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Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Transition metal compounds containing alkynylsilyl groups – complexes with a metal-silicon bond

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ARTICLE INFO

Article history: Received 8 December 2011 Accepted 25 January 2012

Keywords: Iron Cobalt Rhodium Alkynylsilyl complexes Nucleophilic substitution Oxidative addition

ABSTRACT

Two transition metal complexes containing alkynylsilyl groups and a metal-silicon bond (CpFe(CO)₂-SiMe₂C=CPh (1), Co(CO)₄SiMe₂C=CPh (2)) have been synthesized by nucleophilic substitution (salt elimination) using both strongly and weakly nucleophilic metallates. No disturbing interactions of the metallate with the C=C bond were observed. The synthesis of a third complex ((Ph₃P)₂RhClHSi-Me₂C=CPh (3)) by oxidative addition was hampered by transition metal catalyzed reactions of the Si–H with the C=C triple bond. The reactivity of 1 toward complexation and hydrosilylation of the C=C triple bond was studied, leading to the trinuclear dicobaltatetrahedrane compound 1 * Co₂(CO)₆ (4) and the vinylsilyl complex CpFe(CO)₂SiMe₂CH=CPh(SiEt₃) (5), respectively. The complexes were characterized by NMR (1–5), IR (1–5), and UV/VIS spectroscopy (1, 3, 4) as well as X-ray crystallography (1–4).

1. Introduction

Since their first synthesis over 50 years ago transition metal silyl complexes have acquired considerable importance both in bonding theory and catalysis [1]. However, subsequent chemistry is often hampered by the sensitivity of the metal-silicon bond. In this regard, silyl complexes bearing alkenyl or alkynyl groups at the silicon are of particular interest, as their unsaturated hydrocarbon residues may effect an enhanced reactivity in, e.g., complexation, hydrosilylation, or carbon–carbon bond coupling reactions under mild conditions, thus preserving the metal-silicon bond. While there is a lot of research on alkenylsilyl complexes reported in the literature [2] (including the syntheses of vinylsilylene [2c–e] and η^3 -silaallyl complexes [2f,g]), we were surprised to find that the work on alkynylsilyl complexes is rather limited [3–13], though culminating in the η^3 -silapropargyl complexes of Sakaba et al. (Mo, W) [6] and Rosenthal et al. (Ti, Zr) [7a–d].

Most of the known alkynylsilyl complexes were synthesized by oxidative addition of Si-H bonds to transition metal compounds (Pt [3], Co [4a-h], Rh [5], W [6a,e], Mo [6c], Ti [7a,b,d], Zr [7b,c]). In the particular case of reactions with dicobaltoctacarbonyl $Co_2(CO)_8$ the alkynyl group reacts much faster with $Co_2(CO)_8$ than the Si-H bond, thus furnishing at first hydrosilvl substituted and subsequently trinuclear cobalt-silvl substituted alkyne cobalt complexes [4a-h]. Hence, cobalt alkynylsilyl compounds require an alternative synthetic route. Nucleophilic substitution, the second preeminent synthetic method for silyl complexes, has been reported so far only for a dinuclear iron complex (normal salt elimination: anionic metallate + silyl halide) [8] and a zirconium oligosilyl compound (inverse salt elimination: metal halide + silyl anion) [9]. In both syntheses strong nucleophiles (Fp^{-1} or oligosilyl anion, resp.) were employed. Further preparation methods toward alkynylsilyl complexes are: silicon-carbon bond formation in a chromium silyl complex [10], oxidative Si-H addition of diphenylsilane Ph₂SiH₂ to an Ir−C≡C complex and rearrangement [11], oxidative addition of a Si–C bond to a platinum complex [12], and rearrangement of an oligosilylalkyne cobalt complex [13].

To our knowledge no comparative assessment of nucleophilic substitution with strong and weak nucleophiles and oxidative addition for the synthesis of alkynylsilyl complexes has been made. Herein we present such a comparison as well as three new transition metal alkynylsilyl complexes, among them the first alkynylsilyl cobalt compound with a non-complexed $C \equiv C$ triple bond [14].





Abbreviations: AIM, atoms in molecules; as, asymmetric; br, broad; comb, combination; Cp, cyclopentadienyl C₅H₅; dec., decomposition; d, doublet; δ , bending vibration (IR), chemical shift (NMR); Et, ethyl C₂H₅; γ , wagging vibration; Fp, CpFe(CO)₂; m, medium (IR), multiplet (NMR); Me, methyl CH₃; ν , stretching vibration; ν^{\sim} , wave number; Ph, phenyl C₆H₅; q, quartet; "qn", apparent quintet; ρ , rocking vibration; s, singlet (NMR), strong (IR), symmetric (IR); sh, shoulder; t, triplet; "t", apparent triplet; TMS, tetramethylsilane; vbr, very broad; vs, very strong; vw, very weak; w, weak.

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Scheme 1. Synthesis of compounds 1–3.

2. Results and discussion

2.1. Nucleophilic substitution

Regarding nucleophilic substitution in silyl halides (normal salt elimination), dicarbonyl(η^5 -cyclopentadienyl)ferrate(0) Fp⁻ and tetracarbonylcobaltate(-I) Co(CO)₄ were reported as the strongest and the weakest known nucleophilic metallate, respectively [15]. Thus, these two metallates were chosen for investigating the salt elimination reaction with an alkynylhalosilane.¹

For the synthesis of dicarbonyl(η^5 -cyclopentadienyl)[dimethyl(phenylethynyl)silyl]iron(II) $FpSiMe_2C \equiv CPh$ (1) the corresponding chlorosilane chlorodimethyl(phenylethynyl)silane PhC=CMe₂SiCl was reacted with sodium dicarbonyl(η^{5} -cyclopentadienyl)ferrate NaFp in different solvents (THF/hexane, THF/ pentane, cyclohexane) (Scheme 1). In all cases mixtures of 70-85% 1 and 15–30% of the by-product 1,1,3,3-tetramethyl-1,3bis(phenylethynyl)-disiloxane (PhC=CMe₂Si)₂O were obtained as judged by ²⁹Si NMR, with THF/pentane giving the best results. The oxygen source for the disiloxane is a CO ligand [16a], further byproducts are tetracarbonyl-di(η^5 -cyclopentadienyl)-diiron Fp₂ and an unidentified second compound. The use of solid NaFp in cyclohexane [16] had no advantages. In the work-up of the reaction mixture a chromatography on silica gel proved to be essential for the isolation of solid crystalline 1 although the disiloxane could not be removed completely this way. Nevertheless, subsequent recrystallization gave 1 as a yellow-brown low-melting solid in 53% vield. The solid compound is quite stable showing no signs of decomposition even after one week exposure to air. The NMR, IR, and X-ray diffraction data were consistent with the structure of 1. The ${}^{1}J_{SiFe}$ coupling constant (15 Hz) is in accord with a direct Fe–Si bond [17], and the Fe-Si bond length (231.0 pm) is equal to the average value of all known Fe–Si bond lengths (Fig. 1 and Table 1).²

In contrast to the preparation of **1** the synthesis of tetracarbonyl [dimethyl(phenylethynyl)silyl]cobalt(I) $Co(CO)_4SiMe_2C\equiv CPh(2)$ by reaction of PhC=CMe_2SiCl with sodium tetracarbonylcobaltate NaCo(CO)₄ (Scheme 1) was very sensitive to the reaction conditions. Upon using a solution of NaCo(CO)₄ in THF, the IR and NMR spectra of the reaction mixture suggested the disiloxane (PhC=CMe_2Si)₂O and alkyne cobalt complexes PhC=CMe_2SiX * Co₂(CO)₆ [X = Cl,O_{1/2}] to be the main products. These were most likely formed by THF-catalyzed decomposition of **2** which is a known limiting factor in preparing and handling silyl complexes

[1a,2a,16]. In contrast, a suspension of solid NaCo(CO)₄ in hexane afforded **2** as the main product (as judged by ²⁹Si NMR). Byproducts (including (PhC=CMe₂Si)₂O) were formed only in minor amounts. Work-up gave **2** as colourless low-melting crystals in 82% yield. The complex is very sensitive to oxidation and hydrolysis. The resulting dark brown oil can be removed by recrystallization.

The ¹H, ¹³C, and ²⁹Si NMR data were consistent with the structure of **2**. The ⁵⁹Co NMR spectrum showed a broad signal at -2975 ppm which is comparable to other tetracarbonylcobalt silyl complexes [18]. The IR spectrum featured four bands in the CO region, thus indicating a trigonal-bipyramidal coordination of the cobalt atom with the silyl ligand in axial position and *C*_S symmetry of the molecule [19].

This conclusion was corroborated by the X-ray crystal structure determination of **2** (Fig. 2 and Table 1): apart from the orientation of the phenyl ring the molecule has approximately C_S symmetry. The cobalt is trigonal-bipyramidally coordinated with the silyl ligand in axial position. The three equatorial carbonyl ligands are not coplanar with the cobalt atom but bent toward the silyl ligand by about 10°. This feature has previously been attributed to packing effects [19]. However, ab-initio calculations indicate that it is indeed an electronic effect [20]. Owing to the strong trans-effect of the silyl ligands (178.5–179.2 pm). In accordance with the observed high reactivity of **2** the Co–Si bond (236.8 pm) is distinctly longer than the average of all known Co–Si bond lengths (230 pm) but is comparable to other tetracarbonylcobalt silyl complexes (234–238 pm).²

Efforts to react PhC=CMe₂SiCl with sodium tetracarbonylferrate Na₂Fe(CO)₄ did not result in anionic silyl or neutral bis(silyl)



Fig. 1. Molecular structure of **1** (hydrogens omitted). Selected bond lengths [pm] and angles [°]: Fe1–Si1 231.01(7), Fe1–Cp1 172.27(11), Fe1–C6 173.9(3), Fe1–C7 175.4(3), Si1–C8 187.6(2), Si1–C9 188.1(2), Si1–C10 184.8(3), C10–C11 120.7(3), C6–Fe1–C7 95.42(12), C6–Fe1–Si1 84.88(7), C7–Fe1–Si1 84.97(8), Fe1–Si1–C8 112.14(8), Fe1–Si1–C9 114.01(8), Fe1–Si1–C10 111.38(8), C8–Si1–C9 107.57(11), C8–Si1–C10 105.93(11), C9–Si1–C10 105.26(10), Si1–C10–C11 176.7(2), C6–Fe1–Si1–C8 162.05(12), C7–Fe1–Si1–C10 107.534(11).

¹ The associated inverse reaction (inverse salt elimination) is a less common entry to silyl complexes as there is no generally applicable synthetic procedure for the required silyl anions (which are strong nucleophiles). Nevertheless, this route has been used for the synthesis of a zirconium alkynylsilyl complex [9].

² All average values are search results from the Cambridge Structural Database (CSD) of the CCDC.

| Table 1 | | |
|-----------------------|-------------------|-----|
| Crystal structure dat | a for complexes 1 | 1–4 |

| Compound | 1 | 2 | 3 | 4 |
|---|---|---|----------------------------|---|
| Mol. formula | C ₁₇ H ₁₆ FeO ₂ Si | C ₁₄ H ₁₁ CoO ₄ Si | C46H42ClP2RhSi | C ₂₃ H ₁₆ Co ₂ FeO ₈ Si |
| M (g/mol) | 336.24 | 330.25 | 823.19 | 622.16 |
| T (K) | 93(2) | 123(2) | 93(2) | 93(2) |
| λ (pm) | 71.073 | 71.073 | 71.073 | 71.073 |
| Crystal system | orthorhombic | monoclinic | triclinic | triclinic |
| Space group | Pbca | $P2_1/c$ | P1 | P1 |
| a (pm) | 1015.89(6) | 642.89(3) | 1006.77(10) | 844.09(7) |
| <i>b</i> (pm) | 1708.65(11) | 750.96(4) | 1252.57(12) | 1157.68(9) |
| <i>c</i> (pm) | 1881.31(11) | 3068.76(16) | 1625.50(17) | 2555.77(19) |
| α (°) | 90 | 90 | 76.107(6) | 90.243(4) |
| β(°) | 90 | 92.125(2) | 74.553(5) | 94.184(4) |
| γ (°) | 90 | 90 | 87.354(5) | 93.597(4) |
| $V(10^6 \text{ pm}^3 = \text{Å}^3)$ | 3265.6(3) | 1480.53(13) | 1917.6(3) | 2485.8(3) |
| Ζ | 8 | 4 | 2 | 4 |
| ρ_{calc} (g/cm ³) | 1.368 | 1.482 | 1.426 | 1.662 |
| $\mu ({\rm mm}^{-1})$ | 0.997 | 1.248 | 0.663 | 1.988 |
| F(000) | 1392 | 672 | 848 | 1248 |
| Crystal size (mm) | $0.28 \times 0.25 \times 0.05$ | $0.36 \times 0.25 \times 0.14$ | $0.18\times0.15\times0.05$ | $0.35 \times 0.11 \times 0.02$ |
| θ range (°) | 2.17-25.20 | 2.66-27.50 | 2.10-25.00 | 0.80-25.00 |
| hkl ranges | $-11 \le h \le 11$ | $-8 \le h \le 8$ | $-11 \le h \le 11$ | $-10 \le h \le 9$ |
| | $-20 \le k \le 20$ | $0 \le k \le 9$ | $-14 \le k \le 14$ | $-13 \le k \le 13$ |
| | $-22 \le l \le 22$ | $0 \le l \le 39$ | $-19 \leq l \leq 16$ | $0 \le l \le 30$ |
| Refl. coll./unique | 18600/2928 | 62741/3371 | 20946/6746 | 16139/8674 |
| R _{int} | 0.0560 | 0.0456 | 0.0288 | 0.0355 |
| Completeness (%) | 99.4 | 98.9 | 99.9 | 99.0 |
| Absorption corr. | semi-emp. from equiv. | semi-emp. from equiv. | semi-emp. from equiv. | semi-emp. from equiv. |
| Max./min. transm. | 0.9518/0.7901 | 0.8447/0.6784 | 0.9676/0.8414 | 0.9708/0.5189 |
| Refinem. method | full-matrix least | full-matrix least | full-matrix least | full-matrix least |
| | squares on F ² | squares on F ² | squares on F ² | squares on F ² |
| Data/restr./param. | 2928/0/190 | 3371/0/184 | 6746/0/463 | 8674/0/632 |
| $GoF(F^2)$ | 1.042 | 1.230 | 1.049 | 1.085 |
| $R_1/wR_2 \ [I \ge 2\sigma(I)]$ | 0.0306/0.0613 | 0.0542/0.1283 | 0.0262/0.0648 | 0.0481/0.1348 |
| R_1/wR_2 (all data) | 0.0524/0.0660 | 0.0564/0.1290 | 0.0331/0.0670 | 0.0798/0.1444 |
| $\rho_{\rm res}$ (max./min.) | 0.390/-0.324 | 0.888/-0.896 | 0.423/-0.405 | 0.676/-0.575 |
| $(10^{-6} e/pm^3 = e/Å^3)$ | | | | |

complexes. Instead, in hydrocarbons no reaction occured while in diethyl ether or THF the disiloxane (PhC=CMe₂Si)₂O was formed.

2.2. Oxidative addition

Oxidative addition of alkynylhydrosilanes to coordinatively unsaturated compounds has been used for the synthesis of several alkynylsilyl complexes [3,4a-h,5,6a,c,e,7a-d] although interferences by metal-catalyzed side reactions between the Si–H bond and the C=C triple bond, e.g. hydrosilylation, should have to be expected, especially in the case of platinum metal compounds.



Fig. 2. Molecular structure of **2** (hydrogens omitted). Selected bond lengths [pm] and angles [$^{\circ}$]: Co1–Si1 236.81(12), Co1–C1 183.8(5), Co1–C2 178.5(4), Co1–C3 179.2(4), Co1–C4 179.1(4), Si1–C5 187.2(4), Si1–C6 186.1(4), Si1–C7 183.1(4), C7–C8 121.2(6), C1–Co1–Si1 177.51(13), C1–Co1–C2 95.77(18), C1–Co1–C3 98.78(18), C1–Co1–C4 98.44(18), Co1–Si1–C5 109.47(14), Co1–Si1–C6 111.64(15), Co1–Si1–C7 108.38(13), C5–Si1–C7 108.19(19),C5–Si1–C7 108.19(19),C6–Si1–C7 108.00(19),Si1–C7–C8 177.0(4), C2–Co1–Si1–C7 -172.5(2),C3–Co1–Si1–C5 –174.5(2), C4–Co1–Si1–C6 –168.8(2).

We attempted the synthesis of alkynylsilyl complexes from dimethyl(phenylethynyl)silane PhC=CMe₂SiH and platinum- or rhodium- phosphane complexes, respectively [3,5]. As to the first, the reaction starting from tris(triphenylphosphane)platinum(0) Pt(PPh₃)₃ [21a,b] proved our expectations true: the ²⁹Si NMR spectra of the reaction mixtures indicated (by several signals between –15 ppm and –30 ppm without coupling to ³¹P or ¹⁹⁵Pt; an intense signal at –23 ppm can be ascribed to 2,5-diphenyl-1,4-disila-cyclohexa-2,5-diene [22]) that no silyl complexes had formed but catalytic reactions between the Si–H and the C=C triple bond had occurred. The same result was obtained when bis(triphenylphosphane)platinum(II)-chloride (Ph₃P)₂PtCl₂ (with or without zinc powder [21c]) or ethylenebis(triphenylphosphane) platinum(0) (Ph₃P)₂Pt(C₂H₄) [3c,21d] were used.

Eventually, the synthetic attempts had more success using tris(triphenylphosphane)rhodium(I)-chloride $(Ph_3P)_3RhCl$ [23], mainly because of the low solubility of the resulting complex chlorohydrido[dimethyl(phenylethynyl)silyl]bis(triphenylphosphane)-rhodium(III) $(Ph_3P)_2RhClHSiMe_2C \equiv CPh$ (3) in organic solvents which shifts the equilibrium of 3 with the starting materials [23a–c] to the product side (Scheme 1). Nevertheless, this reaction was still complicated due to interactions of the Si–H and C \equiv C functionalities. Failure to isolate 3 immediately after synthesis results in its slow decomposition as $(Ph_3P)_3RhCl catalyzes$ irreversible reactions of PhC \equiv CMe₂SiH with itself, thus shifting the equilibrium back to the left side. Upon addition of further PhC \equiv CMe₂SiH the equilibrium can be re-shifted to 3.

The synthesis was favourably carried out in methylene chloride, which supports the formation of **3** under the circumstances outlined above. Upon addition of PhC \equiv CMe₂SiH the deep red solution of (Ph₃P)₃RhCl turned yellow-brown within minutes, and

immediate reduction of the solvent volume under reduced pressure followed by cooling furnished **3** in 73% yield as bright yellow crystals which are air-stable for at least some days. Nevertheless, elemental analyses were only correct if the samples were prepared under argon.

Because of its low solubility and decomposition in solution, NMR spectra of **3** were obtained from a crude reaction mixture in deuterated methylene chloride, which was sufficiently pure for this purpose. The ¹H NMR showed a complex multiplet at +7...+8 ppm for the aromatic protons, a slightly broadened singlet at +0.07 ppm for the methyl groups (doublet splitting intimated), and a doublet of triplets at -14.97 ppm for the hydride which suggests chemical equivalence of the two phosphane ligands. The position of the methyl signal appears unusual for a silyl complex as a down-field shifted signal at +0.5...+1 ppm would have been expected [1b,17b]. This feature is explained by the steric demand of both the silyl group and the phosphane ligands: The location of the methyl



Fig. 3. Topological (AIM) analysis of **3**: Representation of topological properties in the ClHRhSi plane. a: electron density ρ with bond paths and bond-critical points; b: Laplacian of electron density $\nabla^2 \rho$. Positive values of $\nabla^2 \rho$ are drawn with dashed lines and represent regions of charge depletion; negative values of $\nabla^2 \rho$ are drawn with solid lines and represent regions of charge concentration. Contour values for both representations in atomic units are: 0.001, 0.002, 0.004, 0.008, 0.02, 0.04, 0.08, 0.2, 0.4, 0.8, 2, 4, 8, 20, 40, 80, 200, 400, 800.



Fig. 4. Molecular structure of **3** (hydrogens except hydride omitted). Selected bond lengths [pm] and angles [°]: Rh1–Si1 229.23(7), Rh1–H1 153(2), Rh1–Cl1 239.05(6), Rh1–P1 232.40(6), Rh1–P2 230.52(6), Si1–C37 187.6(2), Si1–C38 186.7(2), Si1–C39 185.2(3), C39–C40 120.9(4), H1–Rh1–Cl1 176.1(9), H1–Rh1–P1 91.5(8), H1–Rh1–P2 89.8(9), H1–Rh1–Si1 66.7(8), C11–Rh1–P1 89.07(2), C11–Rh1–P2 88.53(2), C11–Rh1–Si1 17.03(2), P1–Rh1–P2 161.67(2), P1–Rh1–Si1 99.50(2), P2–Rh1–Si1 97.78(2), Rh1–Si1–C37 119.67(8), Rh1–Si1–C38 118.50(8), Rh1–Si1–C39 103.48(12), Si1–C39–C40 175.0(2), C11–Rh1–Si1 –C39 3.21(8).

groups in the closer proximity of the phosphane aryl groups renders the aromatic ring current of the phosphane phenyl rings (favourably facing the methyl groups with the C₆-plane for steric reasons) a notable shielding influence. This interpretation is supported by the molecular structure of **3** (see below). The ¹³C NMR spectrum was consistent with the structure of **3**. The ²⁹Si NMR spectrum showed a doublet of triplets at +17.1 ppm while the ³¹P NMR spectrum featured one doublet at +40.9 ppm. The coupling constants were comparable to similar complexes [1c,23e]. These findings confirm the assumption of chemically equivalent phosphane ligands.

The solid-state IR spectrum (KBr pellet) contained three characteristic bands of medium intensity at 2143 cm⁻¹, 2028 cm⁻¹, and 1974 cm⁻¹. The first one was assigned to the C \equiv C vibration by comparison with other alkynylsilyl compounds. To start with, the other two bands were both assigned to the Rh-H vibration. Actually, there is only one band to be expected [23b,e], but occasionally also two bands are reported and attributed to the presence of a second isomer [23a,d]. Other explanations would be coupling with other vibrations, decomposition of 3, chlorine-bromine exchange with KBr, or an incompletely divided Si-H bond (Rh-Si-H three-centre bond). The latter seems unlikely since M-Si-H bands are rather broad [24] while the two bands in question are not. Unfortunately, the ${}^{1}J_{HSi}$ coupling constant (NMR), which would give further insight, could not be measured because of decomposition (see above). To clarify the origin of the IR bands and to elucidate the bonding situation, 3 was computationally investigated by quantum chemical (DFT) and topological (AIM) analysis (for details see experimental section). The calculations clearly indicated the absence of a bondcritical point between silicon and hydrogen and the presence of bond-critical points between rhodium and silicon and rhodium and hydrogen, thus ruling out the three-centre bond (Fig. 3). Further results (Laplacian analysis) are that the Rh-Si bond is mainly covalent while the Rh-Cl bond is mainly ionic. The Rh-bound



Fig. 5. Structural features of **3.** a: Coordination polyhedron of the rhodium atom; b: CH··· π contacts between methyl protons and phenyl rings (C $_{\pi}$ ···H distances (C $_{\pi}$ ···C_{Me} distances) [pm]: a = 277(333), b = 307(328), c = 315(333), d = 270(328), e = 281(348), f = 291(323), g = 280(323), h = 292(360)).

hydrogen has a hydridic character. The phosphine ligands are bound by donor–acceptor interactions. The quantum chemical simulation of the IR spectra of the model compounds chlorohydridobis-(trimethylphosphane)(trimethylsilyl)rhodium(III) (Me₃P)₂RhClH-SiMe₃ and bromohydridobis(trimethylphosphane)(trimethylsilyl)rhodium(III) (Me₃P)₂RhBrHSiMe₃ furnished wavenumbers for the Rh–H vibration of 2034.7 cm⁻¹ and 2022.6 cm⁻¹, respectively. There are no other bands in the characteristic region between 1500 cm⁻¹ and 3000 cm⁻¹. Thus, the 2028 cm⁻¹ band was assigned to the Rh–H vibration of **3**. The 1974 cm⁻¹ band may be ascribed to the complex formed upon chlorine-bromine exchange. However, we cannot exclude a second isomer or a decomposition product formed in the IR sample preparation as origin of the third band.

The X-ray single crystal structure analysis confirmed the conclusions drawn from the NMR spectra. Apart from the orientation of the phenyl groups, the molecule has an idealized bisecting mirror plane made up of the rhodium, the chlorine, the silicon, the hydride, and the alkyne carbon atoms (Fig. 4 and Table 1). The Rh–Si bond is 229.2 pm in length (average value: 234 pm),² which is comparable to similar complexes [1a,c,d,5c,23e]. The hydride hydrogen atom was found directly by analysis of the residual

electron density map. The Rh–H distance (153 pm) is in the reported range for Rh-H bonds (X-ray 100-224 pm; neutron diffraction 131–205 pm).² The Si–H distance (219 pm) is much longer than Si-H bonds in silanes (average value: X-ray 141 pm; neutron diffraction 150 pm)² but markedly shorter than the sum of the van der Waals-radii (340 pm) [25]. This hints at an interaction between hydrogen and silicon, although there is no spectroscopic or computational support to this deduction. The coordination polyhedron of the metal atom is very similar to those of related rhodium silvl complexes [1a,c,d,5c,23e] and can be regarded as an intermediate state between a square pyramid and a trigonal bipyramid. The trigonality index τ is 0.23, which means that the polyhedron is far more a distorted square pyramid than a distorted trigonal bipyramid [26]. The "square" is made up of the chlorine, the hydrogen and the two phosphorus atoms while the silicon atom forms the apex of the pyramid (Fig. 5a). The "trigonal bipyramid" has the two phosphorus atoms in its axial positions and a bisecting plane made up of the chlorine, the hydrogen, and the silicon atom. Although the hydride hydrogen's bond lengths and angles suffer from the usual uncertainties encountered with H-atom positions near a heavy atom (which thwarts a more detailed discussion of the Rh coordination polyhedron), its position in the rhodium coordination sphere appears reasonable as similar coordination polyhedra are reported for related rhodium silyl [1a,c,d,5c,23e] and even ruthenium silylene [27] complexes (R₃P)₂[M(d⁶)](Si, Cl, H).

The ¹H NMR spectrum had indicated an interaction between the methyl hydrogens and the phenyl rings. Corresponding CH··· π contacts were found in the solid state (Fig. 5b). The minimum C···H distances (C···H 270–315 pm, C···C 323–360 pm) are smaller than the sum of the van-der-Waals radii (C···H 300 pm, C···C 370 pm) [25b]. Obviously these contacts are enforced by the steric demand of both the silvl and the phosphane ligands.

2.3. Reactivity of the triple bond

In order to examine the synthetic potential of the alkynylsilyl complexes in further reactions, we explored their reactivity toward complexation and hydrosilylation of the $C \equiv C$ triple bond.

Reaction of **1** with dicobaltoctacarbonyl Co₂(CO)₈ afforded the trinuclear complex octacarbonyl- $1\kappa^2 C_{,2}\kappa^3 C_{,3}\kappa^3 C_{,2}$ -cyclopentadienyl- $1(\eta^5) - [\mu_3 - \text{dimethyl}(\text{phenylethynyl} - 2\kappa^2 C, C': 3\kappa^2 C, C') \text{silyl} - 1\kappa Si] - 1$ iron(II)-2,3-bis[cobalt(0)](Co-Co) FpSiMe₂CCPh * Co₂(CO)₆ (**4**) in 57% yield as a dark brown solid, which is air-stable for at least one week (Scheme 2). The NMR and IR data were consistent with the anticipated structure. Compared to **1** the ¹J_{SiFe} coupling constant (15 Hz) and the Fe-Si bond lengths (232.5 and 232.8 pm; the asymmetric unit contains two independent molecules with only slightly different bond parameters and conformations) (Fig. 6 and Table 1) are nearly unchanged while the ²⁹Si NMR signal is shifted down-field by about 20 ppm. The ⁵⁹Co NMR spectrum featured a very broad signal at -2300 ppm [28]. Noteworthy, in comparison to **1** the ¹³C NMR signals of the alkyne carbon atoms are only slightly shifted although the C=C triple bond was transformed into a formal single bond within the dicobaltatetrahedrane cage. This



Scheme 2. Synthesis of compounds 4 and 5



Fig. 6. Molecular structure of **4** (hydrogens omitted). Only one of the two molecules in the asymmetric unit is shown. Selected bond lengths [pm] and angles [°]: Fe1–Si1 232.49(15), Fe1–Cp1 172.53(22), Fe1–C6 174.6(6), Fe1–C7 174.3(6), Si1–C8 187.7(5), Si1–C9 188.1(4), Si1–C10 187.4(5), C10–C11 132.5(6), C10–Co1 201.1(4), C10–Co2 200.5(4), C11–Co1 199.4(4), C11–Co2 194.9(4), C01–Co2 246.52(9), C6–Fe1–C7 94.9(2), C6–Fe1–Si1 85.63(18), C7–Fe1–Si1 83.53(16), Fe1–Si1–C8 111.76(18), Fe1–Si1–C9 111.68(16), Fe1–Si1–C10 111.62(15), C8–Si1–C9 107.5(2), C8–Si1–C10 106.0(2), C9–Si1–C10 107.9(2), Si1–C10–Co1 132.6(2), C6–Fe1–Si1 8.5(2), C6–Fe1–Si1 8.5(2), Si1–C10–C01 131.8(2), Si1–C10–C02 132.6(2), C6–Fe1–Si1–C10 -167.9(2), C9–Si1–C10 -177.1(7).

phenomenon has been reported several times in the literature [29]. Considering the correlation between ¹³C NMR chemical shift and hybridization (alkanes (sp³): 0 to +70 ppm; alkenes (sp²): +100 to +165 ppm; alkynes (sp): +60 to +100 ppm [30]), it indicates an intermediate state between sp² and sp³ hybridization corresponding to a C–C bond order between two and one. This is supported by the lowered silicon-alkyne carbon NMR coupling constant (${}^{1}J_{SiC} = 45$ Hz; ${}^{1}J_{SiC(sp)} \sim 75$ Hz, ${}^{1}J_{SiC(sp2)} \sim 65$ Hz, ${}^{1}J_{SiC(sp3)} \sim 50$ Hz [1b,e,31]). The ν_{CC} band of the former triple bond appeared in the IR spectrum of **4** at 1574 cm⁻¹, which is in the characteristic region of bands for alkenes and aromatic double bonds. Finally, the former alkyne triple bonds are 132.5 pm and 133.3 pm long, corresponding to a double bond character in this complex. In conclusion, these data suggest retention of at least partial C=C double bond character in this complex.

Compound **1** undergoes hydrosilylation with triethylsilane Et₃SiH in the presence of Speier's catalyst (H₂PtCl₆ in isopropanol) [32a,b] to yield the complex dicarbonyl(η^5 -cyclopentadienyl) {dimethyl[(*E*)-2-phenyl-2-triethylsilyl-ethen-1-yl]silyl}iron(II) FpSiMe₂CH=CPh(SiEt₃) (**5**) in quantitative yield as a brown oil (Scheme 2). Wilkinson's catalyst ((Ph₃P)₃RhCl) [32c] and aluminium chloride AlCl₃ [32d,e] were also probed, but had no effect or led to reactions other than hydrosilylation, respectively. The spectral data of **5** are in accord with the anticipated structure and confirm that the *E*-isomer (Scheme 2) had formed selectively. Unfortunately, crystals of **5** could not be obtained to date.

Irradiation induced ligand substitutions are quite common, also for silyl [33] and stannyl [34] complexes with unsaturated hydrocarbons. Consequently, a solution of **1** was UV-irradiated with IR and NMR monitoring (0.017 M in benzene, 12 h [34a–c]), but only decomposition occurred and Fp₂ was the only product identified.

| Table 2 | |
|--|-------------------|
| ²⁹ Si NMR data of compounds | 1-5. ^a |

| Compound | δ /ppm | $^{1}J_{Si-C=C}/Hz$ | $^{2}J_{Si-C=C}/Hz$ | $J_{\rm Si-E}/\rm Hz$ |
|---|---------------|---------------------|---------------------|-----------------------|
| $PhC \equiv CMe_2Si - Fp(1)$ | +18.4 | 68 | 12 | Fe: 15 ^b |
| $PhC \equiv CMe_2Si - Co(CO)_4(2)$ | +13.8 | 87 | 16 | - |
| PhC=CMe ₂ Si-RhClH(PPh ₃) ₂ (3) | +17.1 | _ ^c | _ ^c | P: 9.6 |
| | | | | Rh: 31 |
| $PhC \equiv CMe_2Si - Fp * Co_2(CO)_6$ (4) | +39.7 | 45 | _ ^c | Fe: 15 ^b |
| $Fp-SiMe_2CH=CPh(SiEt_3)$ (5) | +32.2/+1.8 | _c | _ ^c | _ ^c |

a 29Si NMR data of PhC=CMe2SiH/Cl: [29].

^b FpSiMe3: ${}^{1}J_{SiFe} = 15$ Hz [17b].

^c Satellites too weak or hidden.

The reaction of **2** with $(Ph_3P)_2Pt(C_2H_4)$ did not yield a platinum alkyne complex. Instead, the NMR spectra of the reaction mixture indicated the formation of *trans*-(tricarbonyl)[dimethyl(phenyl-ethynyl)silyl](triphenylphosphane)cobalt(I) $(Ph_3P)Co(CO)_3SiMe_2C \equiv$ CPh by transfer of a phosphane ligand from platinum to cobalt with carbonyl substitution (¹H NMR (C₆D₆): $\delta = +1.10$ (d, ${}^{4}J_{HP} = 1.5$ Hz, SiMe₂) ppm; ²⁹Si NMR (C₆D₆): $\delta = +14.3$ (d, ${}^{2}J_{SiP} = 34.0$ Hz) ppm; ³¹P NMR (C₆D₆): $\delta = +57.5$ (s) ppm), thus providing evidence that the cobalt-silicon bond was retained. Unfortunately, isolation of this compound was not successful. Complexation of **3** was not attempted because of its low solubility.

2.4. Spectroscopic properties

The ²⁹Si NMR spectroscopic parameters of the synthesized complexes are listed in Table 2. The ²⁹Si NMR signals of the alkynylsilyl complexes 1, 2, and 3 appeared at +13...+19 ppm. Regarding the different complex fragments bound to the silyl group this range is surprisingly narrow. Unsaturated organic groups (especially alkynyl groups) increase the shielding of the ²⁹Si nucleus in silanes, while transition metal complex fragments are known to cause a down-field shift of the ²⁹Si resonance (e.g. *Me*–SiMe₃: $\delta = 0$ ppm, *Fp*–SiMe₃: $\delta = +41.5$ ppm, *Ph*–SiMe₃: $\delta = -4.8$ ppm, *Vi*-SiMe₃: $\delta = -7.0$ ppm, *HC*=C-SiMe₃: $\delta = -17.5$ ppm) [1a-c,17b,35]. Apparently, the opposite trends of transition metal and alkynyl group superimpose, thus resulting in an intermediate position of the ²⁹Si NMR signals. "Removal" or "diminution" of the alkynyl triple bond character by complexation (4) or hydrosilylation (5) also removes or diminishes the shielding influence. Thus, the ²⁹Si NMR shifts of **4** and **5** resemble that of dicarbonyl(cyclopentadienyl)trimethylsilyliron(II) FpSiMe₃.

The ¹H and ¹³C NMR signals appeared in the expected ranges. The alkyne carbon atoms featured signals in the

| a | ble 3 | | | | |
|---|-------|--------------|----|----|---|
| P | data | of compounds | 1_ | -5 | ć |

| Compound | $\nu^{\sim}(C \equiv C)/cm^{-1}$ | v~(C≡0)/cm ⁻¹ |
|---|--|---|
| PhC \equiv CMe ₂ Si-Fp (1) PhC \equiv CMe ₂ Si-Co(CO) ₄ (2) | 2148 ^b ; 2145 ^c 2157 ^b ; 2153 ^d | 2001, 1950 ^b ; 1994, 1937 ^c 2094, 2033, 2008, 1998 ^b ; 2092, 2029, 1994 ^d |
| $PhC \equiv CMe_2Si - RhClH(PPh_3)_2$ (3) | 2143 ^c | - |
| $PhC = CMe_2Si - Fp * Co_2(CO)_6$ (4) | 1574 ^c | 2085, 2047, 2026, 2015, 2001, 1949 ^b ; 2083, 2046, 2020, 2012, 1993, 1933 ^c |
| $Fp-SiMe_2CH=CPh(SiEt_3)(5)$ | _ ^e | 1996, 1943 ^b |
| 2 | (00) | |

^a IR data of PhC=CMe₂SiH/Cl: [29].

^b Solution in hexane.

^c KBr pellet.

^d Neat liquid.

^e Not assigned.

range +95...+111 ppm with the one of the silicon-bound carbon at higher field (assignment by ²⁹Si satellites). The IR spectroscopic data of the synthesized compounds are summarized in Table 3. The bands of the C=C triple bonds appear in the narrow range of 2143–2157 cm⁻¹.

3. Conclusions

Transition metal alkynylsilyl complexes with a metal-silicon bond are accessible both by nucleophilic substitution and oxidative addition. In the first synthetic pathway both strongly and weakly nucleophilic metallates can be used. Disturbing interactions of the metallates with the C \equiv C triple bond were not observed, but formation of siloxanes can interfere. Synthesis by oxidative addition can be hampered by transition metal catalyzed reactions between the Si–H and the C \equiv C triple bond. The metallosilyl functionalized alkynyl groups were shown to undergo further complexation or hydrosilylation while the metal-silicon bond is preserved. Thus, alkynylsilyl complexes may be useful as precursors to novel compounds, e.g. multinuclear heterometallic complexes, or metal- and silicon-containing polymers.

4. Experimental section

4.1. General Remarks

All operations were performed under purified argon using standard Schlenk line or glovebox techniques. If possible, reactions were monitored by NMR or IR spectroscopy. Assignments were made by comparison of the spectra with each other and with literature data. Missing NMR peaks are hidden by other peaks, often by those of the solvent. Melting points were determined between thin glass plates (air) or in sealed capillaries (argon) on a Boëtius type heating microscope with a heating rate of about 4 K/min. Elemental analyses were performed in duplicate with a CHN-O-Rapid (Heraeus) and the values averaged. The NMR spectra were recorded at 22 °C with a Bruker DPX 400 Avance spectrometer using tetramethylsilane Me₄Si (TMS) as internal standard for ¹H (400.13 MHz), 13 C (100.63 MHz), and 29 Si (79.49 MHz). The external standards for 31 P (161.98 MHz) and 59 Co (94.65 MHz) were 85% H_3PO_4 and 0.1 M $K_3[Co(CN)_6]$ in D_2O , respectively [36]. For ²⁹Si NMR spectra the INEPT pulse sequence was employed. IR spectra were recorded with a Specord M 82 (VEB Carl Zeiss JENA) or a Nicolet 510 spectrometer. Liquid samples were prepared between NaCl plates, whereas solids were examined in KBr disks. UV/Vis spectra were recorded with a Specord S 100 (Analytik Jena AG) in the range 190-1000 nm.

4.2. Chemicals

Solvents were dried and deoxygenated by distillation under argon from sodium-benzophenone (diethyl ether, hexane, THF, toluene), calcium hydride (CDCl₃, methylene chloride), lithium aluminium hydride (pentane), or sodium-potassium alloy (C_6D_6) and stored under argon until use. PhC=CMe₂SiCl and PhC=CMe₂SiH were synthesized as previously published [29]. Solid NaCo(CO)₄ was prepared by reaction of Co₂(CO)₈ with NaOH in THF, evaporation of the filtered solution in vacuo, and heating of the residue in vacuo up to 100 °C [37]. Chromatography was performed on "Silica gel L5/40" from LACHEMA (Brno)/CHEMAPOL (Prague). The other chemicals were prepared after common procedures or purchased from commercial suppliers and were used as received.

4.3. Crystal structure analyses

The X-ray single crystal structure analyses were performed on a Bruker-Nonius X8 diffractometer using MoK_a radiation $(\lambda = 71.073 \text{ pm})$ and an APEX2-CCD area detector. For solving, refining, and visualization of the structures the programmes Bruker SMART [38a], Bruker SAINT [38a], Bruker SHELXTL [38b], SHELXS-97 [38c], SHELXL-97 [38d], WinGX [38e], and ORTEP32 [38f] were used. The thermal ellipsoids are drawn at the 50% probability level. The diffraction pattern of the crystal of compound 2 exhibited features of both twinning and high mosaic spread of the reflections. Upon absorption correction with Xabs2 (as implemented in WinGX) the final refinement was carried out using the corrected HKLF4 format data set and the twin law (-100)(010)(001). The twin population parameter BASF refined to 0.0045(5). The data set of **4** was collected from a twin with two populations in ratio 0.60 : 0.40 (according to the BASF of 0.4026(6) refined from a HKLF5 format data set comprising full data of both populations, which was generated using SAINTPLUS [38a]).

4.4. Computational details

The quantum chemical calculations were performed using GAUSSIAN 03 [39]. For the topological analysis the geometry of the X-ray structure of **3** was used for a single point calculation at the density functional theory level (DFT) using Becke's three-parameter hybrid exchange functional and the correlation functional of Lee, Yang and Parr (B3LYP) [40]. All elements were treated with the 3-21G basis set [41]. The wavefunction files for the AIM analysis were generated in Cartesian coordinates with a basis set containing 6d functions. The electron density topology was analysed using the programs AIM2000 [42a] and Xaim [42b].

For the calculation of the IR data of the model compounds (Me₃P)RhCl(H)SiMe₃ and (Me₃P)RhBr(H)SiMe₃ the molecular geometries were fully optimized at the B3LYP level [40]. Rhodium was treated with an effective core potential, a valence double zeta basis set (Hay/Wadt pseudopotential, LANL2DZ), and an additional f-type polarization function [43]. The 6–31G(d) basis set was used for all main group elements [44]. Harmonic vibrational frequencies were determined by analytic second derivative methods. The values of the vibrational frequencies were not scaled since a combination of different basis sets was used for these calculations.

4.5. Syntheses

4.5.1. Dicarbonyl(η⁵-cyclopentadienyl)[dimethyl(phenylethynyl) silyl]iron(II) (**1**)

A solution of NaFp in THF (prepared from Na (115 mg, 5.00 mmol), Hg (2.0 mL, 27.1 g, 135 mmol), Fp₂ (757 mg, 2.14 mmol), and THF (20 mL) by stirring for 3 h at room temperature) was added to PhC=CMe₂SiCl (810 mg, 4.16 mmol) in pentane (40 mL) at 0 °C. The brown suspension was warmed to room temperature overnight and then evaporated in vacuo. The residue was extracted with hexane (3 \times 5 mL). The extract was concentrated to 2 mL and chromatographed on silicagel ($10 \text{ cm} \times 2 \text{ cm}$) with hexane/toluene 8:2 as eluent. The product passed the column as a yellow band. The eluate was evaporated in vacuo (1.31 g, 94% crude yield) and the residue redissolved in 5 mL hexane. On slow cooling to -78 °C a solid deposited which was separated and dried in vacuo (975 mg, 70%). The recrystallization was repeated twice yielding yellowbrown crystals which were directly suitable for X-ray crystallography. The compound is air-stable for several days but should be stored under argon in a refrigerator.

Yield: 740 mg, 2.20 mmol, 53%. Mp: 31–34 °C (argon), 30–33 °C (air). Solubility: hexane, pentane, CHCl₃ (dec.). Anal. found (calcd.) for C17H16FeO2Si (336.246 g/mol): C 60.88 (60.73) %, H 4.93 (4.80) %. ¹H NMR (0.75 M in CDCl₃): δ = 7.45 (m, 2 H, Ph_{ortho}), 7.29 (m, 3 H, $Ph_{meta + para}$), 4.81 (s, ${}^{1}J_{HC} = 180$ Hz, 5 H, Cp), 0.58 (s, ${}^{1}J_{HC} = 121$ Hz, 6 H, SiMe₂) ppm. ¹³C NMR (0.75 M in CDCl₃): $\delta = 214.6$ (s, 2 C, CO), 131.7 (s, ${}^{1}J_{CC} = 57$ Hz, 2 C, Ph_{ortho}), 128.2 (s, 2 C, Ph_{meta}), 128.1 (s, 1 C, Ph_{para}), 123.8 (s, 1 C, Ph_{ipso}), 107.5 (s, ${}^{2}J_{CSi} = 12$ Hz, 1 C, C=C-Si), 99.1 (s, ${}^{1}J_{CSi} = 68 \text{ Hz}$, 1 C, C=C-Si), 84.4 (s, 5 C, Cp), 6.7 (s, ${}^{1}J_{CSi} = 50 \text{ Hz}$, 2 C, SiMe₂) ppm. ${}^{29}Si \text{ NMR}$ (0.75 M in CDCl₃): $\delta = +18.4$ (s (${}^{1}\text{H}$ coupled: septet, ${}^{2}J_{SiH} = 6.8 \text{ Hz}$), ${}^{1}J_{SiC(Me)} = 50 \text{ Hz}$ (2 C), ${}^{1}J_{SiC(C=C)} = 68 \text{ Hz}$ (1 C), ${}^{2}J_{SiC(C=C)} = 12 \text{ Hz}$ (1 C), ${}^{2}J_{SiFe} = 15 \text{ Hz}$) ppm. IR (hexane): $v^{\sim} = 2148$ (w, $v(C \equiv C)$), 2002 (vs, $v(C \equiv O)$), 1951 (vs, $\nu(C=0)$) cm⁻¹. IR (KBr): $\nu^{\sim} = 3095$ (vw, $\nu(CH_{Cp/Ph})$), 3073 (w, v(CH_{Cp/Ph})), 2955 (m, v_{as}(CH₃)), 2930 (vw, v(CH)), 2922 (vw, v(CH)), 2890 (w, v_s(CH₃)), 2858 (vw, v(CH)), 2145 (m, v(C≡C)), 1994 (vs, $\nu(C=0)$), 1937 (vs, $\nu(C=0)$), 1592 (w, $\nu(C=C_{PhC=C})$), 1571 (vw, v(C=C_{PhC≡C})), 1486 (m, v(C=C_{PhC≡C})), 1440 (w, v(C=C_{PhC≡C})), 1431 (w), 1413 (m, $v(C=C_{Cp}) + \delta_{as}(SiCH_3)$), 1359 (vw), 1244 (m, $\delta_s(SiCH_3)$), 1219 (m, $\delta(CH_{PhC} \equiv_{C})$), 1111 (vw, $\nu(C = C_{Cp})$), 1068 (w, $\delta(CH_{PhC} \equiv_{C})$), 1024 (w, $\delta(CH_{PhC} \equiv_C)$), 1015 (w, $\delta(CH_{Cp})$), 1000 (w), 916 (w, $\delta(CH_{PhC} \equiv_C))$, 834 (s, $\gamma(CH_{Cp}) + \rho(SiCH_3))$, 827 (s. $\gamma(CH_{CD}) + \rho(SiCH_3)$, 801 (s, $\rho(SiCH_3)$), 759 (s, $\gamma(CH_{PhC} \equiv_C)$), 690 (m, $\gamma(CH_{PhC} \equiv_C)$), 663 (m), 645 (m, δ (FeCO)), 593 (s, δ (FeCO)), 534 (m, v(FeC_{CO})), 522 (w, v(FeC_{CO})), 465 (vw); 405 (m), 376 (vw), 357 (w) cm⁻¹ [45a,b,46]. UV/VIS (hexane): λ (ε) = 215 (12,000), 250 (12,000), 259 (12,000), 278 (sh, 8000), 285 (sh, 7000), 330 (br/sh, 1300) nm (L/mol*cm) [45c].

4.5.2. Tetracarbonyl[dimethyl(phenylethynyl)silyl]cobalt(I) (2)

NaCo(CO)₄ (1000 mg, 5.16 mmol) was suspended in hexane (25 mL) and mixed with PhC=CMe₂SiCl (1145 mg, 5.88 mmol). The solution was stirred at room temperature for 2 d. The brown mixture was then filtered and evaporated in vacuo. The residue was redissolved in hexane (2 mL) and the solution slowly cooled to -78 °C. A colourless solid deposited which was separated and dried in vacuo (1400 mg, 82%). An adhering dark brown oil could be removed to a large extent by five further recrystallizations resulting in almost colourless crystals which were directly suitable for X-ray crystallography. The product is very air-sensitive and should be stored under argon in a refrigerator.

Yield: 685 mg, 2.07 mmol, 40%. Mp: 22-26 °C (argon). Solubility: hexane, pentane, benzene. Anal. found (calcd.) for C₁₄H₁₁CoO₄Si (330.257 g/mol): C 51.16 (50.92) %, H 3.52 (3.36) %. ¹H NMR (0.12 M in C₆D₆): δ = 7.43 (m, 2 H, Ph_{ortho}), 6.91 (m, 3 H, Ph_{meta + para}), 0.72 (s, ${}^{1}J_{\text{HC}}$ = 122 Hz, 6 H, SiMe₂) ppm. ${}^{13}\text{C}$ NMR (0.12 M in C₆D₆): δ = 199.0 (br,³ $\Delta v_{1/2}$ = 60 Hz, CO), 132.1 (s, 2 C, Phortho), 129.1 (s, 1 C, Phpara), 128.6 (s, 2 C, Phmeta), 123.2 (s, 1 C, Phi_{pso}), 110.5 (s, 1 C, C≡C−Si), 95.1 (s, 1 C, C≡C−Si), 7.6 (s, ¹ $J_{CSi} = 54$ Hz, 2 C, SiMe₂) ppm. ²⁹Si NMR (0.12 M in C₆D₆): $\delta = +13.8$ (s (¹H coupled: septet, ² $J_{SiH} = 7.3$ Hz), ¹ $J_{SiC(Me)} = 54$ Hz (2 C), ¹ $J_{SiC(C=C)} = 87$ Hz (1 C), ² $J_{SiC(C=C)} = 16$ Hz (1 C)) ppm. ⁵⁹Co NMR (0.12 M in C₆D₆): $\delta = -2975$ ($\Delta \nu_{1/2} = 8$ kHz) ppm. IR (hexane): $v^{\sim} = 2157$ (w, $v(C \equiv C)$), 2094 (s, $v(C \equiv O)$), 2033 (s, $v(C \equiv O)$), 2008 (vs, $\nu(C=0)$), 1998 (vs, $\nu(C=0)$) cm⁻¹. IR (neat liquid): $\nu^{\sim} = 3082$ (w, v(CH_{Ph})), 3052 (w, v(CH_{Ph})), 3033 (w, v(CH_{Ph})), 2961 (w, $\nu_{as}(CH_3)$), 2897 (vw, $\nu_s(CH_3)$), 2153 (s, $\nu(C \equiv C)$), 2092 (s, $\nu(C \equiv O)$), 2029 (vs, $\nu(C=0)$), 1994 (vs, $\nu(C=0)$), 1595 (w, $\nu(C=C_{PhC=C})$), 1572 $(vw, v(C=C_{PhC=C})), 1487 (w, v(C=C_{PhC=C})), 1443 (w, v(C=C_{PhC=C})), 1487 (w, v(C=C_{PhC}$ 1406 (w, $\delta_{as}(SiCH_3)$), 1251 (m, $\delta_s(SiCH_3)$), 1223 (w, $\delta(CH_{PhC=C})$), 1069 (w, $\delta(CH_{PhC=C})$), 1028 (w, $\delta(CH_{PhC=C})$), 915 (w, $\delta(CH_{PhC=C})$), 851 (s, $\rho(\text{SiCH}_3)$), 827 (s, $\rho(\text{SiCH}_3)$), 806 (s, $\rho(\text{SiCH}_3)$), 777 (m, $\rho(\text{SiCH}_3)$), 757 (m, $\gamma(\text{CH}_{PhC} \equiv_C)$), 690 (m, $\gamma(\text{CH}_{PhC} \equiv_C)$), 671 (m), 603 (w) cm⁻¹ [47].

4.5.3. Chlorohydrido[dimethyl(phenylethynyl)silyl] bis(triphenylphosphane)rhodium(III) (**3**)

(Ph₃P)₃RhCl (231 mg, 0.25 mmol) was dissolved in CH₂Cl₂ (5 mL). PhC=CMe₂SiH (75 μ L, 70 mg, 0.44 mmol) was then added to the deep red brown solution at room temperature with stirring. The mixture changed its colour to amber within minutes. The solution was then evaporated to half its volume in vacuo and slowly cooled to -78 °C. Without removal of the precipitated crystals the solution was again evaporated to half its volume in vacuo and cooled to -78 °C. The solid was separated, washed with ether (4 × 1 mL), and dried in vacuo yielding bright yellow crystals which were directly suitable for X-ray crystallography. The compound is air-stable for some time but should be stored under argon.

Yield: 150 mg, 0.18 mmol, 73%. Mp: 235 °C (dec., argon), 145 °C (dec., air). Solubility: CH₂Cl₂ (dec.), CHCl₃ (dec.); insoluble in hexane, toluene, diethyl ether. Anal. found (calcd.) for C₄₆H₄₂ClP₂RhSi (823.239 g/mol): C 67.19 (67.11) %, H 5.17 (5.14) %. ¹H NMR (0.1 M in CD₂Cl₂): δ = 7.8...7.7 (m, 14 H, Ph_{ortho}), 7.4...7.3 (m, 21 H, Ph_{meta + para}), 0.07 (s, 4 6 H, SiMe₂), -14.97 (dt, ${}^{1}J_{HRh} = 22.5$ Hz, $^{2}J_{\text{HP}} = 14.2 \text{ Hz}, 1 \text{ H}, \text{RhH}) \text{ ppm.}^{13}\text{C NMR} (0.1 \text{ M in } \text{CD}_2\text{Cl}_2): \delta = 135.4$ $(s, {}^{4} 6 C, PhP_{ipso}), 135.2$ ("t", $J_{CP/Rh} = 6.2$ Hz, 12 C, $PhP_{ortho}),$ 132.5...131.5 (-,⁵ PhC≡C_{ortho}), 130.5 (s, 6 C, PhP_{para}), 129...127 (-,⁵ PhC=C_{meta + para}), 128.5 ("t", J_{CP/Rh} = 4.6 Hz, 12 C, PhP_{meta}), 123.9 (s, 1 C, PhC≡C_{ipso}), 106.4 (s, 1 C, C≡C−Si), 100.8 (s,⁴ 1 C, C≡C−Si), 9.8 (s,⁴ $^{1}J_{CSi} = 53$ Hz, 2 C, SiMe₂) ppm. ²⁹Si NMR (0.1 M in CD₂Cl₂): $\delta = +17.1$ (dt, ${}^{1}J_{\text{SiRh}} = 30.9$ Hz, ${}^{2}J_{\text{SiP}} = 9.6$ Hz) ppm. 31 P NMR (0.1 M in CD₂Cl₂): $\delta = +40.9$ (d, ¹*I*_{PRh} = 123.9 Hz) ppm. IR (KBr): $\nu^{\sim} = 3143$ (vw, v(CH_{Ph})), 3074 (w, v(CH_{Ph})), 3053 (m, v(CH_{Ph})), 3026 (w, v(CH_{Ph})), 3005 (w, v(CH_{Ph})), 2983 (vw, v(CH)), 2972 (w, v(CH₃)), 2951 (w, v(CH₃)), 2889 (vw, v(CH₃)), 2143 (m, v(C=C)), 2028 (m, *ν*(RhH)), 1974 (m), 1891 (vw, *γ*_{comb}(CH_{Ph})), 1817 (vw, *γ*_{comb}(CH_{Ph})), 1775 (vw, $\gamma_{comb}(CH_{Ph})$), 1587 (w, $\nu(C=C_{PhC=C})$), 1572 (w, $\nu(C=C_{PhC=C})), 1482 (s, \nu(C=C_{PhP}) + \nu(C=C_{PhC=C})), 1435 (s, v(C=C_{PhC=C})), 1435 (s, v$ $\nu(C=C_{PhP}) + \nu(C=C_{PhC})$, 1399 (vw, $\delta_{as}(SiCH_3)$), 1332 (vw), 1311 (vw), 1243 (w, $\delta_s(SiCH_3)$), 1219 (vw, $\delta(CH_{PhC=C})$), 1187 (w), 1157 (vw), 1119 (vw), 1098 (s, δ (CH_{PhP})), 1071 (vw, δ (CH_{PhC=C})), 1027 (w, $\delta(CH_{PhC=C}))$, 999 (w), 910 (vw, $\delta(CH_{PhC=C}))$, 842 (m, $\rho(SiCH_3))$, 823 (s, $\rho(SiCH_3)$), 803 (m, $\rho(SiCH_3)$), 764 (m, $\gamma(CH_{PhC})$), 753 (s, γ (CH_{PhP})), 749 (s, γ (CH_{PhP})), 693 (s, γ (CH_{Ph})), 670 (w), 618 (vw), 600 (vw), 535 (w, RhPPh₃), 517 (s, RhPPh₃), 457 (w), 431 (vw), 420 (vw), 405 (vw), 369 (vw) cm⁻¹ [48]. UV/VIS (CH₂Cl₂): $\lambda(\varepsilon) = 235(27,000)$, 248 (26,000), 261 (20,000), 275 (sh, 8500), 282 (sh, 8500), 300 (br/ sh, 8500), 339 (br, 8500), 374 (br/sh, 4300) nm (L/mol*cm).

4.5.4. Octacarbonyl- $1\kappa^2 C_2 \kappa^3 C_3 \kappa^3 C_2$ cyclopentadienyl- $1(\eta^5)$ - $[\mu_3-dimethyl(phenylethynyl-<math>2\kappa^2 C_2 C'_3 \kappa^2 C_2 C'_3$) silyl- 1κ Si]-1-iron(II)-2,3-bis[cobalt(0)](Co-Co) (**4**)

 $Co_2(CO)_8$ (650 mg, 1.90 mmol) in hexane (20 mL) was added at room temperature with stirring to a solution of **1** (650 mg, 1.93 mmol) in hexane (20 mL) whereupon a weak effervescence commenced. After 1 d the dark brown solution was filtered, slowly evaporated in vacuo to a volume of 5 mL, and cooled to -20 °C. The precipitated solid was isolated and dried in vacuo (770 mg, 65% crude yield). From the mother liquor additional solid (110 mg, 9% crude yield) could be obtained by evaporation and cooling. The crude product was recrystallized from hexane (25 mL, evaporation in vacuo to 5 mL, cooling to -20 °C, isolation, washing with 3 x 0.5 mL hexane, drying in vacuo) yielding dark brown crystals which

³ A splitting into two signals (axial/equatorial) was intimated.

⁴ Multiplett intimated.

⁵ Overlap with signals of by-products and impurities.

were directly suitable for X-ray crystallography. They were airstable for at least 1 week but should be stored under argon.

Yield: 670 mg, 1.08 mmol, 57%. Mp: 86–87 °C (argon), 83–84 °C (dec., air). Solubility: hexane, benzene. Anal. found (calcd.) for C₂₃H₁₆Co₂FeO₈Si (622.172 g/mol): C 44.39 (44.40) %, H 2.74 (2.59) %. ¹H NMR (0.05 M in C₆D₆): $\delta = 7.56$ (d, ³J_{HH} = 7.6 Hz, 2 H, Ph_{ortho}), 7.02 ("t", ${}^{3}J_{HH} = 7.4$ Hz, 2 H, Ph_{meta}), 6.93 (t, ${}^{3}J_{HH} = 7.2$ Hz, 1 H, Ph_{para}), 4.05 $(s, {}^{1}J_{HC} = 178 \text{ Hz}, 5 \text{ H}, \text{Cp}), 0.87 (s, {}^{1}J_{HC} = 120 \text{ Hz}, 6 \text{ H}, \text{SiMe}_{2}) \text{ ppm}. {}^{13}\text{C}$ NMR (0.05 M in C₆D₆): δ = 215.6 (s, $\Delta \nu_{1/2}$ = 4 Hz, FeCO), 200.9 (br, $\Delta v_{1/2} = 40$ Hz, CoCO), 139.7 (s, $\Delta v_{1/2} = 3$ Hz, 1 C, Ph_{ipso}), 129.7 (s, \Delta v_{1/2} = 3 Hz, 1 C, Ph_{ip} $_2 = 4$ Hz, 2 C, Ph_{ortho}), 129.2 (s, $\Delta v_{1/2} = 4$ Hz, 2 C, Ph_{meta}), 127.9 (s, 1 C, Ph_{para}), 108.2 (s, $\Delta v_{1/2} = 7$ Hz, 1 C, C=C-Si*Co₂), 91.3 (s, $\Delta v_{1/2} = 6$ Hz, 1 C, C=C-Si*Co₂), 83.8 (s, $\Delta \nu_{1/2} = 4$ Hz, 5 C, Cp), 9.8 (s, $\Delta \nu_{1/2} = 3$ Hz, ¹ $J_{CSi} = 47$ Hz, 2 C, SiMe₂) ppm. ²⁹Si NMR (0.05 M in C₆D₆): $\delta = +39.7$ (s (¹H coupled: septet), ² $J_{SiH} = 6.3$ Hz, ¹ $J_{SiC(Me)} = 47$ Hz (2 C), ¹ $J_{SiC(C \equiv C^*Co2)} = 45$ Hz (1 C), ¹ $J_{SiFe} = 15$ Hz) ppm. ⁵⁹Co NMR (0.05 M in C_6D_6): $\delta = -2300 \pm 100$ (vbr, $\Delta v_{1/2} = 37$ kHz) ppm. IR (hexane): $\nu^{\sim} = 2085 \,(\text{m}, \nu(\text{CoC}=0)), 2047 \,(\text{s}, \nu(\text{CoC}=0)), 2026 \,(\text{c}, \nu(\text{CoC}=0)), 2026 \,(\text{c}, \nu(\text{c}, \nu(\text{CoC}=0)), 2026 \,(\text{c}, \nu(\text{c}, \nu(\text{CoC}=0)), 2026 \,(\text{c}, \nu(\text{c}, \nu(\text$ 2015 (m/sh, v(CoC≡O), 2001 (m, v(FeC≡O)), 1949 (m, v(FeC≡O)) cm^{-1} . IR (KBr): $\nu^{\sim} = 3130$ (vw, $\nu(CH_{Cp/Ph})$), 3068 (vw, $\nu(CH_{Cp/Ph})$), $2959 (w, v_{as}(CH_3)), 2899 (vw, v_s(CH_3)), 2083 (s, v(CoC \equiv 0)), 2046 (vs, v_{as}(CH_3)))$ v(CoC≡O)), 2020 (vs, v(CoC≡O)), 2012 (vs, v(CoC≡O)), 1993 (vs, *v*(FeC≡O)), 1933 (s, *v*(FeC≡O)), 1596 (w, *v*(C=C_{Ph})), 1574 (w, ν (C=C)), 1560 (vw/sh), 1522 (vw), 1476 (w, ν (C=C_{Ph})), 1439 (w, ν(C=C_{Ph})), 1413 (w, ν(C=C_{Cp})), 1407 (w, δ_{as}(SiCH₃)), 1360 (vw); 1249 (w, δ_s (SiCH₃)), 1241 (w, δ_s (SiCH₃)), 1178 (vw), 1165 (vw/sh), 1075 (vw/sh), 1065 (vw), 1015 (vw, δ(CH_{Cp})), 1001 (vw), 861 (w), 845 (sh, $\gamma(CH_{Cp}) + \rho(SiCH_3)$), 828 (m, $\gamma(CH_{Cp}) + \rho(SiCH_3)$), 800 (m, $\rho(SiCH_3)$), 758 (m, γ(CH_{Ph})), 693 (w, γ(CH_{Ph})), 680 (vw/sh), 645 (m, δ(FeCO)), 635 (w/sh), 605 (m/sh), 594 (s, δ(FeCO)), 567 (w), 516 (s, δ(CoCO)), 495 (s, δ(CoCO)), 475 (w/sh), 465 (m), 457 (m, δ(CoCO)), 431 (w), 416 (w), 393 (w) cm⁻¹ [45a,b,d,46,49,50]. UV/VIS (hexane): λ (ε) = 216 (50,000), 290 (br/sh, 20,000), 330 (br/sh, 13,000), 375 (br/sh, 3000), 450 (br/sh, 700), 575 (br/sh, 300) nm (L/mol*cm) [45c,d,51].

4.5.5. Dicarbonyl(η^5 -cyclopentadienyl){dimethyl[(E)-2-phenyl-2-triethylsilyl-ethen-1-yl]silyl}iron(II) (**5**)

Complex **1** (182 mg, 0.54 mmol) and a few mg $H_2PtCl_6 * 6H_2O$ in 2 drops of isopropanol were dissolved in Et_3SiH (2.5 mL, 1.83 g, 15.70 mmol), stirred at room temperature for 6 d, and additionally refluxed for 2 h. The mixture was then evaporated in vacuo and the residue extracted with hexane (5 mL). The extract was again evaporated in vacuo leaving **5** as a brown oil.

Yield: 245 mg, 0.54 mmol, 99.6%. ¹H NMR (0.2 M in C₆D₆): C), 4.13 (s, 5 H, Cp), 0.99 (t, ${}^{3}J_{HH} = 7.8$ Hz, 9 H, $-CH_{2}-CH_{3}$), 0.63 (q, ${}^{3}J_{\text{HH}} = 7.8$ Hz, 6 H, $-CH_2-CH_3$), 0.33 (s, 6 H, SiMe₂) ppm. 13 C NMR $(0.2 \text{ M in } C_6D_6)$: $\delta = 216.0$ (s, 2 C, CO), 157.2 (s, 1 C, HC=C), 151.8 (s, 1 C, HC=C), 145.8 (s, 1 C, Ph_{ipso}), 125.9 (s, 1 C, Ph_{para}), 83.8 (s, 5 C, Cp), 7.7 (s, 3 C, $-CH_2-CH_3$), 6.8 (s, ${}^{1}J_{CSi} = 45$ Hz, 2 C, SiMe₂), 3.3 (s, ${}^{1}J_{CSi} = 52$ Hz, 3 C, $-CH_2-CH_3$) ppm. ${}^{13}C$ NMR (0.2 M in hexane): $\delta = 215.3$ (s, 2 C, CO), 157.1 (s (¹H coupled: s/br), 1 C, HC=C), 152.3 (s ${}^{(1)}$ H coupled: d, ${}^{1}J_{CH} = 132$ Hz), 1 C, HC=C), 146.0 (s (¹H coupled: dt, ${}^{2/3}J_{CH} = 15$ Hz, ${}^{2/3}J_{CH} = 7.5$ Hz), 1 C, Ph_{ipso}), 128.1 (s (¹H coupled: dt, ${}^{1}J_{CH} = 161$ Hz, ${}^{3}J_{CH} = 7$ Hz), 2 C, Ph_{meta}), 128.0 (s (¹H coupled: dt, ${}^{1}J_{CH} = 159$ Hz, ${}^{3}J_{CH} = 6$ Hz), 2 C, Ph_{meta}), 128.0 (s (¹H coupled: dt, ${}^{1}J_{CH} = 159$ Hz, ${}^{3}J_{CH} = 6$ Hz), 2 C, Ph_{ortho}), 126.0 (s (¹H coupled: dt, ${}^{1}J_{CH} = 159$ Hz, ${}^{3}J_{CH} = 7$ Hz), 1 C, Ph_{para}), 83.7 (s (¹H coupled: dt, ${}^{1}J_{CH} = 159$ Hz, ${}^{3}J_{CH} = 7$ Hz), 1 C, Ph_{para}), 83.7 (s (¹H coupled: dt, ${}^{1}J_{CH} = 159$ Hz, ${}^{3}J_{CH} = 7$ Hz), 1 C, Ph_{para}), 83.7 (s (¹H coupled: dt, ${}^{1}J_{CH} = 159$ Hz, ${}^{3}J_{CH} = 7$ Hz), 1 C, Ph_{para}), 83.7 (s (¹H coupled: dt, ${}^{1}J_{CH} = 159$ Hz, ${}^{3}J_{CH} = 7$ Hz), 1 C, Ph_{para}), 83.7 (s (¹H coupled: dt, ${}^{1}J_{CH} = 7$ Hz), 1 C, Ph_{para}), 83.7 (s (¹H coupled: dt, ${}^{1}J_{CH} = 7$ Hz), 1 C, Ph_{para}), 83.7 (s (¹H coupled: dt, ${}^{1}J_{CH} = 7$ Hz), 1 C, Ph_{para}), 83.7 (s (¹H coupled: dt, ${}^{1}J_{CH} = 7$ Hz), 1 C, Ph_{para}), 83.7 (s (¹H coupled: dt, ${}^{1}J_{CH} = 7$ Hz), 1 C, Ph_{para}), 83.7 (s (¹H coupled: dt, ${}^{1}J_{CH} = 7$ Hz), 1 C, Ph_{para}), 83.7 (s (¹H coupled: dt, ${}^{1}J_{CH} = 7$ Hz), 1 C, Ph_{para}), 83.7 (s (¹H coupled: dt, ${}^{1}J_{CH} = 7$ Hz), 1 C, Ph_{para}), 83.7 (s (¹H coupled: dt, ${}^{1}J_{CH} = 7$ Hz), 1 C, Ph_{para}), 83.7 (s (¹H coupled: dt, ${}^{1}J_{CH} = 7$ Hz), 1 C, Ph_{para}), 83.7 (s (¹H coupled: dt, ${}^{1}J_{CH} = 7$ Hz), 1 C, Ph_{para}), 83.7 (s (¹H coupled: dt, ${}^{1}J_{CH} = 150$ Hz, ${}^{$ ${}^{I}_{JCH} = 179 \text{ Hz}, {}^{2/3}_{JCH} = 6.5 \text{ Hz}), 5 \text{ C, Cp}), 7.6 (s ({}^{1}\text{H coupled: qt, }{}^{1}_{JCH} = 126 \text{ Hz}, {}^{2}_{JCH} = 5 \text{ Hz}), 3 \text{ C, } -CH_2-CH_3), 6.5 (s ({}^{1}\text{H coupled: qt, }{}^{1}_{HCH} = 126 \text{ Hz}, {}^{2}_{JCH} = 5 \text{ Hz}), 3 \text{ C, } -CH_2-CH_3), 6.5 (s ({}^{1}\text{H coupled: qt, }{}^{1}_{HCH} = 126 \text{ Hz}, {}^{2}_{JCH} = 5 \text{ Hz}), 3 \text{ C, } -CH_2-CH_3), 6.5 (s ({}^{1}\text{H coupled: qt, }{}^{1}_{HCH} = 126 \text{ Hz}, {}^{2}_{JCH} = 5 \text{ Hz}), 3 \text{ C, } -CH_2-CH_3), 6.5 (s ({}^{1}\text{H coupled: qt, }{}^{1}_{HCH} = 126 \text{ Hz}), 3 \text{ C, } -CH_2-CH_3), 6.5 (s ({}^{1}\text{H coupled: qt, }{}^{1}_{HCH} = 126 \text{ Hz}), 3 \text{ C, } -CH_2-CH_3), 6.5 (s ({}^{1}\text{H coupled: qt, }{}^{1}_{HCH} = 126 \text{ Hz}), 3 \text{ C, } -CH_2-CH_3), 6.5 (s ({}^{1}\text{H coupled: qt, }{}^{1}_{HCH} = 126 \text{ Hz}), 3 \text{ C, } -CH_2-CH_3), 6.5 (s ({}^{1}\text{H coupled: qt, }{}^{1}_{HCH} = 126 \text{ Hz}), 3 \text{ C, } -CH_2-CH_3), 6.5 (s ({}^{1}\text{H coupled: qt, }{}^{1}_{HCH} = 126 \text{ Hz}), 3 \text{ C, } -CH_2-CH_3), 6.5 (s ({}^{1}\text{H coupled: qt, }{}^{1}_{HCH} = 126 \text{ Hz}), 3 \text{ C, } -CH_2-CH_3), 6.5 (s ({}^{1}\text{H coupled: qt, }{}^{1}_{HCH} = 126 \text{ Hz}), 3 \text{ C, } -CH_2-CH_3), 6.5 (s ({}^{1}\text{H coupled: qt, }{}^{1}_{HCH} = 126 \text{ Hz}), 3 \text{ C, } -CH_2-CH_3), 6.5 (s ({}^{1}\text{H coupled: qt, }{}^{1}_{HCH} = 126 \text{ Hz}), 3 \text{ C, } -CH_2-CH_3), 6.5 (s ({}^{1}\text{H coupled: qt, }{}^{1}_{HCH} = 126 \text{ Hz}), 3 \text{ C, } -CH_2-CH_3), 6.5 (s ({}^{1}\text{H coupled: qt, }{}^{1}_{HCH} = 126 \text{ Hz}), 3 \text{ C, } -CH_2-CH_3), 6.5 (s ({}^{1}\text{H coupled: qt, }{}^{1}_{HCH} = 126 \text{ Hz}), 3 \text{ C, } -CH_2-CH_3), 6.5 (s ({}^{1}\text{H coupled: qt, }{}^{1}_{HCH} = 126 \text{ Hz}), 3 \text{ C, } -CH_2-CH_3), 6.5 (s ({}^{1}\text{H coupled: qt, }{}^{1}_{HCH} = 126 \text{ Hz}), 3 \text{ C, } -CH_2-CH_3), 6.5 (s ({}^{1}\text{H coupled: qt, }{}^{1}_{HCH} = 126 \text{ Hz}), 3 \text{ C, } -CH_2-CH_3), 6.5 (s ({}^{1}\text{H coupled: qt, }{}^{1}_{HCH} = 126 \text{ Hz}), 3 \text{ C, } -CH_2-CH_3), 6.5 (s ({}^{1}\text{H coupled: qt, }{}^{1}_{HCH} = 126 \text{ Hz}), 3 \text{ C, } -CH_2-CH_3), 6.5 (s ({}^{1}\text{H coupled: qt, }{}^{1}_{HCH} =$ ${}^{1}J_{CH} = 119$ Hz), 2 C, SiMe₂), 3.5 (s (${}^{1}H$ coupled: t/br, ${}^{1}J_{CH} = 118$ Hz), 3 C, $-CH_2-CH_3$) ppm. ²⁹Si NMR (0.2 M in C₆D₆): $\delta = +32.2$ (s (¹H coupled: octet), ${}^{2}J_{SiH} = 6.5$ Hz, ${}^{1}J_{SiC(Me)} = 45$ Hz, 1 Si, FpSiMe₂), +1.8 (s, ${}^{1}J_{SiC(Me)} = 54$ Hz, 1 Si, SiEt₃) ppm. IR (hexane): $\nu^{\sim} = 1996$ (s, $\nu(C\equiv 0)$, 1943 (s, $\nu(C\equiv 0)$) cm⁻¹.

Acknowledgement

The authors thank the Deutsche Forschungsgemeinschaft and the Fonds der chemischen Industrie for financial support.

Appendix A. Supplementary material

642194(1), 299782(2), 642198(3), and 642195(4) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Appendix B. Supplementary material

Supplementary data related to this article can be found online at doi:10.1016/j.jorganchem.2012.01.019.

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