T_8-OSS-Ethyldiphenylphosphine: A New Functional Oligosilsesquioxane Ligand

Vincent Ruffieux, Günter Schmid,* Pierre Braunstein, and Jacky Rosé

Dedicated to Professor Walter Siebert on the occasion of his 60th birthday

Abstract: Oligosilsesquioxanes (OSS) may be considered as molecular sections of silica. The incompletely condensed (cyclopentyl)$_7$T$_7$(OH)$_3$ (T = SiO$_{3/2}$) has been used to generate a phosphine-functionalized T$_8$-OSS system by reaction with 2-(trichlorosilyl)diphenylphosphinoethane. The resulting model molecule (cyclopentyl)$_7$T$_8$(CH$_2$)$_2$PPh$_2$ (**1**) is well suited to coordinate to transition metal clusters via the phosphorous atom. We selected the tetrahedral bimetallic cluster [HFeCo$_3$(CO)$_{12}$]. Depending on the stoichiometry, one or two phosphine ligands could be added to the cobalt atoms, with substitution of CO molecules. Owing to the cyclopentyl substituents, the resulting complexes [HFeCo$_3$(CO)$_{11}${Ph$_2$P(CH$_2$)$_2$T$_8$(cyclopentyl)$_7$}] (**2**) and [HFeCo$_3$(CO)$_{10}${Ph$_2$P(CH$_2$)$_2$T$_8$(cyclopentyl)$_7$}$_2$] (**3**) are soluble in numerous organic solvents. Therefore, they could be completely characterized by ^{1}H, ^{13}C, ^{29}Si, and ^{31}P NMR spectroscopy.

Keywords
clusters · catalyst models · oligosilsesquioxanes · silica · supported complexes

Introduction

Heterogeneous silica-supported transition metal complexes play a very important role in academic research and in the chemical industry.[1] Oligosilsesquioxanes (OSS) (Figure 1) possess strong structure similarities with silica and may thus serve as valuable molecular models, accessible to various physical methods of investigations.[2–5]

The incomplete T$_7$-OSS systems (Figure 1a) deserve particular attention, since their structure and their surface silanol density are very close to that of the cristobalite form of silica.[4] Furthermore, they can undergo corner-capping reactions with inorganic[6] (e.g. transition metal complexes) or organic Lewis acids, in exactly the same way as silica. It is therefore possible to directly compare the random silica-supported catalysts and their analogous, well-defined OSS-supported ones.

There are two ways of binding a transition metal complex or a cluster to the T$_7$-OSS unit, directly by using the trisilanol part of the molecule[6] or through a ligand covalently attached to the OSS moiety by reaction of the trisilanol moiety with an appropriate group, such as a functionalized silane. The latter method should allow direct comparison with transition metal complexes or clusters anchored to functionalized silica surfaces.[1b, 7] A wide range of silanes containing reactive functional groups, such as amines, phosphines, or thiols, are commercially or synthetically available. It is also possible to match virtually every possible distance between the metal catalyst and the OSS moiety by modifying the length of the carbon chain, as in the case of catalysts supported on functionalized silica surfaces. Only

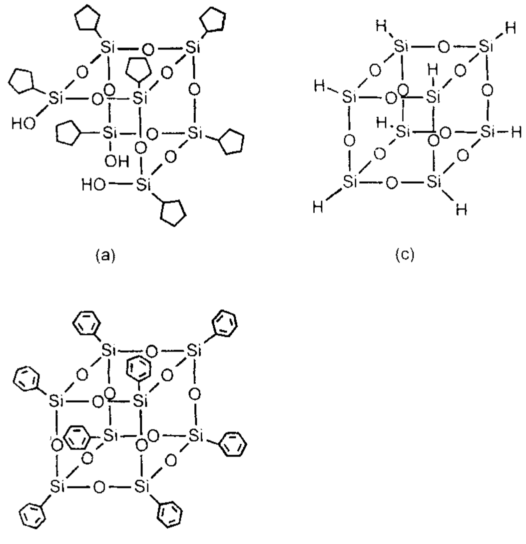

Figure 1. Oligosilsesquioxanes (OSS): a) The incompletely condensed (cyclopentyl)$_7$T$_7$(OH)$_3$. b) The completely condensed (phenyl)$_8$T$_8$. c) The completely condensed H$_8$T$_8$. The notation T refers to the repeating unit RSiO$_{3/2}$.

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monofunctionalized OSS can be obtained in this way. Polyfunctional molecules have been prepared in an important study on aryl and vinyl substitution reactions[9,10] (Figure 1 b) and hydrosilylation[11] (Figure 1 c) of completely condensed T$_8$-OSS.[8]

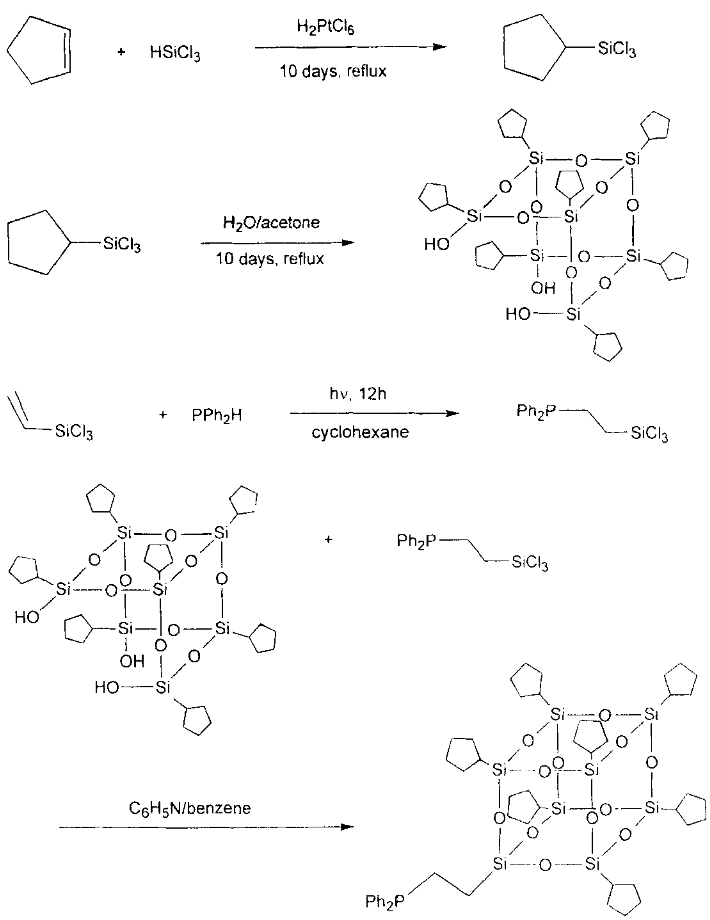
Here we focus our attention on the incompletely condensed (cyclopentyl)$_7$T$_7$(OH)$_3$ system (Figure 1 a) and its reaction with 2-(trichlorosilyl)diphenylphosphinoethane, in order to obtain a well-defined, perfectly characterized prototype for monofunctionalized T$_8$-OSS systems. We then treat this cage compound with the bimetallic cluster [HFeCo$_3$(CO)$_{12}$],[12] whose ability to undergo substitution reactions with phosphine ligands is well established.[13] The resulting new compounds can serve as models for bimetallic clusters or colloids supported on functionalized silica surfaces.

Results and Discussion

The incompletely condensed (cyclopentyl)$_7$T$_7$(OH)$_3$ is the main product of the slow hydrolysis of (cyclopentyl)SiCl$_3$ in water/acetone.[14] In contrast to the preparation of the well-known (cyclohexyl)$_7$T$_7$(OH)$_3$, which takes 3 to 12 months,[2] (cyclopentyl)$_7$T$_7$(OH)$_3$ can be isolated after an acceptable period of 3 to 15 days. (Cyclopentyl)SiCl$_3$ was obtained from the hydrosilylation reaction of cyclopentene and trichlorosilane with H$_2$PtCl$_6$ as the catalyst (Scheme 1).[15] The functionalized silane 2-(trichlorosilyl)diphenylphosphinoethane was synthesized by the photochemical addition of PPh$_2$H to vinyltrichlorosilane.[16] The reaction of 2-(trichlorosilyl)diphenylphosphinoethane and (cyclopentyl)$_7$T$_7$(OH)$_3$ in the presence of pyridine afforded the completely condensed compound **1**.

Compound **1** was fully characterized by IR spectroscopy, ^{1}H, ^{31}P{^{1}H}, ^{13}C{^{1}H}, and ^{29}Si{^{1}H} NMR spectroscopy, and by elemental analysis (see Experimental Section). The typical ^{1}H NMR pattern (phenyl protons omitted) is shown in Figure 2 (left). Figure 2 (right) gives the ^{13}C NMR spectrum of the cyclopentyl carbon atoms bound to Si atoms, whose 1:3:3 ratio is clearly accounted for by the C_{3v} symmetry of the molecule.

Abstract in German: *Oligosilsesquioxane (OSS) können als molekulare Ausschnitte aus dem Siliciumdioxidgitter betrachtet werden. Aus dem unvollständig kondensierten (cyclopentyl)$_7$-T$_7$(OH)$_3$ (T = SiO$_{3/2}$) und 2-(Trichlorsilyl)diphenylphosphinoethan wurde ein Phosphin-funktionalisiertes T$_8$-OSS hergestellt. Die resultierende Modellverbindung (cyclopentyl)$_7$T$_8$-(CH$_2$)$_2$PPh$_2$ **1** ist gut geeignet, über das Phosphoratom Übergangsmetallcluster zu koordinieren. Wir wählten hierzu den tetraedischen Dimetallcluster [HFeCo$_3$(CO)$_{12}$]. In Abhängigkeit von der Stöchiometrie wurden ein oder zwei Phosphinliganden unter Substitution von CO-Molekülen an die Cobaltatome koordiniert. Die resultierenden Komplexe [HFeCo$_3$-(CO)$_{11}${Ph$_2$P(CH$_2$)$_2$T$_8$(cyclopentyl)$_7$}] **2** bzw. [HFeCo$_3$-(CO)$_{10}${Ph$_2$P(CH$_2$)$_2$T$_8$(cyclopentyl)$_7$}$_2$] **3** sind dank der Cyclopentylsubstituenten in organischen Lösungsmitteln löslich und konnten somit ^{1}H-, ^{13}C-, ^{29}Si- und ^{31}P-NMR-spektroskopisch vollständig charakterisiert werden.*



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Scheme 1. Reaction scheme for the formation of (cyclopentyl)$_7$T$_8$(CH$_2$)$_2$PPh$_2$ (**1**).

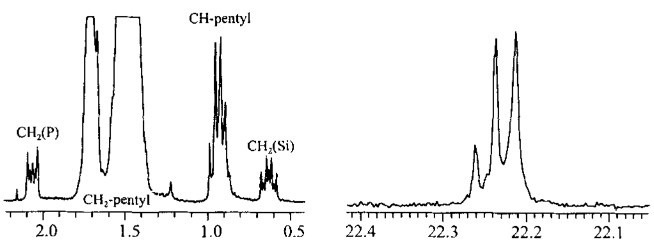


Figure 2. Left: The alkyl signals in the ^{1}H NMR spectrum of (cyclopentyl)$_7$-T$_7$(OH)$_3$ (**1**); the CH_2–Si and CH_2–P resonances appear at $\delta = 0.66$ and 2.07, respectively. Right: ^{13}C NMR spectrum of the cyclopentyl C atoms bound to Si, showing a 1:3:3 pattern of the three resonances at $\delta = 22.25$, 22.23, and 22.20.

Compound **1** dissolves readily in apolar or weakly polar solvents, such as *n*-hexane, cyclohexane, benzene, toluene, chloroform, or dichloromethane, but is insoluble in ethanol, acetone, or acetonitrile. It is thermally stable up to 100 °C. The phosphine group undergoes slow oxidation in the presence of air and water. Despite the similarity of the siloxane structure with that of silica, **1** can be purified by chromatography on silica gel. This is probably possible due to the presence of the apolar cyclopentyl groups.

The CO substitution reaction of **1** with the bimetallic cluster [HFeCo$_3$(CO)$_{12}$] (Figure 3) in equimolar amounts at room temperature in dichloromethane afforded the violet monosubstituted compound **2** (Scheme 2), which was characterized by IR

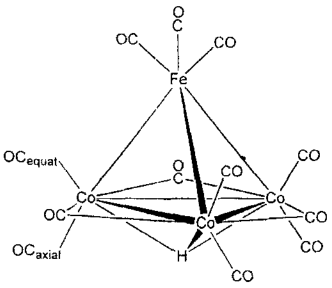
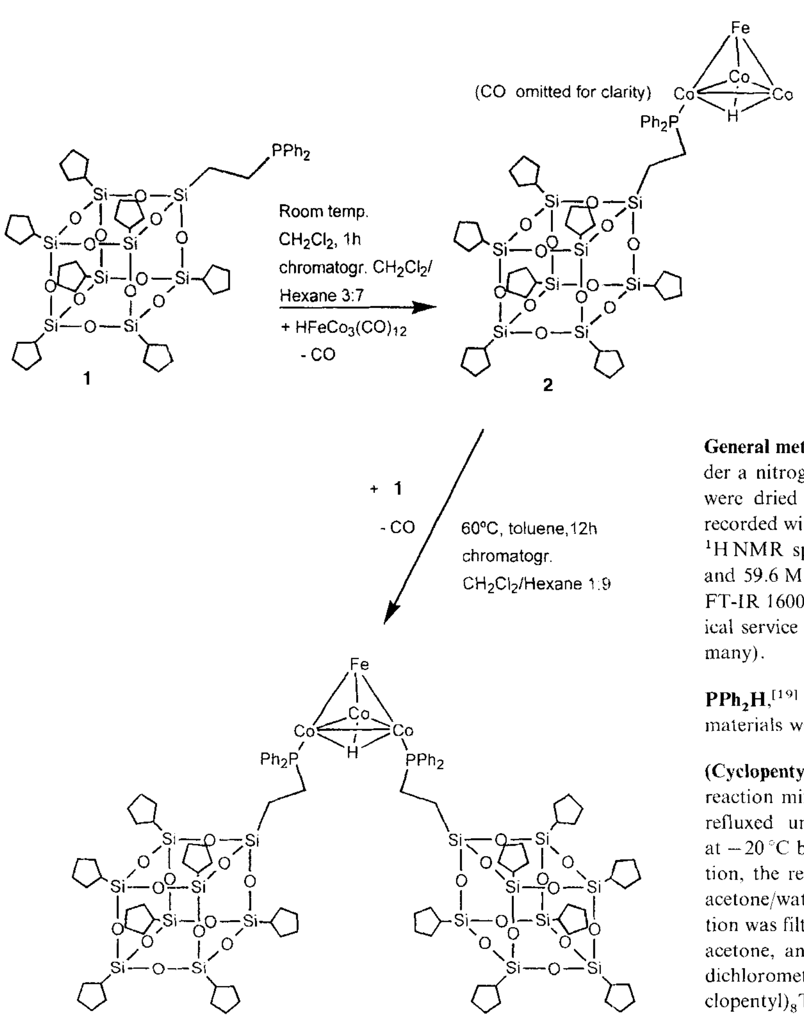


Figure 3. Structure of the bimetallic tetrahedral cluster $[HFeCo_3(CO)_{12}]$.

spectroscopy, ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectroscopy, and by elemental analysis. Spectroscopic data indicated that a cobalt-bound axial CO ligand had been selectively substituted, as observed with other monodentate phosphine ligands.[17] This is accounted for by the high *trans*-labilizing influence of the Fe–Co bond.[18]

After purification by column chromatography, **2** was treated with a further equivalent of **1** in toluene at 60 °C for 12 h to give the disubstituted compound **3** (Scheme 2). By comparison with data for $[HFeCo_3(CO)_{10}(PR_3)_2]$ clusters, it is clear that the second phosphine ligand is also bound to cobalt, in an axial position.

The complete characterization of **2** and **3** is given in the Experimental Section. The ^1H NMR signals corresponding to the CH_2–P and CH_2–Si protons in **3** exhibit a remarkable "mirror" pattern, which arises from the fact that these protons do not lie in the mirror plane of the C_s molecule. The spin system must therefore be described as AA'BB', with four magnetically inequivalent protons. The ^{13}C NMR spectrum exhibits the same type of pattern for the phenyl carbons. In contrast, no such pattern is observed for the carbons of the OSS moiety. This is probably due to the high flexibility of the ethyl group, which allows the ligand to achieve a conformation that minimizes steric hindrance.



Scheme 2. Reaction of **1** with $[HFeCo_3(CO)_{12}]$ yielding monosubstituted **2** and disubstituted **3**.

Conclusion

The new T_8-OSS-ethyldiphenylphosphine complexes described here seem to be valuable prototype models for transition metal complexes or clusters anchored on silica surfaces. Despite their apparently complicated structure, complete characterization has been achieved in a relatively straightforward manner. Since the OSS moiety is quite sensitive to the reaction conditions, it is necessary to check the integrity of the OSS structure after each reaction. For this purpose, ^{13}C and ^{29}Si NMR spectroscopy are most suitable methods, but the latter is more time-consuming.

The ability of T_8-OSS-ethyldiphenylphosphine to readily complex metal centers with low oxidation state in a selective way was clearly demonstrated in this work. The (cyclopentyl)$_7T_7(OH)_3$ is a very interesting precursor for the design of functional T_8-OSS systems for the following reasons:

1) It can be prepared in good yields on an acceptable timescale.
2) It is readily soluble in most common organic solvents, except those of high polarity (e.g., water, alcohols, acetone, and acetonitrile).
3) It is thermally stable up to 100 °C and not sensitive to air or moisture.

Experimental Section

General methods: Air-sensitive reagents and products were manipulated under a nitrogen atmosphere using standard Schlenk techniques. All solvents were dried and purified using standard procedures. NMR spectra were recorded with a Bruker DPX or DMX instrument operating at 300 MHz for ^1H NMR spectroscopy (75.5 MHz for $^{13}C\{^1H\}$, 121.5 MHz for $^{31}P\{^1H\}$, and 59.6 MHz for $^{29}Si\{^1H\}$). IR spectra were recorded on a Perkin-Elmer FT-IR 1600 spectrometer. Elemental analyses were carried out by the analytical service of the Chemistry Department of the University of Essen (Germany).

PPh_2H,[19] (cyclopentyl)$SiCl_3$,[15] and $[HFeCo_3(CO)_{12}]$:[12] These starting materials were synthesized by well-described literature procedures.

(Cyclopentyl)$_7T_7(OH)_3$: According to a modified literature procedure,[14] the reaction mixture, consisting of (cyclopentyl)$SiCl_3$, acetone, and water, was refluxed under nitrogen for two weeks with a condensor maintained at −20 °C by a circulating bath of methanol. In order to simplify the filtration, the resulting solid was allowed to settle, and the clear brownish-red acetone/water solution was transferred to another flask. The remaining solution was filtered. The solid cake was triturated and washed many times with acetone, and finally dried in vacuo. The crude product was dissolved in dichloromethane, and the solution was filtered to remove the insoluble (cyclopentyl)$_8T_8$. The dichloromethane solution was concentrated to ca. 50 mL and layered with ca. 200 mL of acetonitrile, whereupon (cyclopentyl)$_7$-$T_7(OH)_3$ precipitated. After filtration and washing with small amounts of acetonitrile, the pure (cyclopentyl)$_7T_7(OH)_3$ was dried overnight under vacuum. Yield: 81%. The purity of the product was monitored by comparison of the NMR data and elemental analysis (C 47.98 (calcd 48.02), H 7.68 (calcd 7.60)).

$Ph_2P(CH_2)_2SiCl_3$ was prepared by a modification of the procedure described by Holmes-Smith:[16] Diphenylphosphine (10.7 g, 10 mL, 57.5 mmol) and vinyltrichlorosilane (14.7 g, 11.6 mL, 90.9 mmol) were dissolved in dry cyclohexane (100 mL, UV/Vis grad). The solution was transferred through a canula into a 100 mL quartz photochemical reactor and irradiated with stirring for 12 h at 20 °C with a medium-pressure Hg lamp. The solution was then transferred under nitrogen into a 250 mL round-bottom flask. Volatiles were removed under vacuum. The crude product was worked up by distillation (173–174 °C/0.1 mmHg) to yield 17.1 g (85%) of pure product.

(Cyclopentyl)$_7$T$_8$(CH$_2$)$_2$PPh$_2$ (1): $Ph_2P(CH_2)_2SiCl_3$ (4.0 g, 11.4 mmol) was placed in a 500 mL Schlenk round-bottom flask filled with nitrogen. Benzene (250 mL) was added, followed by (cyclopentyl)$_7$T$_7$(OH)$_3$ (10.0 g, 11.4 mmol) and pyridine (2.9 mL, 3.48×10^{-2} mol), under vigorous stirring. The solution was stirred for 12 h at room temperature, then filtered through a 10 cm-pad of Celite and a 5 cm-pad of silica gel, in order to remove pyridine·HCl. The filtration pad was washed with copious amounts of dry benzene. The solution was concentrated to ca. 50 mL and carefully layered with ca. 200 mL acetonitrile, whereupon (cyclopentyl)$_7$T$_8$(CH$_2$)$_2$PPh$_2$ precipitated. The filtration cake was washed with acetonitrile and dried in vacuum. Yield: 11.3 g (89%). IR: $\tilde{\nu}$ = 3071 (w), 3053 (w; νPh), 2950 (s), 2865 (s; νAlk), 1481 (w; νPPh), 1434 (w; νPCH$_2$), 1108 (vs; ν_{asym}Si-O-Si), 739 (w), 696 (w; νSiCH$_2$), 506 (m; ν_{sym}Si-O-Si). ^{1}H NMR (CDCL$_3$, ext. ref. TMS): δ = 0.67 (m, 2H, CH_2–Si), 0.90–1.02 (complex m, 7H, CH pentyl), 1.47–1.73 (complex m, 56H, CH_2 pentyl), 2.07 (m, 2H, CH_2–P), 7.30–7.39 (m, 10H, Ph). ^{13}C{^{1}H} NMR (CDCl$_3$, ext. ref. TMS): δ = 8.05 (d, CH$_2$–Si, 11.8 Hz), 20.82 (d, CH$_2$–P, 13.3 Hz), 22.20, 22.23, 22.25 (s, CH pentyl, 3:3:1), 26.95, 26.99, 27.00, 27.28, 27.29, 27.35 (s, CH$_2$ pentyl, 3:3:1:3:1:3), 128.36 (d, C^3 phenyl, $^3J_{P-C-C-C}$ = 6.4 Hz), 128.44 (s, C^4 phenyl), 132.68 (d, C^2 phenyl, $^2J_{P-C-C}$ = 18.0 Hz), 138.67 (d, J_{P-C} = 14.0 Hz). ^{29}Si{^{1}H} NMR (C$_6$D$_6$, ext. ref. TMS): δ = −65.86, −65.91, −65.94, −66.59 (3:1:3:1). ^{31}P{^{1}H} NMR (CDCl$_3$, ext. ref. H$_3$PO$_4$): δ = −8.5. $C_{49}H_{77}O_{12}PSi_8$ (1113.80): calcd. C 52.84, H 6.97; found C 52.57, H 6.88.

[HFeCo$_3$(CO)$_{11}${Ph$_2$P(CH$_2$)$_2$T$_8$(cyclopentyl)$_7$}] (2): [HFeCo$_3$(CO)$_{12}$] (0.100 g, 1.75×10^{-4} mol) was dissolved in dry dichloromethane (50 mL) under nitrogen. (Cyclopentyl)$_7$T$_8$(CH$_2$)$_2$PPh$_2$ (195 mg, 1.75×10^{-4} mol) was added. The solution was stirred until CO evolution had ceased (ca. 15 min). The solvent was completely evaporated. The violet crude product was purified by chromatography on silica gel with dichloromethane/hexane 7:3. Yield: 0.238 g (82%). IR$_{\nu CO}$ (CH$_2$Cl$_2$): $\tilde{\nu}$ = 2077 (m), 2034s, 2007 (m), 1966 (w; terminal CO), 1862 (m), 1847 (m; bridging CO). ^{1}H NMR: δ = −21.26 (μ_3-H), 0.49 (m, 2H, CH_2–Si), 0.82–1.02 (m, 7H, CH pentyl), 1.47–1.73 (m, 56H, CH_2 pentyl), 2.24 (m, 2H, CH_2–P), 7.28–7.48 (m, 10H, Ph). ^{13}C{^{1}H} NMR: δ = 5.80 (CH$_2$–Si, $^2J_{C-P}$ = 5.3 Hz), 22.14, 22.15, 22.26 (CH pentyl, 3:3:1), 24.55 (CH$_2$–P, J_{C-P} = 22.2 Hz), 26.92, 26.97, 27.00, 27.25, 27.29, 27.33 (CH$_2$ pentyl, 3:3:1:3:1:3), 129.04 (d, Ph, $C^{3,3'}$, $^3J_{C-P}$ = 9.8 Hz), 130.76 (d, Ph, $C^{4,4'}$, $^4J_{C-P}$ = 2.3 Hz), 131.44 (d, Ph, $C^{1,1'}$, J_{C-P} = 40.0 Hz), 131.88 (d, Ph, $C^{2,2'}$, $^2J_{C-P}$ = 9.8 Hz). ^{31}P{^{1}H} NMR: 35.1 ($\Delta\nu_{1/2}$ = 1700 Hz). $C_{60}H_{78}O_{23}PSi_8FeCo_3$ (1655.57) calcd. C 43.53, H 4.75; found C 43.60, H. 4.85.

[HFeCo$_3$(CO)$_{10}${Ph$_2$P(CH$_2$)$_2$T$_8$(cyclopentyl)$_7$}$_2$] (3): Compound **2** (100 mg, 6.04×10^{-5} mol) was dissolved in dry toluene (50 mL) under nitrogen, and **1** (67 mg, 6.04×10^{-5} mol) was added. The solution was stirred for 12 h at 60 °C. After evaporation of the solvent, the green crude product was purified by chromatography on silica gel with dichloromethane/hexane 1:9. Yield 0.101 g (61%). IR$_{\nu CO}$ (CH$_2$Cl$_2$): $\tilde{\nu}$ = 2051 (m), 2020 (s), 1987 (s), 1953 (w; terminal CO), 1837 (m), 1821 (w; bridging CO). ^{1}H NMR (Figure 4, left): δ = −21.42 (μ_3-H), 0.37, 0.52 (m, 4H, H^{2A}, H^{2B}, $H^{2A'}$, $H^{2B'}$), 0.82–1.03 (m, 14H, CH pentyl), 1.47–1.73 (m, 112H, CH_2 pentyl), 2.36, 2.60 (m, 4H, H^{1A}, H^{1B}, $H^{1A'}$, $H^{1B'}$), 6.65–7.43 (m, 20H, Ph^A, Ph^B, Ph$^{A'}$, Ph$^{B'}$). ^{13}C{^{1}H} NMR (Figure 4, right): δ = 5.88 (CH$_2$–Si, $^2J_{C-P}$ = 5.4 Hz), 22.16, 22.20, 22.26 (CH pentyl, 3:3:1), 24.40 (CH$_2$–P, J_{C-P} = 24.3 Hz), 26.94, 27.00, 27.28, 27.34 (CH$_2$ pentyl, 3:4:4:3), 128.48 (t, Ph, $C^{3A,3A',3B,3B'}$, $^3J_{C-P}$ = 8.8 Hz), 129.77, 129.95 (s, Ph, C^{4A}, C^{4B}), 131.84, 133.03 (d, Ph, C^{1A}, C^{1B}, J_{C-P} = 36.4 Hz, J_{C-P} = 34.9 Hz), 132.07, 132.34 (d, $C^{2A,2A'}$, $C^{2B,2B'}$, $^2J_{C-P}$ = 9.2 Hz, $^2J_{C-P}$ = 10.1 Hz), ^{31}P{^{1}H} NMR: δ = 33.3 ($\Delta\nu_{1/2}$ = 730 Hz). $C_{108}H_{155}O_{34}P_2Si_{16}FeCo_3$ (2741.35) calcd. C 47.32, H 5.70; found C 47.19, H 5.80.

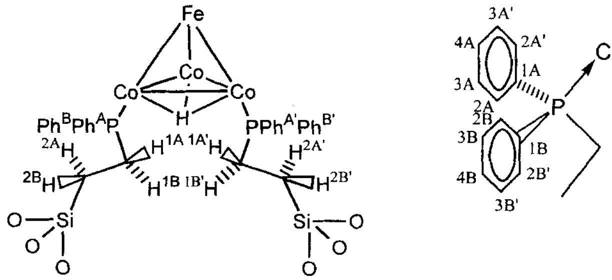


Figure 4.

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