Lithium, titanium and vanadium dithiocarboxylates†

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Reaction of the *in situ* generated lithium aryls 2,6-Mes$_2$C$_6$H$_3$Li and 2,6-Trip$_2$C$_6$H$_3$Li (Mes = 2,4,6-trimethylphenyl, Trip = 2,4,6-triisopropylphenyl) with CS$_2$ afforded the lithium dithiocarboxylates [2,6-Mes$_2$C$_6$H$_3$CS$_2$]Li and [2,6-Trip$_2$C$_6$H$_3$CS$_2$]Li in good yields. These sterically-hindered S-donor ligands proved useful for the salt-metathesis preparation of the paramagnetic Ti(III) and V(III) derivatives [2,6-Mes$_2$C$_6$H$_3$CS$_2$]TiCl$_2$(thf)$_2$ and [2,6-Trip$_2$C$_6$H$_3$-CS$_2$]$_2$VCl(L)$_2$ (L = thf, py). Similarly, reaction of [2,6-Trip$_2$C$_6$H$_3$CS$_2$]Li with TiCl$_4$(thf)$_2$ in the presence of py afforded the diamagnetic Ti(IV) [2,6-Trip$_2$C$_6$H$_3$CS$_2$]$_2$TiCl$_2$(py). Single-crystal X-ray diffraction studies are reported for [2,6-Mes$_2$C$_6$H$_3$]Li(OEt$_2$)$_2$, [2,6-Mes$_2$C$_6$H$_3$CS$_2$]TiCl$_2$(thf)$_2$, [2,6-Trip$_2$C$_6$H$_3$CS$_2$]$_2$TiCl$_2$(py), and [2,6-Trip$_2$C$_6$H$_3$CS$_2$]$_2$VCl(py)$_2$.

Introduction

Coordination complexes supported by sulfur-donor ligands have attracted significant interest due to their interesting electronic and structural properties.[1] These complexes have also frequently been studied in the context of biomimetic chemistry, as metalloproteins featuring metal centers supported by naturally-occurring S-donors perform diverse roles in biology (*e.g.* catalysis, electron transfer, metal sequestration).[2] We have begun exploring extremely sterically-hindered S-donor ligands in the hope that they will allow us to access reactive low-coordination number transition-metal derivatives. In this initial report, we describe two new dithiocarboxylate ligands, based on a versatile terphenyl backbone,[3] and their use in the synthesis of mononuclear titanium and vanadium derivatives.

Results and discussion

Lithium salts of the bulky dithiocarboxylate anions [2,6-Mes$_2$C$_6$H$_3$CS$_2$]$^-$ and [2,6-Trip$_2$C$_6$H$_3$CS$_2$]$^-$ (Mes = 2,4,6-Me$_3$C$_6$H$_2$, Trip = 2,4,6-^{i}Pr$_3$C$_6$H$_2$) were prepared by the reaction of CS$_2$ with the corresponding aryllithium[4] species (Scheme 1). The
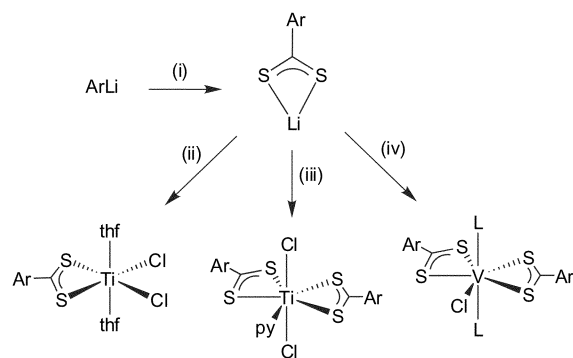
Scheme 1 Ar = 2,6-Mes$_2$C$_6$H$_3$, 2,6-Trip$_2$C$_6$H$_3$; L = py, thf. Reagents and conditions: (i) CS$_2$, Et$_2$O–hexanes, −70 °C; (ii) TiCl$_3$(thf)$_3$, toluene, rt; (iii) TiCl$_4$(thf)$_2$, toluene, py, rt; (iv) VCl$_3$(thf)$_3$, toluene, L, rt.

yellow to orange products were isolated in moderate (*ca.* 55%) yields as simple Lewis base adducts, and their compositions were determined by a combination of NMR spectroscopy and combustion analysis. A single-crystal X-ray diffraction study of [2,6-Mes$_2$C$_6$H$_3$CS$_2$]Li(OEt$_2$)$_2$ was also performed. As shown in Fig. 1, the dithiocarboxylate anion binds to a single Li-center as a symmetric chelate, with Li1–S1 and Li1–S2 distances of
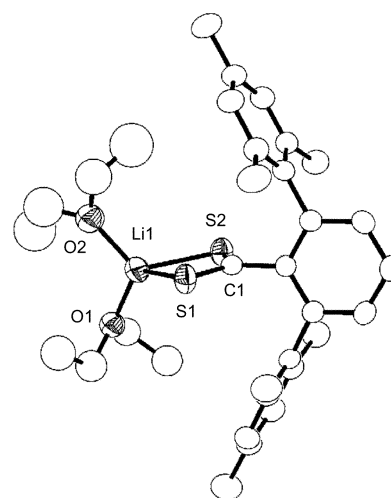
† Electronic supplementary information (ESI) available: additional crystallographic details. See http://www.rsc.org/suppdata/dt/b2/b210691d/

Fig. 1 Molecular structure of [2,6-Mes$_2$C$_6$H$_3$]Li(OEt$_2$)$_2$ drawn with 50% thermal ellipsoids. All hydrogens and the minor components of the disordered Et$_2$O molecules are omitted.

2.467(6) and 2.480(6) Å, respectively (Table 1). The C–S bonds also reflect this binding mode, with essentially identical distances of 1.68 Å. Snaith and coworkers have reported the only other structurally characterized lithium dithiocarboxylates.[5] For comparison, the structure of [(2-MeC$_4$H$_2$N$_2$)CH$_2$CS$_2$]-Li(tmeda) (tmeda = *N,N,N′,N′*-tetramethylethylenediamine) features an asymmetrically chelating dithiocarboxylate anion with much longer Li–S distances of 2.554(4) and 2.688(5) Å. Also of interest, a series of heavy alkali metal (K–Cs) dithiocarboxylates has been reported to adopt bimetallic structures featuring μ-dithiocarboxylate anions.[6] Structures of related Li dithiocarbamate[7] and trithiocarbonate[8] have also been reported.

The Li dithiocarboxylates have proven to be useful reagents for the preparation of a range of transition-metal derivatives. Reaction of [2,6-Mes$_2$C$_6$H$_3$CS$_2$]Li(Et$_2$O)$_2$ with 1 equiv TiCl$_3$-(thf)$_3$ immediately forms a teal solution. The mononuclear Ti(III) species [2,6-Mes$_2$C$_6$H$_3$CS$_2$]TiCl$_2$(thf)$_2$ was isolated in 36% yield from Et$_2$O solution. Solution magnetic susceptibility measurements gave a μ_{eff} = 1.6(1) μ_B, which is consistent with a d^1 metal center. The solid-state structure is shown in Fig. 2. The pseudo-octahedral Ti is ligated to a symmetrically chelating dithiocarboxylate, with the pair of chloride ligands being *trans* to the S-donors. The remaining two coordination sites are occupied by a pair of thf molecules. The small S–Ti–S bite angle of 68.26(3)° results in the relatively large Cl–Ti–Cl angle of 111.23(4)°. The Ti–S distances of 2.554(1) and 2.552(1) are
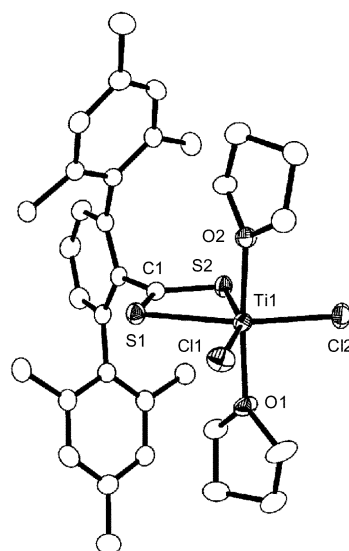
Table 1 Selected bond lengths (Å) and angles (°) for structurally characterized compounds

[2,6-Mes₂C₆H₃]Li(OEt₂)₂

Li1–S1	2.467(6)	S1–Li1–S2	73.77(15)
Li1–S2	2.480(6)	S1–Li1–O1	119.8(3)
Li1–O1	1.919(9)	S1–Li1–O2	112.2(3)
Li1–O2	1.905(9)	S2–Li1–O1	114.5(3)
S1–C1	1.684(3)	S2–Li1–O2	120.1(4)
S2–C1	1.676(3)	O1–Li1–O2	111.9(3)

[2,6-Mes₂C₆H₃]TiCl₂(thf)₂

Ti1–S1	2.552(1)	S1–Ti1–O2	91.65(6)
Ti1–S2	2.554(1)	S2–Ti1–Cl1	157.87(3)
Ti1–Cl1	2.325(1)	S2–Ti1–Cl2	90.91(3)
Ti1–Cl2	2.331(1)	S2–Ti1–O1	91.88(6)
Ti1–O1	2.085(2)	S2–Ti1–O2	92.23(6)
T1–O2	2.089(2)	Cl1–Ti1–Cl2	111.23(4)
S1–C1	1.679(3)	Cl1–Ti1–O1	88.64(6)
S2–C1	1.691(1)	Cl1–Ti1–O2	87.89(6)
S1–Ti1–S2	68.26(3)	Cl2–Ti1–O1	88.63(7)
S1–Ti1–Cl1	89.61(4)	Cl2–Ti1–O2	87.89(6)
S1–Ti1–Cl2	159.14(3)	O1–Ti1–O2	174.66(7)
S1–Ti1–O1	93.05(6)		

[2,6-Trip₂C₆H₃]₂TiCl₂(py)

Ti1–S1	2.5624(8)	S2–Ti1–S4	139.85(3)
Ti1–S2	2.5302(8)	S2–Ti1–Cl1	93.17(3)
Ti1–S3	2.5190(8)	S2–Ti1–Cl2	88.03(3)
Ti1–S4	2.5484(8)	S2–Ti1–N1	143.77(6)
Ti1–Cl1	2.3045(8)	S3–Ti1–S4	67.68(2)
Ti1–Cl2	2.2867(9)	S3–Ti1–Cl1	87.79(3)
Ti1–N1	2.277(2)	S3–Ti1–Cl2	93.77(3)
S1–Ti1–S2	67.30(2)	S3–Ti1–N1	143.44(6)
S1–Ti1–S3	139.36(3)	S4–Ti1–Cl1	92.05(3)
S1–Ti1–S4	152.78(3)	S4–Ti1–Cl2	87.83(3)
S1–Ti1–Cl1	87.05(3)	S4–Ti1–N1	76.07(6)
S1–Ti1–Cl2	92.26(3)	Cl1–Ti1–Cl2	178.27(3)
S1–Ti1–N1	76.71(6)	Cl1–Ti1–N1	88.93(7)
S2–Ti1–S3	72.79(2)	Cl2–Ti1–N1	89.36(7)

[2,6-Trip₂C₆H₃]₂VCl(py)₂

V1–S1	2.5425(9)	S2–V1–S4	156.22(3)
V1–S2	2.5498(8)	S2–V1–Cl1	79.21(3)
V1–S3	2.5489(9)	S2–V1–N1	90.95(6)
V1–S4	2.5380(9)	S2–V1–N2	86.76(6)
V1–Cl1	2.4056(8)	S3–V1–S4	67.10(3)
V1–N1	2.154(2)	S3–V1–Cl1	141.24(3)
V1–N2	2.167(2)	S3–V1–N1	101.37(6)
S1–V1–S2	67.07(3)	S3–V1–N2	82.49(7)
S1–V1–S3	73.65(3)	S4–V1–Cl1	77.64(3)
S1–V1–S4	134.37(3)	S4–V1–N1	83.65(6)
S1–V1–Cl1	145.06(3)	S4–V1–N2	97.17(7)
S1–V1–N1	82.12(7)	Cl1–V1–N1	89.83(6)
S1–V1–N2	99.92(7)	Cl1–V1–N2	86.58(7)
S2–V1–S3	136.64(3)	N1–V1–N2	176.05(9)

Fig. 2 Molecular structure of [2,6-Mes₂C₆H₃]TiCl₂(thf)₂ drawn with 50% thermal ellipsoids. All hydrogens are omitted.
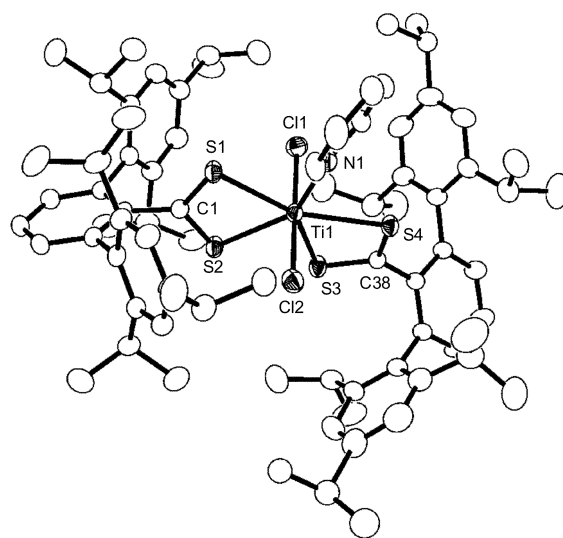
Fig. 3 Molecular structure of [2,6-Trip₂C₆H₃]₂TiCl₂(py) drawn with 50% thermal ellipsoids. All hydrogens and the minor components of the disordered ⁱPr-groups are omitted.

identical, and are comparable to the average Ti–S distances reported for the Ti(IV) species Ti(S₂CNEt₂)₄ (2.564 Å),[9] CpTi(S₂CMe)₃ (2.603 Å),[10] and CpTi(S₂CNMe₂)₃ (2.611 Å).[11] Although [2,6-Mes₂C₆H₃CS₂]TiCl₂(thf)₂ would be expected to have relatively long Ti–S bonds as a result of its larger ionic radius, its lower coordination number relative to the aforementioned Ti(IV) complexes offsets this effect.

The Ti(IV) [2,6-Trip₂C₆H₃CS₂]₂TiCl₂(py) was prepared by the reaction of 2 equiv [2,6-Trip₂C₆H₃CS₂]Li(thf)₃ with TiCl₄(thf)₂ in the presence of excess py. The diamagnetic product was isolated in good yield as red crystals from Et₂O solution. ¹H NMR spectroscopic data indicated a symmetric or fluxional environment, and integration data and combustion analysis revealed a 2 : 1 ratio of dithiocarboxylate to py. The solid-state structure features a 7-coordinate Ti center in an approximate pentagonal bipyramidal environment (Fig. 3). The equatorial ligands include a pair of chelating dithiocarboxylates and the py. The *trans* chlorides occupy the axial positions. In contrast to the aforementioned Li and Ti(III) complexes, the binding of the

dithiocarboxylates in [2,6-Trip₂C₆H₃CS₂]₂TiCl₂(py) is asymmetric. The Ti bonds to S(1) and S(4) (ave 2.555 Å) are about 0.03 Å longer than those to S(2) and S(3). This is explained as a small *trans* influence arising from the weaker donor properties of py relative to the S-donors.

Reaction of two equiv [2,6-Trip₂C₆H₃CS₂]Li(thf)₃ with VCl₃(thf)₃ in toluene solution formed a dark burgundy solution. Following work up in hexanes–HMDSO (hexamethyldisiloxane), [2,6-Trip₂C₆H₃CS₂]₂VCl(thf)₂ was isolated in 28% yield as small burgundy crystals. The low isolated yield for this reaction appears to be due to the extreme solubility of the product in hydrocarbon solvents. A slightly higher yield was achieved for the less soluble py adduct [2,6-Trip₂C₆H₃CS₂]₂VCl(py)₂. Combustion analysis data were consistent with the formulations, and IR spectroscopy revealed the presence of py (ν_{py} = 1604, 1580, 1566 cm⁻¹) in [2,6-Trip₂C₆H₃CS₂]₂VCl(py)₂. Both complexes are paramagnetic with ambient temperature solution magnetic moments (2.8–2.9 μ_B) consistent with d² electronic configurations. The solid-state structure determination of [2,6-Trip₂C₆H₃CS₂]₂VCl(py)₂ confirmed the assignment of the product. As shown in Fig. 4, the V center approximates a pentagonal bipyramidal geometry, with the two py ligands occupying the axial positions. The V–S bond lengths are all
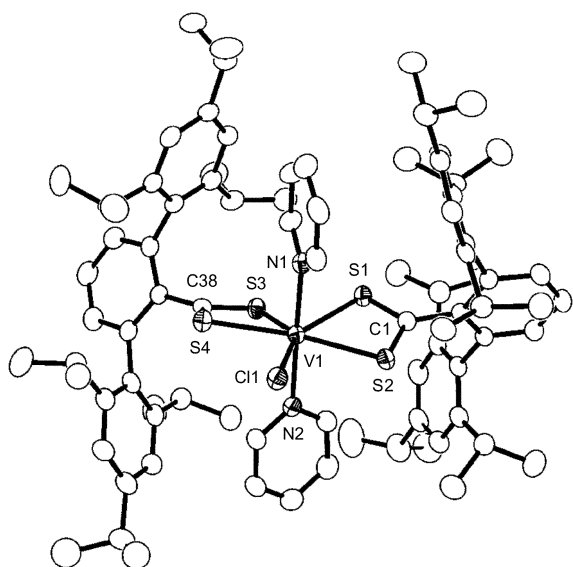
Fig. 4 Molecular structure of [2,6-Trip$_2$C$_6$H$_3$]$_2$VCl(py)$_2$ drawn with 50% thermal ellipsoids. All hydrogens and the minor component of a disordered ^{i}Pr-group are omitted.

very similar with an average value of 2.545 Å. To our knowledge, there are no other structurally characterized V(III) dithiocarboxylates or dithiocarbamates. The only other such V dithiocarboxylates are the pseudo-dodechaderal V(SCPh)$_4$ and V(SCH$_2$Ph)$_4$ which feature average V–S distances of 2.49 and 2.50 Å, respectively.[12]

In summary, we have reported a pair of new sterically-hindered dithiocarboxylate ligands. These have proven to be useful for the preparation of a range of early transition metal derivatives by salt-metathesis methodology. As a result of the bulky 2,6-diaryl-substituted ligands, these Ti and V complexes feature only one or two dithiocarboxylates per metal. This is a feature not commonly observed in early-metal dithiocarboxylate or dithiocarbamate coordination chemistry.

Experimental

General considerations

Standard techniques for air-sensitive chemical manipulations were used unless stated otherwise.[13] 2,6-Mes$_2$C$_6$H$_3$I (Mes = 2,4,6-Me$_3$C$_6$H$_2$),[14] 2,6-Trip$_2$C$_6$H$_3$I (Trip = 2,4,6-^{i}Pr$_3$C$_6$H$_2$),[15] TiCl$_3$(thf)$_3$, TiCl$_4$(thf)$_4$, and VCl$_3$(thf)$_3$ were prepared following literature procedures.[16] Hexanes, Et$_2$O, toluene, tetrahydrofuran (thf), and CH$_2$Cl$_2$ were passed through columns of activated alumina and sparged with N$_2$ prior to use. Hexamethyl-disiloxane (HMDSO) and pyridine (py) were distilled from Na under N$_2$. BuLi was purchased from commercial sources and used as received. CDCl$_3$ was vacuum transferred from CaH$_2$. Chemical shifts (δ) for ^{1}H-NMR spectra are given relative to residual protium in the deuterated solvent at δ 7.24 for CDCl$_3$. ^{13}C{^{1}H}-NMR spectra are given relative to ^{13}CDCl$_3$ at δ 77.00. Infrared spectra were taken as mineral oil mulls between KBr plates unless stated otherwise. Elemental analyses were determined by Desert Analytics. Solution magnetic moments were determined at ambient temperature by ^{1}H NMR spectroscopy using Evans' method.[17]

Syntheses

[2,6-Mes$_2$C$_6$H$_3$CS$_2$]Li(Et$_2$O)$_2$. Hexanes (150 mL) and Et$_2$O (75 mL) were added to 2,6-Mes$_2$C$_6$H$_3$I (15.6 g, 35.3 mmol) to form a colorless suspension. At −20 °C, a hexanes solution of BuLi (20.4 mL, 35.3 mmol) was added dropwise over 30 min and the suspension was stirred for an additional 30 min. At −70 °C, CS$_2$ (2.34 mL, 38.8 mmol) was added dropwise, and the

dark solution was allowed to warm to ambient temperature over several hours. After stirring overnight, the resulting red solution was concentrated slightly and cooled to −40 °C. The product was isolated as orange crystals, which were washed with hexanes (2 × 60 mL) and dried under reduced pressure (9.0 g, 52%). ^{1}H NMR (2% CD$_3$CN in CDCl$_3$): δ 7.14 (t, J = 7.6 Hz, 1H, p-C$_6$H$_3$), 6.83 (d, J = 7.6 Hz, 2H, m-C$_6$H$_3$), 6.72 (s, 4H, m-Mes), 3.38 (q, J = 7.0 Hz, 9H, Et_2O), 2.18 (s, 6H, p-Mes), 2.12 (s, 12H, o-Mes), 1.10 (t, J = 7.0 Hz, 12H, Et_2O). ^{13}C{^{1}H} NMR (2% CD$_3$CN in CDCl$_3$): δ 152.6, 138.8, 137.4, 135.3, 135.1, 128.6, 127.1, 125.8, 116.4, 65.7, 21.5, 21.0, 15.0. IR: 1461 (vs), 1446 (s), 1376 (s), 1216 (m), 1018 (s), 908 (m), 854 (m), 751 (m), 741 (m), 722 (w) cm^{-1}. Anal. Calcd (found) for C$_{33}$H$_{45}$O$_2$S$_2$Li: C, 72.75 (72.52); H, 8.33 (8.34%).

[2,6-Trip$_2$C$_6$H$_3$CS$_2$]Li(py)$_3$. Hexanes (75 mL) and Et$_2$O (25 mL) were added to 2,6-Trip$_2$C$_6$H$_3$I (5.94 g, 9.75 mmol) to give a clear colorless solution. The solution was cooled to −70 °C and BuLi (5.70 mL, 9.75 mmol) was added dropwise to form a cloudy white solution. The mixture was warmed to room temperature and stirred for 0.5 h. After cooling to −70 °C, CS$_2$ (0.600 mL, 9.75 mmol) was added dropwise to give a cloudy pink solution. The reaction was warmed slowly to room temperature resulting in a brown solution. The volatile materials were removed under reduced pressure to afford a mustard yellow solid which was extracted into Et$_2$O (150 mL) and filtered. Pyridine (2 mL) was added, and the solution was concentrated to saturation. Cooling to −40 C yielded the product as a yellow solid (5.0 g, 64%). ^{1}H NMR (CDCl$_3$): δ 8.48 (m, 6H, α-py), 7.72 (m, 3H, γ-py), 7.28 (m, 6H, β-py), 7.2–7.1 (m, 3H, m,p-C$_6$H$_3$), 7.00 (s, 4H, m-$Trip$), 3.09 (sept, J = 6.7 Hz, 4H, m-CHMe$_2$), 2.96 (sept, J = 6.7 Hz, 2H, p-CHMe$_2$), 1.30 (d, J = 7.0 Hz, 12H, p-CHMe_2), 1.20 (d, J = 6.8 Hz, 12H, o-CH(Me)Me), 1.06 (d, J = 6.8 Hz, 12H, o-CH(Me)Me). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 152.9, 150.0, 148.0, 146.9, 137.2, 137.1, 134.0, 130.1, 124.4, 123.7, 119.9, 34.4, 31.1, 26.4, 24.5, 23.2. IR: 3040 (w), 2954 (s), 2924 (s), 1594 (m), 1485 (w), 1461 (s), 1440 (s), 1377 (m), 1360 (w), 1067 (w), 1035 (w), 1021 (m), 1004 (w), 759 (w), 750 (w), 721 (w), 701 (m), 624 (w) cm^{-1}. Anal. Calcd (found) for C$_{52}$H$_{64}$N$_3$S$_2$Li: C, 77.86 (77.16); H, 8.04 (7.95); N, 5.24 (5.20%).

[2,6-Trip$_2$C$_6$H$_3$CS$_2$]Li(thf)$_3$. This compound was prepared analogously to [2,6-Trip$_2$C$_6$H$_3$CS$_2$]Li(py)$_3$ except that thf was used in place of pyridine (65% yield). ^{1}H NMR (CDCl$_3$): δ 7.10 (t, J = 6.7 Hz, 1H, p-C$_6$H$_3$), 7.04 (d, J = 6.6 Hz, 2H, m-C$_6$H$_3$), 6.89 (s, 4H, m-$Trip$), 3.50 (m, 12H, thf), 2.96 (br m, 4H, m-CHMe$_2$), 2.81 (br m, 2H, p-CHMe$_2$), 1.68 (m, 12H, thf), 1.19 (m, 24H), 1.00 (d, J = 6.8 Hz, 12H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 147.7, 146.8, 136.5, 133.5, 129.9, 123.5, 120.8, 119.8, 68.2, 34.1, 30.9, 26.2, 25.5, 24.2, 23.0. IR: 3038 (w), 2952 (s), 2925 (s), 2917 (s), 2871 (s), 2854 (s), 2727 (w), 2671 (w), 1461 (s), 1377 (s), 1316 (w), 1302 (w), 1261 (w), 1169 (w), 1070 (w), 1045 (m), 1019 (m), 940 (w), 913 (w), 892 (w), 871 (w), 803 (w), 759 (w), 722 (w) cm^{-1}.

[2,6-Trip$_2$C$_6$H$_3$CS$_2$]$_2$VCl(thf)$_2$. Toluene (20 mL) was added to [2,6-Trip$_2$C$_6$H$_3$CS$_2$]Li(thf)$_3$ (2.00 g, 2.56 mmol) and VCl$_3$(thf)$_3$ (0.433 g, 1.28 mmol) to form a dark burgundy solution. After stirring overnight, the volatile materials were removed under reduced pressure to give a dark residue which was extracted into hexanes (50 mL). The burgundy solution was filtered and concentrated to 20 mL. The addition of an equal volume of HMDSO resulted in the formation of fine burgundy crystals of product (0.49 g, 28%). ^{1}H NMR (CDCl$_3$): δ ($\omega_{1/2}$, Hz) 18.6 (45), 17.0 (50), 6.72 (400), 4.73 (125), 2.94 (100), 2.84 (115), 2.18 (105), 1.59 (650), 1.18 (280), 1.05 (300), 0.92 (50), 0.74 (300). IR: 2952 (s), 2928 (s), 2922 (s), 2854 (s), 1462 (s), 1378 (s), 1365 (m), 1315 (w), 1305 (w), 1225 (w), 996 (w), 932 (w), 873 (w), 806 (w), 764 (w), 722 (w) cm^{-1}. Anal. Calcd (found) for

Table 2 Crystallographic data and collection parameters

Compound	[2,6-Mes$_2$C$_6$H$_3$CS$_2$]-Li(Et$_2$O)$_2$	[2,6-Mes$_2$C$_6$H$_3$CS$_2$]-TiCl$_2$(thf)$_2$	[2,6-Trip$_2$C$_6$H$_3$CS$_2$]$_2$TiCl$_2$(py)·Et$_2$O	[2,6-Trip$_2$C$_6$H$_3$CS$_2$]$_2$VCl(py)$_2$·2py
Formula	C$_{33}$H$_{45}$LiO$_2$S$_2$	C$_{37}$H$_{51}$Cl$_2$O$_3$S$_2$Ti	C$_{83}$H$_{113}$Cl$_2$NOS$_4$Ti	C$_{94}$H$_{118}$ClN$_4$S$_4$V
M	544.75	726.70	1387.78	1518.55
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/n$ (no. 14)	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)	$P2_1/c$ (no. 14)
T/°C	−89	−140	−138	−138
a/Å	11.5924(13)	14.553(6)	12.7871(7)	22.648(2)
b/Å	11.5958(12)	15.809(6)	16.9214(9)	13.572(1)
c/Å	24.140(3)	16.514(5)	20.390(1)	29.404(3)
V/Å^3	3239.8(6)	3711(2)	3988.6(4)	8718(2)
α/°	90	90	80.002(1)	90
β/°	93.241(2)	102.35(4)	78.030(1)	105.288(2)
γ/°	90	90	68.350(1)	90
Z	4	4	2	4
μ (mm^{-1})	0.190	0.521	0.322	0.286
Reflections collected	26733	36233	56179	85590
Unique reflections	6640	9861	24742	28159
Data/restraints/parameters	6640/2/334	9861/0/406	18248/4/780	17808/0/850
$R1$, $wR2$ (for $I>2\sigma I$)	0.0684, 0.1793	0.0562, 0.1376	0.0619, 0.1628	0.0554, 0.1300
$R1$, $wR2$ (all data)	0.1013, 0.2027	0.0900, 0.1561	0.0827, 0.1722	0.1042, 0.1456
GOF	1.043	1.028	1.054	0.979
Largest peak, hole/e Å^{-3}	0.712, −0.478	0.448, −0.742	0.823, −0.490	0.539, −0.541

C$_{82}$H$_{114}$S$_4$VClO$_2$: C, 73.15 (72.00); H, 8.53 (8.25%). μ_{eff}(CDCl$_3$) = 2.9(1) μ_B.

[2,6-Trip$_2$C$_6$H$_3$CS$_2$]$_2$VCl(py)$_2$. Toluene (20 mL) was added to [2,6-Trip$_2$C$_6$H$_3$CS$_2$]Li(py)$_3$ (0.383 g, 0.477 mmol) and VCl$_3$(thf)$_3$ (0.0807 g, 0.239 mmol) to give a dark red solution. The solution was stirred overnight at room temperature. The volatile materials were removed under reduced pressure to give a dark residue which was extracted into hexanes (50 mL) and filtered. The red-green filtrate was concentrated and cooled to −40 °C. The product was isolated as dark purple crystals (0.12 g, 35%). ^{1}H NMR (CDCl$_3$): δ ($\omega_{1/2}$, Hz) 16.6 (60), 15.5 (400), 13.6 (150), 8.60 (40), 8.00 (70), 7.65 (40), 6.92 (300), 2.06 (140), 1.35 (85), 0.63 (100). IR: 3077 (m), 3051 (m), 3041 (m), 2953 (s), 2924 (s), 2859 (s), 1604 (m, py), 1580 (w, py), 1566 (w, py), 1485 (w), 1461 (s), 1445 (s), 1379 (s), 1360 (m), 1316 (w), 1237 (w), 1217 (w), 1102 (w), 1068 (w), 1044 (w), 1030 (w), 1019 (m), 1009 (m), 939 (m), 877 (m), 804 (w), 778 (w), 755 (m), 743 (w), 722 (w), 701 (m), 694 (m), 690 (m), 690 (m), 651 (w) cm^{-1}. Anal. Calcd (found) for C$_{84}$H$_{108}$S$_4$VClN$_2$: C, 74.16 (73.68); H, 8.00 (7.62); N, 2.06 (2.17%). μ_{eff}(CDCl$_3$) = 2.8(1) μ_B.

[2,6-Trip$_2$C$_6$H$_3$CS$_2$]$_2$TiCl$_2$(py). Toluene (75 mL) was added to [2,6-Trip$_2$C$_6$H$_3$CS$_2$]Li(thf)$_3$ (1.73 g, 2.21 mmol) and TiCl$_4$(thf)$_2$ (0.370 g, 1.11 mmol) to form a red solution. After a few minutes, pyridine (0.40 mL, 4.9 mmol) was added. After stirring overnight, the volatiles were removed under reduced pressure to afford a red solid. The solid was extracted with Et$_2$O (80 mL) and filtered through Celite. Concentration to 10 mL and cooling to −40 °C afforded the product as red crystals (1.11 g, 76.1%). ^{1}H NMR (CDCl$_3$): δ 8.80 (d, J = 5.2 Hz, 2H, α-Py), 7.78 (t, 7.5 Hz, 1H, γ-Py), 7.34–7.27 (m, 4H, β-Py + p-C$_6$H$_3$), 7.19 (d, J = 7.5 Hz, 4H, m-C$_6$H$_3$), 6.80 (s, 8H, m-Trip), 2.78 (sept, J = 6.8 Hz, 4H, p-CHMe$_2$-Trip), 2.54 (sept, J = 6.8 Hz, 8H, o-CHMe$_2$-Trip), 1.19 (d, J = 6.7 Hz, 24H), 1.06 (d, J = 6.7 Hz, 24H), 0.96 (d, J = 6.7 Hz, 24H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 152.3, 148.0, 146.5, 146.3, 139.0, 136.4, 133.8, 129.9, 127.8, 124.7, 120.1, 34.3, 31.0, 26.1, 24.2, 22.1. Anal. Calcd (found) for [2,6-Trip$_2$C$_6$H$_3$CS$_2$]$_2$TiCl$_2$(py)·0.5Et$_2$O: C$_{81}$H$_{108}$Cl$_2$NO$_{0.5}$S$_4$Ti: C, 71.40 (72.02); H, 7.75 (8.06); N, 0.99 (1.04%).

[2,6-Mes$_2$C$_6$H$_3$CS$_2$]TiCl$_2$(thf)$_2$. Toluene (50 mL) was added to [2,6-Mes$_2$C$_6$H$_3$CS$_2$]Li(Et$_2$O)$_2$ (2.10 g, 4.23 mmol) and TiCl$_3$(thf)$_3$ (1.57 g, 4.23 mmol) to form a teal solution. After stirring overnight, the volatiles were removed under reduced pressure. The resulting solid was extracted with Et$_2$O (50 mL)

and filtered. Concentration and cooling to −40 °C afforded the product as green-blue crystals (1.07 g, 36%). IR: 2952 (s), 2855 (s), 1461 (m), 1377 (s), 1015 (s), 1002 (s), 926 (w), 856 (m), 730 (m) cm^{-1}. Anal. Calcd (found) for C$_{37}$H$_{51}$Cl$_2$O$_2$S$_2$Ti: C, 62.53 (62.49); H, 7.23 (7.00%). μ_{eff}(C$_6$D$_6$) = 1.6(1) μ_B.

X-Ray crystallography

Table 2 lists a summary of crystal data and collection parameters for all crystallographically characterized compounds. Single-crystal structure determinations were performed within the Department of Chemistry and Biochemistry at the University of Colorado.

General procedure. Crystals were examined under a light hydrocarbon oil (Paratone-N) and mounted with silicone vacuum grease onto a thin glass fiber affixed to a tapered copper mounting-pin. This assembly was transferred to the goniometer of a Siemens SMART CCD diffractometer equipped with a locally modified LT-2A low-temperature apparatus. Cell parameters were determined using reflections harvested from 3 orthogonal sets of 20 0.3° Ω scans. A minimum of a hemisphere of data was collected using 0.3° Ω scans in two correlated exposures. All data were corrected for Lorentz and polarization effects, and a semi-empirical absorption correction was applied using SADABS.[18] Structure solutions and refinements were performed (SHELXTL-Plus V5.0) on F^2.[18]

CCDC reference numbers 196425–196428.

See http://www.rsc.org/suppdata/dt/b2/b210691d/ for crystallographic data in CIF or other electronic format.

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