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Synthesis of metal dithiolene complexes by Si–S bond cleavage of a bis(silanylsulfanyl)alkene

Simone Friedle, David V. Partyka, Miriam V. Bennett, R.H. Holm *

Department of Chemistry and Chemical Biology, Harvard University, 12 Oxford Street, Cambridge, MA 02138, USA

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Abstract

A new method for the synthesis of metal dithiolenes with alkyl-substituted chelate rings has been investigated. The utility of the protected ene-1,2-dithiolate 3,4-bis-triisopropylsilanylsulfanyl-hex-3-ene as a precursor in reactions with metal halide and oxyhalide complexes was examined. Reaction conditions involve a 2:1 or 3:1 mol ratio of reactants in acetonitrile/THF or toluene at 50–80 °C for 24–36 h. Complex formation was observed as a result of Si–S bond cleavage by bound or free halide and oxo ligands. Members of four major structural families of dithiolene complexes were prepared in ca. 25–70% yields, including planar $[Ni(S_2C_2Et_2)_2]$, square pyramidal $[MI(S_2C_2Et_2)_2]$ (M = Co, Fe), $[Fe(py)(S_2C_2Et_2)_2]^{1-}$, and $[ReO(S_2C_2Et_2)_2]^{1-}$, centrosymmetric $[M_2(S_2C_2Et_2)_4]^{2-}$ (M = Co, Mn), $[M(S_2C_2Et_2)_3]^{1-}$ (M = V, Nb), and trigonal prismatic $[M(S_2C_2Et_2)_3]$ (M = Mo, W). Seven X-ray structure proofs are provided. It is concluded that the method is feasible and potentially extendable to other ring substituents, whose primary effects are on solubility and modulation of redox potentials.

Keywords: Metal dithiolenes; Bis(silanylsulfanyl)alkene; Si–S bond cleavage

1. Introduction

Numerous methods exist for the preparation of metal dithiolene complexes, which contain the generalized ligand *cis*-1,2-$[S_2C_2R_2]^z$ ($z = 2-, 1-, 0$; R = alkyl, aryl, CN, CF_3; RR = 1,2-C_6H_4 or other ring systems). Dithiolenes form large families of complexes, prominent among which are planar $[M(S_2C_2R_2)_2]^z$, square pyramidal $[ML(S_2C_2R_2)_2]^z$, lateral dimeric $[M_2(S_2C_2R_2)_4]^z$, ($z = 2-, 1-, 0$; L = variable ligand), and octahedral to trigonal prismatic $[M(S_2C_2R_2)_3]^z$ ($z = 3-$ to 0). Synthetic methods are often dependent on the substituent R or the backbone ring structure of which the chelating dithiolene fragment is a part. Procedures have been systematized and summarized by Rauchfuss [1]. Once formed, complexes are often susceptible to reversible redox reactions, accounting for the large scope of each family. In general, complexes are prepared from derivatized ligands by removing protecting groups to generate an ene-1,2-dithiolate, which is captured by the metal. This is the case in the original acyloin/benzoin/P_4S_{10} procedure [2,3], which in our hands works best for R = aryl. While the simplest dithiolene reagent, $Na_2[S_2C_2H_2]$, has been prepared [4,5], only one *dialkyl* dithiolene salt has been isolated and used as a reagent in the synthesis of complexes [6]. Dialkyl ligands are of particular interest because of their close relationship to the chelating portion of the pyranopterindithiolene cofactor ligand of molybdenum and tungsten enzymes [7–9]. In our development of active site analogues and analogue reaction systems of these enzymes [9], we have employed extensively the ligand with R = Me. This ligand was not isolated but was transferred from $[Ni(S_2C_2Me_2)_2]$ to $[M(CO)_3(MeCN)_3]$ to afford $[M(S_2C_2Me_2)_2(CO)_2]$ (M = Mo, W) [10,11], which are subject to carbonyl substitution reactions leading to a wide variety of complexes including accurate site analogues.

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* Corresponding author. Tel.: +1 617 495 0853; fax +1 617 495 9289.
E-mail address: holm@chemistry.harvard.edu (R.H. Holm).

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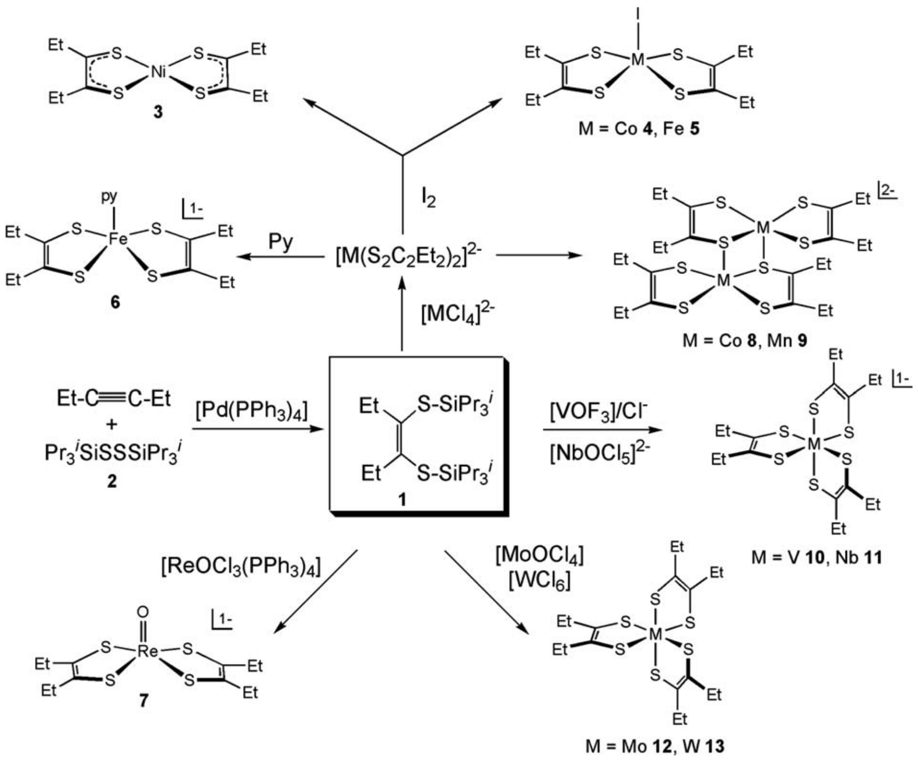


Fig. 1. Synthesis of dithiolene complexes.

In seeking additional and possibly more convenient and general routes to dialkyl and other dithiolene complexes, we noted preparation of the protected ene-1,2-dithiolate 3,4-bis-triisopropylsilanylsulfanyl-hex-3-ene [12] (**1**). **1** and its related compounds are obtained by a Pd^0-catalyzed cross-coupling reaction between an alkyne and bis(triisopropylsilyl)disulfide (**2**) to produce isolable bis(silanylsulfanyl)alkenes [12,13]. The reaction affording **1** is shown in Fig. 1. The possibility that cleavage of the Si–S bonds in **1** might lead to dithiolene complexes is suggested by the ready occurrence of reaction (1), based on 1,2-bis(trimethylsilylthio)benzene [14] and leading to monodithiolene complexes (M = Mo, W) in 70–80% yield [15]. In this investigation, we have examined the feasibility of **1** as a dithiolene precursor in a set of reactions with diverse metal halide sources intended to produce members of the aforementioned dithiolene families

$$[MO_4]^{2-} + 1,2\text{-}C_6H_4(SSiMe_3)_2 \rightarrow [MO_3(S_2C_6H_4)]^{2-} + (Me_3Si)_2O \quad (1)$$

2. Experimental

2.1. Preparation of compounds

All operations were performed under a pure dinitrogen atmosphere using standard Schlenk techniques or in an inert atmosphere box. Acetonitrile, ether, and THF were purified with an Innovative Technology solvent purification system. Hexane and toluene were distilled over sodium benzophenone ketyl; acetonitrile-d_3 was stored over 4-Å molecular sieves. All other reagents were commercially available and used as received. In the following preparations, volume reduction steps were performed in vacuo. Redox potentials are referenced to the SCE. Compounds were identified by a combination of mass spectrometry, elemental analysis, and X-ray structure determinations.

2.1.1. $[Ni(S_2C_2Et_2)_2]$

To a solution of $(Et_4N)_2[NiCl_4]$ [16] (40 mg, 0.087 mmol) in 8 mL of acetonitrile was added a solution of 3,4-bis-triisopropylsilanylsulfanyl-hex-3-ene [12] (84 mg, 0.18 mmol) in 1 mL of THF. The reaction mixture was stirred at 60 °C for 24 h and concentrated to dryness. The residue was washed with hexane and dissolved in 2 mL of acetonitrile. A solution of iodine (66 mg, 0.26 mmol) in 6 mL of THF was added dropwise, and the suspension was stirred for 90 min. The mixture was concentrated to dryness in vacuo and the residue was extracted with toluene/hexane (1:1 v/v). The extract was chromatographed on a small pad of silica gel twice (using the same solvent combination as eluent). The violet band was collected and taken to dryness to give the product as 11 mg (36%) of a dark solid. IR (KBr): 561 (s, br), 1043 (m), 1244 (vs, br), 1383 (s, $\nu_{C=C}$) cm^{-1}. ^1H NMR (C_6D_6): δ 2.34 (q, 2), 1.11 (t, 3). ^{13}C NMR (C_6D_6): δ 15.10 (CH_3), 31.61 (CH_2), 185.90 (C–S). Absorption spectrum (THF): λ_{max} (ϵ_M) 280 (22000), 305 (26000), 410 (sh, 2000), 570 (2000), 774 (19000) nm. Voltammetry (0.1 M $LiClO_4$, DMF): $E_{1/2} = -0.10$ V, -1.13 V. EI-MS: m/z

349.98 (M^+). In multiple preparations with and without the chromatography step, yields as high as 66% were obtained.

2.1.2. $[CoI(S_2C_2Et_2)_2]$

To a solution of $(Et_4N)_2[CoCl_4]$ [16] (30 mg, 0.065 mmol) in 8 mL of acetonitrile was added a solution of 3,4-bis-triisopropylsilanylsulfanyl-hex-3-ene (90 mg, 0.20 mmol) in 1 mL of THF. The reaction mixture was stirred at 50–55 °C for 24 h and taken to dryness. The residue was washed thoroughly with ether twice and dissolved in 2 mL of acetonitrile. A solution of iodine (49 mg, 0.20 mmol) in 4 mL of THF was added dropwise, and the mixture was stirred for 1 h. The solution was concentrated to dryness in vacuo, extracted into 12 mL of toluene/hexane (1:1 v/v), and filtered. The intense blue-green solution was reduced to dryness, the residue was extracted with toluene/hexane, and the extract was filtered. Upon reduction of the filtrate volume, the product was obtained as a black solid (11 mg, 35%). IR (KBr): 1046 (m), 1362, 1384 (s, $\nu_{C=C}$) cm^{-1}. ^1H NMR (C_6D_6): δ 2.54 (q, 2), 1.01 (t, 3). ^{13}C NMR: δ 14.54 (CH_3), 34.11 (CH_2), 203.45 (C–S). Absorption spectrum (toluene): λ_{max} (ϵ_M) 290 (24100), 394 (sh, 5500), 485 (sh, 4200), 655 (9500). Voltammetry (0.1 M $(Bu_4N)PF_6$, acetonitrile): $E_{1/2} = -0.25$ V, -1.22 V. *Anal.* Calc. for $C_{12}H_{20}CoIS_4$: C, 30.13; H, 4.21; S, 26.81. Found: C, 30.38; H, 4.25; S, 26.84%.

2.1.3. $[FeI(S_2C_2Et_2)_2]$

To a solution of $(Et_4N)_2[FeCl_4]$ [16] (18 mg, 0.039 mmol) in 8 mL of acetonitrile was added a solution of 3,4-bis-triisopropylsilanylsulfanyl-hex-3-ene (56 mg, 0.12 mmol) in THF. The reaction mixture was stirred at 60 °C for 24 h, and concentrated to dryness. The residue was washed twice with ether and was suspended in 2 mL acetonitrile. To the suspension was added dropwise a solution of iodine (30 mg, 0.12 mmol) in 6 mL of THF. The mixture was stirred for 45 min, resulting in a deep green color, and was concentrated to dryness. The residue was extracted with toluene/hexane (1:2 v/v) and filtered. Solvent was removed and the extraction procedure was repeated affording the product as a black solid (12 mg, 64%). IR (KBr): 1047 (s, br), 1370, 1374 (m, $\nu_{C=C}$) cm^{-1}. Absorption spectrum (toluene): λ_{max} (ϵ_M) 302 (15000), 382 (sh, 6000), 458 (sh, 8400), 517 (sh, 6000), 607 (7700) nm. Voltammetry (0.1 M $(Bu_4N)PF_6$, acetonitrile): $E_{1/2} = -0.22$, -0.57, -1.19 V. EPR (toluene, 150 K): $g_1 = 2.03$, $g_2 = 2.18$, $g_3 = 2.26$. *Anal.* Calc. for $C_{12}H_{20}FeIS_4$: C, 30.32; H, 4.24; S, 26.99. Found: C, 30.53; H, 4.29; S, 26.86%.

2.1.4. $(Et_4N)[Fe(C_5H_5N)(S_2C_2Et_2)_2]$

To a solution of $(Et_4N)_2[FeCl_4]$ (30 mg, 0.065 mmol) in 8 mL of acetonitrile was added a solution of 3,4-bis-triisopropylsilanylsulfanyl-hex-3-ene (93 mg, 0.20 mmol) in 1 mL of THF. The reaction mixture was stirred at 55 °C for 24 h during which a black solid deposited. The mixture was concentrated to dryness, washed thoroughly with hexane followed by isopropanol and ether. The black solid was collected and extracted into dry pyridine. The deep black-brown solution was filtered through Celite, and ether was diffused into the filtrate. After about 2 days, the product was obtained as large black crystals (18 mg, 50%). Absorption spectrum (pyridine): λ_{max} (ϵ_M) 356 (10800), 442 (6100), 470 (3850), 580 (2470) nm. Voltammetry (0.1 M $(Bu_4N)PF_6$, pyridine): $E_{1/2} = -0.22$ V. *Anal.* Calc. for $C_{25}H_{45}FeN_2S_4$: C, 53.84; H, 8.13; N, 5.02; S, 35.98. Found: C, 53.46; H, 7.92; N, 4.74; S, 35.51%.

2.1.5. $(Ph_4P)[ReO(S_2C_2Et_2)_2]$

To a suspension of $[ReOCl_3(PPh_3)_2]$ [17] (37 mg, 0.044 mmol) in 8 mL of acetonitrile was added Ph_4PCl (18 mg, 0.048 mmol). After the mixture was stirred for 5 min, a solution of 3,4-bis-triisopropylsilanylsulfanyl-hex-3-ene (42 mg, 0.091 mmol) in 1 mL toluene was added. The solution was heated at 80–85 °C for 24 h. The orange solution was concentrated to a residue, which was washed with hexane and ether. The residue was extracted into a minimum volume of acetonitrile, the solution was filtered, and ether was diffused into the filtrate. The solid that crystallized was washed with isopropanol and ether and dried. The product was collected as an orange, microcrystalline solid (18 mg, 50%). IR (KBr): 943 (s, ν_{ReO}) cm^{-1}. ^1H NMR (CD_3CN, anion): δ 2.74 (m, 2), 1.01 (t, 3). Absorption spectrum (acetonitrile): λ_{max} (ϵ_M) 290 (5910), 306 (5790), 348 (2800) nm. Voltammetry (0.1 M $(Bu_4N)PF_6$, acetonitrile): $E_{1/2} = 0.57$ V. *Anal.* Calc. for $C_{36}H_{40}OPReS_4$: C, 51.84; H, 4.83; S, 15.38. Found: C, 51.85; H, 4.68; S, 15.15%.

2.1.6. $(Ph_4P)[V(S_2C_2Et_2)_3]$

To a solution of VOF_3 (11 mg, 0.089 mmol) in 8 mL of acetonitrile was added Ph_4PCl (34 mg, 0.091 mmol). The mixture was stirred for 5 min; to the solution was added dropwise a solution of 3,4-bis-triisopropylsilanylsulfanyl-hex-3-ene (124 mg, 0.027 mmol) in 1 mL of toluene. The reaction mixture was stirred at 50–55 °C for 36 h to give a blue-violet solution, which was concentrated to dryness and washed sequentially with hexane and ether. The residue was extracted into a minimum volume of acetonitrile and the solution was filtered. Ether (2–3 vol. equiv.) was diffused into the acetonitrile solution, which was added to a roughly equal volume of cold ether (−10 °C), and the mixture was stored at this temperature overnight. The deep blue-violet solution and solid that formed were decanted from a small amount of colorless crystals and allowed to stand for several hours. The product was collected as a blue solid (18 mg, 24%). ^1H NMR (CD_3CN): δ 2.93 (q, 2), 1.17 (t, 3). Absorption spectrum (acetonitrile): λ_{max} (ϵ_M) 370 (3510), 532 (7120), 597 (10100), 678 (6380) nm. Voltammetry (0.1 M $(Bu_4N)PF_6$, acetonitrile): $E_{1/2} = 0.04$, -0.92 V. ES-MS: *m*/*z* 489 (M^-).

2.1.7. $(Et_4N)[Nb(S_2C_2Et_2)_3]$

To a solution of $(Et_4N)_2[NbOCl_5]$ [18] (30 mg, 0.055 mmol) in 8 mL of acetonitrile was added a solution of 3,4-bis-triisopropylsilanylsulfanyl-hex-3-ene (77 mg, 0.17 mmol) in 1 mL of toluene. The reaction mixture was stirred at 50 °C for 30 h, and the brown-red solution was concentrated to dryness. The residue was washed with ether, extracted into THF, and filtered. Solvent was removed from the filtrate and the extraction procedure was repeated. The residue was dissolved in a minimum volume of acetonitrile and stored at −20 °C. The product was obtained as a red solid (11 mg, 30%). ^{1}H NMR (CD_3CN, anion): δ 2.68 (q, 2), 1.14 (t, 3). Absorption spectrum (acetonitrile): λ_{max} (ϵ_M) 411 (3600), 493 (3130), 554 (2190) nm. Voltammetry (0.1 M $(Bu_4N)PF_6$, acetonitrile): $E_{1/2} = -1.11$ V. ES-MS: m/z 531 (M^-).

2.1.8. $[Mo(S_2C_2Et_2)_3]$

To a solution of $[MoOCl_4]$ (15 mg, 0.059 mmol) in 8 mL of toluene was added 3,4-bis-triisopropylsilanylsulfanyl-hex-3-ene (84 mg, 0.18 mmol) in 1 mL of toluene. The reaction mixture was stirred for 24 h at 60–65 °C. By the end of the reaction, the solution color was an intense, deep green. Solvent was removed and the residue was suspended in 5 mL of hexane. The suspension was deposited on a 2-in. pad of dry silica, flushed several times with hexane, and eluted with toluene:hexane (3:1 v/v). The bright green band was collected, the solvent was removed to give the product as a red-violet solid (18 mg, 57%). ^{1}H NMR (C_6D_6): δ 2.67 (q, 2), 1.00 (t, 3). Absorption spectrum (toluene): λ_{max} (ϵ_M) 309 (6110), 434 (9990), 642 (12200) nm. Voltammetry (0.1 M $(Bu_4N)PF_6$, acetonitrile/THF 2:1 v/v): $E_{1/2} = -0.36$, −0.90 V. *Anal.* Calc. for $C_{18}H_{30}MoS_6$: C, 40.43; H, 5.65; S, 35.98. Found: C, 41.40; H, 4.91; S, 35.51%.

2.1.9. $[W(S_2C_2Et_2)_3]$

Method A: To a violet solution of $[WCl_6]$ (23 mg, 0.058 mmol) in 6 mL of toluene was added dropwise a solution of 3,4-bis-triisopropylsilanylsulfanyl-hex-3-ene (83 mg, 0.18 mmol) in 1 mL of toluene; the color became deep brown. The reaction mixture was stirred at 65–70 °C for 24 h to yield a deep turquoise-blue solution that was concentrated to dryness. To the residue was added 10 mL of hexane. The suspension was deposited onto a 2-in. pad of dry silica. The suspension was flushed several times with hexane and eluted with toluene. The turquoise-blue band was collected and the solvent was removed to afford the product as a violet solid (21 mg, 59%). ^{1}H NMR (C_6D_6): δ 2.72 (q, 2), 1.01 (t, 3). Absorption spectrum (toluene): λ_{max} (ϵ_M) 390 (4310), 505 (2840), 608 (6380) nm. Voltammetry (0.1 M $(Bu_4N)PF_6$, acetonitrile/THF 2:1 v/v): $E_{1/2} = -0.37$, −0.97 V. ES-MS: m/z 622 (M^-). *Anal.* Calc. for $C_{18}H_{30}S_6W$: C; 34.72; H, 4.86; S, 30.90. Found: C, 34.62; H, 4.78; S, 31.08%.

Method B: To a solution of $[WOCl_4]$ (24 mg, 0.070 mmol) in 6 mL of toluene was added a solution of 3,4-bis-triisopropylsilanylsulfanyl-hex-3-ene (99 mg, 0.21 mmol) in 2 mL of toluene. The solution was stirred at 70 °C for 30 h and allowed to cool. The reaction mixture was taken to dryness; hexane was added and thoroughly mixed with the residue. The suspension (the product is partially soluble) was placed on a 2-in. pad of dry silica, flushed with several volume equivalents of hexane (∼50 mL), and eluted with 2:1 hexane/toluene (v/v). The product (30 mg, 69%) was isolated as above and shown to be analytically and spectroscopically identical to the product of Method A.

2.2. X-ray structure determinations

The structures of the seven compounds in Table 1 were determined. Diffraction-quality crystals were obtained from the indicated solvents: $(Et_4N)_2[Co(S_2C_2Et_2)]_2$, acetonitrile/ether; $[FeI(S_2C_2Et_2)_2]$, toluene; $[CoI(S_2C_2Et_2)_2]$, toluene:hexane (1:1 v/v); $(Et_4N)[Fe(py)(S_2C_2Et_2)_2]$, pyridine; $(Et_4N)_2[Mn(S_2C_2Et_2)]_2$, DMF/ether; $[Mo(S_2C_2Et_2)_3]$, toluene/hexane, −30 °C; $(Ph_4P)[ReO(S_2C_2Et_2)_2]$, acetonitrile/ether. Crystals were coated in Paratone oil and mounted by means of glass capillary fibers on a Bruker CCD area detector instrument operated by the SMART software package. For each crystal, a hemisphere of data was collected at 193 K in 30 or 45 s frames using scans of 0.3 deg/frame. Data reduction were performed with SAINT, which corrects for Lorentz polarization and decay. Absorption corrections were applied using SADABS, and space groups were assigned using XPREP. All structures were solved by direct methods with SHELXTL and refined against all data by full-matrix least squares on F^2. Hydrogen atoms were attached at idealized positions on carbon atoms and were refined as riding atoms with uniform isotropic thermal parameters. The terminal carbon atom of one ethyl group of $[M_2(S_2C_2Et_2)_4]^{2-}$ (M = Mn, Co) and $[Mo(S_2C_2Et_2)_3]$ was disordered over two positions and was refined accordingly. The latter compound and $(Ph_4P)[ReO(S_2C_2Et_2)_2]$ contain two molecules in the asymmetric unit. All structures converged in the final stages of refinement, showing no movement in atom positions. Use of the checking program PLATON did not identify any missing or higher symmetry. Crystallographic parameters and agreement factors are presented in Table 1.

2.3. Other physical measurements

^{1}H NMR spectra were obtained with Bruker AM 400N/500N/600N spectrometers. FT-IR spectra were taken on recrystallized solid samples in KBr on a Nicolet Nexus 470 FT-IR spectrometer, and UV–Vis spectra were recorded on a Varian Cary 50 Bio spectrophotometer. Electrospray mass spectra were recorded on a Platform II quadrupole mass spectrometer (Micromass Instruments, Danvers, MA).

3. Results and discussion

The purpose of this work was to assess the utility of a particular type of protected ene-1,2-dithiolate, a bis(silan-

Table 1
Crystallographic data[a]

	$(Et_4N)_2[Co(S_2C_2Et_2)_2]_2$	$[CoI(S_2C_2Et_2)_2]$	$[FeI(S_2C_2Et_2)_2]$	$(Et_4N)[Fe(py)(S_2C_2Et_2)_2]$	$(Et_4N)_2[Mn(S_2C_2Et_2)_2]_2$	$[Mo(S_2C_2Et_2)_3]$	$(PPh_4)[ReO(S_2C_2Et_2)_2]$
Formula	$C_{40}H_{80}Co_2N_2S_8$	$C_{12}H_{20}CoIS_4$	$C_{12}H_{20}FeIS_4$	$C_{25}H_{45}FeN_2S_4$	$C_{40}H_{80}Mn_2N_2S_8$	$C_{36}H_{60}Mo_2S_{12}$	$C_{72}H_{80}O_2P_2Re_2S_8$
Crystal system	monoclinic	triclinic	tetragonal	monoclinic	monoclinic	triclinic	monoclinic
F_w	963.40	478.35	475.27	557.72	955.42	1069.44	1668.18
Space group	$P2_1/c$	$P\bar{1}$	$P4_1$	$P2_1/n$	$P2_1/c$	$P\bar{1}$	$P2_1$
a (Å)	11.896(4)	7.646(1)	10.571(1)	8.807(1)	11.976(2)	11.610(2)	9.998(2)
b (Å)	17.745(5)	9.024(2)	10.571(1)	16.782(3)	17.763(4)	13.628(3)	20.049(4)
c (Å)	12.149(4)	13.362(2)	16.066(3)	20.328(4)	12.314(3)	15.635(3)	18.051(4)
α (°)	90	82.193(3)	90	90	90	100.36(3)	90
β (°)	104.931(9)	75.076(3)	90	94.64(3)	104.89(3)	105.14(3)	90.93(3)
γ (°)	90	75.265(4)	90	90	90	97.51(3)	90
V (Å^3)	2478(1)	859.2(3)	1795.4(4)	2994.5(1)	2531.5(9)	2307.4(8)	3617.8(1)
Z	2	2	4	4	2	2	2
ρ_{calc} (g/cm^3)	1.291	1.849	1.563	1.237	1.253	1.539	1.531
2θ Range (°)	3.54–52.74	3.16–56.62	3.86–56.58	4.02–56.58	3.52–56.60	3.10–50.00	2.26–56.58
Goodness-of-fit (F^2)	1.026	1.021	1.036	1.014	1.102	1.115	1.105
R_1[b]/wR_2[c] (%)	4.48/11.85	3.42/7.28	2.92/5.86	4.98/11.55	6.51/12.21	5.15/10.78	7.07/13.55

[a] Collected using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at $T = 193$ K.

[b] $R_1 = \sum\|F_o| - |F_c\|/\sum|F_o|$.

[c] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2/\sum[w(F_o^2)^2]\}^{1/2}$.

ylsulfanyl)alkene, as a precursor to metal dithiolenes. Compound **1** was selected because it is accessible from readily handled 3-hexyne (b.p. 81–82 °C) and the disulfide **2** is obtainable by iodine oxidation of the anion of commercial thiol Pr^i_3SiSH [12]. Deprotection by Si–S bond cleavage with coordinated or free halide and (possibly) coordinated oxide is suggested by the bond dissociation energy order 2 [19–21], against which must be balanced the energies of M–X and M=O bonds of the reactant. Product formation is additionally promoted by formation of strong covalent M–S bonds in stable delocalized chelate rings [22]. While only one other diethyldithiolene complex has been reported ($[Ni(S_2C_2Et_2)_2]$ [2]), the main issue is not the preparation of new compounds nor a detailed structural/electronic analysis of those prepared. Rather, it is a test of potential precursor **1** in the formation of examples in the main families of dithiolene complexes, whose structural features have been summarized [23].

$$\begin{aligned} &\mathrm{Si{-}F}(160) > \mathrm{Si{-}O} > (123\text{–}136) > \mathrm{Si{-}Cl}\ (113) > \\ &\quad \mathrm{Si{-}N}\ (92\text{–}109) > \mathrm{Si{-}S}\ (\lesssim 90)\ \ \mathrm{kcal/mol} \end{aligned} \tag{2}$$

Synthetic experiments are summarized in Fig. 1. Quoted yields are averages of at least two preparations but are not necessarily optimal. All products evidence redox reactions; only one oxidation state of each was isolated. For simplicity, the ligand oxidation state is depicted as an ene-1,2-dithiolate, except for $[Ni(S_2C_2Et_2)_2]$. The non-innocent behavior of dithiolene ligands in oxidized complexes is well-recognized and has been considered in some detail recently [24]. While the matter is beyond the purview of this report, we note recent experimental and theoretical investigations of non-innocent bis(dithiolene)nickel and related complexes [22,25–27].

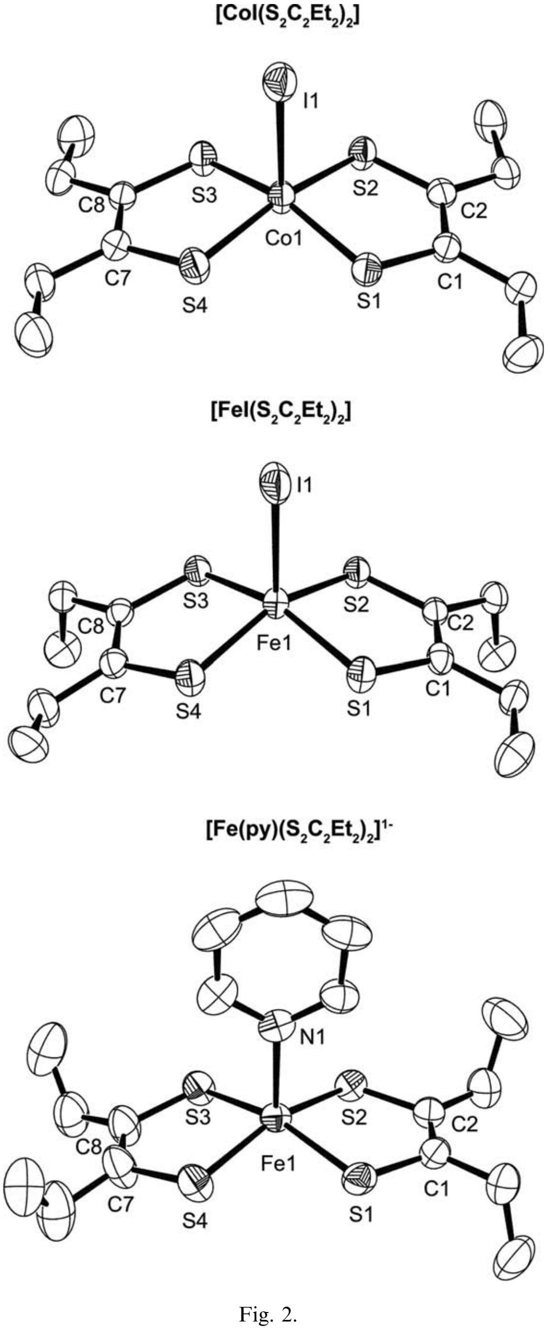
3.1. Bis(dithiolene) complexes

In one set of reactions, the complexes $[MCl_4]^{2-}$ (M = Ni, Co, Fe) were reacted with 2–3 equiv. of **1** in acetonitrile/THF at 50–60 °C for 24 h. The initial complexes formed are the readily oxidized species $[M(S_2C_2Et_2)_2]^{2-}$ (not isolated) which upon treatment with iodine in THF afford $[Ni(S_2C_2Et_2)_2]$ (**3**, 36–66%), $[CoI(S_2C_2Et_2)_2]$ (**4**, 35%), and $[FeI(S_2C_2Et_2)_2]$ (**5**, 64%, $S = 1/2$ ground state) or with pyridine $[Fe(py)(S_2C_2Et_2)_2]^{1-}$ (**6**), isolated as the Et_4N^+ salt (50%). As is typical for $[Ni(S_2C_2R_2)_2]$ complexes, **3** exhibits an intense near-IR transition at 774 nm and a three-member electron transfer series $[Ni(S_2C_2Et_2)_2]^{2-/1-/0}$ at $E_{1/2} = -0.10$ and -1.13 V. The compound is highly similar to planar $[Ni(S_2C_2Me_2)_2]$ (771 (21 500) nm; −0.15, −1.05 V) [25]. Complex **3** is formed by the apparent stoichiometry of reaction (3) (M = Ni); analogous reactions with 3/2 I_2 apply to the formation of **4** and **5**. Evidently under workup conditions $[Fe(S_2C_2Et_2)_2]^{2-}$ or its pyridine adduct underwent a one-electron oxidation. (Note the ready oxidizability of closely related Fe^{II} complexes in the couples $[Fe(S_2C_2H_4)_2]^{2-/1-}$ (−1.12 V)), $[Fe(S_2C_6H_4)_2]^{2-}$ (−0.99 V), and $[Fe(S_2C_6H_3\text{-}4\text{-}Me)_2]^{2-/1-}$ (−0.91 V) [28,29]. Reaction (4) produces $[ReO(S_2C_2Et_2)_2]^{1-}$ (**7**, 50%) in a process requiring an additional equivalent of chloride for stoichiometric discharge of all Si–S bonds. It is noteworthy that the oxo ligand is not silylated in, or silylated and removed from, the isolable product of the reaction.

$$\begin{aligned} &[MCl_4]^{2-} + 2Et_2C_2(SSiPr^i_3)_2 + I_2 \\ &\quad \rightarrow [M(S_2C_2Et_2)_2] + 2I^- + 4Pr^i_3SiCl \end{aligned} \tag{3}$$

$$\begin{aligned} &[ReOCl_3(PPh_3)_2] + 2Et_2C_2(SSiPr^i_3)_2 + Cl^- \\ &\quad \rightarrow [ReO(S_2C_2Et_2)_2]^{1-} + 4Pr^i_3SiCl \end{aligned} \tag{4}$$

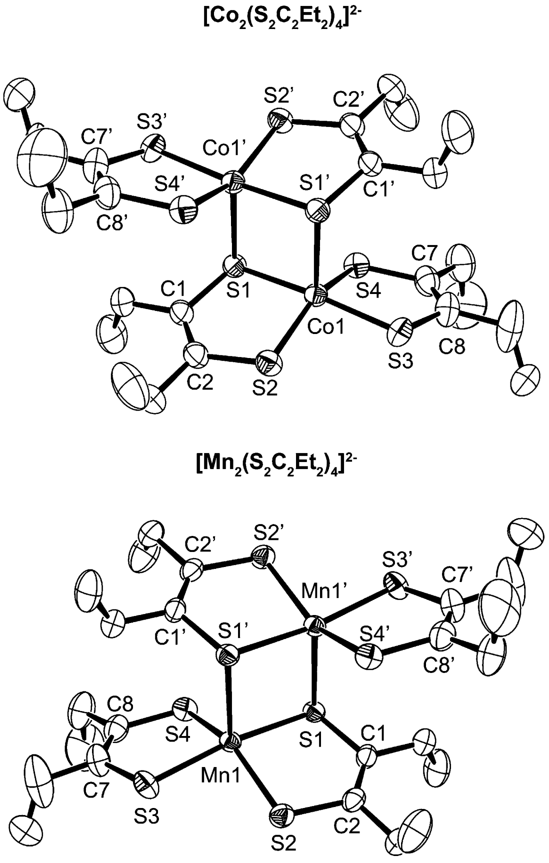
Complexes **4**–**7** exhibit square pyramidal stereochemistry in which the metal atom is displaced 0.31 Å (**4**) to 0.72 Å (**7**) from the S_4 mean plane toward the axial ligand. Structures are shown in Figs. 2 and 3 and metric parameters are summarized in Table 2. Average bond lengths and angle are given for the bis(dithiolene) portions; numerically designated bonds and angles are averages of two of the same type. Complex **7** is precedented by square pyramidal $[ReO(S_2C_6H_4)_2]^{1-}$ [30,31], with which it is isostructural. The chelate ring C–S and C–C bond lengths in **6** and **7** are biased toward an enedithiolate ligand description with a single C–S bond (1.82 Å) and a double C–C bond (1.33 Å). Those of **4** and **5**, which are clearly nonclassical molecules, are intermediate between a dithiolate and dithione in terms of C–S distances.


$[CoI(S_2C_2Et_2)_2]$

$[FeI(S_2C_2Et_2)_2]$

$[Fe(py)(S_2C_2Et_2)_2]^{1-}$

Fig. 2.


$[Co_2(S_2C_2Et_2)_4]^{2-}$

$[Mn_2(S_2C_2Et_2)_4]^{2-}$

Fig. 3.

3.2. M–S dinuclear complexes

Two complexes in this structural category [23] were obtained, but not in analytical purity; consequently detailed preparations are not given. However, both complexes were identified by X-ray structure determinations, justifying their inclusion. Reaction of $[MCl_4]^{2-}$ with 2 equiv. of **1** were performed under conditions used for bis(dithiolene) complexes except that the reaction with M = Mn was conducted without exclusion of air. With M = Co, a limited amount of black crystals was isolated. This material was shown to contain the dinuclear dianion $[Co_2(S_2C_2Et_2)_4]^{2-}$ (**8**) as the Et_4N^+ salt. The complex shows a well-defined reduction at −1.22 V and an oxidation at −0.26 V in acetonitrile. With M = Mn, a mixture of colorless and red crystals was obtained after standard workup and recrystallization from DMF/ether. The red crystals were shown to contain $[Mn_2(S_2C_2Et_2)_4]^{2-}$ (**9**) as the Et_4N^+ salt. The structures of **8** and **9**, provided in Fig. 4, are centrosymmetric lateral dimers whose bridging portion is a $M_2(\mu_2\text{-}SR)_2$ rhomb in which the metal atom has an irregular five-coordinate geometry. The structure of **8** is analogous to that of $[Co_2(S_2C_6Cl_4)_4]^{2-}$ [32] while **9**

Table 2
Selected interatomic distances (Å) and angles (°)

	$[CoI(S_2C_2Et_2)_2]$	$[FeI(S_2C_2Et_2)_2]$	$(Et_4N)[Fe(py)(S_2C_2Et_2)_2]$	$[ReO(S_2C_2Et_2)_2]$
M–L	2.564(1)	2.558(1)	2.172(2)	1.714(1)
M–S[a]	2.150(1)	2.183(4)	2.227(4)	2.307(5)
S–C[a]	1.686(7)	1.699(2)	1.762(7)	1.78(2)
C1–C2[a]	1.340(8)	1.382(7)	1.334(2)	1.32(4)
L–M–S[a]	98(2)	102(2)	99(2)	108(1)
S1–M–S2[a]	88.9(4)	87.7(5)	88.5(6)	84.4(9)
S1–M–S3[a]	164(4)	157(2)	161.5(9)	143(2)
C–S–M[a]	106.6(2)	107.6(2)	105.9(4)	107.1(6)
C2–C1–S1[a]	118.7(3)	118.7(4)	119.9(5)	120(2)
$d_\perp$ (M)[b]	0.31	0.44	0.36	0.73(1)

[a] Mean values.

[b] Perpendicular displacement of M from the mean [S1,S2,S3,S4] plane.

Table 3
Selected interatomic distances (Å) and angles (°)

	$(Et_4N)_2[Co(S_2C_2Et_2)_2]_2$	$(Et_4N)_2[Mn(S_2C_2Et_2)_2]_2$
M–S1	2.194(1)	2.332(1)
M–S2	2.175(1)	2.317(1)
M–S3	2.195(1)	2.297(1)
M–S4	2.195(1)	2.290(1)
M–S1′	2.411(1)	2.618(1)
M–M	3.274(1)	3.463(1)
S–C[a]	1.75(1)	1.768(9)
C–C[b]	1.340(5)	1.339(1)
M–S1–M′	90.47(3)	87.70(3)
S1–M–S2	88.95(4)	87.02(4)
S3–M–S4	89.06(4)	87.17(4)
S2–M–S3	90.10(4)	90.55(4)
S1–M–S4	89.50(4)	89.92(4)
S1–M–S3	174.95(4)	170.12(4)
S2–M–S4	152.57(4)	148.62(4)
S–M–S1′[c]	89.53–104.46	92.3–106.66
C–S–M[a]	105.7(2)	104.8(3)
$d_\perp$(M)[d]	0.31	0.41

[a] Mean values.

[b] Average of chelate ring C–C bond distance.

[c] Range of 4.

[d] Perpendicular displacement of M from the mean [S1,S2,S3,S4] plane. Symmetry equivalents are denoted by primed atoms.

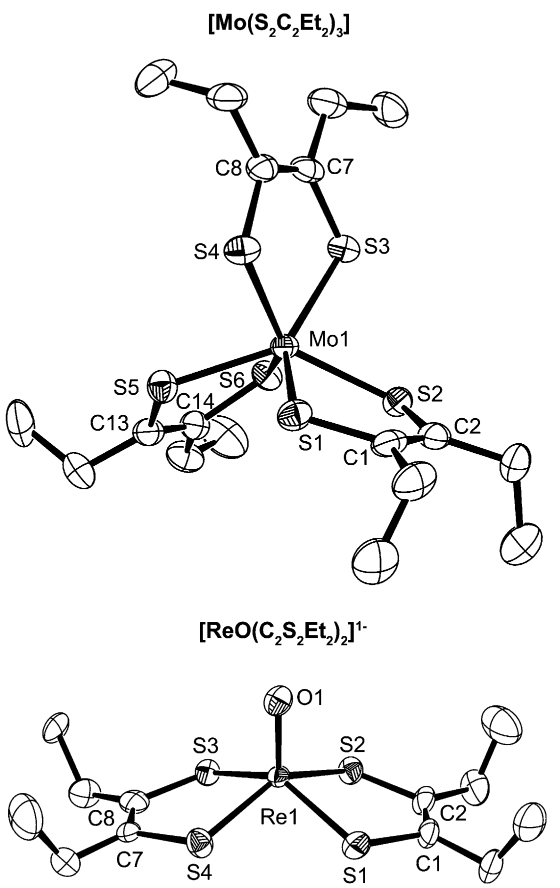


Fig. 4.

is essentially isostructural with $[Mn_2(S_2C_2H_4)_4]^{2-}$ [33] and similar to $[Mn_2(C_3S_5)_4]^{4-}$ [34]. This complex is one of only a small number of homoleptic manganese dithiolenes, which include a group of $Mn^{II,III}$ complexes derived from toluene-3,4-dithiolate(2-) [35]. Bond distances and angles for **8** and **9** are collected in Table 3.

3.3. Tris(dithiolene) complexes

These complexes were prepared by reaction of a metal halide or oxyhalide precursor with three equivalents of **1** at 50–70 °C for 24–36 h. This procedure yields $[M(S_2C_2Et_2)_3]^{1-}$ M = V (**10**, 24%), Nb (**11**, 30%) and $[M(S_2C_2Et_2)_3]$ M = Mo (**12**, 57%), W (**13**, 59%, 69%) by two methods. Reaction stoichiometries are simply formulated; e.g., reactions (5) and (6) for the formation of **13** and **11**, respectively. Note that in contrast to reaction (4), the oxo ligand has been

$$[WCl_6] + 3Et_2C_2(SSiPr^i_3)_2 \rightarrow [W(S_2C_2Et_2)_3] + 6Pr^i_3SiCl \qquad (5)$$

$$[NbOCl_5]^{2-} + 3Et_2C_2(SSiPr^i_3)_2 \rightarrow [Nb(S_2C_2Et_2)_3]^{1-} + 4Pr^i_3SiCl + (Pr^i_3Si)_2O + Cl^- \qquad (6)$$

removed in reaction (6) and in the formation of **10** and **12**. A characteristic feature of tris(dithiolene) complexes in oxidized forms is their close approach to or achievement of trigonal prismatic stereochemistry [23]. This feature is described by the trigonal twist angle θ and the *trans*-SMS angle, whose values are 0° and 136°, respectively, for a trigonal prism and 90° and 180° for an octahedron. For **12**, which crystallizes with two independent isostructural molecules in the asymmetric unit, mean values are $\theta = 0.3°$ and a trans angle of 135°, indicating that the complex is at the trigonal prismatic limit. The mean chelate ring C–C (1.368(5) Å) and C–S (1.714(7) Å) bond distances indicate an intermediate ligand oxidation state. Of previously reported complexes, **12** is essentially isostructural with $[Mo(S_2C_6H_4)_3]$ ($\theta = 0°$, *trans*-SMS = 136°) [36] and $[Mo(S_2C_2Me_2)_3]$ ($\theta = 3°$, *trans*-SMS = 137°) [11]. On this basis, **13** is expected to the isostructural with $[W(S_2C_2Me_2)_3]$ ($\theta = 2°$, *trans*-SMS = 137°) [37]. Diffraction quality crystals of the Et_4N^+ salts of **10** and **11** were not obtained.

4. Summary

This study contributes a new method of synthesis of metal dithiolenes by Si–S bond cleavage of a bis(silanylsulfanyl)alkene (**1**), exemplified by the preparation of complexes belonging to four major structural families: $[M(S_2C_2R_2)_2]^z$ (**3**), $[ML(S_2C_2R_2)_2]^z$ (**4–7**), $[M_2(S_2C_2R_2)_4]^z$ (**8**, **9**), and $[M(S_2C_2R_2)_3]^z$ (**10–13**). Seven X-ray structure proofs are provided. The procedure introduced here is an elaboration of reaction (1), which is the first example of dithiolene complex formation by Si–S bond cleavage. Stoichiometric reactions require sufficient equivalents of bound or free halide and/or bound oxide to deprotect the ligand precursor by formation of R_3SiX or $(R_3Si)_2O$. The method appears capable of extension. Symmetrical and unsymmetrical alkynes R–C≡C–R′ with primary, secondary, and tertiary alkyl groups form bis(triisopropylsilanylsulfanyl)alkenes in reported yields of 42–96% [12]. Published results suggest that hydroxyl groups removed from the triple bond by one or more carbon atoms are tolerated in reactions affording the protected ligand [13]. Hence, the potential exists for substantial variation in chelate ring substituents. These influence solubility in non-aqueous and aqueous media and modulate redox potentials [38]. Lastly, the use of a disulfide reagent $(R_3SiS)_2$ with substituents smaller than $R = Pr^i$ may improve yields and eliminate heating the reaction mixture. This is the case with reaction (1), which proceeds readily at room temperature.

5. Supplementary material

Crystallographic data for structural analysis have been deposited at the Cambridge Crystallographic Data Center. Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK, e-mail: deposit@ccdc.cam.ac.uk or www:www.ccdc.cam.ac.uk.

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