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1,1,2,2-Tetramethyl-1,2-bis(phenylthiomethyl)disilane, a Flexible Ligand for the Construction of Macrocyclic, Mesocyclic, and Bridged Dithioether Complexes. Synthesis of the Bis-silylated Olefins *Z*-$(PhSCH_2)Me_2SiC(H){=}C(Ar)SiMe_2(CH_2SPh)$ by Catalytic Activation of the Si−Si Bond

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The functionalized disilane $(PhSCH_2)Me_2SiSiMe_2(CH_2SPh)$ (**1**) has been prepared and coordinated as a dithioether ligand on $[PtCl_2(PhCN)_2]$ to afford the fluxional seven-membered chelate complex *cis*-$[PtCl_2\{(PhSCH_2)_2Si_2Me_4\}]$ (**2a**). After metathesis reaction of **2a** with NaI the diiodo derivative *cis*-$[PtI_2\{(PhSCH_2)_2Si_2Me_4\}]$ (**2b**) was obtained. Treatment of $[Re(\mu\text{-}Br)(CO)_3THF]_2$ with 1 equiv of **1** yields the bromo-bridged dinuclear complex *fac*-$[\{Re(\mu\text{-}Br)(CO)_3\}_2\{\mu\text{-}(PhSCH_2)_2Si_2Me_4\}]$ (**5**), which is spanned by **1** forming a 10-membered mesocycle. Addition of a further equivalent of **1** yields the dinuclear macrocyclic compound *fac*-$[\{ReBr(CO)_3\}_2\{\mu\text{-}(PhSCH_2)_2Si_2Me_4\}_2]$ (**4**), forming a 14-membered ring system. The chloro-bridge of $[RuCl(\mu\text{-}Cl)(CO)_3]_2$ is cleaved by **1** to give the dinuclear compound *fac*-$[\{RuCl_2(CO)_3\}_2\{\mu\text{-}(PhSCH_2)_2Si_2Me_4\}]$ (**6**), in which the two metal fragments are linked by the thioether functions. In the presence of catalytic amounts of $Pd(OAc)_2$/CNR, the Si−Si bond of **1** is cleaved and addition across the triple bond of phenylacetylene or *p*-tolylacetylene affords the bis-silylated olefins *Z*-$(PhSCH_2)Me_2SiC(H){=}C(Ar)SiMe_2(CH_2SPh)$ (**7a** Ar = Ph; **7b** Ar = *p*-Tol). The new compounds have been studied by multinuclear NMR techniques; the crystal structures of **2a**, **2b**, **4**, **5**, **6**, and **7a** have been determined by X-ray diffraction studies.

Introduction

The catalytic cleavage of the Si−Si bond of disilanes by transition metals is an elegant route for the bis-silylation (double silylation) of unsaturated organic substrates such as alkynes, olefins, isonitriles, and aldehydes.[1−11] As catalysts, $Pd(PPh_3)_4$, $Pd(CNR)_2$, $Pd(OAc)_2$, $[Pt(C_2H_4)(PPh_3)_2]$, the mutual *syn*-arrangement of the two $SiCH_2SPh$ substituents, or $[RuHCl(CO)(PPh_3)_3]$[12] are often employed to activate the disilane, whose Si−Si σ-bond possesses a high-lying HOMO and a low-lying LUMO. This energetic feature of the frontier orbitals, which has also been theoretically investigated, confers properties that are similar to the C=C bond.[13,14] A recent DFT computational study on the bis-silylation of acetylenes catalyzed by Pd complexes has shown that the oxidative addition is an easy process with almost no barrier.[15] The isolation of some reaction intermediates such as bis-silyl complexes or silylated alkenyl complexes allows conceiving a catalytic cycle involving the following steps: (i) oxidative addition of the Si−Si bond across a metal center, (ii) subsequent insertion of the unsaturated substrate into a M−Si bond, and (iii) finally reductive elimination of the bis-silylated substrate (Scheme 1).[16,17]

In the context of our interest on organosilicon compounds[18−20] and transition metal silyl complexes,[21−25] we have recently prepared a series of organosilanes functionalized by phenyl-

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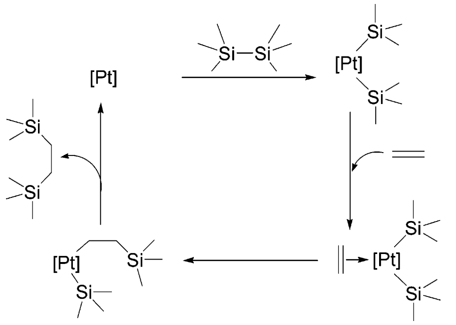
Scheme 1. Catalytic Cycle for the Bis-silylation of Unsaturated Organic Substrates

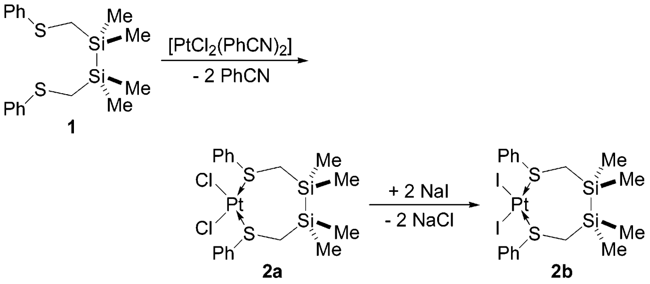


thiomethyl substituents such as $Ph_2Si(PhSCH_2)_2$ or Me(H)Si-$(PhSCH_2)_2$ and coordinated these ligands via their thioether function or via a covalent M−Si bond on Pt and Re.[26] In light of a potential application for bis-silylation reactions, we have now extended our research on the compound 1,1,2,2-tetramethyl-1,2-bis(diphenylthiomethyl)disilane (**1**). In addition to an oxidative addition of the Si−Si bond across a low-valent metal center, the two thioether functions of this disilane may also interact with soft metal centers. We have therefore undertaken a study to evaluate first the coordination chemistry of this promising hybrid ligand system **1** on various transition metals before exploiting its potential for catalytic or stoichiometric bis-silylation reactions. A point of interest was the evaluation of the influence of the incorporation of a disilane motif in the chain and the comparison with dithioether ligand systems of the type $RS(CH_2)_nSR$. Due to its flexibility, this ligand system may a priori adopt chelating and bridging bonding modes. The syntheses and the crystal structures of some dithioether complexes ligated by **1** are presented in this paper together with some results on the catalytic activation of the Si−Si bond of **1** in the presence of 1-alkynes. In addition to multinuclear NMR studies, the molecular structure of the resulting bis-silylated olefins has also been determined.

Results and Discussion

Synthesis of 1 and Coordination on Platinum as Chelating Dithioether Ligand. The functionalized disilane **1** was prepared by reaction of [(phenylthio)methyl]lithium with dichlorotetramethyldisilane in hexane/Et_2O and isolated in 78% yield as a colorless solid. The detailed multinuclear NMR data of air-stable 1,1,2,2-tetramethyl-1,2-bis(diphenylthiomethyl)disilane (**1**) are presented in the Experimental Section.[27] Upon reaction of $[PtCl_2(PhCN)_2]$ with a slight excess of **1** in dichloromethane at 303 K, the stable yellow square-planar chelate complex *cis*-$[PtCl_2\{(PhSCH_2)_2Si_2Me_4\}]$ (**2a**) was isolated as sole product.

Scheme 2



Metathesis reaction in the presence of NaI in a CH_2Cl_2/acetone mixture transformed **2a** into the orange-red derivative *cis*-$[PtI_2\{(PhSCH_2)_2Si_2Me_4\}]$ (**2b**) (Scheme 2).

Like numerous literature-known dithioether complexes, also **2a** and **2b** exhibit temperature-dependent ^1H NMR spectra. The study of inversion processes at the sulfur atoms in solution giving rise to *meso*- and *dl*-isomers has been the topic of several publications; therefore we have not studied this phenomenon in detail.[28−30] It is known that the relative invertomer populations are a function of a sensitive balance of factors such as the nature of the metal, substituents on sulfur, ring size, coordinated ligand, and temperature. We have recently examined the pyramidal inversion of the related six-membered chelate complex *cis*-$[PtCl_2\{(PhSCH_2)_2SiPh_2\}]$.[26] In the case of **2a**, the proton NMR spectrum recorded in $CDCl_3$ at 298 K consists of two mutually coupled doublets ($^2J_{H,H} = 11.8$ Hz) at δ 3.36 and 2.28; the latter display an additional $^3J_{Pt,H}$ coupling of 52 Hz. Apart from these methylene resonances, two distinct singlets at δ 0.54 and 0.41 are assigned to the Si-methyl substituents. At 323 K, the four methyl groups give rise to a single resonance at δ 0.55 and the methylene protons have lost their splitting and appear as broad humps at δ 3.34 and 2.37. The observation that the coalescence temperature for the inversion process of square-planar complexes $[MX_2\{RS(CH_2)_nSR\}]$ (M = Pd, Pt; X = Cl, Br, I) falls in the order Cl > Br > I has been rationalized by the *trans*-influence of the halide on the strength of the M−S bond.[28] In agreement with the crystallographic data (see below), this interpretation may also account for the signal form of the proton NMR spectrum of **2b**. This exhibits already at 298 K a very broad singlet at δ 0.51 and two extreme broadened resonances at δ 2.32 and 3.53 due to the methylene protons. At 318 K, the latter signals have almost disappeared in the baseline, and the four $Si-CH_3$ groups now give rise to a sharpened singlet at δ 0.54.

Consistent with a dynamic behavior is also the temperature dependency of the $^{195}Pt\{^1H\}$ NMR spectrum of **2a** (see Supporting Information). At 298 K, three broadened resonances in an approximate 1:2:1 ratio are observed at $\delta = -1844$, -1847, and -1850 ppm. Raising the temperature to 323 K causes the appearance of a narrow singlet at $\delta = -1846$. In addition, a second less intense resonance is now found at $\delta = -1825$. The ^{29}Si NMR INEPT spectrum of **2a** (recorded at 298 K) consists of a broad singlet, which appears slightly downfield shifted with respect to noncoordinated **1** (δ −14.8 vs −16.7).

Crystal Structures of 2a and 2b. Suitable single crystals of the two compounds were grown from CH_2Cl_2/hexane. **2a** shows a highly disordered phenyl substituent on S(1). The disordered carbon atoms were refined on split positions. The molecular

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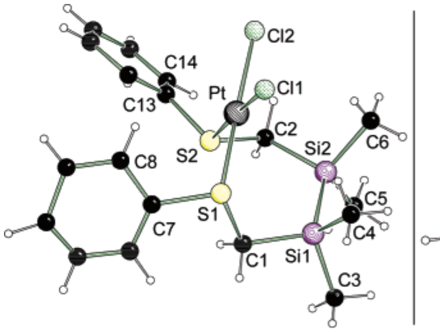

Figure 1. Molecular structures of **2a** (only one of two disordered atoms for C8−C12 shown) and **2b** in the solid state (Schakal plot). Selected bond lengths (Å) and angles (deg) **2a**: C(1)−S(1) 1.803(9), C(1)−Si(1) 1.909(9), C(2)−S(2) 1.800(9), C(2)−Si(2) 1.923(11), Cl(1)−Pt 2.318(2), Cl(2)−Pt 2.311(2), Pt−S(2) 2.267(2), Pt−S(1) 2.281(2), Si(1)−Si(2) 2.357(4); S(2)−Pt−S(1) 91.15(8), Cl(2)−Pt−Cl(1) 90.04(9); **2b**: C(3)−S(1) 1.790(6), C(3)−Si(1) 1.899(6), C(12)−S(2) 1.788(6), C(12)−Si(2) 1.898(6), I(1)−Pt 2.6004(5), I(2)−Pt 2.6042(8), Pt−S(2) 2.2773(12), Pt−S(1) 2.2990(14), Si(1)−Si(2) 2.348(2); S(2)−Pt−S(1) 89.48(5), I(1)−Pt−I(2) 91.771(18).

structure of **2a** reveals a square-planar coordination sphere around the Pt(II) atom and forms a seven-membered chelate ring as shown in Figure 1. The root-mean-square deviation from the plane defined by Cl(1)−Cl(2)−Pt−S(1)−S(2) amounts to 0.011 Å. The closely related platinum complex *cis*-$[PtCl_2\{PhS(CH_2)_4SPh\}]$ ligated by a 1,4-bis(phenylthio)butane ligand is known in the literature, but (apart from IR data) no structural data are available.[31] **2a** is therefore best compared to *cis*-$[PtCl_2\{(PhSCH_2)_2SiPh_2\}]$ forming a six-membered chelate complex.[26] The Pt atom is ligated by two chloro ligands in a *cis*-arrangement [Cl(1)−Pt−Cl(2) = 90.02(8)°]. The Pt−S(1) and Pt−S(2) bond distances of 2.281(1) and 2.267(2) Å parallel those of $[PtCl_2\{(PhSCH_2)_2SiPh_2\}]$ [2.281(2) and 2.271(2) Å]. The average Pt−Cl bond length of **2a** [2.315 Å] is somewhat shorter that of the diphenyl[bis(phenylthio)methyl]silane derivative [2.321 Å]. In contrast to the latter complex, where the phenyl substituents of the sulfur atoms are *syn*-orientated with respect to the chelate ring (corresponding to a *meso*-conformation), the phenyl groups of **2a** and **2b** are *anti*-orientated in the solid state (*dl* invertomer). The S(1)−Pt−S(2) angle of **2b** is more acute than in **2a** [89.48(5)° vs 91.15(8)°], probably due to the stronger thermodynamic *trans*-influence of iodide compared to chloride, and the average Pt−S distance of **2b** is slightly longer than that of **2a** [2.288 vs 2.274 Å]. The same tendency of the Pt−S bond lengths of the series $[PtX_2\{PhS(CH_2)_2SPh\}]$ (X = Cl, Br, I) has been discussed in detail by Marangoni et al.[28b]

Alkylation of 2a. A convenient method to alkylate $[PtCl_2(1,5\text{-cyclooctadiene})]$ is transmetalation by tetramethylstannane to produce $[PtCl(CH_3)(1,5\text{-cyclooctadiene})]$ and Me_3SnCl.[32] Similarly, a solution of **2a** reacts gradually after addition of 1.5 equiv of Me_4Sn and stirring for 2 days at ambient temperature. In the dark dried residue, the characteristic smell of Me_3SnCl is noticeable. Although we could not obtain a satisfactory elemental analysis due to the presence of a small amount of side-products, which could not be removed by recrystallization, the formation of $[PtCl(CH_3)\{(PhSCH_2)_2Si_2Me_4\}]$ (**3**) is evidenced by the proton NMR spectrum. As expected for a Pt-bound methyl group, a singlet at δ 0.91 with a ^2JPt−H coupling of 73 Hz is observed. For comparison, the methyl resonance of $[PtCl(CH_3)(1,5\text{-cod})]$ gives rise to a singlet at δ 0.93 with a ^3JPt−H coupling of 71 Hz. Note that a recent study on the methylated Pd complex $[PdCl(CH_3)\{Pr^iS(CH_2)_3S^iPr\}]$ and $[Pd(CH_3)\{Pr^iS(CH_2)_3S^iPr\}][BAr_4]$ has demonstrated the ability of these dithioether complexes to catalyze the copolymerization of CO/ethylene leading to polyketones.[33]

Tanaka and Ito have demonstrated that Pt(II) and Pt(IV) silyl complexes are accessible through oxidative addition of a Si−Si bond to the Pt center.[34] With the aim to prepare a bis(silyl) complex $[Pt(PEt_3)_2\{SiCH_2SPh\}_2]$, *cis*-$[PtCl_2(PEt_3)_2]$ was treated with 2 equiv of **1** in refluxing toluene overnight. Instead of the hoped-for oxidative addition of the Si−Si bond across platinum, quantitative *cis*−*trans* isomerization of the starting material occurred to afford *trans*-$[PtCl_2(PEt_3)_2]$, as evidenced by NMR and an X-ray diffraction study of the isolated yellow-greenish crystals.

Synthesis of Cyclic Rhenium Complexes with 1 Acting as Bridging Dithioether Ligand. Previous studies have shown that dithioether $RS(CH_2)_nSR$ react with hexacarbonyl-μ-dihalogenobis(tetrahydrofuran)dirhenium(I)[35] to form mononuclear complexes when $n = 2$ or 3[29,39,40] and dinuclear complexes when $n = 0$.[36,37] In a previous paper, we have also demonstrated that treatment of the dimeric compound $[Re(\mu\text{-}Br)(CO)_3THF]_2$ with $Ph_2Si(PhSCH_2)_2$ results in formation of the conformational rigid dithioether complex *fac*-$[Re(Br)(CO)_3\{(PhSCH_2)_2SiPh_2\}]$, chelated by the dithioether ligand forming a six-membered cycle.[26]

Attempting to isolate a similar stable chelate compound, a solution of $[Re(\mu\text{-}Br)(CO)_3THF]_2$ in CH_2Cl_2 was reacted with 2 equiv of **1** at 298 K. Surprisingly, the stable white solid obtained was identified unambiguously by an X-ray study (see below) as the macrocyclic compound *fac*-$[\{ReBr(CO)_3\}_2\{\mu\text{-}(PhSCH_2)_2Si_2Me_4\}_2]$ (**4**). The dithioether acts as a bridging ligand connecting the two rhenium atoms, thus forming a 14-

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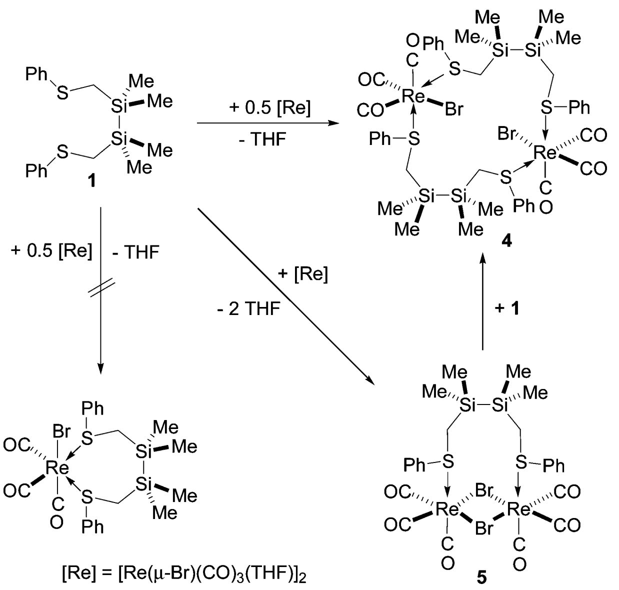
Scheme 3



membered ring system. This unexpected assembling of a macrocycle without precedent in rhenium-thioether chemistry contrasts with the finding that in the case of platinum formation of seven-membered chelate complexes such as **2a**,**b** with this dithioether ligand is observed (see above). When only 1 equiv of the dithioether is added, the dinuclear complex *fac*-$[\{Re(\mu\text{-}Br)_2(CO)_3\}_2\{\mu\text{-}(PhSCH_2)_2Si_2Me_4\}]$ (**5**) is isolated in 68% yield. The framework of **4** is similar to the one reported for 1,1′-bis(mesitylthio)ferrocene bridging a $Re_2(CO)_6Br_2$ dinuclear core.[38] Addition of a second equivalent of **1** to a CH_2Cl_2 solution of **5** splits quantitatively within 1 h (NMR monitoring) the bromo-bridges, forming the macrocyclic compound **4** (Scheme 3). ^1H NMR studies at variable temperature revealed also a dynamic behavior for **4**. Thus, at 298 K two singlets are observed for the $SiMe_2$ groups at δ 0.37 and 0.38, and raising the temperature to 323 K results in convergence to a single resonance at δ 0.37 for the eight methyl groups.

Crystal Structures of 4 and 5. Suitable single crystals of **4** and **5** were grown from CH_2Cl_2/heptane. Complex **4** contains a center of inversion (Figures 2a and 2b), and the symmetry of **5** results from the presence of a proper C_2 axis perpendicular to the Re_2Br_2 unit (Figure 5). In both cases, the rhenium centers are in a slightly distorted octahedral environment with a facial arrangement of the carbonyl groups. Note that the distortion is more pronounced in compound **4**, the *cis* angles being in the range 80.73(6)−98.5(3)° [82.01(3)−94.73(19)° for complex **5**]. The Re−S and Re−Br distances [**4**: Re−S(1) 2.530(2), Re−S(2) 2.518(2), Re−Br 2.6212(13) Å; **5**: Re−S 2.5056(13), Re−Br 2.6479(8) and 2.6526(9) Å] lie in the range of what is generally observed for these bonds.[39−41] In particular the Re−S bond distances are almost unaffected by the dithioether coordination modes, e.g., chelating vs bridging. The Re_2Br_2 unit remains almost planar in complex **5**, in opposition to what is observed in the more strained disulfide derivatives $Re_2Br_2(CO)_6S_2R_2$ (R = Me or Ph).[36,37] The two rhenium atoms are at a nonbonding distance of 3.996 Å. The flexible dithioether adopts a conformation in which the two $SiMe_2$ groups are eclipsed, leading thus to a C_2 symmetry. In compound **4**, the two rhenium centers are only linked by the adaptable dithioether ligands. In this case, the two $SiMe_2$ units are staggered and the 14-membered centrosymmetrical cycle thus generated exhibits a transannular Re⋯Re separation of 8.639 Å. The shortest nonbonding distance between two opposite atoms in this macrocycle is a S⋯S contact of 5.235 Å.[42]

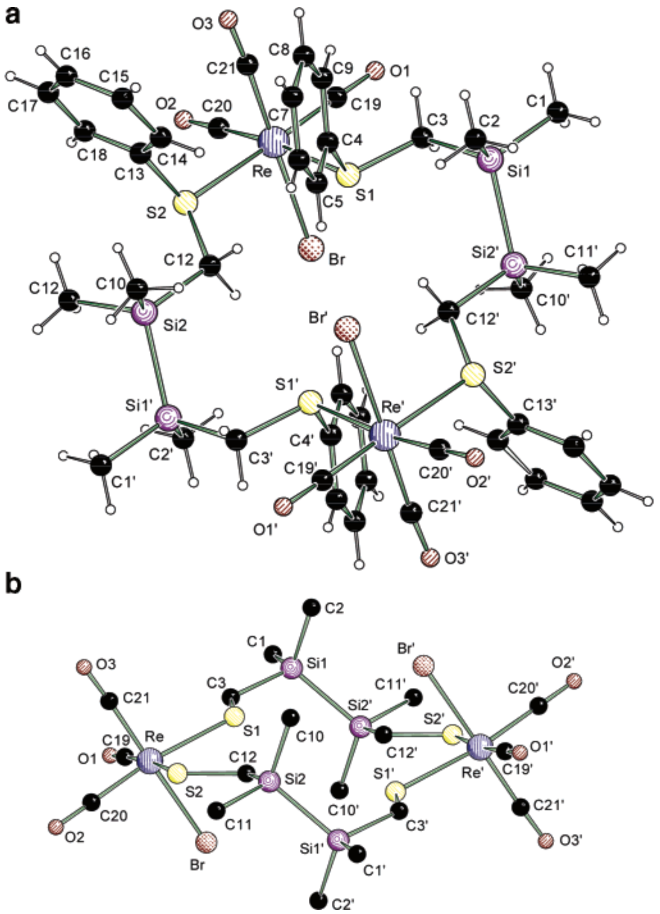


Figure 2. (a) Molecular structure of **4** in the solid state (Schakal plot). Selected bond lengths (Å) and angles (deg): Re−Br 2.6212(13), Re−C(19) 1.894(10), Re−C(20) 1.901(11), Re−C(21) 1.911(10), Re−S(1) 2.530(2), Re−S(2) 2.518(2), S(1)−C(3) 1.807(9), S(2)−C(12) 1.799(8), Si(1)−C(3) 1.908(10), Si(2)−C(12) 1.918(9) Si(1)−Si(2) 2.340(3), C(19)−Re−C(20) 88.8(4), C(19)−Re−C(21) 87.5(3), C(20)−Re−C(21) 88.7(4), C(19)−Re−S(2) 174.6(3), C(20)−Re−S(2) 86.1(2), C(21)−Re−S(2) 93.9(3), C(19)−Re−S(1) 93.0(3), C(20)−Re−S(1) 172.6(3), C(21)−Re−S(1) 98.5(3), C(19)−Re−Br 92.3(2), C(20)−Re−Br 92.0(3), C(21)−Re−Br 179.2(3), S(2)−Re−S(1) 91.89(7), S(2)−Re−Br 86.38(6), S(1)−Re−Br 80.73(6), C(3)−S(1)−Re 107.5(3), C(3)−Si(1)−Si(2) 111.3(3). (b) View of the macrocyclic core structure of **4** (Schakal plot). The phenyl groups have been omitted for clarity.

Synthesis of a Dinuclear Ruthenium Complex. The dimeric compound $[RuCl(\mu\text{-}Cl)(CO)_3]_2$ is known to be cleaved by various nucleophiles such as PR_3 or DMSO to give adducts of the type $[RuCl_2(CO)_3L]$.[43,44] In the case of thioethers R_2S, formation of an adduct with 2,5-dihydrothiophene has been reported.[45] The functional ligand $Ph_2PCH_2CH_2SPh$ is coordinated as both a monodentate and bidentate chelating ligand in

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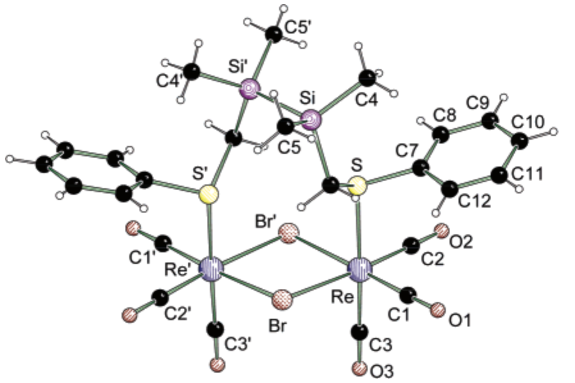


Figure 3. Molecular structure of **5** in the solid state (Schakal plot). Selected bond lengths (Å) and angles (deg): Re−Br 2.6479(8), Re′−Br 2.6526(9), Re−C(1) 1.904(6), Re−C(2) 1.905(7), Re−C(3) 1.924(6), Re−S 2.5056(13), S−C(6) 1.820(5), Si−C(6) 1.904(5), Si−Si 2.357(3), Re−Br−Re′ 97.87(3), C(1)−Re−C(2) 90.9(3), C(1)−Re−C(3) 90.1(2), C(2)−Re−C(3) 90.0(2), C(1)−Re−S 94.06(15), C(2)−Re−S 88.55(15), C(3)−Re−S 175.61(17), C(1)−Re−Br 94.73(19), C(2)−Re−Br 174.36(18), C(3)−Re−Br 89.64(15), S−Re−Br 91.45(3), C(1)−Re−Br′ 176.29(19), C(2)−Re−Br′ 92.39(18), C(3)−Re−Br′ 91.65(16), S−Re−Br′ 84.29(3), Br−Re−Br′ 82.01(3), C(6)−S−Re 114.68(16), C(6)−Si−Si′ 110.06(16).

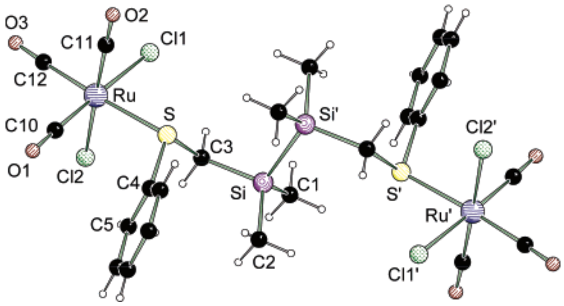


Figure 4. Molecular structure of **6** in the solid state (Schakal plot) and selected bond lengths (Å) and bond angles (deg): Ru−S 2.4349(6), Ru−Cl(1) 2.4018(7), Ru−Cl(2) 2.3938(6), S−C(4) 1.785(2), S−C(3) 1.805(2), Si−C(2) 1.863(3), Si−Si 2.3533(12), Si−C(1) 1.871(3), Cl(1)−Ru−Cl(2) 91.45(2), C(10)−Ru−S 91.71(7), C(12)−Ru−S 173.41(8), Cl(2)−Ru−S 91.26(2), Cl(1)−Ru−S 86.32(2), C(3)−S−Ru 108.16(8), C(4)−S−Ru 109.75(7), C(2)−Si−C(1) 109.77(14), C(2)−Si−Si 110.3(10), C(1)−Si−Si 113.51(10).

[RuCl$_2$(CO)L$_2$].[46] We reacted **1** with 1 equiv of [RuCl(μ-Cl)(CO)$_3$]$_2$ in CCl$_4$ solution at ambient temperature and obtained the chain complex *fac*-[(OC)$_3$Cl$_2$Ru{μ-(PhSCH$_2$)$_2$Si$_2$Me$_4$)}RuCl$_2$(CO)$_3$] (**6**), in which the two metal fragments are linked by the thioether functions (Scheme 4). IR monitoring shows that the three ν(CO) vibrations of the starting material at 2139, 2081, and 2075 cm^{-1} are replaced within 15 min by three bathochromic shifted vibrations at 2132, 2074, and 2048 cm^{-1}, indicating a facial carbonyl arrangement. The NMR spectrum of yellowish **6** is quite simple and consists of a sharp singlet at δ −0.04 due to four identical SiMe groups and a broad singlet at δ 3.09 attributed to the SCH$_2$Si groups, which sharpens upon heating to 318 K. The high symmetry of the dinuclear array is also maintained in the solid state, as shown by an X-ray diffraction study (see below).

Crystal Structure of 6. Figure 4 shows two octahedral ruthenium(II) centers that are linked by the disilane via its thioether substituents, the midpoint of the Si−Si bond being an inversion center. The separation between the two metal centers amounts to 11.031 Å. Each ruthenium moiety has two *cis*-arranged chloro ligands [Cl(1)−Ru−Cl(2) 91.45(2)°] and a facial arrangement of the three carbonyl ligands. The SPh function of the disilane ligand occupies the sixth position of the octahedron, the two halide atoms being *cis* relative to the Ru−S bond [2.4349(6) Å]. A comparable Ru−S bond length [2.416(2) Å] has been established for *trans*-(Cl,Cl′)-[RuCl$_2$(ptdmp)$_2$], chelated by the phosphine-thioether ligand Me$_2$PCH$_2$CH$_2$SPh.[47] The fact that the disilane is now part of an linear array without ring strain has no effect on the Si−Si bond length, since it is almost identical with that found for the chelate complex **2a** [2.3533(12) vs 2.357(4) Å].

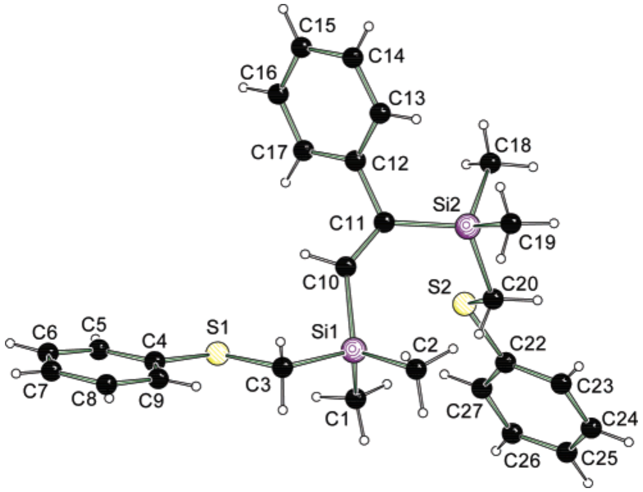
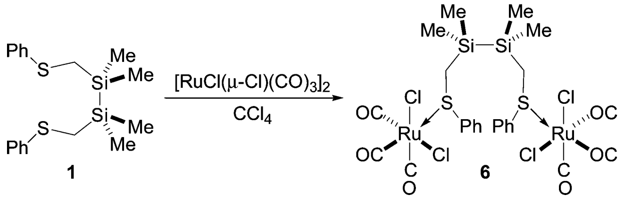


Figure 5. Molecular structure of **7a** in the solid state (Schakal plot) and selected bond lengths (Å) and bond angles (deg): C(1)−Si(1) 1.875(10), C(3)−S(1) 1.809(10), C(3)−Si(1) 1.895(8), C(4)−S(1) 177.4(11), C(10)−C(11) 1.341(10), C(10)−Si(1) 1.912(8), C(11)−C(12) 1.517(11), C(11)−Si(2) 1.886(9), C(18)−Si(2) 1.880(8), C(20)−S(2) 1.790(10), C(20)−Si(2) 1.919(7), C(21)−S(2) 1.763(11); C(4)−S(1)−C(3) 105.2(4), Si(1)−C(3)−S(1) 110.1(5), C(11)−C(10)−Si(1) 135.1(7), C(12)−C(11)−Si(2) 116.9(5), C(11)−Si(2)−C(20) 113.9(3), S(2)−C(20)−Si(2) 111.6(5), C(20)−S(2)−C(21) 104.8(4), C(3)−Si(1)−C(10) 103.4(4), C(1)−Si(1)−C(10) 112.1(4), C(11)−Si(2)−C(18) 108.8(4), C(10)−C(11)−Si(2) 128.7(6).

Scheme 4



Catalytic Bis-silylation of Terminal Aromatic Acetylenes. We have also attempted to prepare Pd-dithioether complexes analogous to **2**, which are ligated by **1**. However, on treatment of [PdCl$_2$(PhCN)$_2$] with a slight excess of **1** in dichloromethane at ambient temperature, progressive darkening and precipitation of large amounts of colloidal Pd was noticed. Since several examples of stable Pd-dithioether complexes are known (see above),[28,48,49] this reduction to elemental Pd may be explained by a competing oxidative addition of the Si−Si bond leading to a labile silylated Pd(IV) species. This intermediate may then decompose via reductive elimination of chlorosilanes. Note that

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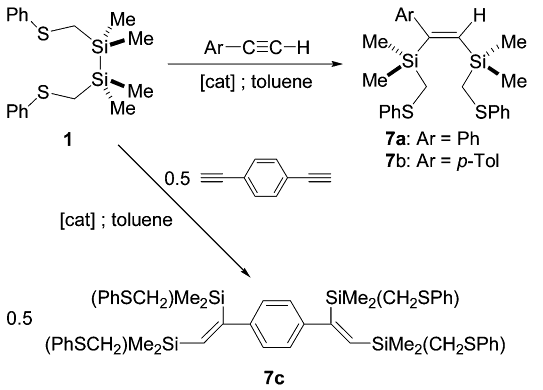
(47) Taguchi, N.; Kashiwabara, K.; Nakajima, K.; Kawaguchi, H.; Tatsumi, K. *J. Organomet. Chem.* **1999**, *587*, 290.

Scheme 5



recently the existence of silylated Pd(IV) complexes has been confirmed by an X-ray diffraction study.[50]

After exploring the propensity of **1** to act as a dithioether ligand in coordination chemistry, we set out to study the possibility of a metal-mediated activation of the Si−Si bond. In light of the above-mentioned reduction of $[PdCl_2(PhCN)_2]$ in the presence of **1**, it seemed promising to probe the bis-silylation of phenylactylene and *p*-tolylacetylene using $Pd(OAc)_2$/CNR as catalyst according to Scheme 5. Upon heating a toluene solution of **1** containing an excess of Ar−C≡C−H and 5 mol % of the catalyst for 20 h, the mixture rapidly turned red. After workup, the bis-silylated olefins *Z*-$(PhSCH_2)Me_2SiC(H){=}C(Ar)SiMe_2(CH_2SPh)$ (**7a** Ar = Ph; **7b** Ar = *p*-Tol) were isolated in the form of reddish crystals in the case of **7a** or as a brownish oil in the case of **7b** in 71−81% yield. Bis-silylation can even be performed across both triple bonds of 1,4-diethynylbenzene to afford the redidsh compound **7c**. Comparison of the spectroscopic data with those of **7a**,**b** indicates also a mutual *syn*-arrangement of the $SiCH_2SPh$ substituents of this diolefin. We also probed the catalytic activity of $Pd(PPh_3)_4$ toward **1** and phenylacetylene in an NMR tube experiment. NMR monitoring in C_6D_6 at 45 °C revealed that in the presence of 10 mol % of this Pd(0) catalyst almost quantitative formation of **7a** took place. In contrast, no catalytic activity was observed employing **2a** or $[RuCl(\mu\text{-}Cl)(CO)_3]_2$ in hot toluene.

Consistent with the proton NMR data, the *syn*-arrangement of the two $SiCH_2SPh$ substituents of **7a** has been confirmed by an X-ray diffraction study (Figure 5). The bond distance of 1.341(10) Å between C(10) and C(11) is in the usual range for olefinic double bonds; despite their bulkiness, the two silyl substituents are almost coplanar, the dihedral angle Si(1)−C(10)−C(11)−Si(2) being 3.05°. The bond lengths C(10)−Si(1) and C(11)−Si(2) [1.875(10) and 1.886(9) Å] parallel those reported for the cyclic compound 5,6-carboranylene-1,1,4,4-tetraethyl-2-phenyl-1,4-disilacyclohexene-2-ene [1.859(3) vs 1.873(3) Å], resulting from the reaction of 3,4-carboranylene-1,1,2,2-tetraethyl-1,2-disilacyclobutene-3-ene with phenylacetylene.[51]

Conclusion and Perspectives

We have shown that dithioether ligand **1** incorporating a disilane unit forms stable complexes with various transition metals such as Ru, Re, and Pt, but reduces Pd(II). Due to its flexibility, this ligand system can form seven-membered chelates, may assemble dinuclear complexes as bridging ligand, and even permits the construction of macrocyclic ring systems. Apart from this application in coordination chemistry, a promising potential for bis-silylation reaction also exists. Thus, in the presence of aromatic terminal acetylenes and a Pd catalyst, the Si−Si bond of **1** is cleaved, forming the bis-silylated olefin *Z*-$(PhSCH_2)Me_2SiC(H){=}C(Ar)SiMe_2(CH_2SPh)$, **7**. We are currently investigating the scope of the catalytic bis-silylation of other unsaturated organic substrates and are trying to trap reaction intermediates of this Pd-mediated reaction. Preliminary studies indicate that **1** is furthermore a useful precursor for the construction of cyclic trisilapentanes, which themselves are prone to insert acetylenes (catalytically mediated by $Pd(PPh_3)_4$), forming cyclic organosilicon compounds.[52]

Experimental Section

General Procedures. 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, and dichloromethane from P_4O_{10}. IR spectra have been recorded on a Nicolet Nexus 470 spectrometer. Elemental C and H analyses were performed on a Leco CHN 900 elemental analyzer. The ^{1}H and $^{29}Si\{^{1}H\}$ NMR spectra were recorded at 300.13 and 39.76 MHz, respectively, on a Bruker Avance 300 and a Bruker ACP 200 instrument. ^{195}Pt chemical shifts were measured on a Bruker ACP 200 instrument (42.95 MHz) and externally referenced to K_2PtCl_4 in water with downfield chemical shifts reported as positive. NMR spectra were recorded in pure $CDCl_3$, unless otherwise stated. The reactions were generally monitored by IR spectroscopy in the ν(CO) region.

Preparation of $(PhSCH_2)Me_2SiSiMe_2(CH_2SPh)$ (1). To a cooled suspension of 62 mmol of (phenylthiomethyl)lithium in 100 mL of diethyl ether, prepared from thioanisole and *n*-BuLi in diethyl ether, was added at −50 °C a solution of dichlorotetramethylsilane (5.20 g, 28 mmol) in 20 mL of hexane. The reaction mixture was allowed to warm to room temperature, stirred for 12 h, and then filtered. The solvent was evaporated in vacuo, and the residue was purified by Kugelrohr distillation. Recrystallization of the oily product from EtOH afforded **1** as a colorless solid (7.80 g, 78% yield). Mp = 54 °C. Anal. Calcd for $C_{18}H_{26}Si_2S_2$ (362.7): C, 59.61; H, 7.22. Found: C, 59.0; H, 7.30. ^{1}H NMR: δ 0.24 (s, 12H, SiCH_3, $^{2}J_{H,Si}$ = 6.5 Hz), 2.30 (s, 4H, SiCH_2S, $^{2}J_{H,Si}$ = 6.1 Hz), 7.0−7.34 (m, 10H, SC_6H_5). $^{13}C\{^{1}H\}$ NMR: δ −3.7 (4C, SiCH_3), 17.2 (2C, SiCH_2S), 124.8 (2C, C-4 of SC_6H_5), 126.2 (4C, C-2/C-6 of SC_6H_5), 128.7 (4C, C-3/C-5 of SC_6H_5), 140.2 (2C, C-1 of SC_6H_5). $^{29}Si\{^{1}H\}$ NMR: δ −16.7.

Preparation of $[PtCl_2\{(PhSCH_2)_2Si_2Me_4\}]$ (2a). To a solution of $[PtCl_2(PhCN)_2]$ (472 mg, 1 mmol) in 10 mL of dichloromethane was added **1** (370 mg, 1.1 mmol). The solution was stirred at 303 K for 24 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 (534 mg, 85% yield). Anal. Calcd for $C_{18}H_{26}Cl_2PtS_2Si_2$ (628.69): C, 34.39; H, 4.17. Found: C, 34.04; H, 4.11. ^{1}H NMR (298 K): δ 0.41 (s, SiCH_3), 0.54 (s, SiCH_3), 2.28 (d, 2H, H_A, $^{2}J_{HA,HB}$ = 11.8, $^{3}J_{Pt,HB}$ = 52 Hz), 3.36 (d, 2H, H_B, $^{2}J_{HA,HB}$ = 11.8 Hz). $^{195}Pt\{^{1}H\}$ NMR (323 K): δ −1846 (s, Pt).

Preparation of $[PtI_2\{(PhSCH_2)_2Si_2Me_4\}]$ (2b). To a solution of **2a** (315 mg, 0.5 mmol) in a 50:50 mixture of 12 mL of dichloromethane/acetone was added a 10-fold excess of NaI. The

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Table 1. Crystal Data, Data Collection, and Structure Refinement

	2a	**2b**	**4**	**5**	**6**	**7**
formula	$C_{18}H_{26}Cl_2PtS_2Si_2$	$C_{19}H_{28}Cl_2I_2PtS_2\ Si_2$	$C_{42}H_{52}Br_2O_6Re_2S_4Si_4$	$C_{24}H_{26}Br_2O_6Re_2S_2Si_2$	$C_{25}H_{28}Cl_6O_6Ru_2S_2Si_2$	$C_{26}H_{32}S_2Si_2$
fw	628.68	896.50	712.83	1062.97	480.82	464.82
T (K)	173(2)	173(2)	173(2)	173(2)	193(2)	173(2)
cryst size (mm)	0.30 × 0.20 × 0.20	0.30 × 0.20 × 0.20	0.30 × 0.20 × 0.10	0.30 × 0.30 × 0.10	0.30 × 0.30 × 0.20	0.40 × 0.20 × 0.20
cryst syst	triclinic	monoclinic	triclinic	monoclinic	triclinic	orthorhombic
space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$C2/c$	$P\bar{1}$	$Pca2_1$
a (Å)	7.472(2)	12.815(4)	10.282(2)	12.631(3)	8.1419(8)	25.243(4)
b (Å)	9.403(2)	11.1543(14)	10.615(2)	18.693(4)	8.9171(9)	6.464(2)
c (Å)	17.115(5)	19.862(4)	12.989(3)	13.998(3)	13.2822(13)	31.369(6)
α (deg)	98.43(3)	90	109.11(3)	90	101.2800(10)	90
β (deg)	91.64(4)	101.93(3)	94.25(3)	100.09(3)	90.773(2)	90
γ (deg)	104.07(3)	90	96.90(3)	90	100.8300(10)	90
V (Å^3)	1151.3(5)	2777.6(11)	1320.0(5)	3253.8(11)	927.58(16)	5119.0(2)
Z	2	4	1	4	2	8
ρ_{calc} (g·cm^{-3})	1.814	2.144	1.793	2.170	1.721	1.206
μ (mm^{-1})	6.612	7.710	6.385	10.126	1.459	0.313
F(000)	612	1680	692	1992	478	1984
θ range, deg	2.26 to 26.00	2.44 to 27.00	2.45 to 26.00	2.28 to 27.00	2.55 to 25.00	2.07 to 25.00
index ranges	$-9 \le h \le 9$, $-11 \le k \le 11$, $-21 \le l \le 21$	$-16 \le h \le 16$, $-14 \le k \le 14$, $-25 \le l \le 23$	$-12 \le h \le 11$, $-13 \le k \le 13$, $-16 \le l \le 16$	$-16 \le h \le 16$, $-23 \le k \le 21$, $-17 \le l \le 17$	$-9 \le h \le 9$, $-10 \le k \le 10$, $-15 \le l \le 15$	$-30 \le h \le 28$, $-5 \le k \le 7$, $-36 \le l \le 31$
no. of collected reflns	13 259	25 065	12 551	12 393	17 764	13 649
no. of indep reflns	4243	6019	4835	3324	3248	8206
no. of data/restraints/ params	4243/0/270	6019/0/257	4835/0/275	3324/0/174	3248/0/201	8206/1/549
largest diff peak and hole, e Å^{-3}	4.310 and −4.990	1.952 (near Pt and I) and −3.196	3.978 and −3.317	1.679 and −2.286	0.887 and −0.790	0.464 and −0.323
absolute structure factor						0.07(17)
final R indices [$I > 2\sigma(I)$]	R1 = 0.0570, wR2 = 0.1521	R1 = 0.0421, wR2 = 0.1057	R1 = 0.0530, wR2 = 0.1246	R1 = 0.0377, wR2 = 0.0909	R1 = 0.0222, wR2 = 0.0569	R1 = 0.0617, wR2 = 0.1143
R indices (all data)	R1 = 0.0589, wR2 = 0.1539	R1 = 0.0447, wR2 = 0.1080	R1 = 0.0640, wR2 = 0.1309	R1 = 0.0412, wR2 = 0.0929	R1 = 0.0226, wR2 = 0.0573	R1 = 0.1274, wR2 = 0.1291
GOF on F^2	1.054	1.031	1.011	1.058	1.047	1.011

suspension was then stirred for 24 h. The solvent was then removed under reduced pressure and the residue extracted with CH_2Cl_2. After concentration of the extract, layering with hexane gave orange-red crystals solvated by one molecule of CH_2Cl_2, which was lost after prolonged drying in vacuo (265 mg, 79% yield). Anal. Calcd for $C_{18}H_{26}I_2PtS_2Si_2$ (810.88): C, 26.64; H, 3.23. Found: C, 26.32; H, 3.02. ^{1}H NMR (298 K): δ 0.51 (s, br Si*CH*$_3$), 2.32 (v br, unresolved, H_A), 3.53 (v br, unresolved, H_B), 6.95−8.02 (m, phenyl).

Preparation of *fac*-[{ReBr(CO)$_3$}$_2${*μ*-(PhSCH$_2$)$_2$Si$_2$Me$_4$}$_2$] (4). [{Re(μ-Br)(CO)$_3$THF]$_2$ (100 mg, 0.118 mmol) was dissolved in 10 mL of dichloromethane, and 2 equiv of **1** (86 mg, 0.236 mmol) was added to the solution. The reaction mixture was stirred at room temperature for 5 h and then concentrated under reduced pressure. Addition of hexane and cooling gave pale yellow crystals, which were filtered off and dried under vacuum (121 mg, 72% yield). Anal. Calcd for $C_{42}H_{52}Br_2O_6Re_2S_4Si_4$ (1425.66): C, 33.70; H, 3.68. Found: C, 33.43; H, 3.83. IR (CH_2Cl_2) ν(CO): 2034s, 1942s, 1909s cm^{-1}. ^{1}H NMR: δ 0.38 (s, 3H, Si*CH*$_3$), 0.37 (s, 3H, Si*CH*$_3$), 2.66 (d, 2H, $^2J_{HA-HB}$ = 12 Hz), 3.71 (d, 2H, $^2J_{HA-HB}$ = 12 Hz), 7.28−7.66 (m, 10H, C_6H_5).

Preparation of *fac*-[{Re(*μ*-Br)(CO)$_3$}$_2$-{*μ*-(PhSCH$_2$)$_2$Si$_2$Me$_4$}] (5). Compound **5** was obtained in an analogous manner by reaction of [{Re(μ-Br)(CO)$_3$THF]$_2$ (100 mg, 0.118 mmol) with 1 equiv of **1** (43 mg, 0.118 mmol) (85 mg, 68% yield). Anal. Calcd for $C_{24}H_{26}Br_2O_6Re_2S_2Si_2$ (1062.97): C, 27.12; H, 2.47. Found: C, 26.87; H, 2.54. IR (CH_2Cl_2) (νCO): 2023s, 1928s, 1905s cm^{-1}. ^{1}H NMR: δ −0.03 (s, 3H, Si*CH*$_3$), −0.11 (s, 3H, Si*CH*$_3$), 2.86 (d, 2H, $^2J_{HA-HB}$ = 15 Hz), 3.26 (d, 2H, $^2J_{HA-HB}$ = 15 Hz), 7.28−7.75 (m, 10H, C_6H_5).

Preparation of *fac*-[(OC)$_3$Cl$_2$Ru{*μ*-(PhSCH$_2$)$_2$Si$_2$Me$_4$)}RuCl$_2$-(CO)$_3$]$_2$ (6). To a solution of [Ru(μ-Cl)(CO)$_3$]$_2$ (51 mg, 0.1 mmol) in dry CCl_4 (7 mL) was added **1a** (0.043 g, 0.12 mmol). The mixture was stirred at room temperature for 0.5 h and then the solvent removed in vacuo. Yellowish single crystals were grown from CH_2Cl_2/hexane (0.058 g, 67% yield). Anal. Calcd for $C_{24}H_{26}Cl_4O_6Ru_2O_6S_2Si_2$: C, 32.95; H, 3.00. Found: C, 32.80; H, 2.88. IR (CCl_4) ν(CO): 2132 (s), 2074 (s), 2048 (m) cm^{-1}. ^{1}H NMR δ −0.04 (s, 12H, Si*CH*$_3$), 3.09 (s, 4H, S*CH*$_2$), 7.30−7.93 (m, 10H, SC_6H_5).

Preparation of *Z*-(PhSCH$_2$)Me$_2$SiC(H)═C(Ph)SiMe$_2$(CH$_2$SPh) (7a). To a toluene solution (10 mL) containing **1** (0.492 g, 1.36 mmol), phenylacetylene (0.210 g, 2.06 mmol), and palladium acetate (0.006 g, 0.028 mmol) was added 1,1,3,3 tetramethylbutyl isocyanide (0.048 g, 0.42 mmol). The yellow mixture quickly turned red after heating to 80 °C. Agitation was continued for 20 h, then all volatiles were removed under reduced pressure. Extraction of the oily residue with hexane and storing in a freezer at 5 °C gave an analytically pure sample (0.448 g, 71% yield). Anal. Calcd for $C_{26}H_{32}S_2Si_2$ (464.85): C, 67.18; H, 6.94. Found: C, 67.49; H, 7.02. ^{1}H NMR: δ 0.33 (s, 6H, Si*CH*$_3$, $^2J_{H,Si}$ = 6.6 Hz), 0.39 (s, 6H, Si*CH*$_3$, $^2J_{H,Si}$ = 6.6 Hz), 2.29 (s, 2H, Si*CH*$_2$S), 2.39 (s, 2H, Si*CH*$_2$S), 6.62 (s, 1H, ═C*H*, $^2J_{H,Si}$ = 16.7 Hz), 6.74−7.84 (m, 15H, C_6H_5). ^{13}C{^{1}H} NMR: δ 0.00 (2C, *Si*CH$_3$), 0.02 (2C, Si*C*H$_3$), 19.11 (1C, Si*C*H$_2$S), 19.46 (1C, Si*C*H$_2$S), 125.21−129.75 (1C, phenyl), 140.53 (1C, SC_6H_5), 140.68 (1C, SC_6H_5), 148.07 (1C, ═*C*H), 150.2 (1C, phenyl), 164.47 (1C, ═*C*-C_6H_5). ^{29}Si{^{1}H} NMR: δ −6.62 (s, 1Si), −9.65 (s, 1Si).

Preparation of *Z*-(PhSCH$_2$)Me$_2$SiC(H)═C(*p*-Tol)SiMe$_2$-(CH$_2$SPh) (7b). A toluene solution (2 mL) containing **1** (0.246 g, 0.64 mmol), *p*-tolylacetylene (0.120 g, 1.03 mmol), palladium acetate (0.003 g, 0.014 mmol), and 1,1,3,3-tetramethylbutyl isocyanide (0.029 g, 0.21 mmol) was heated under reflux for 7 h. The solution was stood at room temperature, and then all volatiles were removed under reduced pressure. The oily residue was dissolved in pentane, filtered, and kept in a freezer at −25 °C. A brownish-red solid precipitated, which melted again at ambient temperature (0.248 g, 81% yield). Anal. Calcd for $C_{27}H_{34}S_2Si_2$ (478.86): C, 67.72; H, 7.16. Found: C, 67.49; H, 7.32. ^{1}H NMR: δ 0.36 (s, 6H, Si*CH*$_3$), 0.43 (s, 6H, Si*CH*$_3$), 2.28 (s, 2H, Si*CH*$_2$S), 2.35 (s, 3H, C_6H_4*CH*$_3$), 2.37 (s, 2H, SiCH$_2$S), 6.59 (s, 1H, ═C*H*), 7.01−7.30 (m, 14H, C_6H_5). ^{29}Si{^{1}H} NMR: δ −6.97 (s, 1Si), −10.05 (s, 1Si).

Preparation of (7c). This derivative was prepared as described for **7a** by heating a mixture of **1** (0.492 g, 1.36 mmol) and 1,4-diethynylbenzene (0.126 g, 1.03 mmol) in the presence of the catalyst (0.452 g, 84% yield). Anal. Calcd for $C_{46}H_{58}S_4Si_4$ (851.55): C, 64.88; H, 6.87. Found: C, 65.27; H, 7.11. ^{1}H NMR: δ 0.59 (s, 12H, Si*CH*$_3$), 0.67 (s, 12H, Si*CH*$_3$), 2.49 (s, 4H, Si*CH*$_2$S), 2.61 (s, 4H, Si*CH*$_2$S), 6.84 (s, 2H, ═C*H*), 6.27−7.25 (m, 24 H, C_6H_5). ^{13}C{^{1}H} NMR: δ −0.02 (4C, *Si*CH$_3$), 0.04 (4C, Si*C*H$_3$), 19.13 (2C, Si*C*H$_2$S), 19.45 (2C, Si*C*H$_2$S), 125.42−129.37 (1C, phenyl), 140.52 (2C, SC_6H_5), 140.68 (2C, SC_6H_5), 147.85 (2C, ═*C*H), 148.09 (2C, phenyl), 164.18 (2C, ═*C*-C_6H_5). ^{29}Si{^{1}H} NMR: δ −6.68 (s, 1Si), −9.69 (s, 1Si).

Crystal Structure Determinations. Data of **2a**, **2b**, **4**, **5**, and **7** were collected on a Stoe IPDS diffractometer (Stoe & Cie GmbH) using graphite-monochromated Mo Kα radiation (λ = 0.71069 Å). The intensities were determined and corrected by the program INTEGRATE in IPDS (Stoe & Cie, 1999). An empirical absorption correction was employed using the FACEIT-program in IPDS (Stoe & Cie, 1999). Data of **6** were collected on a Bruker APEX-CCD (D8 three-circle goniometer) (Bruker AXS) using graphite-monochromated Mo Kα radiation (λ = 0.71069 Å). The intensities were determined and corrected by the programs Smart version 5.622 (Bruker AXS, 2001) and SaintPlus version 6.02 (Bruker AXS, 1999). An empirical absorption correction was employed using Sadabs version 2.01 (Bruker AXS, 1999).

The structures were solved applying direct and Fourier methods, using SHELXS-90 and SHELXL-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 riding model. The phenyl group on S(1) of **2a** is disordered, and the corresponding carbon atoms were refined on split positions. 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. Crystal data, data collection parameters, and details of the structure refinement are given in Table 1. ORTEP diagrams for **2a**, **2b**, **4**, **5**, **6**, and **7** are included in the Supporting Information.

Crystallographic data (excluding structure factors) for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 247286 for **2a**, 247290 for **2b**, 247289 for **4**, 247288 for **5**, 247287 for **6**, and 247291 for **7**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax +44-1223-336033; e-mail deposit@ccdc.cam.ac.uk; web http://www.ccdc.cam.ac.uk).

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Supporting Information Available: Tables of X-ray structural data, including data collection parameters, positional and thermal parameters, bond distances and angles, and ORTEP plots for **2a**, **2b**, **4**, **5**, **6**, and **7**. UV−vis spectra of **1** and **2a** and the ^{195}Pt{^{1}H} NMR spectrum of **2a** at variable temperature are also depicted. This material is available free of charge via the Internet at http://pubs.acs.org.

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