nu_{\mathrm{Si–O}}$]. ^{1}H NMR ($\mathrm{CDCl_3}$): δ −0.02 (s, 24 H, SiMe), 0.4–0.7 (m, 8 H, $\mathrm{SiOCH_2CH_2C}\mathit{H}_2\mathrm{SiO}$), 1.4–1.8 (m, 8 H, $\mathrm{SiOCH_2C}\mathit{H}_2\mathrm{CH_2SiO}$), 3.6–3.9 (m, 8 H, $\mathrm{SiOC}\mathit{H}_2\mathrm{CH_2CH_2SiO}$), 4.25 (d, 8 H, J_{PH} = 67.5 Hz, $\mathrm{SiOCH_2P}$), 7.2–7.7 (m, 40 H, Ph). ^{13}C{^{1}H} NMR ($\mathrm{CDCl_3}$): δ −3.1 (SiMe), 11.7 ($\mathrm{SiOCH_2CH_2}\mathit{C}\mathrm{H_2SiO}$), 25.6 ($\mathrm{SiOCH_2}\mathit{C}\mathrm{H_2CH_2SiO}$), 63.0 (d, J_{PC} = 37.9 Hz, $\mathrm{SiOCH_2P}$), 66.0 ($\mathrm{SiO}\mathit{C}\mathrm{H_2CH_2CH_2SiO}$), 128.5 (d, J_{PC}= 9.6 Hz, ^{m}C/Ph), 129.0 (^{p}C/Ph), 130.3 (d, J_{PC}= 10.6 Hz, ^{o}C/Ph), 133.8 (d, J_{PC} = 40.3 Hz, ^{i}C/Ph), 196.7 (d, J_{PC} = 8.2 Hz, *cis*-CO), 199.1 (d, J_{PC} = 21 Hz, *trans*-CO). ^{31}P{^{1}H} NMR ($\mathrm{CDCl_3}$): δ 17.3. Anal. Calc. for $\mathrm{C_{92}H_{96}O_{28}P_4Si_5W_4}$ (2649.47); C, 41.70, H, 3.65. Found: C, 42.61, H, 3.93%.

3.9. *Synthesis of* $\mathit{Si(OCH_2CH_2CH_2SiMe[OCH_2PPh_2Ni(CO)_3]_2)_4}$ *(**8**)*

Dendrimer **8** can be synthesised by following the procedure described for the synthesis of **7a**. Thus, 0.35 g (0.16 mmol) of **5** are reacted with 0.33 g (1.92 mmol) of $\mathrm{Ni(CO)_4}$ (**6a**). After appropriate work-up the title compound can be isolated as a yellow viscous oil. Yield: 0.51 g (0.15 mmol, 94% based on **5**).

IR ($\mathrm{CaF_2}$) ν [$\mathrm{cm^{-1}}$]: 2069 (s), 1984 (vs) [$\nu_{\mathrm{C\equiv O}}$]; 1256 (vs) [$\delta_{\mathrm{Si–C}}$]; 1093 (vs) [$\nu_{\mathrm{Si–O}}$]. ^{1}H NMR ($\mathrm{CDCl_3}$): δ 0.00 (s, 12 H, SiMe), 0.4–0.7 (m, 8 H, $\mathrm{SiOCH_2CH_2C}\mathit{H}_2\mathrm{SiO}$), 1.3–1.8 (m, 8 H, $\mathrm{SiOCH_2C}\mathit{H}_2\mathrm{CH_2SiO}$), 3.5–3.9 (m, 8 H, $\mathrm{SiOC}\mathit{H}_2\mathrm{CH_2CH_2SiO}$), 4.3 (bs, 16 H, $\mathrm{SiOCH_2P}$), 7.3–7.8 (m, 80 H, Ph). ^{13}C{^{1}H} NMR ($\mathrm{CDCl_3}$): δ −6.1 (SiMe), 8.7 ($\mathrm{SiOCH_2CH_2}\mathit{C}\mathrm{H_2SiO}$), 24.4 ($\mathrm{SiOCH_2}\mathit{C}\mathrm{H_2CH_2SiO}$), 63.4 (d, J_{PC} = 30.7 Hz, $\mathrm{SiOCH_2P}$), 65.4 ($\mathrm{SiO}\mathit{C}\mathrm{H_2CH_2CH_2SiO}$), 128.3 (d, J_{PC}= 9.6 Hz, ^{m}C/Ph), 129.8 (^{p}C/Ph), 132.5 (d, J_{PC} = 12.3 Hz, ^{o}C/Ph), 133.7 (d, J_{PC} = 33.1 Hz, ^{i}C/Ph), 196.0 (CO). ^{31}P{^{1}H} NMR ($\mathrm{CDCl_3}$): δ 30.5. Anal. Calc. for $\mathrm{C_{144}H_{132}Ni_8O_{36}P_8Si_5}$ (3296.19); C, 52.40, H, 4.04. Found: C, 53.33, H, 4.35%.

3.10. *Synthesis of* $\mathit{Me_2Si(OCH_2CH_2CH_2SiMe(OCH_2PPh_2))_2}$ *(**10**)*

Compound **10** can be prepared as described earlier for **4** (vide supra). In this respect 1.04 g (4.80 mmol) of **3**, 0.27 g (2.40 mmol) of DABCO and 0.48 g (1.20 mmol) of **9** are reacted. After appropriate work-up **10** can be isolated as a colourless, air sensitive viscous oil. Yield: 1.15 g (1.02 mmol, 86% based on **9**).

IR (NaCl) ν [$\mathrm{cm^{-1}}$]: 1257 (vs) [$\delta_{\mathrm{Si\ –C}}$], 1068 (vs) [$\nu_{\mathrm{Si–O}}$]. ^{1}H NMR ($\mathrm{CDCl_3}$): δ 0.02, 0.1 (12 H, $\mathit{Me}_2\mathrm{SiOCH_2CH_2CH_2Si}\mathit{Me}$), 0.2–0.4 (m, 4 H, $\mathrm{SiOCH_2CH_2C}\mathit{H}_2\mathrm{SiO}$), 1.7–1.9 (m, 4 H, $\mathrm{SiOCH_2C}\mathit{H}_2\mathrm{CH_2SiO}$), 3.7–3.9 (m, 4 H, $\mathrm{SiOC}\mathit{H}_2\mathrm{CH_2CH_2SiO}$), 4.30 (d, 8 H, J_{PH} = 5.8 Hz, $\mathrm{SiOCH_2P}$), 7.2–7.6 (m, 40 H, Ph). ^{13}C{^{1}H} NMR ($\mathrm{CDCl_3}$): δ −4.7, −2.7 ($\mathit{Me}_2\mathrm{SiOCH_2CH_2CH_2Si}\mathit{Me}$), 9.9 ($\mathrm{SiOCH_2CH_2}\mathit{C}\mathrm{H_2SiO}$), 26.1 ($\mathrm{SiOCH_2}\mathit{C}\mathrm{H_2CH_2SiO}$), 63.6 (d, J_{PC} = 8.1 Hz, $\mathrm{SiOCH_2P}$), 65.2 ($\mathrm{SiO}\mathit{C}\mathrm{H_2CH_2CH_2SiO}$), 128.7 (d, J_{PC} = 6.7 Hz, ^{m}C/Ph), 129.1 (^{p}C/Ph), 133.6 (d, J_{PC} = 18.2 Hz, ^{o}C/Ph), 136.9 (d, J_{PC} = 12.0 Hz, ^{i}C/Ph). ^{29}Si{^{1}H} NMR ($\mathrm{CDCl_3}$): δ −3.7, −2.4 ($\mathrm{Me_2SiO_2}$, $\mathrm{MeSiO_2}$). ^{31}P{^{1}H} NMR ($\mathrm{CDCl_3}$): δ −11.9. Anal. Calc. for $\mathrm{C_{62}H_{72}O_6P_4Si_3}$ (1121.46); C, 66.40, H, 6.47. Found: C, 66.39, H, 6.52%.

3.11. *Synthesis of* $\mathit{Me_2Si(OCH_2CH_2CH_2SiMe[OCH_2PPh_2Ni(CO)_3]_2)_2}$ *(**11**)*

In a similar manner to the preparation of **7a**, 0.20 g (0.18 mmol) of **10** are reacted with 0.18 g (1.08 mmol) of $\mathrm{Ni(CO)_4}$ (**6a**) in diethyl ether. Appropriate work-up gives the metallo dendrimer **11** as a pale yellow viscous oil in 0.29 g (0.15 mmol, 93% based on **10**) yield.

IR (NaCl) ν [$\mathrm{cm^{-1}}$]: 2070 (s), 1997 (vs) [$\nu_{\mathrm{C\equiv O}}$]; 1257 (vs) [$\delta_{\mathrm{Si–C}}$]; 1068 (vs) [$\nu_{\mathrm{Si–O}}$]. ^{1}H NMR ($\mathrm{CDCl_3}$): δ 0.17, 0.29 (m, 12 H, $\mathit{Me}_2\mathrm{SiOCH_2CH_2CH_2Si}\mathit{Me}$), 0.6–0.8 (m, 4 H, $\mathrm{SiOCH_2CH_2C}\mathit{H}_2\mathrm{SiO}$),1.6–1.9 (m, 4 H, $\mathrm{SiOCH_2C}\mathit{H}_2\mathrm{CH_2SiO}$),3.1–3.5 (m, 4 H, $\mathrm{SiOC}\mathit{H}_2\mathrm{CH_2CH_2SiO}$), 4.3 (bs, 8 H, $\mathrm{SiOCH_2P}$), 7.4–7.9 (m, 40 H, Ph). ^{13}C{^{1}H} NMR ($\mathrm{CDCl_3}$): δ −3.7, −3.1 ($\mathit{Me}_2\mathrm{SiOCH_2CH_2CH_2Si}\mathit{Me}$),8.8 ($\mathrm{SiOCH_2CH_2}\mathit{C}\mathrm{H_2SiO}$), 25.6 ($\mathrm{SiOCH_2}\mathit{C}\mathrm{H_2CH_2SiO}$), 62.3 (d, J_{PC} = 28.1 Hz, $\mathrm{SiOCH_2P}$), 65.8 ($\mathrm{SiO}\mathit{C}\mathrm{H_2CH_2CH_2SiO}$), 128.3 (d, J_{PC} = 9.1 Hz, ^{m}C/Ph), 129.8 (^{p}C/Ph), 132.6 (d,

J_{PC} = 12.9 Hz, ^{o}C/Ph), 134.1 (d, J_{PC} = 32.6 Hz, ^{i}C/Ph), 195.5 (CO). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 28.7. Anal. Calc. for $C_{74}H_{72}Ni_4O_{20}P_4Si_3$ (1724.21); C, 42.92, H, 4.21. Found: C, 43.79, H, 4.30%.

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