Synthesis and reactivity of silylated tetrathiafulvalenes†

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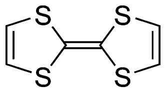
Novel organosilylated tetrathiafulvalenes (TTFs) possessing Si–H or Si–Si bonds have been synthesised. The crystal structures of several derivatives have been determined by X-ray diffraction, including that of dimeric $(Si_2Me_4)(TTF)_2$ (**11**) incorporating a diatomic $SiMe_2$–$SiMe_2$ linker. Cyclic voltammetry measurements in all cases show two oxidation waves. DFT calculations were performed to rationalize the absence of an electronic communication between the two TTF moieties of **11** through the disilanyl spacer. The reactivity of the Si–H bond has been exploited to prepare the dinuclear complex $[\{Ru(CO)_4\}_2\{\mu\text{-}(Me_2Si)_4TTF\}]$ (**14**), starting from $Ru_3(CO)_{12}$ and $TTF(SiMe_2H)_4$ (**1**). Treatment of **14** with 2 equiv. of PPh_3 or dppm results in selective substitution of a CO ligand *trans* to a $SiMe_2$ group to afford *mer*-$[\{Ru(PPh_3)(CO)_3\}_2\{\mu\text{-}(Me_2Si)_4TTF\}]$ (**13**) and *mer*-$[\{Ru(CO)_3\}_2(\eta^1\text{-}dppm)\{\mu\text{-}(Me_2Si)_4TTF\}]$ (**16**). Attempts to transform the Si–H bonds of some $TTF(SiMe_2H)_n$ ($n = 1$, 2) into Si–O functions using stoichiometric amounts of water in the presence of tris(dibenzylideneacetone)dipalladium(0) were unsuccessful. Quantitative cleavage of the C_{TTF}–Si bond was observed instead of formation of TTF-based-siloxanes. Essays of catalytic bis-silylation of phenylacetylene with **11** and $TTF(SiMe_2\text{-}SiMe_3)$ (**9**) in the presence of $Pd(OAc)_2$/1,1,3,3-tetramethylbutylisocyanide failed. Again, cleavage of the C_{TTF}–Si bond was noticed.

Introduction

The remarkable properties of the "venerable" tetrathiafulvalene (TTF, Scheme 1) (reversible redox processes at relatively low potential, stacking in the solid state) continue to focus interest not only for the synthesis of conducting organic metals[1] but also for alternative applications[2] such as sensors[3] or molecular motors.[4]



TTF

Scheme 1

Until the 1990's, development of TTF chemistry concerned mainly the modification of the skeleton with the aim of increasing the dimensionality of the charge transfer materials and consequently their electrical conducting properties.[5] Among the variety of chemical modifications realized, the most exploited strategies were the introduction of chalcogens in a peripheral position and the synthesis of TTF derivatives containing extended π-electron conjugation.[6] The incorporation of silyl groups has also been explored, but to a lesser extend compared to thiolate or thioether. The synthesis of flexible[7] or rigid bis(tetrathiafulvalene)[8] containing dimethylsilyl linkers has been reported, the tetrasilylated derivative $TTF(SiMe_3)_4$ has been obtained under high-pressure conditions by cycloaddition of bis(trimethylsilylacetylene) with CS_2,[9] while mono-silylated derivatives have been isolated starting from mono-lithiated TTF.[10] Recently we described the synthesis of functionalized TTFs with $SiMe_2$–H moieties[11] and detailed studies on a series of functionalized sulfur systems.[12] The reactivity of the Si–H bond for oxidative addition reactions has been exploited to link covalently a Pt(0) centre with a TTF moiety.[11] In the last decade, there has been an increasing interest in functionalized TTFs with substituents allowing coordination to transition metal. Besides the quest for materials of high dimensionality, such molecules are particularly attractive for the elaboration of hybrid organic/inorganic multifunctional materials.[13] The first TTF transition metal complexes were obtained by the covalent coordination of metal fragments to tetrathiolate tetrathiafulvalene ($TTFS_4^{4-}$).[14] Since that time, in addition to the above-mentioned synthesis of TTF-based silyl complexes, new strategies consisting of the synthesis of TTF incorporating a potentially coordinating function such as thioether,[15] phosphane,[16] pyridine,[17] acetylacetone[18] or oxazoline[19] have been developed.

The reactivity of Si–H bond being not restricted only to platinum,[20] an extension to other metal centres appeared as a logical continuation to our previous studies. The presence of one or more Si–H bonds on silyl substituted TTFs seemed also promising for the preparation of TTF-based siloxanes since it can

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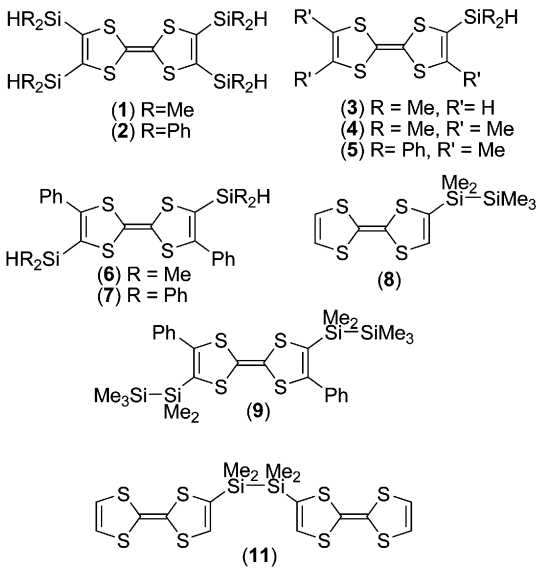
† Electronic supplementary information (ESI) available: $^{29}Si\{^1H\}$ and 2D-HMQC spectra of **8** and details on computational studies performed on compounds **11** and **12**. CCDC reference numbers 671046, 671047, 680221 and 680222. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b803947j

be easily transformed into a Si–O function under mild conditions.[21] Moreover, the hydrosilylation reaction across unsaturated organic substrates may allow the formation of other silylated TTF derivatives.[22] Besides the intrinsic photophysical properties of the Si–Si bond,[23] functionalization of TTFs with these moieties is particularly of interest since it may be an alternative strategy for the synthesis of original silylated TTFs. Indeed, the catalytic activation of the Si–Si bond of disilanes by transition metals is an elegant route for the bis-silylation of unsaturated organic substrates such as alkynes, olefins, isocyanides and aldehydes.[24] The synthetic potential of these above-mentioned reactions has motivated us to continue our previous studies on silylated TTFs. We report in this paper on the preparation and characterization of novel compounds with Si–H or Si–Si bonds and the study of their reactivity.



Scheme 2

Results and discussion

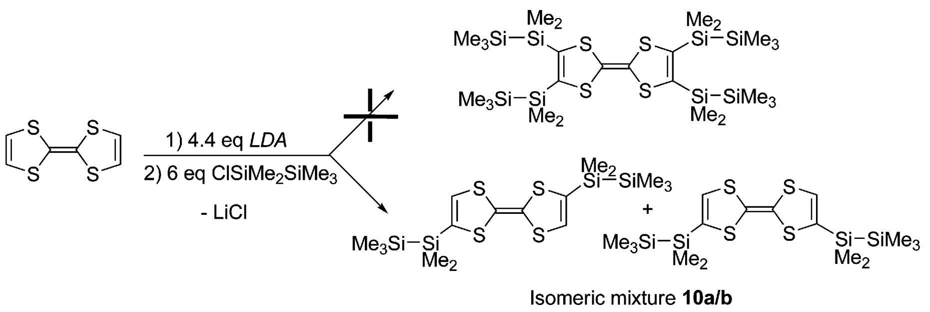
Synthesis of silylated TTF derivatives

We recently described the synthesis of tetra-silylated tetrathiafulvalene TTF(SiR$_2$H)$_4$ (R = Me: **1**, Ph: **2**)[11b] by a classical one-pot method used for the preparation of substituted TTF, which takes advantage of the acidity of the TTF hydrogen atoms.[25] The silylation was achieved by reaction at −78 °C between the appropriate chlorosilane and TTFLi$_4$ generated by deprotonation of TTF with a slight excess of LDA (lithium diisopropylamide, 5 equiv.). Using a similar methodology, mono-substituted TTFs (**3–5**) and di-substituted diphenyltetrathiafulvalene with a functional group attached to the 5-membered TTF core (**6–7**) have been prepared in order to gain insight into the potentialities of TTF functionalized by SiR$_2$H groups (Scheme 2). All these compounds were isolated as orange-red crystalline powders which are air-stable for prolonged periods. Note that compounds **6** and **7** were obtained using as starting material commercially available (Aldrich) diphenyltetrathiafulvalene which is considered to be a mixture of *cis*- and *trans*-isomers. Previous studies have shown that the *trans* product is predominant[26] and an X-ray crystallography study on **7** reveals a *trans* structure (see below). The IR spectra of all these compounds present a broadened ν(Si–H) vibration in the range between 2150–2180 cm^{-1}. TTF derivatives **8** and **9** possessing Si–Si bonds were respectively prepared by reaction of mono-lithiated TTF and di-lithiated dipenyltetrathiafulvalene with chloropentamethyldisilane.

Attempts to prepare the tetrakis-disilanyl derivative starting from tetralithiated tetrathiafulvalene failed. The yellow powder isolated after purification was identified by elemental and GC/MS analysis to be a mixture of *cis*/*trans* bis(disilanyl)tetrathiafulvalene (**10a** and **10b** in Scheme 3). A 75 : 25 ratio has been determined, but the spectroscopic data do not allow unambiguous assignment to the corresponding isomer (see Experimental section). The bis(TTF) compound **11**, linked by a Si–Si bond, was obtained by treating 2 equiv. of mono-lithiated TTF with 1,2-dichlorotetramethyldisilane in 55% yield in the form of a yellow crystalline solid. As expected, the ^{29}Si NMR spectrum of **11** displays a single singlet resonance at δ −22.8, whereas two resonances are observed in the spectra of **8–10** due to the presence of two non-equivalent silicon atoms.

Crystal structures of some silyl- and disilany-TTFs

The suggested molecular structures of compounds **2** (Fig. 1), **7** (Fig. 2), **9** (Fig. 3) and **11** (Fig. 4) have also been confirmed by X-ray diffraction studies. The TTF derivatives **2**, **7** and **9** present an inversion centre located at the middle of the central C=C bond of the TTF core. The TTF moieties in these molecules deviate only slightly from planarity giving rise to a chair-like conformation. In contrast, the TTF moieties adopt a boat-like conformation in compound **11**, the midpoint of the bridging Si–Si bond being an inversion centre. Except for this conformational view, the nature of the substituents on the TTF core has no significant influence on the



Scheme 3

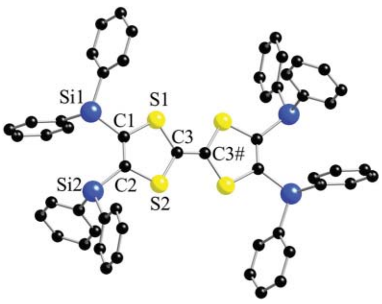


Fig. 1 Molecular structure of **2**. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles (°): C(3)–C(3)# 1.342(4), C(3)–S(1) 1.756(2), C(3)–S(2) 1.759(2), S(1)–C(1) 1.763(2), S(2)–C(2) 1.764(2), C(2)–C(1) 1.350(3), C(1)–Si(1) 1.880(2), C(2)–Si(2) 1.881(2); C(3)#–C(3)–S(1) 123.1(2), C(3)#–C(3)–S(2) 123.7(2), S(1)–C(3)–S(2) 113.23(11), C(3)–S(1)–C(1) 96.57(9), C(3)–S(2)–C(2) 96.45(10), S(2)–C(2)–C(1) 116.68(16), S(1)–C(1)–C(2) 116.71(16), S(2)–C(2)–Si(2) 116.51(11), S(1)–C(1)–Si(1) 116.44(11), C(1)–C(2)–Si(2) 126.45(16), C(2)–C(1)–Si(1) 126.82(16). Symmetry operation used to generate equivalent atoms: #: $-x$, $-y$, $1 - z$.

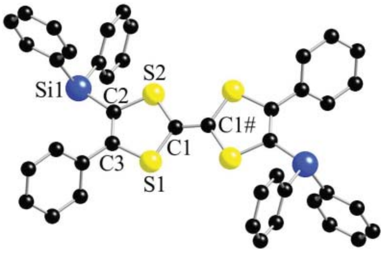


Fig. 2 Molecular structure of **7**. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles (°): C(1)–C(1)# 1.326(12), C(1)–S(1) 1.743(7), C(1)–S(2) 1.768(7), S(2)–C(2) 1.750(7), S(1)–C(3) 1.762(7), C(2)–C(3) 1.365(9), C(2)–Si(1) 1.872(7); C(1)#–C(1)–S(1) 124.6(7), C(1)#–C(1)–S(2) 121.5(8), S(2)–C(1)–S(1) 113.9(4), C(1)–S(1)–C(3) 96.3(3), C(1)–S(2)–C(2) 96.0(3), S(2)–C(2)–C(3) 116.9(5), S(1)–C(3)–C(2) 116.5(5), S(2)–C(2)–Si(1) 115.3(4). Symmetry operation used to generate equivalent atoms: #: $1 - x$, $2 - y$, $1 - z$.

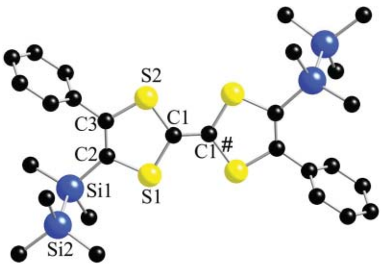


Fig. 3 Molecular structure of **9**. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles (°): C(1)–C(1)# 1.331(4), C(1)–S(1) 1.7548(17), C(1)–S(2) 1.7506(19), S(2)–C(3) 1.7606(17), S(1)–C(2) 1.7542(18), C(2)–C(3) 1.345(2), C(2)–Si(1) 1.8891(18), Si(1)–Si(2) 2.3361(8); C(1)#–C(1)–S(1) 122.63 (19), C(1)#–C(1)–S(2) 123.83(18), S(1)–C(1)–S(2) 113.54(10), C(1)–S(1)–C(2) 96.96(8), C(1)–S(2)–C(3) 95.58(8), S(1)–C(2)–C(3) 115.41(13), S(2)–C(3)–C(2) 118.24(14), S(1)–C(2)–Si(1) 114.30(9), C(2)–Si(1)–Si(2) 109.66(6). Symmetry operation used to generate equivalent atoms: #: $-x + 2$, $-y$, $-z + 1$.

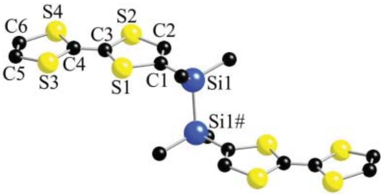


Fig. 4 Molecular structure of **11**. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles (°): C(4)–C(3) 1.349(7), C(4)–S(3) 1.748(5), C(4)–S(4) 1.744(5), S(4)–C(6) 1.719(7), S(3)–C(5) 1.715(6), C(6)–C(5) 1.312(9), C(3)–S(1) 1.754(5), C(3)–S(2) 1.741(5), S(2)–C(2) 1.738(5), S(1)–C(1) 1.758(5), C(2)–C(1) 1.346(7), C(1)–Si(1) 1.862(5), Si(1)–Si(1)# 2.327(3); C(3)–C(4)–S(3) 123.0(4), C(3)–C(4)–S(4) 122.5(4), S(4)–C(4)–S(3) 114.4(3), C(4)–S(4)–C(6) 94.1(3), C(4)–S(3)–C(5) 94.4(3), S(4)–C(6)–C(5) 118.3(5), S(3)–C(5)–C(6) 118.1(6), C(4)–C(3)–S(1) 121.5(4), C(4)–C(3)–S(2) 123.9(4), S(2)–C(3)–S(1) 114.5(3), C(3)–S(1)–C(1) 96.0(2), C(3)–S(2)–C(2) 95.1(3), S(1)–C(1)–C(2) 115.1(4), S(2)–C(2)–C(1) 119.2(4), S(1)–C(1)–Si(1) 119.2(3), C(1)–Si(1)–Si(1)# 107.34(18). Symmetry operation used to generate equivalent atoms: #: $-x + 2$, $-y$, $-z + 1$.

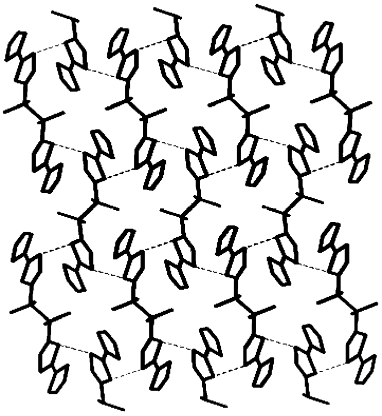


Fig. 5 View of the *bc* plane in **11** showing short S···S contacts of 3.518 Å (dashed lines).

structural parameters of the TTF unit. For these four compounds, the C–Si distances lie in the range between 1.86–1.89 Å and are similar to those reported for $(TTF)_2SiMe_2$ [1.868 Å][7] and **1** [1.876 and 1.883 Å].[11b] The Si–Si bond lengths are almost identical in **9** and **11** [2.336(1) and 2.327(3) Å respectively] and similar to the values generally observed for this bond in non-sterically-crowded organosilanes.[27] The coordination geometry around each Si atom is essentially tetrahedral. In compound **11**, the two TTF moieties are almost parallel, with the Si–Si bond which is normal to the TTF planes. Worth mentioning are the intermolecular interactions observed in the solid state packing diagram of molecule **11** with short S···S contacts of 3.518 and 3.705 Å (Fig. 5). Due to the steric hindrance of the phenyl substituent, no significative intermolecular interactions deserving a detailed discussion were noticed in the case of the other derivatives.

Electrochemistry

The redox properties of each new compound have been investigated by cyclic voltammetry in dichloromethane and acetonitrile solution at a scan rate of 100 $mV\ s^{-1}$. The results are collected in Table 1. It should be noted that two reversible redox processes are observed for diphenyltetrathiafulvalene in both solvents whereas the second wave of TTF is found to be irreversible in CH_2Cl_2

Table 1 Electrochemical data: reference electrode $AgClO_4$ (0.1 M in MeCN)/Ag

Compound	Solvent	$E_1^{1/2}$/V	$E_2^{1/2}$/V
TTF	CH_2Cl_2	+0.07	Irreversible
	MeCN	−0.01	+0.36
Ph_2TTF	CH_2Cl_2	+0.13	+0.62
	MeCN	+0.025	+0.375
1	CH_2Cl_2	+0.01	+0.54
	MeCN	−0.05	+0.33
2	CH_2Cl_2	+0.07	+0.57
	MeCN	+0.02	+0.38
4	CH_2Cl_2	−0.02	+0.52
	MeCN	−0.10	+0.28
6	CH_2Cl_2	+0.02	+0.53
	MeCN	+0.01	+0.39
7	CH_2Cl_2	+0.10	+0.56
	MeCN	Insoluble	
8	CH_2Cl_2	+0.01	Irreversible
	MeCN	−0.07	+0.32
9	CH_2Cl_2	−0.02	+0.50
	MeCN	−0.04	+0.35
11	CH_2Cl_2	−0.03	Irreversible
	MeCN	−0.08	+0.36
14	CH_2Cl_2	−0.08	+0.50
15	CH_2Cl_2	−0.23	+0.41

solution, as already mentioned by Wudl *et al.*[28] The silylated TTFs present the same features as their parent compounds (Fig. 6). Substitution of the TTF hydrogen by $SiPh_2H$ groups induces no significant change in the potential of the two redox processes. However, they are lowered by *ca.* 0.05 V per Si_2Me_5 substituent introduced in the case of **8** and **9**. No oxidative cleavage of the Si–Si bond is observed for the complexes **8–11** in the potential range explored. According to the electrochemical data, no electronic coupling between the two redox units for disilanyl compound **11** occurs. Indeed, only two distinct oxidation waves are present, indicating that monocationic and dicationic species are formed simultaneously, followed by a further oxidation to generate the tetracationic species (Fig. 6). This finding contrasts to what is noticed for the $(TTF)_2(SiMe_2)$ (**12**) incorporating a *monoatomic* $–SiMe_2–$ spacer, since three oxidation steps are observed in this case.[7] Note that a recent study devoted to dinuclear ferrocenes of type $[\{Fe(Cp^*)(C_5H_4)\}_2X]$ (X = CMe_2, $SiMe_2$, $GeMe_2$, Si_2Me_4; $Cp^* = C_5Me_5$) has shown that the electronic coupling is more important with the CMe_2 linker than with the $SiMe_2$ bridge.[29] This has been rationalized by the closer approach of the two ferrocenes (Fcs) due to the shorter Fc–C–Fc separation compared to the Fc–Si–Fc separation. The CV data presented in this report indicate a single wave in the case of the disilanyl-bridged compound $[\{Fe(Cp^*)(C_5H_4)\}_2Si_2Me_4]$, ruling out a significant interaction between the two redox centres. These findings are somewhat contradictory with another electrochemical study of ferrocenyloligosilane of type $[\{Fe(Cp)(C_5H_4)\}_2(SiMe_2)_n]$.[30] In the latter example, electrochemical communication was established even across a trisilanyl spacer.

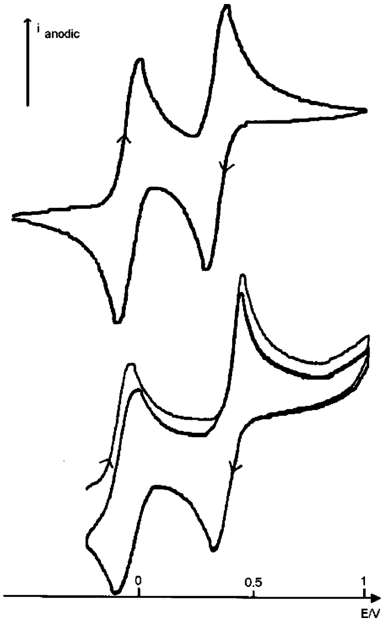
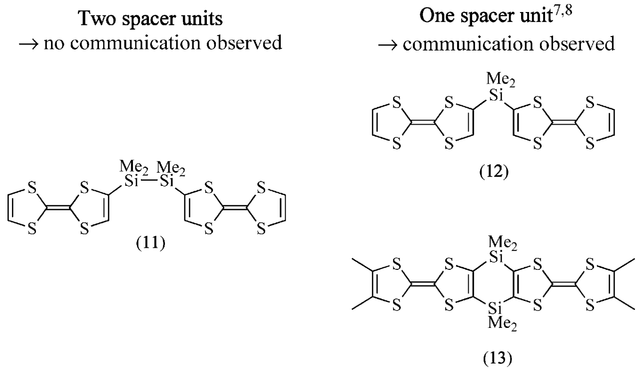


Fig. 6 Cyclic voltammograms of **8** (top) and **11** (5 scans) recorded in MeCN solution on a platinum electrode at a scan rate of 100 mV s^{-1}; reference electrode $AgClO_4$ (0.1 M in MeCN)/Ag.

Electronic structure of silyl-bridged TTFs

According to the experimental CV results of the disilyl-bridged compound **11**, there is no electronic communication between the two TTF units in this molecule. Contrary to this, Fourmigué *et al.* observed a considerable communication in $(TTF)_2SiMe_2$ (**12**), where both TTF units are separated by only one silyl group.[7] Most recently, a communication between the two TTF units has also been reported in the "double" mono-silyl bridged system **13**.[8] Thus, the two TTF units are able to communicate with each other if there is only one silicon spacer in-line between them (**12** and **13**) whereas a communication appears impossible with two spacers in-line between the TTF units of **11** (Scheme 4). Therefore the question arises, what are the origins for the divergent electrochemical behaviour of the TTF compounds depicted in Scheme 4? In the early 1990's, a sandwich structure with some degree of sharing of the π-electrons between the two TTF units was postulated to explain the stabilization of the mono-radical cation in flexible TTF dimers.[31] However, extended Hückel calculations performed on $(TTF)_2X$ (X = $SiMe_2$, Hg, S, PPh) dimers interpreted the splitting of the oxidation waves as due rather to Coulombic repulsions between the two TTF units and not arising from through space or bond orbital overlap.[7] In this study, we have re-examinated this problem using DFT calculations at the B3LYP/6-31+G(d) level[32] on compounds **11** and **12**.



Scheme 4 Electronic communication between the TTF units of **11–13**.

The starting coordinates were constructed using the solid state structures. In addition to the conformer found in the crystal, a second energetically comparable conformer exists for **11** and **12**, respectively, where the TTF units are twisted against each other (other imaginable conformers were neglected as the energy of these conformers is too high). Since the second conformer shows similar results to the dominant one (in both cases), we limit our discussion to the one found in the crystal. Fig. 7 visualizes the calculated frontier orbitals (LUMO, HOMO and HOMO−1) of the investigated compounds. DFT studies on the same level also showed that the frontier orbitals of radical cations $\mathbf{11}^{+\bullet}$ and $\mathbf{12}^{+\bullet}$ are comparable to the neutral TTF derivatives. The basic requirement for an electronic communication of spatial separated TTF units is the presence of a low lying frontier orbital, capable of electron transfer. For this electron transfer, the relevant frontier orbital has to connect the different parts of the molecule to each other. In both systems, HOMO−1 and HOMO are analogous, principally located at the TTF units. The crucial and important difference between both compounds concerns the lowest unoccupied molecular orbital. In the disilyl-bridged compound **11**, the LUMO is exclusively located at the TTF units without any part at the $–SiMe_2SiMe_2–$ bridge. In contrast, the LUMO of **12** connects both TTF units over the monosilyl-bridge through space. Due to this decisive difference, an electron transfer is possible from the first TTF unit along the silicon bridge to the second TTF unit. This transfer is facilitated since the LUMO is close in energy to the occupied orbitals (*e.g.* HOMO).

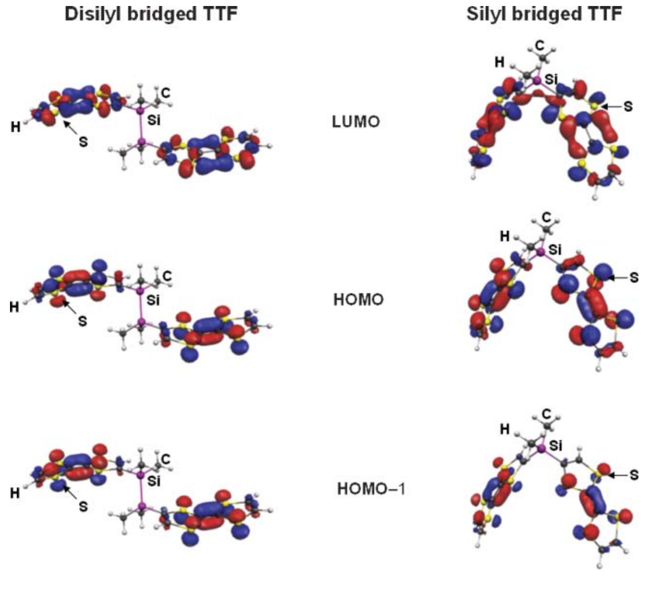
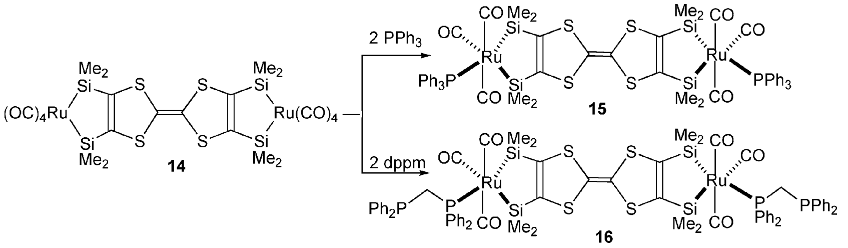


Fig. 7 Presentation of the frontier orbitals (HOMO−1, HOMO and LUMO) of the two di-TTF derivates **11** (left) and **12** (right).

To corroborate these results, we compared our theoretical findings with the one very recently performed on the rigid $(o\text{-DMTTF})_2(SiMe_2)_2$ (*o*-DMTTF = *ortho*-dimethyltetrathiafulvalene) using DFT calculations with the B-P86 exchange–correlation functional.[8] In this case, only one main conformer exists since the two TTF units are fixed by two $–SiMe_2–$ bridges. The TTF units are able to communicate with each other (like in **12**) as the LUMO of **13** is spread over both $–SiMe_2–$ units. Therefore, the electronic situation of **12** and **13** can be compared and significantly separated from the one dominant in **11**. To conclude, a communication between spatial separated TTF units is possible if they are connected over the spacer by a low lying, suitable, unoccupied molecular orbital which is capable of accepting an excited electron.

Activation of the Si–H bond for oxidative addition across Ru(0)

We have previously shown that **1** reacts by oxidative addition with 2 equiv. of $[Pt(C_2H_4)(PPh_3)_2]$ in toluene to afford the dinuclear diplatinum complex $[\{Pt(PPh_3)_2\}_2\{\mu\text{-}(Me_2Si)_4TTF\}]$.[11b] In order to develop further the organometallic coordination chemistry of this novel type of silyl complexes, we have investigated the reactivity of $[Ru_3(CO)_{12}]$ towards **1**. The pioneering work of the research groups of Stone and Graham has demonstrated that silanes R_3SiH oxidatively add across $[Ru_3(CO)_{12}]$ or $[Ru(CO)_5]$ to afford first hydridosilyl complexes of the type $[Ru(H)(SiR_3)(CO)_4]$. The latter may then evolve photochemically or thermally in the presence of excess of R_3SiH to bis(silyl) complexes $[Ru(SiR_3)_2(CO)_4]$, with concomitant extrusion of H_2.[33] This route has quite recently been applied to the preparation of bis(silyl) complexes chelated by the ligand (9,9-dimethylxanthene-4,5-diyl)bis(dimethylsilyl).[34] Fink has shown that treatment of $[Ru_3(CO)_{12}]$ with tetrakis(dimethylsilyl)benzene $C_6H_2(SiMe_2H)_4$ produces in a one-pot reaction the dinuclear compound $[\{Ru(CO)_4\}_2\{\mu\text{-}(Me_2Si)_4C_6H_2\}]$, in which the two ruthenium(II) tetracarbonyl units are linked through the bis(chelating) silylated benzene spacer.[35] In a similar manner, reaction of 0.67 molar equiv. of $[Ru_3(CO)_{12}]$ with **1** in cyclohexane at 65 °C provided $[\{Ru(CO)_4\}_2\{\mu\text{-}(Me_2Si)_4TTF\}]$ (**14**) in the form of a stable orange-brown microcrystalline powder in 72% yield. The proposed structure of **14** was ascertained by IR spectra, NMR and elemental analysis. The presence of four distinct ν(CO) vibrations (2102 m, 2044 s, 2033 vs, 2024 vs), whose positions and intensities are quite similar to those reported for *cis*-$[Ru(Me_2SiCH_2CH_2SiMe_2)(CO)_4]$ and *cis*-$[Ru(SiMe_3)_2(CO)_4]$, confirms the local C_{2v} symmetry around each octahedral $Ru(SiR_3)_2(CO)_4$ fragment. The proton NMR spectrum recorded in $CDCl_3$ consists of just one singlet at δ 0.33 indicating the equivalence of the four $SiMe_2$ groups. Upon prolonged heating a solution of **14** in cyclohexane in the presence of 2 equiv. of PPh_3, selective substitution of a CO ligand *trans* to a $SiMe_2$ group occurred to yield *mer*-$[\{Ru(PPh_3)(CO)_3\}_2\{\mu\text{-}(Me_2Si)_4TTF\}]$ (**15**) (Scheme 5). The meridional carbonyl arrangement is deduced from the IR spectrum, which displays three ν(CO) vibrations at 2054 m, 2000 s and 1986 vs cm^{-1}.[36] The ^1H NMR spectrum gives rise to two $SiMe_2$ resonances at δ 0.13 and 0.61. Due to a *trans*-coupling $^4J_{P,H}$ of 2.4 Hz, the signal at δ 0.13 is split into a doublet. Addition of 2 equiv. of dppm afforded, as the main compound, *mer*-$[\{Ru(CO)_3(\eta^1\text{-dppm})\}_2\{\mu\text{-}(Me_2Si)_4TTF\}]$ (**16**), possessing two pendant η^1-dppm ligands (Scheme 5). The crude product was contaminated by small amounts (*ca.* 15%) of another uncharacterized complex displaying a singlet resonance at δ −5.3 in the $^{31}P\{^1H\}$ spectrum. Analytically pure **16** was separated from this byproduct by recrystallisation. The ^1H NMR spectrum of **16** is similar to that of **15** with two sets of $SiMe_2$ groups. The $^{31}P\{^1H\}$ spectrum proves unambiguously the coordination of a phosphorus atom to ruthenium at δ 21.4 Hz, whereas the dangling phosphorus gives rise to a doublet at δ = −25.0 Hz, a region typical for non-coordinated dppm phosphorus.



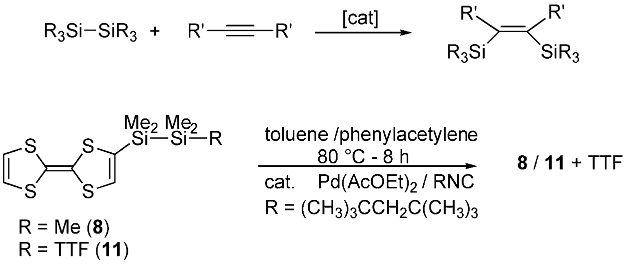
Scheme 5

Both doublets are coupled through a $^{2}J_{\text{P–P}}$ coupling of 90 Hz. These data also match well with those reported for [Ru(CO)$_4$(η^1-dppm)] (δ 39.8 and −25.7; $^{2}J_{\text{P–P}} = 91$ Hz).[37]

CV experiments performed in CH_2Cl_2 at a scan rate of 100 mV s^{-1} on compounds **14** and **15** evidence the same electrochemical behaviour as previously encountered for [{Pt(PPh$_3$)$_2$}$_2${μ-(Me$_2$Si)$_4$TTF}]. For both systems, two reversible oxidation waves are observed. No additional oxidation involving the Ru$^{\text{II}}$ centres is noticed below 1.2 V (*vs.* Ag$^+$/Ag). However, the potential depends strongly on the nature of the metallic fragment as already observed with carbonyl complexes chelated with tetrakis(diphenylphosphino)tetrathiafulvalene.[16] Changing the metallic fragment ligated on the [TTF(Me$_2$Si)$_4$]$^{4-}$ entity from [Pt(PPh$_3$)$_2$]$^{2+}$ to [Ru(CO)$_4$]$^{2+}$ species induces a shift of 0.3 V towards anodic potential. Moreover, this study evidences that the half-wave potential can be fine-tuned by substituting a carbonyl by a more electron-donating phosphane ligand. Indeed, there is a significant shift of the anodic waves from **14** to **15** (Table 1).

Attempts to activate the Si–Si bond for double silylation reactions

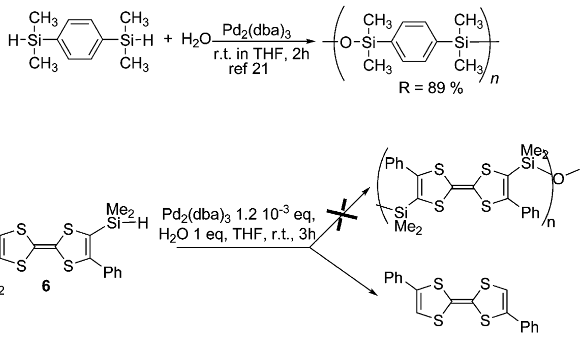
The activation of the silicon–silicon bond has been studied extensively in the past and among the numerous reactions which can be performed, the bis-silylation of alkynes has attracted much attention (Scheme 6). We have recently reported on the formation of bis-silylated olefins by catalytic cleavage of the Si–Si bond of 1,1,2,2-tetramethyl-1,2-bis(phenylthiomethyl)disilane in the presence of phenylacetylene, diethynylbenzene or 4-ethynyl[2.2]paracyclophane.[38] Using the same methodology, we reacted compounds **8** and **11** with phenylacetylene in the presence of Pd(OAc)$_2$/1,1,3,3-tetramethylbutylisocyanide as catalyst. To our disappointment, monitoring the reactions by ^{29}Si and ^{1}H NMR evidences no formation of bis-silylated olefin but a partial cleavage of the C$_{\text{TTF}}$–Si bond (Scheme 6). Note that there is a precedent in the literature where C–Si cleavage is preferred over Si–Si rupture.[39]



Scheme 6

Attempts to form siloxanes by conversion of Si–H to Si–O

Kawakami *et al.* have recently reported that the catalytic cross-dehydrocoupling polymerization of 1,4-bis(dimethylsilane)-benzene under mild reaction conditions leads to a poly(carbo-siloxane) chain (Scheme 7).[21] In light of this result, it seemed promising to probe this reaction with our silylated TTFs. Compounds **3**, **4**, **6** and **7** were reacted with stoichiometric amounts of water in the presence of tris(dibenzylideneacetone)-dipalladium(0)–chloroform adduct (Pd$_2$(dba)$_3$) in THF. In all cases, IR spectroscopy confirms the disappearance of the Si–H bond. However, melting point and a ^{1}H NMR study of the resulting materials reveal the quantitative cleavage of the C$_{\text{TTF}}$–Si bond and the formation of unsilylated TTFs according to a protodesilylation reaction (Scheme 7).



Scheme 7

Conclusion

We have shown that TFFs can be easily functionalized with several SiR$_2$H groups and have prepared the first TTF-representatives bearing disilanyl units. This synthetic part is completed by some crystallographic and electrochemical studies. The absence of an electrochemical communication between the two TTF units in the disilanyl-bridged compound **11** has been rationalized by means of DFT calculations. Unfortunately, the a priori promising concept to combine TTF chemistry with the literature-known reactivity of the Si–Si bond suffers from a serious drawback. Instead of a transition metal-mediated activation of the Si–Si bond, homolytic cleavage of the C$_{\text{TTF}}$–Si bond is noticed. Similarly, several attempts to convert the Si–H function of SiMe$_2$H bearing TTFs to siloxane Si–O–Si failed. Again, rupture of the C$_{\text{TTF}}$–Si bond is evidenced. However, oxidative addition of the Si–H function across low-valent transition metals works straightforwardly and allows the preparation of stable dinuclear platinum(II) and ruthenium(II) bis(silyl) chelate complexes. The later octahedral complex readily loses one meridional carbonyl ligand in the presence of PR_3. Notably the complex *mer*-[{Ru(CO)$_3$(η^1-dppm)}$_2${μ-($Me_2Si)_4$TTF}] (**16**), which may be considered as a metalloligand,[40] is a very promising precursor to assemble further metal centres for the construction of polymetallic TTFSi$_4$-bridged arrays. Although the aim of the present work rather concerns organometallic chemistry than materials science, future electrocrystallization studies will reveal whether disilanyl-funtionalized TTFs may find an application as precursors in this domain.

Experimental section

Preparation of compounds

All reactions were performed in Schlenk-tube flasks under purified nitrogen. Solvents were dried and distilled prior to use by standard procedures. LDA (1.8 M or 2.0 M in THF–heptane–ethylbenzene), TTF and Ph_2TTF were purchased from Aldrich while Me_3TTF was prepared according to a published procedure.[41] Chlorosilanes have been purchased from Wacker Chemie. Syntheses of compounds **1** and **2** have been already reported elsewhere.[11b]

TTF(SiMe$_2$H) (3). LDA (0.85 mmol) was added dropwise to a solution of TTF (160 mg, 0.8 mmol) in diethyl ether (15 mL) at −78 °C. After stirring for 1.5 h, 1.05 equiv. of freshly distilled chlorodimethylsilane (100 µL, 0.85 mmol) were added and the reaction was allowed to warm slowly to room temperature overnight. Filtration and evaporation under reduced pressure of the solvent gave a red oil which was purified by precipitation from hexane at −60 °C (139 mg, 62% yield). Anal. calcd for $C_8H_{10}S_4Si$ (262.94): C, 36.60; H, 3.84; S, 48.86. Found: C, 36.58; H, 3.81; S, 47.98%. ^{1}H NMR (298 K, C_6D_6): δ 0.54 (d, 6H, SiCH_3, $^3J_{H,H}$ = 3.7 Hz), 4.48 (hept, 1H, SiH, $^3J_{H,H}$ = 3.7 Hz), 5.39 (AB system, 2H, $^3J_{AB}$ = 6.3 Hz), 5.68 (s, 1H).

Me$_3$TTF(SiMe$_2$H) (4). Prepared in an analogous manner to **3** starting from Me_3TTF (36% yield). Anal. calcd for $C_{11}H_{16}S_4Si$ (304.59): C, 43.38; H, 5.29; S, 42.11. Found: C, 43.49; H, 5.26; S, 42.06%. ^{1}H NMR (298 K, C_6D_6): δ 0.54 (d, 6H, SiMe$_2$, $^3J_{H,H}$ = 3.9 Hz), 2.30 (s, 3H, CH_3) 2.31 (s, 3H, CH_3), 2.35 (s, 3H, CH_3), 4.40 (hept, 1H, SiH, $^3J_{H,H}$ = 3.9 Hz, $^1J_{H,Si}$ = 196 Hz).

Me$_3$TTF(SiPh$_2$H) (5). Prepared in an analogous manner to **3** starting from Me_3TTF and chlorodiphenylsilane (41% yield). Anal. calcd for $C_{21}H_{20}S_4Si$ (304.59): C, 58.83; H, 4.70; S, 29.92. Found: C, 58.85; H, 4.70; S, 30.07%. ^{1}H NMR (298 K, $CDCl_3$): δ 2.15 (s, 3H, CH_3) 2.17 (s, 3H, CH_3), 2.33 (s, 3H, CH_3), 5.40 (s, 1H, SiH, $^1J_{H,Si}$ = 208 Hz), 7.53–7.94 (m, 10H, H$_{ar}$). ^{29}Si-{^{1}H} NMR (C_6D_6): δ −19.35.

Ph$_2$TTF(SiMe$_2$H)$_2$ (6). A solution of Ph_2TTF (0.3 g, 0.84 mmol) in THF (10 mL) was treated at −78 °C with 2.2 equiv. of LDA. The reaction temperature was allowed to rise slowly to −15 °C and the mixture was stirred at this temperature for 4 h. Chlorodimethylsilane (3 equiv. 280 µL, 2.52 mmol) was added after renewed cooling at −78 °C, then the temperature was allowed to rise slowly overnight up to room temperature. After evaporation of the solvent and the excess of chlorodimethylsilane, the target product was extracted with diethyl ether and crystallized in hexane at −20 °C (278 mg, 70% yield). Anal. calcd for $C_{22}H_{24}S_4Si_2$ (472.86): C, 55.88; H, 5.12; S, 27.12. Found: C, 55.81; H, 5.09; S, 27.53%. ^{1}H NMR (298 K, $CDCl_3$): δ 0.09 (d, 12H, SiCH_3, $^3J_{H,H}$ = 3.92 Hz), 4.34 (hept, 2H, SiH, $^3J_{H,H}$ = 3.92 Hz), 6.95–7.55 (m, 10H, H$_{ar}$). mp 115–117 °C.

Ph$_2$TTF(SiPh$_2$H)$_2$ (7). Prepared in an analogous manner to **6** starting from Ph_2TTF and chlorodiphenylsilane except the crystallisation which was performed using dichloromethane (50% yield). Anal. calcd for $C_{42}H_{32}S_4Si_2$ (721.10): C, 69.96; H, 4.47; S, 17.79. Found: C, 69.23; H, 4.40; S, 18.59%. ^{1}H NMR (298 K, C_6D_6): δ 5.31 (m, 2H, SiH, $^1J_{Si,H}$= 215 Hz), 7.95–7.35 (m, 30H, H$_{arom}$). ^{29}Si-{^{1}H} NMR (C_6D_6): δ −19.16. mp 231–233 °C.

TTF(Si$_2$Me$_5$) (8). LDA (5.8 mmol) was added dropwise to a solution of TTF (1.08 g, 5.28 mmol) in diethyl ether (50 mL) at −78 °C. After stirring for 1.5 h, 1.5 equiv. of pentamethylchlorodisilane (1.52 mL, 7.92 mmol) were added, then the temperature was allowed to rise slowly overnight up to room temperature. After filtration and evaporation of the solvent, the crude product was then warmed under reduced pressure (40 °C under 12 mbar) to eliminate the excess of pentamethylchlorodisilane. The yellow powder was purified by a first crystallisation from hexane (10 mL) at 0 °C to recuperate 130 mg of TTF; a second crystallisation from heptane (15 mL) at −30 °C permitted the isolation of the target compound (970 mg, 55% yield). Anal. calcd for $C_{11}H_{18}S_4Si_2$ (334.70): C, 39.47; H, 5.42; S, 38.32. Found: C, 39.61; H, 5.30; S, 38.14%. ^{1}H NMR (298 K, C_6D_6): δ 0.06 (s, 9H, SiCH_3), 0.12 (s, 6H, SiCH_3), 5.43 (AB system, 2H, H$_a$, H$_b$, $^3J_{AB}$ = 6.5 Hz), 5.72 (s, 1H). ^{29}Si-{^{1}H} NMR (C_6D_6): δ −19.16 (*Si*CH$_3$), −22.37 (*Si*CH$_3$). ^{13}C NMR (C_6D_6): δ 136.29, 124.10, 119.21, 119.06, 113.39, 109.13, −2.34, −3.80. mp 61–62 °C.

Ph$_2$TTF(Si$_2$Me$_5$)$_2$ (9). To a solution of Ph_2TTF (1.02 g, 2.8 mmol) in diethyl ether (60 mL) at −78 °C were added 2.2 equiv. of LDA. The reaction temperature was allowed to rise slowly to −15 °C and the mixture was stirred at this temperature for 4 h. Pentamethylchlorodisilane (3 equiv., 1.65 mL, 8.58 mmol) was added after renewed cooling at −78 °C, then the temperature was allowed to rise slowly overnight up to room temperature. Filtration and evaporation of all volatiles under reduce pressure (45 °C under 10 mbar) yielded **9** as a red powder which was crystallized from a mixture of heptane–diethyl ether (*V*: 20/15) at −30 °C (967 mg, 56% yield). Anal. calcd for $C_{28}H_{40}S_4Si_4$ (617.2): C, 54.49; H, 6.53; S, 20.78. Found: C, 54.53; H, 6.38; S, 20.59%. ^{1}H NMR (298 K, C_6D_6): δ 0.05 (s, 12H, SiCH_3), 0.07 (s, 18H, SiCH_3), 6.96–7.32 (m, 10H, H$_{ar}$). ^{29}Si-{^{1}H} NMR (C_6D_6): δ −18.02 (*Si*CH$_3$), −22.77 (*Si*CH$_3$). ^{13}C NMR (C_6D_6): δ 131.80, 131.78, 130.86, 130.45, 130.40, 130.19, 128.33, 0.01, −0.29. mp 158–159 °C.

TTF(Si$_2$Me$_5$)$_2$ (10a/b). To a solution of TTF (0.5 g, 2.44 mmol) in diethyl ether (30 mL) at −78 °C were added 4.5 equiv. of LDA. The reaction temperature was allowed to rise slowly to −15 °C and the mixture was stirred at this temperature for 4 h. Pentamethylchlorodisilane (6 equiv., 2.82 mL, 14.6 mmol) was added after renewed cooling at −78 °C, then the temperature was allowed to rise slowly overnight up to room temperature. Filtration and evaporation of all volatiles under reduce pressure (45 °C under 10 mbar) yielded 1.45 g of a red oil which was purified by precipitation from pentane at −80 °C to afford a mixture of *cis* and *trans* isomers (535 mg, 47% yield). Anal. calcd for $C_{16}H_{32}S_4Si_4$ (465.03): C, 41.32; H, 6.94; S, 27.58. Found: C, 41.23; H, 6.99; S, 26.98%. ^{1}H NMR (298 K, C_6D_6): δ major isomer: 0.07 (s, SiCH_3), 0.13 (s, SiCH_2), 5.72 (s, 2H); minor isomer 0.05 (s, SiCH_3), 0.12 (s, SiCH_2), 5.74 (s, 2H), ^{29}Si-{^{1}H} NMR (C_6D_6): δ major isomer −19.17 (*Si*CH$_3$), −22.48 (*Si*CH$_2$); minor isomer, −19.17 (*Si*CH$_3$), −22.48 (*Si*CH$_2$); −22.51 (*Si*CH$_2$). GC/MS *m*/*z*: 464.

(TTF)$_2$(Si$_2$Me$_4$) (11). LDA (7.32 mmol) was added dropwise to a solution of TTF (1.36 g, 6.65 mmol) in diethyl ether (60 mL) at −78 °C. After stirring for 1.5 h, 1.5 equiv. of 1,2-dichloro-1,1,2,2-tetraamethyldisilane (0.62 mL, 3.33 mmol) were added, then the temperature was allowed to rise slowly overnight up to room temperature. After filtration, the precipitate was washed with pentane and extracted with hot toluene. Slow evaporation of toluene afforded **11** as yellow plates suitable for X-ray measurement (700 mg, 55% yield). Anal. calcd for $C_{16}H_{18}S_8Si_2$ (522.96): C, 36.74; H, 3.47; S, 49.05. Found: C, 36.61; H, 4.39; S, 49.18%. ^{1}H NMR (298 K, C_6D_6): δ 0.12 (s, 12H, SiCH_3), 5.43 (AB system, 4H, $^3J_{AB}$= 6.5 Hz), 5.66 (s, 2H). ^{29}Si-{^{1}H} NMR (C_6D_6): δ −22.77 (*Si*CH$_3$). ^{13}C NMR (C_6D_6): δ 134.55, 125.48, 119.20, 119.06, 112.92, 109.65, −3.76. mp 160 °C (decomp.).

[{Ru(CO)$_4$}$_2${μ-(Me$_2$Si)$_4$TTF}] (14). To a solution of **1** (437 mg, 1.0 mmol) in cyclohexane (15 ml) was added [$Ru_3(CO)_{12}$] (422 mg, 0.66 mmol). After stirring for 1 d at 65 °C, the red-brown solution was filtered and concentrated to *ca.* 6 ml until precipitation of **14** began. The precipitation was completed by addition of hexane. The orange-brown solid, which is air stable for short periods of time, was then dried *in vacuo.* (620 mg, 72% yield). Anal. calcd for $C_{22}H_{24}O_8S_4Si_4Ru_2$ (859.25): C, 30.75; H, 2.82; S, 14.93 Found: C, 30.93; H, 3.10; S, 14.31%. ^{1}H NMR (298 K, $CDCl_3$): δ 0.62 (s, SiCH_3). IR (C_6H_{12}) νCO: 2102 m, 2044 s, 2033 vs, 1926 vs cm^{-1}.

***mer*-[{Ru(CO)$_3$(PPh$_3$)}$_2${μ-(Me$_2$Si)$_4$TTF}] (15).** A mixture of **12** (172 mg, 0.2 mmol) and PPh$_3$ (105 mg, 0.4 mmol) in methylcyclohexane (15 ml) was heated for 1 d at 90 °C. After *ca.* 12 h, a small amount of **13** began to precipitate as a yellowish solid. After almost complete consumption of **12** (IR monitoring), the red-brown solution was concentrated to *ca.* 5 ml with concomitant precipitation of **13**. The precipitation was completed by addition of hexane. The yellowish solid, which is air stable for short periods of time, was filtered off and then dried *in vacuo.* (171 mg, 64% yield). Anal. calcd for $C_{56}H_{54}O_6P_2S_4Si_4Ru_2$ (1327.77): C, 50.65; H, 4.10. Found: C, 50.90; H, 4.32%. ^{1}H NMR ($CDCl_3$): δ 0.13 (d, 12H, SiCH_3, $^4J_{P,H}$ = 2.4 Hz), 0.61 (s, 12H, SiCH_3, $^4J_{P,H}$ not resolved), 7.45 (30H, *Ph*). ^{31}P-{^{1}H} NMR: δ 30.4 (s). IR (C_6H_{12}): νCO: 2054 m, 2000 s, 1986 vs cm^{-1}.

***mer*-[{Ru(CO)$_3$(η^1-dppm)}$_2${μ-(Me$_2$Si)$_4$TTF}] (16).** A mixture of **12** (172 mg, 0.2 mmol) and dppm (155 mg, 0.4 mmol) in methylcyclohexane (15 ml) was heated for 1 d at 90 °C. After almost complete consumption of **12** (IR monitoring), the red-brown solution was concentrated to *ca.* 5 ml with concomitant precipitation of **16**. The precipitation was completed by addition of hexane. The yellowish solid, which is air stable for short periods of time, was filtered off. IR and ^{31}P NMR examination of the crude product revealed the presence of *ca.* 10% of the dppm-chelated complex [{Ru(η^2-dppm)(CO)$_2$}$_2${(Me$_2$Si)$_4$TTF}] as by-product. Recrystallisation from CH_2Cl_2–Et_2O yielded **16** with more than 95% purity, so that a satisfying elemental analysis was obtained. (214 mg, 68%). Anal. calcd For $C_{70}H_{68}O_6P_4S_4Si_4Ru_2$ (1571.96) C, 53.48; H, 4.36; S, 8.16 Found: C, 53.41; H, 4.10; S, 7.84%. ^{1}H NMR: δ 0.13 (d, 12H, SiCH_3, $^4J_{P,H}$ = 2.2 Hz), 0.62 (s, 12H, SiCH_3, $^4J_{P,H}$ not resolved), 3.33 (d br, 4H, CH_2, $^2J_{P,H}$ = 7.6 Hz), 7.39–7.48 (4 m, 40H, *Ph*). ^{31}P-{^{1}H} NMR: δ 21.4 0 (d, $^2J_{P,P}$ = 90.0 Hz), −25.0 (d, $^2J_{P,P}$) = 90.0 Hz). IR (C_6H_{12}) νCO: 2053 m, 1998 s, 1983 vs cm^{-1}.

Electrochemical set-up

Voltammetric analyses were carried out in a standard three-electrode cell with a Radiometer PGP 201 potentiostat at ambient temperature. The electrolyte consisted of a 0.2 M *n*Bu$_4$PF$_6$ solution in CH_2Cl_2 or MeCN. The working electrode was a platinum disk electrode and the auxiliary electrode was a platinum wire. The reference electrode was a silver–silver ion electrode, Ag/Ag$^+$ (0.1 M AgClO$_4$ in MeCN), separated from the analyzed solution by a sintered glass disk. After each measurement the reference was checked against the ferrocene–ferrocenium couple (+ 0.025 V and + 0.16 V against this reference electrode in acetonitrile solution and in dichloromethane solution respectively).

Computational studies

All calculations were performed with predetermined symmetry. Starting coordinates were taken from the crystal structure analysis of compounds **11** and **12** prior to energy optimization at the B3LYP/6-31+G(d) level. Additional harmonic vibrational frequency analyses (to establish the nature of the stationary point on the potential energy surface) were performed on the same level and showed no imaginary frequency.

Crystal structure determinations

A suitable crystal of each complex was mounted in an inert oil (perfluoropolyalkyl ether) and used for X-ray crystal structure determinations. Data were collected on a Stoe IPDS diffractometer at 173(2) K for **9** and **11** and at 293(2) K for **2** and **7**. The intensities were determined and corrected by the program INTEGRATE in IPDS (Stoe & Cie, 1999). Numerical absorption corrections were employed using the FACEIT-program in IPDS (Stoe & Cie, 1999) (**9** and **11**), while multi-scan type absorption corrections were applied for the compounds **2** and **7**. All structures were solved applying direct and Fourier methods, using SHELXS-97 and SHELXL-97.[42,43] The completeness of data set was only 0.91 in the case of compound **2**, which is a recurrent problem encountered with Image Plate detectors. The *R*(int) value for compound **7** is high, very likely because of the shape of the crystals which were thin needles. However the final *R* factor and the esds were reasonably low. 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. 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. Crystallographic parameters are listed in Table 2.

CCDC numbers: 671046 (**2**), 671047 (**7**), 680222 (**9**) 680221 (**11**).

Table 2 Crystal data, data collection and structure refinement

Compound	**2**	**7**	**9**	**11**
Formula	$C_{54}H_{44}S_4Si_4$	$C_{42}H_{32}S_4Si_2$	$C_{28}H_{40}S_4Si_4$	$C_{16}H_{18}S_8Si_2$
Formula weight	933.49	721.10	617.2	522.96
Temperature/K	293(2)	293(2)	173(2)	173(2)
Wavelength/Å	0.71073	0.71073	0.71073	0.71073
Crystal system	Triclinic	Monoclinic	Orthorhombic	Monoclinic
Space group	$P\bar{1}$	*P*2(1)*c*	*Pbca*	*P*2(1)/*c*
a/Å	10.2738(14)	17.299(4)	8.0210(16)	7.9799(16)
b/Å	10.9233(16)	5.9428(11)	18.440(4)	8.5086(17)
c/Å	11.8812(15)	19.486(4)	23.144(5)	16.715(3)
α/°	98.430(16)			
β/°	94.867(16)	112.20(2)		93.12(3)
γ /°	107.326(16)			
Volume/Å^3	1247.4(3)	1854.7(7)	3423.2(12)	1133.2(4)
Z	1	2	4	2
Density (calculated)/g cm^{-3}	1.243	1.291	1.198	1.533
Absorption coefficient/mm^{-1}	0.322	0.351	0.434	0.895
F(000)	488	752	1312	540
Crystal size/mm	0.60 × 0.80 × 0.30	0.50 × 0.1 × 0.06	0.20 × 0.20 × 0.20	0.30 × 0.30 × 0.10
Theta range for data collection/°	1.99 to 26.09	2.13 to 26.02	2.21 to 27	2.44 to 24.99
Index ranges	$-12 \le h \le 12$, $-13 \le k \le 13$, $-14 \le l \le 14$	$-21 \le h \le 21$, $-7 \le k \le 7$, $-23 \le l \le 24$	$-10 \le h \le 10$, $-23 \le k \le 23$, $-27 \le l \le 28$	$-9 \le h \le 8$, $-10 \le k \le 10$, $-19 \le l \le 19$
Reflections collected	12471	17431	34993	8329
Independent reflections	4520 [*R*(int) = 0.0363]	3626 [*R*(int) = 0.4321]	3634 [*R*(int) = 0.0669]	1974 [*R*(int) = 0.0804]
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 on F^2
Data/restraints/parameters	4520/0/288	3626/0/221	3634/0/168	1974/0/120
Goodness-of-fit on F^2	0.920	0.637	1.091	1.007
Final *R* indices [$I > 2\sigma(I)$]	$R1 = 0.0374$, $wR2 = 0.0838$	$R1 = 0.0511$, $wR2 = 0.0696$	$R1 = 0.0511$, $wR2 = 0.1407$	$R1 = 0.0555$, $wR2 = 0.1259$
R indices (all data)	$R1 = 0.0602$, $wR2 = 0.0914$	$R1 = 0.2775$, $wR2 = 0.1333$	$R1 = 0.0558$, $wR2 = 0.1468$	$R1 = 0.0894$, $wR2 = 0.1368$
Largest diff. peak and hole/e Å^{-3}	0.269 and −0.144	0.221 and −0.220	0.548 and −0.363	0.334 and −0.387

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