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(Phenylthiomethyl)silanes and (butyltelluromethyl)silanes as novel bifunctional ligands for the construction of dithioether-, ditelluroether- and transition metal-silicon complexes

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Dedicated to Pierre Braunstein.

Abstract

The functionalized silanes (PhSCH₂)₂SiPh₂ (1a), (PhSCH₂)₂Si(vinyl)Me (1b), (PhSCH₂)₂Si(H)Me (1c) and (PhSCH₂)₃SiH (1d) have been prepared and co-ordinated as chelating dithioether ligands or via a covalent M–Si bond to various transition metal centers. Thus, reaction of 1a with [PtCl₂(PhCN)₂] affords the dithioether complex *cis*-[PtCl₂{(PhSCH₂)₂SiPh₂}] (3), which exist in solution as mixtures of DL- and *meso*-invertomers. Treatment of [Re(μ -Br)(CO)₃THF]₂ with 1a-c yielded the stereochemically rigid chelate complexes *fac*-[ReBr(CO)₃{(PhSCH₂)₂SiR¹R²}] (R¹, R² = Ph (4a)), (R¹ = vinyl, R² = Me (4b)), (R¹ = H, R² = Me (4c)). Due to the presence of two different substituents R¹ and R² on Si, 4b and 4c are isolated as 50:50 mixtures of diastereomers. The presence of a Si-H function in 1c,d can be exploited for Si-H activation reactions. Thus, oxidative addition on [Pt(PPh₃)₂(CH₂=CH₂)] yields the fluxional hydrido silyl complex [Pt(H)(PPh₃)₂{Si(CH₂SPh)₂Me}] (5a) and the rigid derivative [Pt(H)(PPh₃)₂{Si(CH₂SPh)₃] (5b). The ditelluroether complexes *cis*-[PtCl₂{(RTeCH₂)₂SiMe₂] (6a, R = Ph), (6b, R = n-Bu) are obtained by treatment of [PtCl₂(PhCN)₂] with (PhTeCH₂)₂SiMe₂ (2a) and (n-BuTeCH₂)₂SiMe₂ (2b), respectively. The complex *fac*-[ReBr(CO)₃{(n-BuTeCH₂)₂SiMe₂] (7) results from the reaction of [Re(μ -Br)(CO)₃THF]₂ with (2b). The new compounds have been studied by multinuclear NMR techniques, the crystal structures of 3, 4a, 5 and 6b have been determined by X-ray diffraction studies.

Keywords: Silyl complexes; Platinum; Rhenium; Dithioether complexes; Ditelluroether complexes

1. Introduction

Thioether ligands SR_2 co-ordinated on transition metal centers are in general easily substituted by other donor molecules. Incorporation of the thioether function in a chelating ligand system may significantly enhance the stability of the dative $M \leftarrow SR_2$ bond. Numerous literature known dithioether ligands $R_2SX_nSR_2$ contain mostly CH₂-groups as spacer units. More recently, chiral dithioether complexes have been successfully used in homogeneous catalysis [1,2]. Another recent domain, where dithioether complexes were investigated are bioinorganic chemistry and biomedical applications [3–5]. Two possibilities exist to fine-tune the steric and electronic properties of this ligand system: (i) modification of the SR end groups and/or (ii) variation of the length and kind of the spacer units between the two sulfur atoms. Thus, the significant influence of the number of methylene groups in complexes ligated by dithioether ligands $R_2S(CH)_nSR_2$ on the conformation and molecular structure has been extensively studied [6]. In the context of our work on organosilicon compounds [7–9] and transition metal silyl complexes, [10–13] we have prepared a series of organosilanes functionalized by phenylthiomethyl

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PhSCH₂-, phenyltelluromethyl PhTeCH₂- and butyltelluromethyl BuTeCH₂-substituents. In order to evaluate the influence of silicon in these potentially chelating ligand systems of the type $R-E-CH_2-SiR_2-CH_2-E-R$ (E = S, Te) for coordination chemistry, we have undertaken a study to ligate these dithioether and ditelluroether on various transition metals. An additional aspect of this study was the utilization of dithioether ligands bearing potentially reactive groups like Si-H or Si-vinyl functions. During this work was in progress, a paper of Rheingold and Rabinovich describing the coordination of the very related tridentate thioether (PhSCH₂)₃SiMe (which has been independently prepared by us [9]), on a Cr(CO)₃ fragment appeared [14].

2. Experimental

All reactions were performed in Schlenk-tube flasks under purified nitrogen. Solvents were dried and distilled under nitrogen before use, toluene and hexane over sodium, dichloromethane from P_4O_{10} . Nitrogen was passed through BASF R3-11 catalyst and molecular sieve columns to remove residual oxygen and water. IR spectra have been recorded on a Nicolet Nexus 470 spectrometer. Elemental C, H analyses were performed on a Leco Elemental Analyzer CHN 900. The ¹H, $^{13}C{^{1}H}, ^{31}P{^{1}H}, ^{125}Te{^{1}H}$ and $^{29}Si{^{1}H}$ NMR spectra were recorded at 200.13, 50.32, 81.01, 63.16 and 39.76 MHz, respectively, on a Bruker ACP 200 instrument and a Bruker Avance 300 instrument (300.13 MHz for ¹H). ¹⁹⁵Pt chemical shifts were measured on a Bruker ACP 200 instrument (42.95 MHz) and externally referenced to K₂PtCl₄ in water with downfield chemical shifts reported as positive. NMR spectra were recorded in pure CDCl₃, unless otherwise stated. The reactions were generally monitored by IR spectroscopy in the v(CO) region for the rhenium derivatives.

2.1. Preparations

2.1.1. Preparation of $(PhSCH_2)_2SiHMe$ (1c) and $(PhSCH_2)_3SiH$ (1d)

A cooled solution of 0.24 mol of (phenylthiomethyl)lithium in 200 ml of diethyl ether-hexane, prepared from thioanisole and n-BuLi in diethyl ether, was added at -40 °C to a solution of 0.08 mol of trichlorosilane or 0.12 mol of methyldichlorosilane in 30 ml of diethyl ether. The reaction mixture was warmed to room temperature (r.t.) and filtered. The solvent was evaporated in vacuo, and the residue was purified by Kugelrohr distillation.

2.1.1.1. Compound 1c. Anal. Calc. for $C_{15}H_{18}SiS_2$ (290.5): C, 62.02; H, 6.24. Found: C, 61.7; H, 6.3%. ¹H NMR: $\delta = 0.34$ (d, 3H, SiCH₃, ³ $J_{H,H} = 3.3$ Hz, ²*J*_{H,Si} = 7.2 Hz), 2.35, 2.38 (AB-system, 4H, SiCH₂S *J*_{AB} = 12.5 Hz, ³*J*_{H,H} = 3.1 Hz), 4.19 (m, 1H, SiH, ³*J*_{H,H} = 3.3 Hz), 7.0–7.35 (m, 10 H; SC₆H₅). ¹³C{¹H} NMR: δ = -6.3 (SiCH₃), 14.4 (2 C) (SiCH₂S), 125.2 (2 C) (C-4 of SC₆H₅), 126.8 (4 C), 128.8 (4 C) (C-2/C-6 and C-3/C-5 of SC₆H₅), 138.9 (2 C) (C-1 of SC₆H₅). ²⁹Si{¹H} NMR: δ = -14.0.

2.1.1.2. Compound 1d. Anal. Calc. for $C_{21}H_{22}SiS_3$ (398.7): C, 63.27; H, 5.56. Found: C, 63.1; H, 5.8%. ¹H NMR: $\delta = 2.45$ (d, 6H, SiCH₂S, ³J_{H,H} = 3.1 Hz), 4.24 (septuplet, 1H, SiH, ³J_{H,H} = 3.1 Hz), 7.0–7.35 (m, 15 H; SC₆H₅). ¹³C{¹H} NMR: $\delta = 12.9$ (3 C) (SiCH₂S), 125.5 (3 C) (C-4 of SC₆H₅), 127.2 (6 C), 128.9 (6 C) (C-2/ C-6 and C-3/C-5 of SC₆H₅), 138.2 (3 C) (C-1 of SC₆H₅). ²⁹Si{¹H} NMR: $\delta = -14.6$.

2.1.2. Preparation of $(PhTeCH_2)_2SiMe_2$ (2a) and $(BuTeCH_2)_2SiMe_2$ (2b)

A cooled solution of 0.16 mol of RTeLi (R = phenyl, butyl) in 200 ml of THF-hexane, prepared from Te and n-BuLi or PhLi in THF, was added at -78 °C to a solution of 0.08 mol of bis(chloromethyl)dimethylsilane in 60 ml of THF. The reaction mixture was warmed to r.t., the solvent removed in vacuo and the reaction mixture extracted with hexane. The solvent was evaporated in vacuum, and the oily residue was purified by Kugelrohr distillation.

2.1.2.1. Compound 2a. Boiling point (b.p.): $151 \circ C/10^{-3}$ mm (oven temperature); yellowish oil. Yield 81%. Anal. Calc. for C₁₆H₂₀SiTe₂ (476.5): C, 38.77; H, 4.07. Found: C, 38.90; H, 4.0%. ¹H NMR: $\delta = 0.23$ (s, 6H, SiCH₃, ²J_{H,Si} = 6.4 Hz), 2.13 (s, 4H, TeCH₂Si, ²J_{H,Te} = 11.7 Hz, ²J_{H,Si} = 4.9 Hz), 7.1–7.75 (m, 10 H; TeC₆H₅). ¹³C{¹H} NMR: $\delta = -9.9$ (s, SiCH₂Te, ¹J_{C,Te} = 174 Hz, ¹J_{C,Si} = 50 Hz, ³J_{C,Te} = 6.4 Hz), -0.9 (s, SiCH₃, ¹J_{C,Si} = 54 Hz, ³J_{C,Te} = 9 Hz), 113.1 (C-1 of TeC₆H₅, ¹J_{C,Te} = 291 Hz), 127.2 (C-4 of TeC₆H₅), 129.1 (C-3 of TeC₆H₅), 137.0 (C-2 of TeC₆H₅, ²J_{C,Te} = 22 Hz). ¹²⁵Te{¹H} NMR: $\delta = 365.5$. ²⁹Si{¹H} NMR: $\delta = 5.9$ (s, ²J_{Si,Te} = 24 Hz).

2.1.2.2. Compound **2b.** B.p.: $140 \text{ °C}/10^{-3}$ mm (oven temperature); yellowish oil. Yield 87%. Anal. Calc. for $C_{12}H_{28}SiTe_2$ (455.6): C, 31.63; H, 6.19. Found: C, 31.91; H, 6.10%. ¹H NMR: $\delta = 0.14$ (s, ${}^{2}J_{H,Si} = 6.5$ Hz, 6 H; SiCH₃), 0.87 (t, 6H, n-butyl- CH_3 , ${}^{3}J_{H,H} = 14.6$ Hz), 1.2–1.5 (m, 4H, n-butyl- CH_2CH_3), 1.5–1.8 (m, 4H, n-butyl- $CH_2CH_2CH_3$), 1.5–1.8 (m, 4H, n-butyl- $CH_2CH_2CH_3$), 1.5–1.8 (m, 4H, n-butyl- $CH_2CH_2CH_2CH_3$, ${}^{3}J_{H,H} = 15.1$ Hz). ¹³C{¹H} NMR: $\delta = -16.2$ (${}^{1}J_{C,Te} = 171.0$ Hz, ${}^{1}J_{C,Si} = 51.0$ Hz, ${}^{3}J_{C,Te} = 7$ Hz; SiCH₂Te), -1.1 (${}^{1}J_{C,Si} = 54$ Hz, ${}^{3}J_{C,Te} = 8.4$ Hz; SiCH₃), 4.4 (${}^{1}J_{C,Te} = 155$ Hz; TeCH₂C), 13.4 (CCH₃), 25.0 (${}^{3}J_{C,Te} = 11.0$ Hz, CCH₂CH₃), 33.9 (${}^{2}J_{C,Te} = 10.4$ Hz, TeCH₂CH₂C). ${}^{125}Te\{{}^{1}H\}$ NMR: $\delta = 143.1$. ${}^{29}Si\{{}^{1}H\}$ NMR: $\delta = 5.6$ (${}^{2}J_{Si,Te} = 23$ Hz).

2.1.3. Preparation of $PtCl_2\{(PhSCH_2)_2SiPh_2\}$ (3)

To a suspension of $[PtCl_2(PhCN)_2]$ (471.8 mg, 1 mmol) in 8 ml of toluene was added **1a** (428 mg, 1 mmol). The solution was stirred at 75 °C for 48 h. The solvent then was removed under reduced pressure and the residue rinsed with hexane. Recrystallization from dichloromethane-hexane gave yellow crystals, which were filtered off and dried under vacuum (619 mg, 89% yield). *Anal.* Calc. for C₂₆H₂₄Cl₂PtS₂Si (695.69): C, 44.96; H, 3.46. Found: C, 44.77; H, 3.65%. ¹H NMR (233K): invertomer I δ = 3.64 (d, 2H, H_A, ²J_{H_A,H_B = 13.4 Hz), 3.06 (d, 2H, H_B, ²J_{H_A,H_B = 13.4 Hz). Invertomer II δ = 2.90 (d, 2H, H_A, ²J_{H_A,H_B = 13.8 Hz), 3.06 (d, overlapped with the signal of H_A of invertomer I). ¹⁹⁵Pt{¹H} NMR: δ = -2167 (s, Pt), -2197 (s, Pt).}}}

2.1.4. Preparation of ReBr(CO)₃{(PhSCH₂)₂SiPh₂} (4a)

[Re(μ-Br)(CO)₃THF]₂ (84 mg, 0.1 mmol) was dissolved in 10 ml of dichloromethane and **1a** (86 mg, 0.2 mmol) was added to the solution. The reaction mixture was stirred at r.t. for 45 min and then concentrated to approximately 4 ml under reduced pressure. Addition of hexane gave a white powder, which was filtered off and dried under vacuum (120 mg, 77% yield). *Anal.* Calc. for C₂₉H₂₄BrO₃ReS₂Si (778.1): C, 44.72; H, 3.08. Found: C, 44.33; H, 3.25%. IR (KBr): ν (CO): 2035s, 1942s, 1897s cm⁻¹. ¹H NMR: δ = 2.83 (d, H_A, 2H, ²J_{H_A,H_B} = 12.2 Hz), 4.29 (d, H_A, 2H, ²J_{H_A,H_B} = 12.2 Hz). ²⁹Si{¹H} NMR: δ = -13.9 (s, Si).

2.1.5. Preparation of

$ReBr(CO)_3\{(PhSCH_2)_2Si(CH_3)(CH = CH_2)\}$ (4b and 4b')

[Re(μ-Br)(CO)₃THF]₂ (100 mg, 0.118 mmol) was dissolved in 5 ml of dichloromethane and **1b** (82 μl, 0.26 mmol) was added to the solution. After stirring at r.t. for 1 h, the solvent was removed under vacuum and the oily residue was washed with petroleum ether. The product was obtained as a white powder, which was dried in vacuum (116 mg, 74% yield). *Anal.* Calc. for C₂₀H₂₀BrO₃ReS₂Si (666.1): C, 36.03; H, 3.00. Found: C, 35.82; H, 3.21%. IR (KBr): ν (CO): 2034s, 1942s, 1888s cm⁻¹. ¹H NMR: δ = 2.42 (d, 2H, H_A, ²J_{H_A,H_B} = 11.9 Hz) and 3.89 (d, 2H, H_B, ²J_{H_A,H_B} = 11.9 Hz); δ = 2.56 (d, 2H, H_A, ²J_{H_A,H_B} = 11.9 Hz) and 3.72 (d, 2H, H_B, ²J_{H_A,H_B} = 11.9 Hz), 0.48 (s, 3H, CH₃), 0.53 (s, 3H, CH₃), 5.96–6.33 (m, 6H, CH=CH₂).

2.1.6. Preparation of

$ReBr(CO)_3\{(PhSCH_2)_2Si(CH_3)H\}$ (4c and 4c')

 $[\text{Re}(\mu-\text{Br})(\text{CO})_3\text{THF}]_2$ (84 mg, 0.1 mmol) was dissolved in 10 ml of dichloromethane and **1c** (63.8 µl, 0.22 mmol) was added to the solution. The reaction mixture was stirred at r.t. for 45 min and then concentrated to approximately 3 ml under reduced pressure. Addition of

hexane gave a white powder, which was filtered off and dried under vacuum (35 mg, 27% yield). *Anal.* Calc. for $C_{18}H_{18}BrO_3ReS_2Si$ (640.1): C, 33.75; H, 2.83. Found: C, 33.91; H, 3.04%. IR (CH₂Cl₂): v(Si-H): 2159m, v(CO): 2036s, 1946s, 1908s cm⁻¹. (KBr): v(Si-H): 2148w, v(CO): 2028s, 1940s, 1886s cm⁻¹. ¹H NMR: $\delta = 0.46$ (d, 3H, CH₃Si, ³ $J_{H,H} = 3.5$ Hz), 0.53 (d, 3H, CH₃Si, ³ $J_{H,H} = 3.8$ Hz), 3.78 (m, H_A), 2.45 (m, H_B), 4.32 (m, 1H, Si-H), 4.48 (m, 1H, Si-H). ²⁹Si{¹H} NMR: $\delta = -21.92$ (s, Si).

2.1.7. Preparation of

$PtH\{(PhSCH_2)_2Si(CH_3)\}(PPh_3)_2(5a)$

To a solution of $[Pt(PPh_3)_2(C_2H_4)]$ (750 mg, 1 mmol) in 10 ml of toluene was added 1c (348 µl, 1.2 mmol). The solution was stirred at r.t. for 20 min and then concentrated to approximately 3 ml under reduced pressure. Crystallization in toluene–hexane gave a pale yellow powder, which was filtered off and dried under vacuum (911 mg, 90% yield). *Anal.* Calc. for $C_{51}H_{48}P_2PtS_2Si$ (1010.19): C, 60.64; H, 4.8. Found: C, 60.39; H, 5.01%. IR (KBr, cm⁻¹): v(Pt-H): 2066w. ¹H NMR: $\delta = -0.04$ (d, 3H, CH₃, ${}^{3}J_{Pt,H} = 27$ Hz, ${}^{4}J_{P,H} =$ 2.4 Hz), 2.16 (d, 2H, H_A, ${}^{2}J_{H_A,H_B} = 11.0$ Hz), 2.27 (d, 2H, H_B, ${}^{2}J_{H_A,H_B} = 11.0$ Hz), -2.66 (dd, 1H, PtH, ${}^{2}J_{P,H} = 19.6$ Hz, ${}^{2}J_{P,H} = 152.7$ Hz, ${}^{1}J_{Pt,H} = 972.3$ Hz). ${}^{13}C{}^{1}H{}$ NMR: $\delta = 2.6$ (s, C, CH₃, ${}^{2}J_{Pt,C} = 67$ Hz), 23.4 (s, 2C, CH₂, ${}^{2}J_{Pt,C} = 94$ Hz). ${}^{31}P{}^{1}H{}$ NMR (243 K): $\delta = 30.8$ (d, P, PPh₃, ${}^{2}J_{P,P} = 13$ Hz, ${}^{1}J_{Pt,P} = 2509$ Hz), 33.2 (d, P, PPh₃, ${}^{2}J_{P,P} = 13$ Hz, ${}^{1}J_{Pt,P} = 1682$ Hz). ${}^{195}Pt{}^{1}H{}$ NMR (C₆D₆): $\delta = -3410$ (dd, Pt, ${}^{1}J_{Pt,P} =$ 1647 Hz, ${}^{1}J_{Pt,P} = 2531$ Hz).

2.1.8. Preparation of $PtH\{(PhSCH_2) (5b)\}$

Compound **5b** was obtained in an analogous manner by reaction of [Pt(PPh₃)₂(C₂H₄)] with **1d** and isolated in 48% yield. *Anal.* Calc. for C₅₇H₅₂P₂PtS₂Si (1118.33): C, 61.22; H, 4.69. Found: C, 61.18; H, 4.86%. ¹H NMR: $\delta = 2.41$ (s, 6H, CH₂, ³J_{Pt,H} = 23.5 Hz), -3.21 (dd, 1H, PtH, ²J_{P,H} = 21.2 Hz, ²J_{P,H} = 155.3 Hz, ¹J_{Pt,H} = 934.5 Hz). ³¹P{¹H} NMR: $\delta = 29.8$ (d, P, PPh₃, ²J_{P,P} = 14 Hz, ¹J_{Pt,P} = 2518 Hz), 31.0 (d, P, PPh₃, ²J_{P,P} = 14 Hz, ¹J_{Pt,P} = 1756 Hz). ¹⁹⁵Pt{¹H} NMR (C₆D₆): $\delta = -3570$ (dd, Pt, ¹J_{Pt,P} = 2522 Hz, ¹J_{Pt,P} = 1757 Hz).

2.1.9. Preparation of $PtCl_2(PhTeCH_2)_2SiMe_2$ (6a)

A solution of $[Pt(Cl)_2(PhCN)_2]$ (236 mg, 0.5 mmol) in 10 ml of CH₂Cl₂ was treated with **2a** (428 mg, 0.5 mmol) and stirred for 1 day at ambient temperature. All volatiles were removed under reduced pressure and the residue rinsed with hexane. Recrystallization from CH₂Cl₂-hexane gave a yellow microcystalline powder, which was filtered off and dried under vacuum (339 mg, 89% yield). *Anal.* Calc. for C₁₆H₂₀Cl₂PtSiTe₂ (761.62): C, 25.23; H, 2.65. Found: C, 25.45; H, 2.67%.

2.1.10. Preparation of $[PtCl_2(BuTeCH_2)_2SiMe_2)$ (6b)

A solution of [Pt(Cl)₂(PhCN)₂] (471.8 mg, 1 mmol) in 10 ml of CH₂Cl₂ was treated with **2b** (456 mg, 1 mmol). and stirred for 1 day at ambient temperature. All volatiles were removed under reduced pressure and the residue rinsed with hexane. Recrystallization from CH₂Cl₂-hexane gave air stable orange-yellow crystals (512 mg, 71% yield). *Anal.* Calc. for C₁₂H₂₈Cl₂PtSiTe₂ (721.64): C, 19.97; H, 3.91. Found: C, 19.99; H, 3.83%. ¹H NMR: $\delta = 0.23$ (s, SiMe), 0.25 (s, SiMe₂), 0.29 (s, SiMe), 0.87 (t, n-butyl-CH₃), 1.38 (m, n-butyl-CH₂CH₃), 1.70 (m, n-butyl-CH₂CH₂CH₃), 1.85 (m, nbutyl-CH₂CH₂CH₂CH₃), 3.10 (m, TeCH₂Si). ¹⁹⁵Pt{¹H} NMR: $\delta = -2652$ (s, ¹J_{Pt,Te} = 1063 Hz), -2665 (s). ¹²⁵Te{¹H} NMR: $\delta = 436.7$ (s), 398.8 (s, ¹J_{Pt,Te} = 1063 Hz). ²⁹Si{¹H} NMR: $\delta = 11.0$ (s), 7.1 (s) (²J_{Si,Te} = 21 Hz).

2.1.11. Preparation of $ReBr(CO)_3\{(n-BuTeCH_2)_2SiMe_2\}$ (7)

To a solution of $[\text{Re}(\mu-\text{Br})(\text{CO})_3\text{THF}]_2$ (84 mg, 0.1 mmol) in 10 ml of dichloromethane was added **2b** (91 mg, 0.2 mmol). The reaction mixture was stirred at r.t. for 15 min and then concentrated to 2 ml under reduced pressure. Addition of hexane gave a white powder, which was filtered off and dried under vacuum (111 mg, 69% yield). *Anal.* Calc. for C₁₅H₂₈BrO₃ReSiTe₂ (805.78): C, 22.36; H, 3.50. Found: C, 22.69; H, 3.65%. IR (CH₂Cl₂): *v*(CO): 2022vs, 1933s, 1886vs cm⁻¹.

2.2. Crystal structure determinations

A suitable crystal of each complex was mounted in a glass capillary and used for X-ray crystal structure determinations at 293(2) K. Data of 3 and 6b were collected on a Siemens AED2 diffractometer using graphite-monochromated Mo K α radiation ($\lambda =$ 0.71069 Å). The intensities were collected using $\Omega - 2\theta$ scans, and the intensities of three standard reflections, which were measured after every 100 reflections, remained stable throughout each data collection. The intensities were corrected for Lorentz and polarization effects. An empirical absorption correction based on the Ψ -scans of three reflections was employed: Data of 4a and 5a were collected on a Stoe IPDS diffractometer. The intensities were determined and corrected by the program INTEGRATE in IPDS (Stoe and Cie, 1999). An empirical absorption correction was employed using the FACEIT-program in IPDS (Stoe and Cie, 1999).

The structures were generally solved by direct and Fourier methods using SHELXS-97. For each structure, the non-hydrogen atoms were refined anisotropically. All of the H-atoms were placed in geometrically calculated positions and each was assigned a fixed isotropic displacement parameter based on a ridingmodel. H1 of compound 5 bonded to Pt was refined free with an isotropic displacement parameter. Quite reasonable bond length and bond angles were obtained for H1, although hydrogen atoms can't be localized certainly near heavy atoms like Pt. Refinement of the structures was carried out by full-matrix least-squares methods based on F_o^2 using SHELXL-97. All calculations were performed using the WINGX crystallographic software package, using the programs SHELXS-97 and SHELXL-97 [15]. The crystallographic data for each complex are given in Table 5. The figures were drawn using SCHAKAL-99.

3. Results and discussion

3.1. Synthesis of the dithio- and ditelluroether ligands

The [(phenylthio)methyl]hydridosilanes (1c,d) were prepared in analogy to the published synthesis of 1a,b by reaction of [(phenylthio)methyl]lithium with Cl₂Si-Me(H) or Cl₃SiH [7b]. Compound 1c was isolated as a yellowish oil, 1d was obtained as a waxy solid. The ditelluroether ligands (PhTeCH₂)₂SiMe₂ (2a) and (n-BuTeCH₂)₂SiMe₂ (2b) were obtained as yellowish, bad smelling oils by reaction of LiTeR with bis(chloromethyl)dimethylsilane according Scheme 1. The detailed multinuclear NMR data of 1c,d and 2a,b are presented in Section 2.

3.2. Synthesis of platinum and rhenium complexes with chelating (phenylthiomethyl)silane ligands

In order to study the ability of the (phenylthiomethyl)silanes (1) to chelate metal complexes and the stereochemical problems associated with, we first prepared simple model compounds using diphenylbis[(phenylthio)methyl]silane (1a). Upon reaction of 1a with [PtCl₂(PhCN)₂] in toluene, the very stable yellow square planar chelate complex *cis*-[PtCl₂{(PhSCH₂)₂SiPh₂}] (3)



was isolated. ¹H NMR investigations at variable temperature showed, that due to a facile inversion process at the sulfur atoms in solution, meso- and DL-isomers coexist in a temperature dependent equilibrium (Scheme 2). At 325 K the pyramidal inversion is sufficiently fast so that only one 'averaged planar' conformation is observed resulting in singlet for the methylene protons at δ 3.11 with a ${}^{3}J_{\text{Pt,H}}$ coupling of 54 Hz. At 298 K, the signal has collapsed to a very broad hump. Progressive cooling of the solution resulted in a separation in two distinct resonances for the methylene protons. The observation of two mutually coupled doublets at δ 3.64 and 3.06 $({}^{2}J_{H_{A},H_{B}} = 13.4 \text{ Hz})$ at 233 K indicates that the inversion process is frozen on the NMR time scale. In addition to the first set of doublets, a second AB system due a second isomer is present, the ratio being approximately 70:30. The coexistence of meso- and DLisomers of 3 can also be deduced from the ${}^{195}Pt{}^{1}H$ NMR spectrum, which displays at 298 K two singlets at δ -2167 and -2197 in an approximate 60:40 ratio.

3.2.1. Crystal structure of 3

Suitable single crystals were grown from CH₂Cl₂hexane. Fig. 1 shows a platinum(II) center in a square planar environment with a cis-arrangement of the two chloro ligands $[Cl(1)-Pt-Cl(2) = 90.02(8)^{\circ}]$. The root mean square (RMS) deviation from the plane defined by Cl(1)-Cl(2)-Pt-S(1)-S(2) amounts to 0.046 Å. The sixmembered Pt-S(1)-S(2)-C(1)-C(2)-Si chelate ring adopts a distorted chair conformation very similar to that reported for *cis*-[PtCl₂{PhS(CH₂)₃SPh}] ligated by a 1.3-bis(phenvlthio)propane ligand [16]. In contrast to the latter complex, in which the phenyl substituents of the sulfur atoms are in an *anti*-mode with respect to the chelate ring, the two phenyl groups of 3 are synorientated corresponding to a meso-conformation. The Pt-S(1) and Pt-S(2) bond distances of 228.1(1) and 227.1(2) pm parallel that of [PtCl₂{PhS(CH₂)₃SPh}] [227.1(2) and 227.42(19) pm]. The averaged Pt-Cl bond length of 3 [232.1 pm] is also almost identical to that of the 1,3-bis(phenylthio)propane counterpart [232.5 pm] (Table 1).

Extensive NMR studies have been carried out in the past on the $[ReX(CO)_3(RS\cdots SR) \ (X = Cl, Br, I)$ to study the sulfur inversion, which gives rise to two DL-



Fig. 1. View of the molecular structure of 3.

Table 1 Selected bond lengths (pm) and bond angles (°) of **3**

Bond lengths	
Pt-S(1)	228.1(2)
Pt-S(2)	227.1(2)
Pt-Cl(1)	231.7(2)
Pt-Cl(2)	232.5(2)
S(1)-C(1)	182.2(6)
S(2)-C(2)	182.2(6)
S(1)-C(15)	179.3(7)
S(2)-C(21)	179.8(7)
Si-C(1)	189.5(6)
Si-C(2)	188.3(7)
Bond angles	
Cl(1)-Pt-Cl(2)	90.02(8)
Cl(1)-Pt-S(1)	84.49(7)
Cl(2)-Pt-S(1)	174.49(6)
Cl(1)-Pt-S(2)	173.02(6)
Cl(2)-Pt-S(2)	85.20(7)
S(1)-Pt-S(2)	100.25(6)
C(1)-S(1)-C(5)	109.8(2)
S(1)-C(1)-Si	115.9(3)
S(2)-C(2)-Si	118.4(4)
C(1)-S(1)-Pt	112.0(2)
C(2)-S(2)-Pt	108.4(2)

and two *meso*-conformations [6a,6b]. A stable chelate complex of this type is also formed, when **1a** is reacted with $[\text{Re}(\mu-\text{Br})(\text{CO})_3\text{THF}]_2$ in CH₂Cl₂ (Scheme 3). Both ¹H and ²⁹Si NMR spectra of colorless *fac*-[Re-Br(CO)₃{(PhSCH₂)₂SiPh₂}] (**4a**) indicate, that in contrast to the case of **3**, in solution only one invertomer



Scheme 2.



Scheme 3.

exists at ambient temperature. Thus, the proton NMR spectrum of this off-white air stable compound consists in a well defined AX pattern centered at δ 4.29 and 2.83 $(J_{\rm H,H} = 12.2 \text{ Hz})$ due to two mutually coupled CH₂ protons. The absence of other conformational isomers is also confirmed by the ²⁹Si INEPT NMR spectrum, which exhibits just a single resonance at δ -13.9 ppm (1a δ -11.3 ppm). At present we can not conclude, whether the solution conformation of 4a corresponds to the meso-ligand arrangement found in the solid state structure of 4a (see below). Note, that the fac-[Re- $Br(CO)_{3}{MeS(CH_{2})_{3}SMe}]$, in which the dithioether ligand forms also a six-membered chelate ring with a ReBr(CO)₃-fragment, is fluxional at ambient temperature [6a,6b]. At the moment, we cannot state which steric and/or electronic parameter causes the augmentation of the barrier of pyramidal inversion at the S-donor atoms in the case of 4. This may be due to the replacement of a methylene unit by SiR₂ or alternatively due to the presence of phenyl substituents on S instead of methyl groups.

When $[\text{Re}(\mu-\text{Br})(\text{CO})_3\text{THF}]_2$ was reacted with $(\text{PhSCH}_2)_2\text{Si}(\text{vinyl})\text{Me}$ (1b) in CH_2Cl_2 , two diastereomers *fac*-[ReBr(CO)_3{(PhSCH}_2)_2\text{SiMe}(\text{vinyl})}] (4b, 4b') were formed in a 50:50 ratio. Due to the dissymmetric substitution on silicon, one diastereomer possesses the vinyl group directed towards the Re-Br (4b), the second one (4b') the methyl group directed towards the Re-Br bond. As in the case of 4a, the NMR data of 4b, 4b' indicate that the two isomers are stereochemically rigid

at ambient temperature. Thus, the proton NMR displays two distinct sets of AX pattern for the methylene protons and an overlapped multiplet for the vinyl resonances. Rising the temperature to 50 °C in CDCl₃ had no effect on the shape of the NMR signals.

The same case was encountered upon reaction of $[Re(\mu-Br)(CO)_3THF]_2$ with $(PhSCH_2)_2Si(H)Me$ (1c). The IR spectrum of [ReBr(CO)₃{(PhSCH₂)₂Si(H)Me}] (4c) shows in addition to the three v(CO) stretches at 2036, 1946 and 1909 cm⁻¹ diagnostic for a facarrangement, a band of medium intensity at 2159 cm^{-1} assigned to a v(Si-H) vibration. This proves that formation of the chelate complex 4c is preferred instead of oxidative addition of the Si-H bond on Re (see below). The proton NMR data are indicative for the formation of two stereochemically rigid diastereomers 4c and 4c' in a 50:50 ratio. Due the additional coupling with Si–H, the two resonances of the SiMe groups at δ 0.46 and 0.53 ppm are splitted in doublets by ${}^{3}J_{H,H}$ couplings of 3.5 and 3.8 Hz, respectively. Selective irradiation of the two broad Si-H signals at δ 4.48 and 4.32 ppm permitted to correlate the SiMe resonance at δ 0.46 ppm with that at 4.32 ppm and the SiMe resonance at δ 0.53 ppm with that at 4.48 ppm.

3.2.2. Crystal structure of 4a

Suitable single crystals were grown from CH_2Cl_2 -hexane. Fig. 2 shows a rhenium(I) center in an octahedral environment with a facial arrangement of the three carbonyl ligands. The diphenylbis[(phe-

Table 2



Fig. 2. View of the molecular structure of 4a.

nylthio)methyl]silane ligand forms a six-membered cycle with the rhenium center adopting a chair conformation. The phenyl rings of the thioether groups are both *syn*orientated in the same direction as the bromo ligand corresponding to a *meso*-invertomer. The Re–S bond lengths of 251.0(2) and 252.0(2) pm are close to that reported for [ReBr(CO)₃{(-CH₂S(CH₂)Cl)}] (252.5(3)

Bond lengths		
Re-S(1)	251.0(2)	
Re-S(2)	252.0(2)	
Re-Br	262.93(11)	
S(1)-C(4)	181.8(7)	
S(2)-C(5)	179.3(6)	
Si-C(4)	188.1(7)	
Si-C(5)	189.2(6)	
Bond angles		
C(3)-Re-S(1)	176.2(2)	
C(1)-Re-S(1)	95.7(2)	
C(2)-Re-S(1)	88.9(2)	
C(3)-Re-S(2)	93.6(2)	
C(1)-Re-S(2)	177.4(2)	
C(2)-Re-S(2)	86.7(2)	
S(1)-Re-S(2)	83.04(5)	
C(3)–Re–Br	90.5(2)	
C(1)-Re-Br	91.3(2)	
C(2)–Re–Br	177.6(2)	
S(1)-Re-Br	91.14(5)	
S(2)-Re-Br	90.91(4)	
C(4)-S(1)-Re	109.8(2)	
C(5)-S(2)-Re	111.9(2)	
S(1)-C(4)-Si	119.2(3)	
S(2)-C(5)-Si	111.9(3)	

Selected bond lengths (nm) and bond angles (°) of 49

displaying a bridging bonding mode, or (iii) to attach a second metal center by formation of inorganic ring systems of type (\mathbf{C}).



and 253.7(2) pm), the Re–Br bond distance of 262.93(11) pm is somewhat longer compared with the latter complex [260.87(10) pm] [3] (Table 2).

3.3. Synthesis of platinum hydrido silyl complexes

The oxidative addition of tertiary hydridosilane H– SiR₃ on transition metal centers offers a convenient method to generate hydrido silyl complexes of the type $L_n M(H)SiR_3$. Our aim was to extend this Si–H activation route using functionalized hydridosilanes bearing donor groups in order to achieve (i) an intramolecular coordination in monometallic complexes (A), (ii) to synthesize and stabilize bimetallic complexes of type (B) The pioneering work of Eaborn on platinum silyl complexes has shown, that a wide range of commercially available hydridosilanes can be oxidatively added on $[Pt(PPh_3)_2(CH_2=CH_2)]$ to afford hydrido silyl complexes of the type *cis*- $[Pt(H)(SiR_3)(PPh_3)_2]$ [17]. NMR studies at variable temperature on *cis*- $[Pt(H)(SiPh_3)_2]$ have revealed that this complex is fluxional in solution [18]. This fluxionality is due to an temperature depend equilibrium between a square-planar Pt(II) species $[Pt(H)(SiR_3)(PPh_3)_2]$ and a Pt(0) species $[(H-SiR_3)Pt(PPh_3)_2]$ having a side-on coordinated H–SiR₃ ligand.

As expected, the Si-H bond of **1c** is reactive for oxidative addition towards low valent metal centers such





The fluxional complex 5a has been fully characterized in solution by multinuclear NMR techniques. In CDCl₃ at 243 K, the data are consistent with a cis-arrangement of the hydride and the silvl ligand. In the proton NMR spectrum of 5a, the hydride resonance is found at δ -2.66 and consists of a doublet of doublet (${}^{2}J_{P,H} =$ 19.6, 152.7 Hz), which is flanked by platinum satellites $({}^{1}J_{Pt,H} = 972.3 \text{ Hz})$. Due to a trans-coupling ${}^{4}J_{P,H}$ of 2.4 Hz, the SiMe resonance at $\delta -0.04$ is splitted in a doublet with an additional ${}^{3}J_{\text{Pt,H}}$ coupling of 27.0 Hz. At ambient temperature, all resonances give rise to broad signals without any fine structure. Similarly, in the ${}^{31}P{}^{1}H$ NMR spectrum the two broadened resonances of the PPh₃ ligands have lost their mutual coupling at ambient temperature. However, at 243 K the expected well resolved AX-pattern at δ 30.8 and 33.2. with a ${}^{2}J_{P,P}$ of 13 Hz is observed. The ${}^{1}J_{Pt,P}$ couplings of 2509 and 1682 Hz are also present in the ¹⁹⁵Pt{¹H} NMR spectrum of **5a** giving rise to a doublet of doublets centered at δ -3410 ppm.

In an analogous manner, the stable derivative **5b** was obtained after oxidative addition of $(PhSCH_2)_3SiH$ (**1d**) on Pt(0). Surprisingly, both phosphorous and proton NMR spectra are well resolved and easy to interpret due to the symmetry of the silyl moiety. These findings let suggest that **5b** is almost rigid at ambient temperature. Extended studies on hydrido-silyl manganese have evidenced that electron withdrawing substituents on Si favor pronounced oxidative addition on the reaction trajectory starting with non classical silane adducts [CpMn(I)(CO)₂(H–SiR₃)] to complete oxidative addition leading finally to [CpMn(III)(CO)₂(H)SiR₃)] [19]. In the case of **5a,b**, the third CH₂SPh substituent is slightly more electron withdrawing compared with CH₃.



Fig. 3. View of the molecular structure of 5a.

Maybe this subtle electronic modification combined with the increased steric bulkiness of SiR_3 is sufficient to stabilize a Pt(II) center.

3.3.1. Crystal structure of 5a

Suitable single crystals were grown from toluenehexane. Fig. 3 shows a platinum(II) center in a severely distorted square-planar environment with a cis-arrangement of the two PPh₃ ligands, the angles P(2)-Pt-P(1)and P(2)-Pt-Si [107.52(5) and 97.80(5)°] being substantially larger than the 90° expected for an ideal squareplanar geometry. There is, however, no significant deviation from planarity, since the RMS deviation from the plane defined by P(1), P(2), Pt and Si is only 0.057 Å. Although there is some electron density close to Pt, which could be refined for a hydride position, a precise localization of a hydride ligand in the proximity of a heavy atom is not possible. Therefore, the given Pt-H(1) bond distance of 153.8 pm of 5a may have much impreciseness. For comparison, 154.4 pm have been determined for the bimetallic complex [(OC)₃Fe{Si(O- $Me_{3}(\mu-Ph_{2}PNHPPh_{2})Pt(H)(PPh_{3})$ [13]. The overall geometry of 5a is quite similar to that of cis-[Pt(H)(SiPh₃)(PPh₃)₂] [20], the Pt-Si bond length of 5a [235.59(12) pm] being almost identical with that of the triphenylsilyl counterpart [235.7(3) pm]. The single crystal X-ray determination reveals furthermore, that in the solid state intramolecular short contacts between a thioether group and the platinum center are absent, the closest Pt-S distance being 4.146 Å (Table 3).

3.4. Synthesis of platinum complexes with chelating ditelluroether ligands

For comparison with the dithioether complex cis-[PtCl₂(PhSCH₂)₂SiPh₂)] (**3**), we were interested in to synthesize related ditelluroether chelate complexes. The

Table 3 Selected bond lengths (pm) and bond angles (°) of **5a**

Bond lengths		
Pt-P(2)	231.04(13)	
Pt-P(1)	234.54(11)	
Pt-Si	235.59(12)	
S(1)-C(3)	175.9(5)	
S(1)-C(2)	180.5(5)	
S(2)-C(10)	176.1(5)	
S(2)-C(9)	179.0(5)	
Si-C(1)	188.6(5)	
Si-C(2)	190.3(5)	
Si-C(9)	191.8(5)	
Bond angles		
P(2) - Pt - P(1)	107.52(5)	
P(2)-Pt-Si	97.80(5)	
P(1)-Pt-Si	153.42(4)	
C(3)-S(1)-C(2)	105.2(2)	
C(10)-S(2)-C(9)	105.3(2)	
C(1)-Si-C(2)	106.3(2)	
C(1)-Si-C(9)	100.3(2)	
C(2)-Si-C(9)	105.0(2)	
C(1)-Si-Pt	121.3(2)	
C(2)-Si-Pt	112.6(2)	
C(9)-Si-Pt	109.59(14)	
S(1)-C(2)-Si	111.8(2)	
S(2)-C(9)-Si	113.2(2)	

telluro-congeners cis-[PtCl₂(RTeCH₂)₂SiMe₂)] (6a R = Ph, **6b** R = n-Bu) were readily formed upon reaction of [PtCl₂(PhCN)₂] with a slight excess of **2a,b** in CH₂Cl₂ with 89% yield (Scheme 5). Since the very stable yellow complex 6a was not sufficient soluble in CDCl₃ for multinuclear NMR studies, we focussed our investigations on the much more soluble n-butyl derivative **6b**. ¹H NMR studies at 295 K showed that the inversion barrier at the tellurium atoms is low enough to observe mesoand DL-isomers as encountered for 3. Thus, the SiMe₂ groups give rise to singlet at δ 0.25 ppm, which appears in middle of two other SiMe resonances of equal intensities. We tentatively attribute the singlet to the DL-invertomer (see the molecular structure below, possessing a C_2 axes passing through Pt and Si), for which the two methyl groups on Si should be identical. In the case of a meso-conformation, the two n-butyl groups are orientated in the same sense, rendering the two methyl groups on Si non-equivalent. Therefore, they give rise to two singlets with the appearance of a 'pseudo-doublet'. Rising the temperature to 313 K has no significant effect on the shape of the over all proton NMR spectrum, the integration ratio between the SiMe₂ singlet of the DL-invertomer and the 'pseudo-doublet' of the *meso*-invertomer being approximately 70:30.

The ¹⁹⁵Pt{¹H} NMR spectrum, which displays two broadened singlets at δ –2652 and –2665 in an approximate 3:1 ratio, the first being intense enough to determine a ¹J_{Pt,Te} coupling of 1063 Hz. The same ¹J_{Pt,Te} coupling of 1063 Hz was also found in the ¹²⁵Te{¹H} NMR spectrum, which exhibits two singlets at δ 436.7 and 398.8 in an approximate 1:3 ratio (**2b** 143.1 ppm). The same 1:3 intensity ratio was also encountered in the ²⁹Si INEPT NMR spectrum (Fig. 4), which showed two singlets at δ 11.0 and 7.1. The later resonance is flanked by tellurium satellites with an averaged ²J_{Si,Te} coupling of 21 Hz. For comparison, the ligand **2b** gives rise to a singlet at δ 5.6 with an averaged ²J_{Si,Te} coupling of 23 Hz.

3.4.1. Crystal structure of 6b

Suitable single crystals were grown from CH₂Cl₂hexane. Fig. 5 shows a platinum(II) center in a square planar environment with a *cis*-arrangement of the two chloro ligands. The RMS deviation from the plane defined by Cl(1)-Cl(2)-Pt-Te(1)-Te(2) amounts to 0.009 Å. The dimethylbis[(butyltelluro)methyl]silane ligand forms a distorted six membered cycle with the Pt center, the Pt-Te(1) and Pt-Te(2) bond distances being 249.71(14) and 250.60(16) pm, respectively. The two n-butyl groups are oriented in the opposite sense corresponding to a DL-conformation. The averaged Pt-Te bond length of 250.15 pm parallels that of $[PtCl{MeS(CH_2)_3Te(CH_2)_3SMe}][PF_6] [252.58(11) pm],$ the averaged Pt-Cl bond length of **6b** [234.4 pm] is very comparable to that of the cationic complex [235.4 pm] [21] (Table 4).



Scheme 5.



Fig. 4. ²⁹Si INEPT NMR spectrum of 6b recorded in CDCl₃.



Fig. 5. View of the molecular structure of 6b.

3.5. Synthesis of a rhenium complexes with a chelating ditelluroether ligands

After addition of 2 equiv. of **2b** to a solution of $[\text{Re}(\mu-\text{Br})(\text{CO})_3\text{THF}]_2$ in CH₂Cl₂, IR monitoring indicated instantaneous formation of *fac*-[ReBr(CO)₃{(n-Bu-TeCH₂)₂SiMe₂}] (7). Compared with the dithioether derivative **4c**, the position of the three ν (CO) stretching modes at 2022, 1933 and 1895 cm⁻¹ is shifted approximately ten wave numbers to lower frequency. This is probably due to the stronger donor ability of the n-BuTe groups compared with the SPh groups of **4c** (Scheme 6).

Bond lengths	
Pt-Te(1)	249.71(14)
Pt-Te(2)	250.60(16)
Pt-Cl(1)	233.5(6)
Pt-Cl(2)	235.3(5)
Te(1)-C(1)	213.6(18)
Te(1)-C(5)	216.1(18)
Te(2)-C(2)	210.7(19)
Te(2)-C(9)	213.6(18)
Si-C(4)	181.6(19)
Si-C(3)	183.0(19)
Bond angles	
Cl(1)-Pt-Cl(2)	90.3(3)
Cl(1)-Pt-Te(1)	175.51(18)
Cl(2)-Pt-Te(1)	85.25(18)
Cl(1)-Pt-Te(2)	86.00(18)
Cl(2)-Pt-Te(2)	176.19(18)
Te(1)-Pt-Te(2)	98.49(5)
C(1)-Te(1)-C(5)	109.8(2)
C(2) - Te(2) - C(9)	90.9(9)
C(1) - Te(1) - C(5)	92.1(8)
C(1)-Te(1)-Pt	107.1(5)
C(2)-Te(2)-Pt	107.6(5)

4. Conclusion and perspectives

We have shown that dithioether and ditelluroether ligands incorporating a silicon atom form stable complexes with various transition metals. The ease of variation of the substituents on Si offers a promising

Table 5 Crystallographic data for compounds **3**, **4a**, **5a**, and **6b**

Identification code	SHELX816 5a	shelxs967 6b	shelxs826 4a	SHELX870 3
Empirical formula	$C_{51}H_{48}P_2PtS_2Si$	C ₁₂ H ₂₈ Cl ₂ PtSiTe ₂	C ₂₉ H ₂₄ BrO ₃ ReS ₂ Si	C ₂₆ H ₂₄ Cl ₂ PtS ₂ Si
Formula weight	1010.13	721.62	778.80	694.65
Temperature (K)	293(2)	293(2)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	triclinic	triclinic	monoclinic	triclinic
Space group	<i>P</i> 1	<i>P</i> 1	P2(1)/n	<i>P</i> 1
Unit cell dimensions				
a (Å)	13.238(3)	9.113(2)	11.141(2)	10.476(2)
b (Å)	13.628(3)	9.740(2)	21.754(4)	11.574(2)
c (Å)	14.383(3)	11.906(2)	12.584(3)	12.709(3)
α (°)	72.31(3)	93.68(3)	90	66.87(3)
β (°)	69.73(3)	94.26(3)	107.40(3)	66.43(3)
γ (°)	77.82(3)	91.18(3)	90	78.08(3)
Volume (Å ³)	2302.7(9)	1051.3(4)	2910.3(10)	1296.6(5)
Z	2	2	4	2
Density (calculated) (Mg $^{-3}$)	1.457	2.280	1.777	1.779
m)	2.267	0.601	5 7(2	5 927
Absorption coefficient $(1 - 1)$	3.207	9.691	5.762	5.837
(mm ⁻¹)	1016	(())	1512	(7)
F(000)				6/6
Crystal size (mm ⁻)	$0.30 \times 0.20 \times 0.20$	$0.20 \times 0.20 \times 0.10$	$0.20 \times 0.20 \times 0.10$	$0.40 \times 0.40 \times 0.20$
<i>θ</i> Range for data	1.56-27.50	2.24-23.98	2.13-26.30	2.16-24.12
collection (°)				
Index ranges	$-15 \le h \le 14, -16 \le k \le$	$-10 \le h \le 1, -1 \le k \le 10,$	$-13 \le h \le 13, -26 \le k \le 26,$	$-12 \le h \le 11, -12 \le k \le$
	$1/, 0 \le l \le 18$	$-13 \le l \le 13$	$-14 \le l \le 14$	$12, -14 \le l \le 14$
Reflections collected	10059	3114	22 984	8311
Independent reflections	10059	3114	$5529 [R_{int} = 0.0537]$	$3815 [R_{int} = 0.061/]$
Refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares or F^2
Data/restraints/para-	10 059/0/519	3114/0/167	5529/0/335	3815/0/289
meters				
Goodness-of-fit on F^2	1.029	0.913	1.075	1.036
Final R indices	$R_1 = 0.0365, wR_2 = 0.0976$	$R_1 = 0.0650, wR_2 = 0.1566$	$R_1 = 0.0477, wR_2 = 0.1233$	$R_1 = 0.0389, wR_2 = 0.1073$
$[I > 2\sigma(I)]$				
R indices (all data)	$R_1 = 0.0432, wR_2 = 0.1018$	$R_1 = 0.0824, wR_2 = 0.1627$	$R_1 = 0.0546, wR_2 = 0.1281$	$R_1 = 0.0398, wR_2 = 0.1095$
Extinction coefficient	•	-	0.0057(4)	-
Largest difference peak	1.930 and -1.989	2.606 and -2.949	1.873 and -2.273	1.800 and -1.968
and hole (e Å ^{-3})				



Scheme 6.

access to functionalized ligand systems. Notably the

presence of a reactive Si-H function offers additional

coordination modes by oxidative addition. In an forth-

coming paper we will report on the construction of

(hetero)bimetallic systems of type C (see above) exploit-

ing the propensity of **1c**,**d** to ligate metal centers both via

dative $M \leftarrow SR_2$ bonds as well via a covalent M-Si

bond.

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