Structure and Reactivity of (η^5-Cyclopentadienyl)(triphenylphosphine)-(undecamethylcyclohexasilyl)nickel(II)-Hexane (2/1)

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Dedicated to Professor Hubert Schmidbaur on the occasion of his 75th birthday

The nickel cyclohexasilyl complex $CpNi(PPh_3)Si_6Me_{11}$ was synthesized from nickelocene, triphenylphosphine, and undecamethylcyclohexasilyl potassium and was fully characterized. It shows a relationship between its Si–Si bond lengths and its reactivity towards oxygen. The cleavage of one cyclopentadienyl ligand from nickelocene by silyl anions in the presence of additional ligands opens a promising new pathway to nickel silyl complexes of the type $CpNi(L)$-SiR_3.

Key words: Cyclohexasilyl Complexes, Nickel Silyl Complexes, Nickelocene, Silyl Anions, Structure-Reactivity Relationship

Introduction

Cyclohexasilyl complexes are model compounds to investigate the electronic and steric influences of a metal complex moiety on an oligo- or polysilane backbone. It is known that silicon-silicon bonds are weakened and activated by neighboring transition metal atoms, leading to, *e. g.*, a rearrangement of oligosilyl groups [1, 2]. In order to examine the correlation between the extent of these effects and the nature of the transition metal moiety we became interested in nickel cyclohexasilyl complexes. In this article we report a novel pathway to such compounds starting from nickelocene and silyl anions as well as the structure and reactivity of a complex thus synthesized, namely (η^5-cyclopentadienyl)(triphenylphosphine)(undecamethylcyclohexasilyl)nickel(II), $CpNi(PPh_3)Si_6Me_{11}$ (**1**) [3].

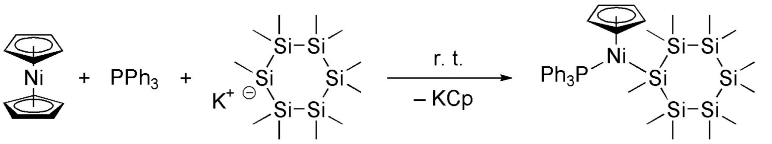
Results and Discussion

Complex **1** is not accessible *via* salt elimination from cyclopentadienyl(triphenylphosphine)nickel chloride, $CpNi(PPh_3)Cl$, and undecamethylcyclohexasilyl potassium, KSi_6Me_{11} [4], although analogous preparations of alkyl, aryl, and alkynyl compounds have been published [5]. Thus, we had to search for a different synthetic pathway.

It is known that one Cp ligand in nickelocene, Cp_2Ni, can be cleaved by organolithium, LiR, or Grignard compounds RMgX, leading to coordinatively unsaturated fragments CpNi-R [6]. If additional ligands L are present, these reactive intermediates form complexes of the type CpNi(L)-R [7, 8], otherwise they decompose to multinuclear nickel complexes [6].

We wondered whether silyl anions would behave analogously, finally leading to nickel silyl complexes $CpNi(L)$-SiR_3. Thus, KSi_6Me_{11} was added at r. t. to a solution of Cp_2Ni and triphenylphosphine PPh_3 in dimethoxyethane (DME) (Scheme 1). Indeed, a color change from dark-green to dark-brown indicated a reaction, and work-up of the mixture gave dark brownish-green crystals which were identified by NMR spectroscopy, elemental analysis, and X-ray diffraction analysis as (η^5-cyclopentadienyl)(triphenylphosphine)(undecamethylcyclohexasilyl)nickel(II)-hexane (2/1), $CpNi(PPh_3)Si_6Me_{11} \cdot 0.5\ C_6H_{14}$ ($\mathbf{1} \cdot 0.5\ C_6H_{14}$), a hexane hemi-solvate of the anticipated complex **1**.

Attempts to improve the rather low yield (20 %) were only of minor success. Lowering the reaction temperature had an adverse effect. At 0 °C the yield was only slightly diminished but at −78 °C no product at all was obtained, although **1** was detected in the reaction mixture by NMR spectroscopy (besides many by-



Scheme 1. Synthesis of **1**.

products). Changing the solvent to toluene gave a small improvement in yield. The use of an excess of PPh_3 (100 %) also led to a slightly improved yield, but the product was contaminated with considerable amounts of triphenylphosphine oxide, Ph_3PO. Thus, the best result was obtained at room temperature with toluene as the solvent and without an excess of PPh_3 (25 % yield).

If the reaction was carried out without PPh_3 (DME or toluene, r. t. or −78 °C), extensive rearrangements and decomposition of the cyclohexasilane ring occured, leading to unidentified silanes (evaluation by ^{29}Si NMR spectroscopy). Undecamethylcyclohexasilane, $Me_{11}Si_6H$, the "acid" corresponding to KSi_6Me_{11}, and bis(undecamethylcyclohexasilyl), $(Me_{11}Si_6)_2$, the oxidation product corresponding to KSi_6Me_{11}, were never observed (neither in experiments with PPh_3). The only identifiable compound in the mixture was potassium cyclopentadienide, KCp, the expected by-product from Cp cleavage of Cp_2Ni. At −78 °C. A deep red-violet color of the reaction mixture, which persisted up to −20 °C and then gradually changed into dark brown upon warming to r. t. (either in experiments with PPh_3), hints at an unstable reaction intermediate. At r. t., the color changes directly from dark-green to dark-brown. In an additional experiment, Cp_2Ni and PPh_3 were treated with $Me_{11}Si_6H$ in hexane, THF, toluene or nonane under reflux conditions. But, except for decomposition of the Cp_2Ni on prolonged heating, no reaction occurred.

From these experiments we conclude that KSi_6Me_{11} behaves analogously to organolithium and Grignard compounds and cleaves one Cp ligand from Cp_2Ni leading to the unstable intermediate cyclopentadienyl-(undecamethylcyclohexasilyl)nickel, $CpNi\text{-}Si_6Me_{11}$, and KCp. Only a minor fraction of this intermediate can be trapped by PPh_3 to give **1**. The main reaction is its decomposition into unidentified nickel complexes and silanes. Redox or acid-base reactions of the silyl anion do not seem to occur.

Compound **1** · 0.5 C_6H_{14} forms dark brownish-green crystals, which are often millimeter-sized. They are soluble in hexane, benzene, and chloroform (in the latter with decomposition). On contact with air they show signs of decomposition only after 6 – 7 d. Solutions are much more air-sensitive and decompose immediately within a few hours. Under the microscope the crystals seemed to be dichroitic: depending on the direction of observation their color was emerald or brownish-green, respectively. On heating in air they decompose at 140 – 145 °C, while under argon they melt at 187 – 190 °C with slow decomposition starting at 176 °C. Curiously, under argon a slow color change from green to dark-brown was observed at 80 – 90 °C which did not occur in air.

The ^{1}H and ^{13}C NMR spectra of **1** are in full agreement with the expected structure except one feature. The ^{1}H NMR peak of the methyl group of the silicon atom bearing the transition metal moiety appeared at −0.47 ppm instead at the expected +0.5 to +1.0 ppm [9]. This strong shielding indicates that this methyl group is influenced by the ring current of the phenyl groups of the PPh_3 ligand, which was confirmed by X-ray single-crystal structure analysis (see below). The ^{31}P NMR spectrum showed a signal at +54.4 ppm which is in the typical range for phosphine complexes [10, 11]. The ^{29}Si NMR spectrum featured four signals in a ratio of 1 : 2 : 2 : 1 at −37.3 ppm, −29.4 ppm, −40.5 ppm, and −42.8 ppm, respectively, typical for cyclohexasilyl complexes [4, 12 – 19]. Three of them were split into doublets by coupling to ^{31}P nuclei, thus clearly indicating the presence of a PPh_3 ligand in the molecule [20].

The UV/Vis spectrum showed a medium-intensive band at 366 nm with a shoulder at 431 nm, and a weak band at 591 nm besides the strong aromatic absorptions between 200 and 300 nm. They correspond to yellow and blue light, respectively, and cause the brownish-green color of **1**.

Complex **1** · 0.5 C_6H_{14} crystallizes in the monoclinic space group type *C*2/*c* with *Z* = 8 (Fig. 1 and Table 1). The Si–Si bond lengths in the cyclohexasilane ring are somewhat elongated in comparison with the unsubstituted dodecamethylcyclohexasilane, Si_6Me_{12}, (234 pm [21], Table 2). The elongation is largest at the transition metal-bearing silicon atom Si1 (5 pm) and vanishes with increasing distance from it. This phenomenon is known [4, 22, 23] but is especially distinct in **1**. Additionally, also the bond to the corresponding

Table 1. Crystal structure data for **1** · 0.5 C_6H_{14}.

Formula	$C_{37}H_{60}NiPSi_6$
M_r	763.07
Crystal size, mm	0.11 × 0.1 × 0.1
Temperature, K	173(2)
Crystal system	monoclinic
Space group	*C*2/*c*
a, Å	29.3739(9)
b, Å	9.8769(3)
c, Å	32.44(1)
β, deg	111.543(2)
V, Å^3	8754.3(5)
Z	8
D_{calcd}, g cm^{-3}	1.16
μ(MoK_α), cm^{-1}	6.7
F(000), e	3272
hkl range	±34, ±11, ±38
θ_{max}, deg	25.00
Refl. measured	149301
Refl. unique	7711
R_{int}	0.0734
Param. refined	440
$R(F)/wR(F^2)$ [$I \geq 2\sigma(I)$]	0.0370 / 0.0891
$R(F)/wR(F^2)$ [all refls.]	0.0641 / 0.0948
GoF (F^2)	1.088
ρ_{fin} (max/min), e Å^{-3}	+0.931 / −0.447

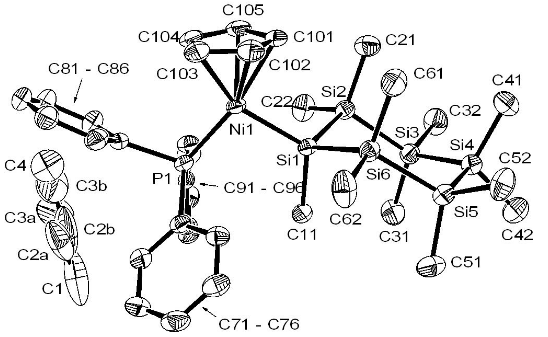


Fig. 1. Molecular structure of **1** · 0.5 C_6H_{14} (ORTEP; displacement ellipsoids at the 50 % probability level, H atoms omitted for clarity).

methyl group (Si1−C11 193 pm) is longer than the other Si–CH_3 bonds (190 – 191 pm). This can be attributed to the activating effect of the transition metal moiety. The Ni−Si bond is markedly longer than the average value of other nickel silyl complexes (229 pm *vs.* 224 pm [24]), probably due to the steric demand of the cyclohexasilyl ligand. All other bond lengths appear in the expected ranges.

The angle P1–Ni1–Si1 between the PPh_3 ligand and the silyl group is 99°. The phosphorus atom and the silicon atom Si1 are distorted tetrahedrally coordinated. The torsion angles C81−P1−Ni1−Si1 and P1−Ni1−Si1−C11 are close to 180° and 0°, respectively, *i. e.* the molecule, apart from the orientation of the phenyl groups and the Cp ligand, has nearly a mirror plane defined by these atoms. As indicated by the ^{1}H NMR spectrum the phenyl groups of the PPh_3 ligand come very close to the methyl group C11 (Fig. 2). Their distance in the solid is below the sum of the van der Waals radii ($d(H_{Me}–C_{Ph})$ = 300 pm, $d(C_{Me}–C_{Ph})$ = 370 pm [25, 26]).

The crystal structure of **1** · 0.5 C_6H_{14} consists of alternating layers of undecamethylcyclohexasilyl rings and transition metal fragments parallel to the crystallographic *ab* plane (Fig. 3). Between the phenyl groups of the PPh_3 ligands remain voids which contain the hexane molecules. However, these solvate molecules are disordered. Obviously, the voids are larger than a hexane molecule so that the molecules can occupy different positions.

Table 2. Selected bond lengths (pm), angles (deg), and dihedral angles (deg) for **1** with estimated standard deviations in parentheses.

Si(1)−Si(2)	239.4(1)	Si(1)−Si(6)	238.8(1)
Si(2)−Si(3)	237.1(1)	Si(5)−Si(6)	235.3(1)
Si(3)−Si(4)	234.4(1)	Si(4)−Si(5)	235.4(1)
Si(1)−C(11)	192.7(2)	Ni(1)−Si(1)	229.4(1)
Ni(1)−P(1)	214.6(1)		
P(1)−Ni(1)−Si(1)	99.0(1)		
Ni(1)−Si(1)−Si(2)	113.2(1)	Si(6)−Si(1)−Si(2)	107.3(1)
Ni(1)−Si(1)−Si(6)	111.0(1)	C(11)−Si(1)−Si(2)	101.0(1)
C(11)−Si(1)−Ni(1)	118.8(1)	C(11)−Si(1)−Si(6)	104.5(1)
C(71)−P(1)−Ni(1)	120.0(1)	C(71)−P(1)−C(81)	99.2(1)
C(81)−P(1)−Ni(1)	110.5(1)	C(91)−P(1)−C(81)	103.8(1)
C(91)−P(1)−Ni(1)	115.7(1)	C(71)−P(1)−C(91)	105.5(1)
P(1)–Ni(1)–Si(1)–C(11)	−3.4(1)		
Si(1)–Ni(1)–P(1)–C(81)	−178.2(1)		

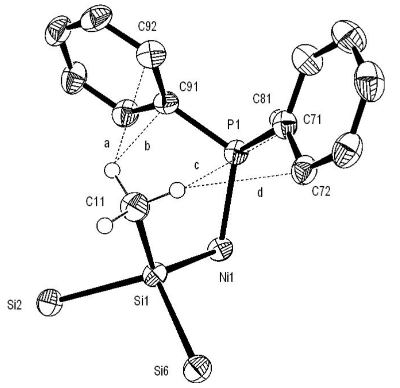


Fig. 2. CH-π interactions between methyl and phenyl groups in **1** · 0.5 C_6H_{14}. Distances (pm) involved: $d(H_{Me}–C_{Ph})/d(C_{Me}–C_{Ph})$: *a* = 285 / 362, *b* = 289 / 354, *c* = 303 / 368, *d* = 264 / 347 (ORTEP; displacement ellipsoids 50 %).

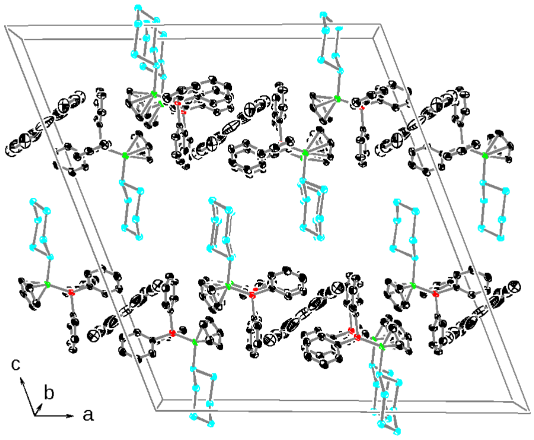
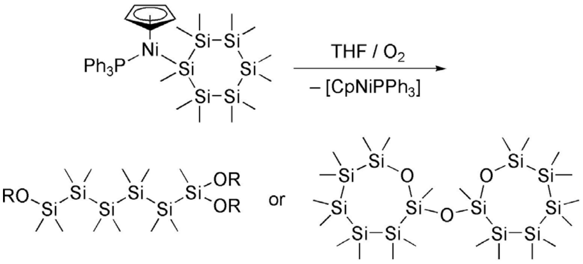


Fig. 3. Crystal structure of $\mathbf{1} \cdot 0.5\ C_6H_{14}$. View of the unit cell along the *b* axis (ORTEP; H atoms and methyl groups omitted for clarity; displacement ellipsoids 50 %).

The observed Si–Si bond elongation at Si1 corresponds to an increased reactivity of these bonds towards oxygen [3]. If a solution of **1** in THF was exposed to the air, the NMR spectra showed that decomposition had started immediately, and the green solution turned yellow within two days. In wet THF the solution of **1** was decolorized within one day. Water without oxygen had no effect on the stability of **1** in THF. The ^{29}Si NMR spectrum of the final solutions (with and without added water) showed six signals of equal intensity with no coupling to phosphorus (+7.0 ppm, −8.4 ppm, −42.2 ppm, −42.7 ppm, −46.7 ppm, −49.6 ppm). Thus, we conclude that the cyclohexasilane ring was oxidatively opened at the NiSi–Si bond, and a nickel- and phosphorus-free linear or cyclic silane with two different chain ends had formed. Based on its ^{29}Si NMR data it is assigned the composition $ROMe_2Si\text{-}(SiMe_2)_4\text{-}SiMe(OR)_2$ (Scheme 2) [27]. Unfortunately, the product could not be isolated, and a comprehensive characterization was not possible.

Conclusion

The cleavage of one cyclopentadienyl ligand from nickelocene by silyl anions in the presence of additional ligands opens a promising new pathway to nickel silyl complexes of the type $CpNi(L)\text{-}SiR_3$. Its usefulness was demonstrated by the synthesis of cyclopentadienyl(triphenylphosphine)(undecamethylcyclohexasilyl)nickel, $CpNi(PPh_3)Si_6Me_{11}$ (**1**), from nickelocene, triphenylphosphine, and undecamethylcyclohexasilyl potassium. However, further investigations to improve the yield of the products and to study the applicable range of substituted nickelocenes, ligands, and silyl anions will be necessary. Complex **1** shows a selective ring cleavage reaction with oxygen which was correlated to the Si–Si bond lengths in its solid-state structure, thus establishing a structure-reactivity relationship.



Scheme 2. Proposed oxidative cleavage of **1** (R = H, alkyl, silyl).

Experimental Section

All operations were carried out under an atmosphere of dry purified argon using Schlenk or glovebox techniques. Solvents were dried by distillation from the following reagents and stored under argon prior to use: Na/benzophenone-ketyl (tetrahydrofuran THF, 1,2-dimethoxyethane DME, toluene, hexane), CaH_2 ([D_6]acetone, $CDCl_3$, nonane), $LiAlH_4$ (pentane), Na/K alloy (C_6D_6). Cp_2Ni [28] and KSi_6Me_{11} [29] were prepared according to published procedures. PPh_3 was laboratory stock from Lachema (Brno) / Chemapol (Prague).

Melting points were determined in sealed capillaries (under argon) and between thin glass plates (in air) on a Boëtius-type heating microscope. The heating rate was about 4 K min^{-1}. Elemental analyses were performed on a CHN-O-Rapid instrument (Heraeus). NMR spectra were measured on a DPX 400 Avance spectrometer (Bruker) at 22 °C with tetramethylsilane Me_4Si (TMS) as internal standard for ^{1}H, ^{13}C, and ^{29}Si. The external standard for ^{31}P was 85 % phosphoric acid [10]. IR spectra were recorded on a Specord M 82 (VEB Carl Zeiss Jena) or a Nicolet 510 spectrometer. Samples were examined in KBr disks. UV/Vis spectra were recorded on a Specord S 100 instrument (Analytik Jena AG) in the range 190 to 1000 nm.

All reactions were monitored by NMR spectroscopy. Assignments were made by comparison of the spectra among each other and with literature data [4, 12 – 19, 27]. The IR bands were assigned based on literature data [30 – 38].

*(η^5-Cyclopentadienyl)(triphenylphosphine)(undecamethylcyclohexasilyl)nickel(II)–hexane (2/1) (**1** · 0.5 C_6H_{14})*

Cp_2Ni (97 mg, 0.51 mmol) and PPh_3 (135 mg, 0.51 mmol) were dissolved in DME (10 mL), and KSi_6Me_{11}

in DME (13.5 mL 0.037 M solution, 0.50 mmol) was added dropwise at r. t., whereupon the green solution turned dark-brown. After 1 d the solvent was removed *in vacuo* and the dark brown residue extracted with hexane (5 × 5 mL). The combined extracts were concentrated to 5 mL and cooled slowly to −20 °C. The precipitated dark brownish-green crystals were separated, washed with pentane (2 × 1 mL), and dried *in vacuo*. They can be handled in air but should be stored under argon. Yield: 75 mg (0.10 mmol, 20 %). – M. p.: 140–145 °C (dec., air), 187–190 °C (see text, argon). – $C_{34}H_{53}NiPSi_6 + 0.5 \cdot C_6H_{14} = C_{37}H_{60}NiPSi_6$ (719.978 + 0.5 · 86.178 = 763.067): calcd. C 58.24, H 7.93; found C 58.07, H 7.98. – ^{1}H NMR (400.13 MHz, 0.031 M in C_6D_6) [39]: δ = 7.61 (m, 6 H, Ph_{ortho}), 7.05 (m, 9 H, $Ph_{meta+para}$), 5.22 (s, $^1J_{HC}$ = 174 Hz, 5 H, Cp), 1.23 (m, 4 H, hexane), 0.89 (t, $^3J_{HH}$ = 6.9 Hz, 3 H, hexane), 0.59 (s, 6 H, SiMe), 0.58 (s, 6 H, SiMe), 0.33 (s, 6 H, SiMe), 0.32 (s, 3 H, Si_δMe), 0.23 (s, 3 H, Si_δMe), 0.18 (s, 6 H, SiMe), −0.47 (d, $^4J_{HP}$ = 1.6 Hz, 3 H, Si_αMe). – ^{13}C NMR (100.63 MHz, 0.031 M in C_6D_6): δ = 136.7 (d, $^1J_{CP}$ = 44 Hz, 3 C, Ph_{ipso}), 134.4 (d, $^2J_{CP}$ = 12 Hz, 6 C, Ph_{ortho}), 129.8 (s, 3 C, Ph_{para}), (Ph_{meta} hidden by solvent), 90.8 (d, $^2J_{CP}$ = 1.5 Hz, 5 C, Cp), 31.9 (s, 1 C, hexane), 23.0 (s, 1 C, hexane), 14.3 (s, 1 C, hexane), 0.04 (s, 2 C, SiMe), −1.5 (d, $^3J_{CP}$ = 10 Hz, 1 C, Si_αMe), −2.3 (s, 2 C, SiMe), −4.3 (s, 2 C, SiMe), −4.7 (s, 1 C, Si_δMe), −5.7 (s, 2 C, SiMe), −6.2 (s, 1 C, Si_δMe). – ^{13}C NMR (100.63 MHz, [D$_6$]acetone): δ = 137.0 (d, $^1J_{CP}$ = 44 Hz, 3 C, Ph_{ipso}), 134.9 (d, $^2J_{CP}$ = 12 Hz, 6 C, Ph_{ortho}), 130.7 (s, 3 C, Ph_{para}), 128.8 (d, $^3J_{CP}$ = 10 Hz, 6 C, Ph_{meta}), 91.0 (d, $^2J_{CP}$ = 1.5 Hz, 5 C, Cp), 32.3 (s, 1 C, hexane), 23.3 (s, 1 C, hexane), 14.3 (s, 1 C, hexane), 0.0 (s, 2 C, SiMe), −1.5 (d, $^3J_{CP}$ = 9 Hz, 1 C, Si_αMe), −2.4 (s, 2 C, SiMe), −4.3 (s, 2 C, SiMe), −4.7 (s, 1 C, Si_δMe), −5.9 (s, 2 C, SiMe), −6.3 (s, 1 C, Si_δMe). – ^{29}Si NMR (79.49 MHz, 0.031 M in C_6D_6): δ = −29.4 (d, $^3J_{SiP}$ = 1.8 Hz, 2 Si, Si_β), −37.3 (d, $^2J_{SiP}$ = 32 Hz, 1 Si, Si_α), −40.5 (d, $^4J_{SiP}$ = 1.5 Hz, 2 Si, Si_γ), −42.8 (s, 1 Si, Si_δ). – ^{31}P NMR (161.98 MHz, 0.031 M in C_6D_6): δ = 54.4 (s). – IR (KBr): ν = 3070 (w, $\nu(CH_{Cp/Ph})$), 3051 (w, $\nu(CH_{Cp/Ph})$), 2945 (m, $\nu_{as}(CH_3)$), 2888 (m, $\nu_s(CH_3)$), 2790 (vw, ν(CH)), 1479 (m, $\nu(C{=}C_{Ph})$), 1434 (s, $\nu(C{=}C_{Ph})$), 1403 (m, $\nu(C{=}C_{Cp}) + \delta_{as}(SiCH_3)$), 1348 (w), 1310 (vw), 1242 (s, $\delta_s(SiCH_3)$), 1184 (vw), 1156 (vw), 1096 (m, $\delta(CH_{Ph})$), 1050 (vw), 1030 (vw/sh), 1016 (w, $\delta(CH_{Cp})$), 999 (vw), 990 (vw), 887 (w), 837 (m, $\rho(SiCH_3)$), 827 (m/sh), 801 (s, $\gamma(CH_{Cp}) + \rho(SiCH_3)$), 782 (s, $\rho(SiCH_3)$), 763 (m, $\rho(SiCH_3)$), 746 (m, $\gamma(CH_{Ph})$), 732 (m/sh), 696 (s, $\gamma(CH_{Ph})$), 650 (s, ν(SiC ?)), 596 (vw), 534 (s, $NiPPh_3$), 511 (m, $NiPPh_3$), 492 (m, $NiPPh_3$), 460 (w), 420 (w) cm^{-1}. – UV/Vis (hexane): λ_{max} (lg ε_{max}) = 215 nm (4.48), 227 nm (sh, 4.43), 273 nm (sh, 4.11), 366 nm (br, 3.80), 431 nm (br/sh, 3.38), 591 nm (br, 2.18).

Crystal structure determination

The crystal structure of **1** was determined on a Bruker-Nonius X8 diffractometer with an APEX2-CCD detector using MoK_α radiation. Suitable single crystals were grown from hexane at 5 °C. The structure was solved by Direct Methods (SHELXTL) and refined with full-matrix least-squares on F^2 (SHELXTL) [40]. Non-H atoms were refined anisotropically while H atoms were considered in idealized positions (riding model). The hexane molecule was found to be disordered. Graphical representations were created with ORTEP-32 [41].

CCDC 255854 contains 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.

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[39] Abbreviations: as – asymmetric; br – broad; d – doublet; δ - bending vibration; γ – wagging vibration; m – medium (IR), multiplet (NMR); ν – stretching vibration; ρ – rocking vibration; s – singlet (NMR), strong (IR), symmetric (IR); sh – shoulder; vw – very weak; w – weak; ? – assignment ambiguous; $Si_{\alpha,\beta,\gamma,\delta}$ - position of the Si atoms in substituted oligosilanes referring to the substituent.

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