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Early transition metal thiolates

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Abstract

This article presents a comprehensive and systematic review of the syntheses, structures and reactivities of thiolate complexes of group 4 and 5 metals (i.e. Ti, Zr, Hf, V, Nb and Ta). This includes a discussion of monometallic and polymetallic species as well as recent advances in heterobimetallic derivatives. Specifically excluded are dithiolene derivatives of the early metals as these compounds have been previously reviewed.

Keywords: Early transition metal thiolates; Synthesis; Chemistry

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1. Introduction

Continuing interest in complexes which incorporate thiolate ligands is prompted by several motivating facts. Among these are the relevance to biological systems [1], the potential of chemistry relating to S—C bond cleavage reactions and desulfurization [2], the novel structure of such complexes and the potential of applications in organosulfur chemistry. All of these features spurred the study of late transition metal thiolate chemistry over the last 30 years, resulting in a considerable body of important and interesting work [3]. Parallel study of early metal thiolate chemistry was left underdeveloped until about 10 years ago when this area was revived. This article will review the progress in this area. While every attempt has been made to make this review comprehensive to mid-1993, the scopes has been limited to thiolate complexes of the early metals, specifically Ti, Zr, Hf, V, Nb and Ta. As thiolato-bridged heterobimetallics described prior to 1988 have been reviewed in 1989 [4], data are not provided on these compounds. Only more recent reports of such compounds are incorporated in the present review. In addition, dithiolene, dithiocarbamate and xanthate derivatives are specifically excluded as these are electronically distinct from thiolate systems [5].

2. Homoleptic thiolate complexes

Homoleptic thiolate derivatives of the early metals are generally a class of compounds that has received little attention. While few structural studies of such compounds have been described, the known chemistry of such species is very limited. A summary is provided in Table 1.

2.1. Titanium

The first report of a homoleptic titanium thiolate derivative appeared in 1974. Clark and Kaminaris [6] described the preparation of the thermally unstable $Ti(SC_6F_5)_4$ **1**. At 70 °C **1** was reported to degrade (Eq. (1)). It was further reported that **1** did not act as a Lewis acid towards common donors such as PPh_3 or pyridine.

$$Ti(SC_6F_5)_4 \rightarrow TiS_2 + (SC_6F_5)_2 + (C_6F_5)_2 \quad (1)$$

The first structurally characterized homoleptic titanium thiolate was the dianion $[Ti(SCH_2CH_2S)_3]^{2-}$ **2** reported by Holm and coworkers in 1985 [7]. This species is prepared from the reaction of the disodium dithiolate, $TiCl_3$ and Et_4NCl. The

Table 1
Homoleptic thiolate complexes of the early metals

No.	Compound	Information	Ref.
1	$Ti(SC_6F_5)_4$	Synthesis, IR	[6]
2	$[Ti(SCH_2CH_2S)_3]^{2-}$	Synthesis, X-ray, CV, coulometry, UV–visible, NMR	[7–10]
3	$[Ti(S\text{-}2,4,6\text{-}i\text{-}Pr_3C_6H_2)_4]^-$	Synthesis, UV-visible, X-ray	[11]
4	$Ti(S\text{-}t\text{-}Bu)_4$	Synthesis, NMR	[12]
5	$Hf(SC_6F_5)_4$	Synthesis	[6]
6	$[Hf(SCH_2CH_2S)_3]^{2-}$	Synthesis, UV-visible, NMR	[10]
7	$[V_2(SCH_2CH_2S)_4]^{2-}$	Synthesis, Electrochemistry, UV-visible, X-ray	[8,9,13–16]
8	$[V_2(SCH_2CH_2S)_4]^-$	Generation	[8,9,16]
9	$V(S\text{-}t\text{-}Bu)_4$	Synthesis, EPR, Electrochemistry, MS, X-ray	[17–19]
10	$[V(S\text{-}t\text{-}Bu)_4]^-$	Synthesis, X-ray	[18,19]
11	$Nb(SC_6F_5)_5$	Synthesis	[6]
12	$[Nb(SCH_2CH_2S)_3]^-$	Synthesis, NMR, UV-visible, X-ray, IR	[10,20–22]
14	$[Nb(SCH_2CH_2CH_2S)_3]^-$	Synthesis, NMR, UV-visible, X-ray, IR	[21,23]
15	$[Nb_2(SCH_2CH_2CH_2S)_5]^-$	Synthesis, IR, NMR	[23]
17	$[Nb(S_2C_7H_{10})_3]^-$	Synthesis, NMR, UV-visible, IR, X-ray, Electrochemistry	[24]
18	$[Nb(SPh)_6]^{2-}$	Synthesis, X-ray	[25]
19	$(THF)_3NaNb(SPh\text{-}p\text{-}Me)_6$	Synthesis, X-ray	[25]
20	$[Nb_2(SPh)_{10}]^-$	Synthesis, NMR	[25]
22	$[Ta(SCH_2CH_2S)_3]^-$	Synthesis, NMR, UV-visible	[22]
23	$[Ta(SCH_2CH_2CH_2S)_3]^-$	Synthesis, NMR, UV-visible	[21]
24	$[Ta(S_2C_7H_{10})_3]^-$	Synthesis, NMR, UV-visible, IR, X-ray, Electrochemistry	[24]
25	$[Ta(SPh)_6]^{2-}$	Synthesis, X-ray	[25]

CV, cyclic voltammetry; NMR, nuclear magnetic resonance; EPR, electron paramagnetic resonance; MS, mass spectroscopy.

resulting diamagnetic Ti(IV) product **2** is apparently derived as a result of the oxidative instability of Ti(III). Compound **2** can also be derived from $TiCl_4$ [8]. The structural data show the geometry about Ti is pseudo-octahedral with Ti—S bond distances falling into two ranges 2.434(4) and 2.419(1) Å (Fig. 1). Subsequent electrochemical studies show that **2** is reduced irreversibly at −2.09 V vs. saturated calomel electrode (SCE) [9]. Salts of the dianion of **2** have also been prepared via the reaction of $Ti(NEt_2)_4$ with ethanedithiol and subsequent cation exchange [10].

Sigel and Power [11] reported the use of a bulky thiolate to stabilize a Ti(III) homoleptic anion complex $[Li(OEt_2)_3][Ti(SC_6H_2\text{-}2,4,6\text{-i-}Pr_3)_4]$ **3** (Fig. 2). This compound is derived from reaction of the lithium thiolate and $TiCl_3$. The structure of **3** shows that the Ti adopts a pseudotetrahedral geometry with Ti—S distances averaging 2.361(2) Å.

One potential use of neutral homoleptic Ti(IV) thiolates is as molecular precursors to thin films. Bochmann et al. [12] have demonstrated this potential. The red crystalline material $Ti(S\text{-}t\text{-}Bu)_4$ **4** was prepared from the reaction of $Ti(NMe_2)_4$ and HS-*t*-Bu. This very air-sensitive species is volatile, decomposing under vacuum at 130 °C (Eq. (2)). The nature of the film produced was confirmed by energy-dispersive X-ray analysis and stands in contrast to decomposition route reported for **1**. Nonetheless, it demonstrates the extension of the concepts of metal–organic chemical vapor deposition (MOCVD) to titanium thiolates and TiS.

$$Ti(S\text{-}t\text{-}Bu)_4 \rightarrow TiS + t\text{-}Bu_2S + (S\text{-}t\text{-}Bu)_2 \qquad (2)$$

2.2. *Zirconium*

A brief and somewhat dubious report of a blue compound formulated as $Zr(SPh)_4$ appeared in the literature in 1966 [26]. Although Clark and Kaminaris [6] also described attempts to react ZrI_4 or $ZrCl_4$ with HSC_6F_5, no products were isolated. Since then, no other homoleptic thiolates of Zr have been reported.

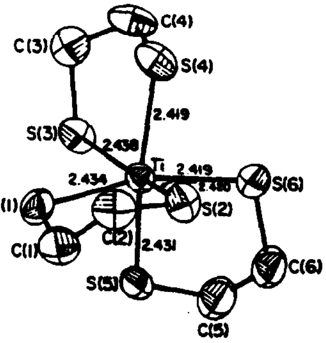


Fig. 1. ORTEP drawing of the homoleptic dianion $[Ti(SCH_2CH_2S)_3]^{2-}$ **2**. Reproduced with permission from Ref. [7]. Copyright 1985 American Chemical Society.

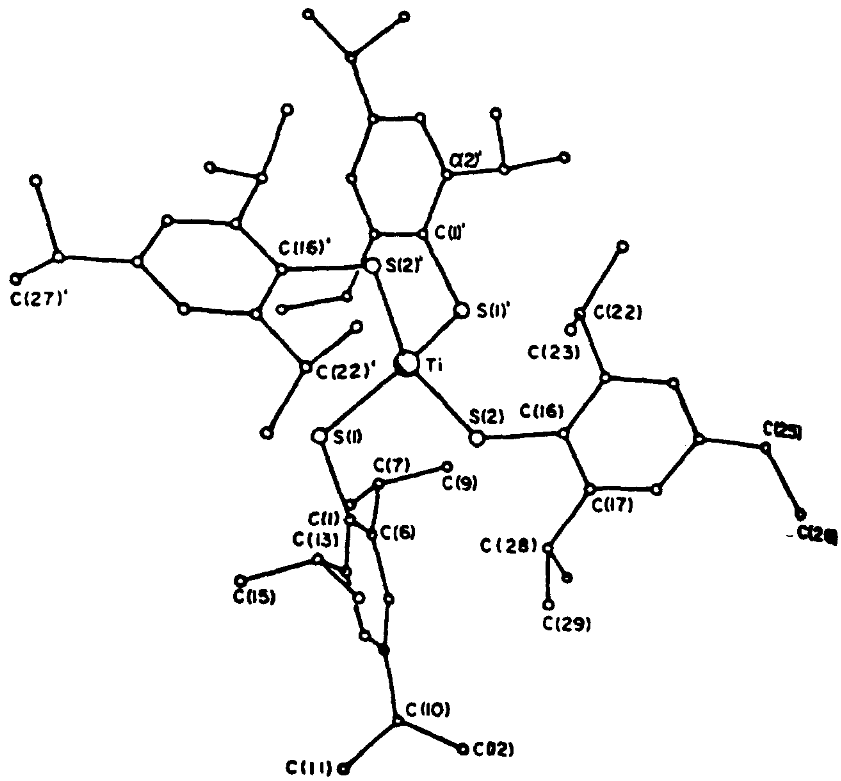


Fig. 2. ORTEP drawing of the homoleptic dianion $[Ti(SC_6H_2,2,4,6\text{-}i\text{-}Pr_3)_4]^-$ 3. Reproduced with permission from Ref. [11]. Copyright 1987 American Chemical Society.

2.3. *Hafnium*

Employing a synthetic route similar to that used for **1** the compound $Hf(SC_6F_5)_4$ **5** was reportedly prepared in 1974, although full details of its characterization were not described [6]. Salts of the homoleptic dianion $[Hf(SCH_2CH_2S)_3]^{2-}$ **6** are derived from the reaction of $Hf(NEt_2)_4$ with ethanedithiol, followed by cation exchange [10]. These two reports represent the only efforts describing hafnium homoleptic thiolate derivatives, while no structural data have been presented.

2.4. *Vanadium*

In 1983, the first homoleptic vanadium thiolate derivative $[V_2(SCH_2CH_2S)_4]^{2-}$ **7** was prepared simultaneously by three groups, via reaction of VCl_3 with $(NaSCH_2)_2$, followed by cation exchange (Fig. 3) [13–15]. In this dianion, two of the ethanedithiolate ligands provide four bridging sulfur atoms between the two V(III) centers. The dianion **7** has D_2 symmetry, while the VS_6 coordination unit has C_{2v} symmetry and is of unusual non-octahedral stereochemistry. The species **7** is weakly paramagnetic

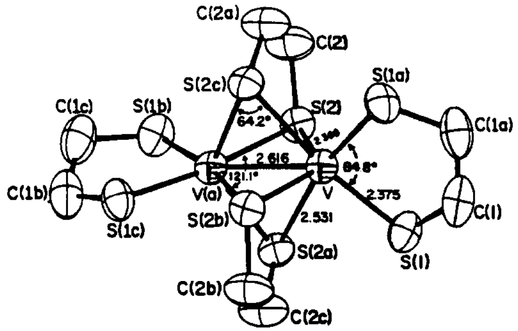


Fig. 3. ORTEP drawing of the homoleptic dianion $[V_2(SCH_2CH_2S)_4]^{2-}$ **7**. Reproduced with permission from Ref. [15]. Copyright 1983 American Chemical Society.

as a result of the low lying triplet state as suggested by molecular orbital (MO) calculations [9]. Further, this species was shown to be reversibly oxidized by one electron to $[V_2(SCH_2CH_2S)_4]^-$ **8** at −0.61 V vs. SCE; however, **8** was not stable, as it did not remain in solution 20–30 min after being generated coulometrically [8,16].

The mononuclear V(IV) species $[V(S\text{-}t\text{-}Bu)_4]$ **9** was first prepared by the reaction of VCl_4, *t*-BuSH and NEt_3 [17]. It was subsequently prepared by reaction of $VCl_3(THF)_3$ with NaS-*t*-Bu and $(S\text{-}t\text{-}Bu)_2$ [18,19]. This paramagnetic species has $\bar{4}$ symmetry corresponding to a slightly flattened T_d symmetry. Compound **9** undergoes a reversible one-electron reduction to $[V(S\text{-}t\text{-}Bu)_4]^-$ **10** at −0.68 V vs. SCE. The reaction of $VCl_3(THF)_3$ with NaS-*t*-Bu in the presence of bipyridine afforded the salt $[V(S\text{-}t\text{-}Bu)_2(bipy)_2][V(S\text{-}t\text{-}Bu)_4]$, which contains the homoleptic anion **10**. This anion also adopts a distorted tetrahedral geometry, with slightly longer V—S bonds than in **9** (2.280(7)–2.309(7) Å vs. 2.2184(24) Å). Mass spectral data of **9** reveal that S—C bond cleavage occurs en route to $[VS_x]^+$ ($x = 0$–3) and suggest a mechanism for the formation of V_2S_3 during upgrading of heavy petroleum crudes containing V impurities [19].

2.5. Niobium

The poorly characterized compound $Nb(SC_6F_5)_5$ **11** was briefly described in 1974 [6] but it was not until 1986 that Nakamura and coworkers [20] reported the first fully characterized niobium homoleptic thiolate derivative. The species $[Nb(SCH_2CH_2S)_3]^-$ **12** was prepared by reaction of $NbCl_5$ and $LiSCH_2CH_2SLi$ [20]. The anion **12** has C_3 symmetry with Nb–sulfur geometry midway between trigonal prismatic and octahedral. A subsequent study described a second salt of this anion [10]. IR and Raman studies imply that this perturbation of the geometry arises as a result of crystal packing forces and electronic factors [21]. This anion, on exposure to water, methanol or phenol, undergoes an unexpected isomerization to the species $[NbS(SCH_2CH_2S)(SCH_2CH_2SCH_2CH_2S)]^-$ **13** (Fig. 4) [22]. The

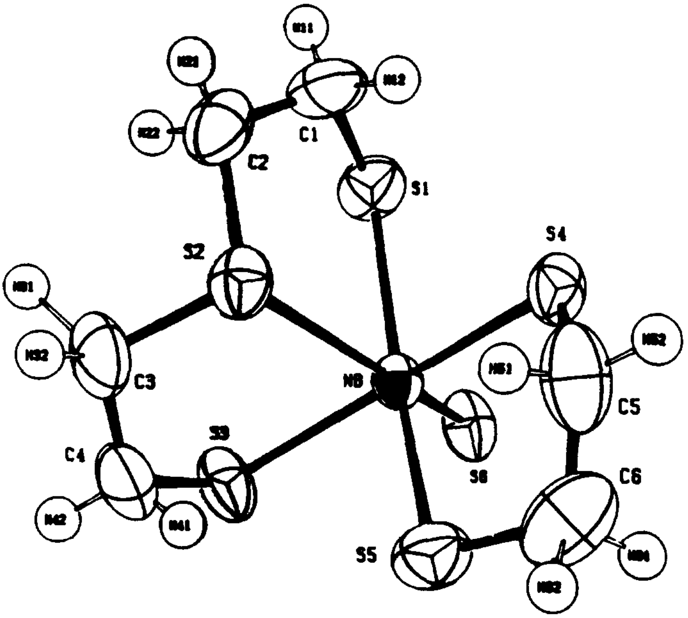


Fig. 4. ORTEP drawing of the anion $[NbS(SCH_2CH_2S)(SCH_2CH_2)_2S)]^-$ **13**. Reproduced with permission from Ref. [22]. Copyright 1986 American Chemical Society.

Nb=S bond distance in this pseudo-octahedral species is 2.192(3) Å while the Nb—S(thioether) distance is 2.740(4) Å

The species $[Nb(SCH_2CH_2CH_2S)_3]^-$ **14** was prepared in a manner similar to that used for **12** [21]. It has been shown to undergo a self-reduction reaction on standing in solution for a month, yield the binuclear species $[Nb_2(SCH_2CH_2CH_2S)_5]^-$ **15** [23]. This species undergoes a further reaction with methanol to give $[Nb_2(OMe)_3(SCH_2CH_2CH_2S)_3]^-$ **16** (Fig. 5) [23].

Reactions of the chiral dithiolate norbornane-*exo*-2,3-dithiolate (nbt) with $NbCl_5$ affords the anion $[Nb(nbt)_3]^-$ **17** [24]. With this ligand two geometrical forms are possible, synclastic and anticlastic (Fig. 6). Structural data show that **17** is anticlastic in the solid state (Fig. 7) while ^1H nuclear magnetic resonance (NMR) data confirm an intramolecular anticlastic–synclastic interconversion process.

Coucouvanis and coworkers [25] have reported the synthesis of $[PPh_4]_2[Nb(SPh)_6]$ **18** and $[Na(THF)_3Nb(SPh\text{-}p\text{-}Me)_6]$ **19** from the reaction of

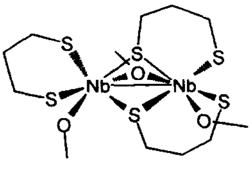
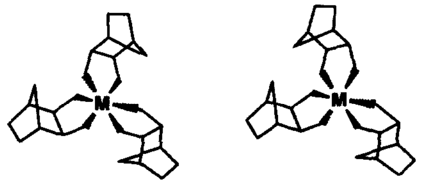


Fig. 5. Structure of the compound $[Nb_2(OMe)_3(SCH_2CH_2CH_2S)_3]^-$ **16**.



Synclastic **Anticlastic**

Fig. 6. Synclastic and anticlastic isomers of $[M(ndt)_3]^-$.

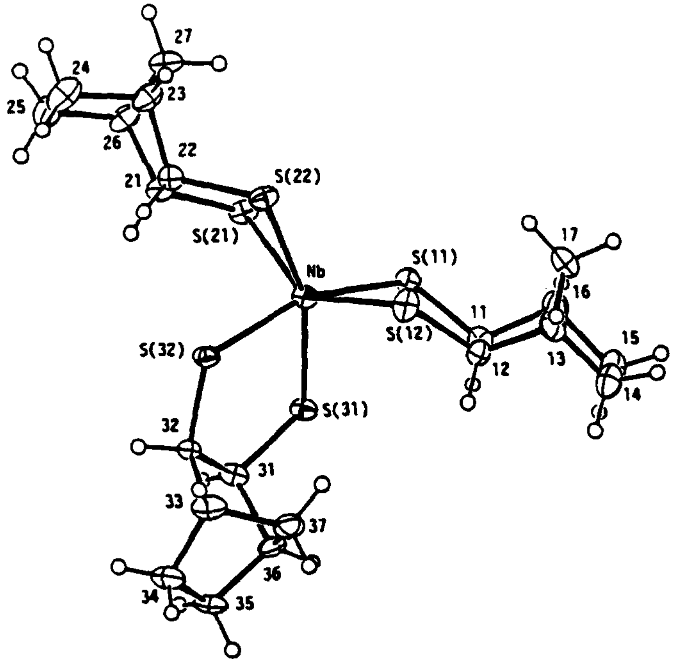


Fig. 7. ORTEP drawing of the homoleptic anion $[Nb(ndt)_3]^-$ **17**. Reproduced with permission from Ref. [24]. Copyright 1989 American Chemical Society.

$NbCl_5$ with NaSPh (Fig. 8). The implication of these results is that the Nb(V) in **19** is stabilized by coordination of $Na(THF)_3^+$. The Nb—S distances in **18** and **19** are 2.488(3) Å and 2.447(3) Å respectively, consistent with the Nb oxidation states. Also in this report preliminary data imply the formation of the species $[NEt_4][Nb_2(SPh)_{10}]$ **20**, although this species was not fully characterized [25].

2.6. Tantalum

Initial attempts to prepare homoleptic Ta thiolates were reported by Clark and Kaminaris [6]. Reaction of $TaCl_5$ with HSC_6F_5 led only to the formation of the ill-characterized $TaCl_3(SC_6F_5)_2$ **21**. Subsequent isolation of verified homoleptic

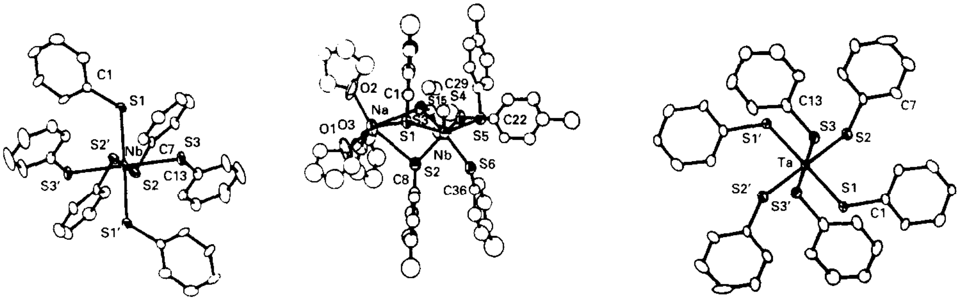


Fig. 8. ORTEP drawings of $[Nb(SPh)_6]^{2-}$ **18**, $Na(THF)_3Nb(SC_6H_4Me)_6$ **19** and $[Ta(SPh)_6]^-$ **25**. Reproduced with permission from Ref. [25]. Copyright 1990 American Chemical Society.

tantalum thiolates occurred in conjunction with the studies of Nb analogs described above. For example, the species $[Ta(SCH_2CH_2S)_3]^-$ **22** and $[Ta(SCH_2CH_2CH_2S)_3]^-$ **23** were prepared in a manner similar to that described for **12** [21,22]. The compound $[Ta(nbt)_3]^-$ **24** was prepared and an X-ray structure of **24** showed that the synclastic isomer was obtained [24]. The species $[Ta(SPh)_6]^-$ **25** (Fig. 8) was prepared in a synthetics route analogous to that used for **18** although reduction of the metal did not occur affording the isolation of the octahedral Ta(V) species **25** [25].

3. Thiolate derivatives of coordination compounds

Here, as in Section 2, comparatively few studies have described simple thiolate derivatives of the early metals (Table 2). The exception has been vanadium where significantly more effort has been expended. The greater degree of study has been associated with the implications of a role for vanadium in biological systems.

3.1. Titanium

One of the first reports of simple thiolate derivatives of Ti was described by Bradley and Hammersley in 1967 [27]. They described the reaction of metal amides with several thiols in their attempts to prepare homoleptic Ti thiolates. Instead, red, insoluble compounds formulated as $Ti(SR')_4(R'SH)_x(R_2NH)_y$ ($R' = Me$, Et, i-Pr; $R = Me$, Et) **26** were suggested to be adducts of the desired homoleptic compounds. The researchers suggested that these compounds were polymeric although this was not confirmed. Several soluble species of the form $Ti(SR)(NMe_2)_3$ ($R = Et$ **27**, i-Pr **28**) and $Ti(SR)_2(NMe_2)_2$ ($R = Et$ **29**, i-Pr **30**) were isolated (Eq. (3)). Molecular weight determinations suggested that these species were oligomeric in solution.

$$Ti(NR_2)_4 + xR'SH \rightarrow Ti(SR')_x(NR_2)_{4-x} + xR_2NH \qquad (3)$$

Employing a similar approach to Ti—S bond formation, Chatterjee et al. [28]

Table 2
Thiolate derivatives of coordination compounds

No.	Compound	Information	Ref.
Titanium			
27	$Ti(SEt)(NMe_2)_3$	Synthesis, NMR, MW	[27]
28	$Ti(S\text{-}i\text{-}Pr)(NMe_2)_3$	Synthesis, NMR, MW	[27]
29	$Ti(SEt)_2(NMe_2)_2$	Synthesis, NMR, MW	[27]
30	$Ti(S\text{-}i\text{-}Pr)_2(NMe_2)_2$	Synthesis, NMR, MW	[27]
31	$Ti(O\text{-}i\text{-}Pr)_2(SCH_2CH_2O)$	Synthesis	[28]
32	$Ti(O\text{-}i\text{-}Pr)_2(SCH_2CH_2CO_2)$	Synthesis	[28]
33	$Ti(O\text{-}i\text{-}Pr)_2(SCH(CH_3)CO_2)$	Synthesis	[28]
34	$Ti(O\text{-}i\text{-}Pr)_2(SCH_2CH_2S)$	Synthesis	[28]
35	$Ti(O\text{-}i\text{-}Pr)_2(SCH_2CH_2NHCH(Me)COMe)$	Synthesis	[29]
36	$Ti(O\text{-}i\text{-}Pr)_2(SCH_2CH_2NHCH(Me)CC_6H_4O)$	Synthesis	[29]
37	$Ti(O\text{-}i\text{-}Pr)_2(SCH_2CH_2N{=}CHC_6H_4O)$	Synthesis	[29]
38	$Ti(SCH_2CH_2O)_2$	Synthesis	[28]
39	$Ti(SCH_2CH_2CO_2)_2$	Synthesis	[28]
40	$Ti(SCH(CH_3)CO_2)_2$	Synthesis	[28]
41	$Ti(SCH_2CH_2S)_2$	Synthesis	[28]
42	$Ti(SCH_2CH_2NHCH(Me)COMe)_2$	Synthesis	[29]
43	$Ti(SCH_2CH_2NHCH(Me)CC_6H_4O)_2$	Synthesis	[29]
44	$Ti(SCH_2CH_2N{=}CHC_6H_4O)_2$	Synthesis	[29]
45	$Ti(O\text{-}i\text{-}Pr)_3(SEt)$	Synthesis, NMR	[30]
46	$Ti(O\text{-}i\text{-}Pr)_2(SCH(Me)CH_2S)$	Synthesis, IR, NMR, MW	[31]
47	$Ti(O\text{-}i\text{-}Pr)_2(SCH_2CH_2CH_2S)$	Synthesis, IR, NMR, MW	[31]
48	$Ti(O\text{-}i\text{-}Pr)_2(SCH_2CH_2SH)_2$	Synthesis, IR, NMR, MW	[31]
49	$Ti(O\text{-}i\text{-}Pr)_2(SCH(Me)CH_2SH)_2$	Synthesis, IR, NMR, MW	[31]
50	$Ti(O\text{-}i\text{-}Pr)_2(SCH_2CH_2S)(phen)$	Synthesis, IR, NMR, MW	[31]
51	$Ti(O\text{-}i\text{-}Pr)_2(SCH_2CH_2S)(bipy)$	Synthesis, IR, NMR, MW	[31]
52	$Ti(O\text{-}i\text{-}Pr)_2(SCH_2CH_2S)(py)_2$	Synthesis, IR, NMR, MW	[31]
53	$Ti(O\text{-}i\text{-}Pr)_2(SCH(Me)CH_2S)(phen)$	Synthesis, IR, NMR, MW	[31]
54	$Ti(O\text{-}i\text{-}Pr)_2(SCH(Me)CH_2S)(bipy)$	Synthesis, IR, NMR, MW	[31]
55	$Ti(O\text{-}i\text{-}Pr)_2(SCH(Me)CH_2S)(py)_2$	Synthesis, IR, NMR, MW	[31]
56	$Ti(O\text{-}i\text{-}Pr)_2(SCH_2CH_2CH_2S)(phen)$	Synthesis, IR, NMR, MW	[31]
57	$Ti(O\text{-}i\text{-}Pr)_2(SCH_2CH_2CH_2S)(bipy)$	Synthesis, IR, NMR, MW	[31]
58	$Ti(O\text{-}i\text{-}Pr)_2(SCH_2CH_2CH_2S)(py)_2$	Synthesis, IR, NMR, MW	[31]
59	$Ti(O\text{-}i\text{-}Pr)_2(SC_6H_4\text{-}2\text{-}NH_2)_2$	Synthesis, IR, NMR, MW	[31]
60	$[Ti(SEt)((OCH_2CH_2)_3N)]_2$	Synthesis, NMR, IR, MS	[32]
61	$[Ti(S\text{-}i\text{-}Pr)((OCH_2CH_2)_3N)]_2$	Synthesis, NMR, IR, MS	[32]
62	$[Ti(SCMe_2Et)((OCH_2CH_2)_3N)]_2$	Synthesis, NMR, IR, MS	[32]
63	$[Ti(S\text{-}allyl)((OCH_2CH_2)_3N)]_2$	Synthesis, NMR, IR, MS	[32]
64	$[Ti(SPh)((OCH_2CH_2)_3N)]_2$	Synthesis, NMR, IR, MS	[32]
65	$TiCl_2(SCH_2CH_2S)(bipy)$	Synthesis	[33]
66	$TiCl_2(SCH_2CH_2S)(py)_2$	Synthesis	[33]
67	$TiCl_2(SCH_2CH_2S)(py\text{-}N\text{-}oxide)_2$	Synthesis	[33]
68	$TiCl_2(SCH_2CH_2S)(4\text{-}Me\text{-}py)_2$	Synthesis	[33]
69	$TiCl_2(S\text{-}t\text{-}Bu)_2(diars)$	Synthesis, NMR, IR, X-ray	[34]
70	$TiCl_2(S\text{-}t\text{-}Bu)_2(dmpe)$	Synthesis, NMR, IR	[34]
71	$TiCl_2(S\text{-}t\text{-}Bu)_2(dppe)$	Synthesis, NMR, IR	[34]
72	$Ti(TPP)(SPh)$	Synthesis, UV-visible, IR, EPR	[35]

Table 2 (continued)

No.	Compound	Information	Ref.
Zirconium			
73	$Zr_3S_3(S\text{-}t\text{-}Bu)_2(BH_4)_4(THF)_2$	Synthesis, IR, X-ray	[36]
74	$Zr_6S_6(S\text{-}t\text{-}Bu)_2(BH_4)_8(THF)_2$	Synthesis, IR, X-ray	[36]
75	$Zr_3S(S\text{-}t\text{-}Bu)_{10}$	Synthesis, NMR, X-ray	[37]
Vanadium			
76	$VO(SC_6H_4NH_2)_2$	Synthesis, UV–visible	[38]
77	$VO(SCH_2CH_2NH_2)_2$	Synthesis, IR, UV–visible	[39]
78	$VO(SCH_2CH_2N(decyl)H)_2$	Synthesis, IR, UV–visible	[39]
79	$VO(SC_6H_4NO)_2$	Synthesis, IR, UV–visible	[39]
80	$VO(SC_6H_4NH_2)_2$	Synthesis, IR, UV–visible	[39]
81	$VO(SC_9H_6N)_2$	Synthesis, IR, UV–visible, EPR, Magnetic susceptibility, Conductivity, Electrochemistry	[40–44]
82	$VO(SC_6H_4NH_2)_2py$	Synthesis, IR, UV–visible	[39]
83	$VO(SC_6H_4NO)_2py$	Synthesis, IR, UV–visible	[39]
84	$VO(SC_6H_4CO_2)_2$	Synthesis, UV–visible, IR	[45]
85	$VO(SC_6H_4CO_2)_2py$	Synthesis, UV–visible, IR	[45]
86	$[VO(SCH_2C(CO_2)NH_2)_2]^{2-}$	Synthesis, UV–visible, EPR	[46]
87	$VO(SCH_2C(CO_2Me)NH_2)_2$	Synthesis, EPR, UV–visible, IR, Electrochemistry, X-ray	[47–50]
88	$VO(SC(CH_3)_2CH(CO_2Me)NH_2)_2$	Synthesis, IR, UV–visible, Electrochemistry	[49]
89	$VO(SCH_2CH_2NHC_6H_5)_2$	Synthesis, IR, Electrochemistry, Stability constant	[51]
90	$VO(SCH_2CH_2NHC_6H_4\text{-}p\text{-}Cl)_2$	Synthesis, IR, Electrochemistry, Stability constant	[51]
91	$VO(SCH_2CH_2NHC_6H_4\text{-}Me)_2$	Synthesis, IR, Electrochemistry, Stability constant	[51]
92	$VO(SCH_2CH_2NHC_6H_4\text{-}OMe)_2$	Synthesis, IR, Electrochemistry, Stability constant	[51]
93	$VO((SC_6H_4CH{=}N(CH_2))_2)$	Synthesis, MS, Magnetic properties, UV–visible, EPR, X-ray	[52]
94	$VO(SC_6H_4CH{=}N(CH_2))_2(CH_2)$	Synthesis, MS, Magnetic properties, UV–visible, EPR	[52]
95	$VO((SC_6H_4CH{=}N)_2(o\text{-}C_6H_4))$	Synthesis, MS, Magnetic properties, UV–visible, EPR	[52]
96	$VO((SC_6H_4CH{=}N)_2(o\text{-}C_6H_4\text{-}4{,}5\text{-}Me_2))$	Synthesis, MS, Magnetic properties, UV–visible, EPR	[52]
97	$VO(SCH_2CH_2N(Me)CH_2)_2$	Synthesis, UV–visible, X-ray	[53,54]
98	$V_2O(SCH_2CH_2NMe_2)_4$	Synthesis, UV–visible, Electrochemistry, Magnetic susceptibility, X-ray	[55]
99	$V_2(SCH_2CH_2NH_2)_4$	Synthesis, UV–visible, Electrochemistry, Magnetic susceptibility	[55]
100	$VO(SEt)_3$	Synthesis, NMR	[56]
101	$VO(S\text{-}i\text{-}Pr)(O\text{-}i\text{-}Pr)_2$	Synthesis, NMR, ^{51}V NMR	[57]
102	$VO(S\text{-}i\text{-}Pr)_3$	Synthesis, NMR, ^{51}V NMR	[57]

Table 2 (continued)

No.	Compound	Information	Ref.
103	$VO(S\text{-}t\text{-}Bu)(O\text{-}t\text{-}Bu)_2$	Synthesis, NMR, ^{51}V NMR	[17]
104	$VO(S\text{-}t\text{-}Bu)_2(O\text{-}t\text{-}Bu)$	NMR, ^{51}V NMR	[17]
105	$VO(S\text{-}t\text{-}Bu)_3$	Synthesis, NMR, ^{51}V NMR	[17]
106	$VO(SSiPh_3)_3$	Synthesis, NMR, ^{51}V NMR	[17]
107	$VS(S\text{-}t\text{-}Bu)(O\text{-}t\text{-}Bu)_2$	Synthesis, NMR, ^{51}V NMR	[17]
108	$VS(S\text{-}t\text{-}Bu)_2(O\text{-}t\text{-}Bu)$	Synthesis, NMR, ^{51}V NMR	[17]
109	$VS(SSiPh_3)_3$	Synthesis, NMR, ^{51}V NMR	[17]
110	$[VO(SCH_2CH_2S)_2]^{2-}$	Synthesis, EPR, UV–visible, IR, X-ray	[13,58–60]
111	$[VO(SCH_2CH_2CH_2S)_2]^{2-}$	Synthesis, EPR, UV–visible, IR	[59,60]
112	$[VS(SCH_2CH_2S)_2]^{2-}$	Synthesis, EPR, UV–visible, IR, X-ray	[58–60]
113	$[V(OSiMe_3)(SCH_2CH_2S)_2]^{-}$	Synthesis, EPR, UV–visible, IR, X-ray	[60]
114	$[VS(SPh)_4]^{2-}$	Synthesis, UV–visible, IR, X-ray	[61]
115	$[VSe(SPh)_4]^{2-}$	Synthesis, UV–visible, IR, X-ray	[61]
116	$[VSe(SCH_2CH_2S)_2]^{2-}$	Synthesis, UV–visible, IR, X-ray	[61]
117	$[VS_2(S_2)(SPh)]^{2-}$	Synthesis, X-ray	[62]
118	$[V_2O_2(SCH_2CH_2S)_3]^{2-}$	Synthesis, X-ray	[18]
119	$[V_2S_5(SCH_2CH_2S)]^{3-}$	Synthesis, UV–visible, IR, Electrochemistry	[16]
120	$[V_2OS_4(SCH_2CH_2S)]^{3-}$	Synthesis, UV–visible, IR, Electrochemistry, X-ray	[16,62]
121	$[V_3S_4(SCH_2CH_2S)_3]^{3-}$	Synthesis, UV–visible, IR, Electrochemistry, X-ray	[16]
122	$[V_2S_2(SCH_2CH_2S)_6]^{2-}$	Synthesis, Electrochemistry, X-ray	[63]
123	$[V_4O(SCH_2CH_2S)_2Cl_8]^{2-}$	Synthesis, X-ray, MO calculations	[64]
124	$V(N\text{-}t\text{-}Bu)(S\text{-}t\text{-}Bu)_3$	Synthesis, NMR, ^{51}V NMR	[65]
125	$V(N\text{-}t\text{-}Bu)(S\text{-}t\text{-}Bu)Cl_2$	Synthesis, NMR, ^{51}V NMR	[65]
126	$V(N\text{-}t\text{-}Bu)(S\text{-}t\text{-}Bu)_2Cl$	Synthesis, NMR, ^{51}V NMR	[65]
127	$V(N\text{-}t\text{-}Bu)(O\text{-}t\text{-}Bu)(S\text{-}t\text{-}Bu)_2$	Synthesis, NMR, ^{51}V NMR	[65]
128	$V(N\text{-}t\text{-}Bu)(O\text{-}t\text{-}Bu)_2(S\text{-}t\text{-}Bu)$	Synthesis, NMR, ^{51}V NMR	[65]
129	$V(N\text{-}t\text{-}Bu)(SSiPh_3)_3$	Synthesis, NMR, ^{51}V NMR, X-ray	[65]
130	$[V(N\text{-}t\text{-}Bu)(S\text{-}t\text{-}Bu)_2]_2O$	Synthesis, NMR, ^{51}V NMR, X-ray	[65]
131	$[V(SCH_2C(CO_2)NH_2)_3]^{4-}$	Electrochemistry	[66]
132	$[V(OC(CH_3)CHC(CH_3){=}NCH_2)_2(SPh)]_n$	Synthesis, IR, Magnetic moment	[67]
133	$V(SC_6H_2\text{-}2,4,6\text{-}i\text{-}Pr)_3(THF)_2$	Synthesis, UV–visible, Magnetic moment, Electrochemistry, X-ray	[68]
134	$[V_3(SC_6H_4O)_6]^{-}$	Synthesis, IR, NMR, X-ray	[69]
135	$[V(S\text{-}t\text{-}Bu)_2(bipy)_2]^{+}$	Synthesis, X-ray	[19]
136	$[V(SNC_5H_4)_3]^{-}$	Synthesis, X-ray	[70]
137	$[V(SNH_2C_6H_4)_2(SNHC_6H_4)]^{-}$	Synthesis, X-ray	[70]
138	$V(SC_9H_6N)_3$	Synthesis, X-ray	[70]
Niobium			
139	$[Nb_4S_2(SPh)_{12}]^{4-}$	Synthesis, X-ray	[71]
140	$Nb_4S_2(SPh)_8(PMe_3)_4$	Synthesis, X-ray	[72]
141	$Nb_4S_2(SPh)_8(PMe_2Ph)_4$	Synthesis, X-ray	[72]

Table 2 (continued)

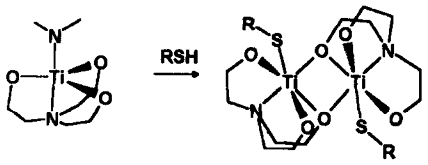
No.	Compound	Information	Ref.
142	$Nb_2(SPh)_4(SPh)_2Cl_2(NCEt)_2$	Synthesis, X-ray	[25]
143	$[NbS(S\text{-}t\text{-}Bu)_4]^-$	Synthesis, X-ray	[73]
144	$[NbS_2(S\text{-}t\text{-}Bu)_2]^-$	Synthesis, X-ray	[73]
145	$[NbS(SPh)_4]^-$	Synthesis, X-ray	[74]
146	$[(\eta^6\text{-}C_6H_5Me)Nb(SMe)_2]_2$	Synthesis, NMR	[75]
147	$[(\eta^6\text{-}C_6H_5Me)Nb(SBu)_2]_2$	Synthesis, NMR	[75]
148	$[(\eta^6\text{-}C_6H_5Me)Nb(SBz)_2]_2$	Synthesis, NMR	[75]
16	$[Nb_2(OMe)_3(SCH_2CH_2CH_2S)_3]^-$	Synthesis, NMR, UV–visible, IR, X-ray	[23]
13	$[NbS(SCH_2CH_2S)(S(CH_2)_2S(CH_2)_2S)]^-$	Synthesis, NMR, IR, UV–visible, X-ray	[22]
Tantalum			
149	$[TaCl_3(Me_2S)]_2(SPh)_2$	Synthesis, IR, MS, X-ray, MO calculations	[76]
150	$[TaCl_2(SM2)]_2(SEt)_2(Cl)$	Synthesis, IR, X-ray	[77]
151	$Ta(S\text{-}2,4,6\text{-}C_6H_2\text{-}i\text{-}Pr_3)_3(THF)(CH\text{-}t\text{-}Bu)$	Synthesis, NMR	[78]
152	$Ta(S\text{-}2,4,6\text{-}C_6H_2\text{-}i\text{-}Pr_3)_3(py)(CH\text{-}t\text{-}Bu)$	Synthesis, NMR	[78]
153	$Ta(S\text{-}2,4,6\text{-}C_6H_2\text{-}i\text{-}Pr_3)_3(SEt_2)(CH\text{-}t\text{-}Bu)$	Synthesis, NMR, X-ray	[79]
154	$[Ta(S\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)_3(THF)]_2(N_2)$	Synthesis, NMR, X-ray	[80]
155	$[Ta(S\text{-}2,4,6\text{-}C_6H_2\text{-}i\text{-}Pr_3)_3(THF)]_2(N_2)$	Synthesis, NMR	[80]
21	$TaCl_3(SC_6F_5)_2$	Synthesis	[6]

MW, molecular weight determination.

described the reactions of $Ti(O\text{-}i\text{-}Pr)_4$ with the thiochelates, $HSCH_2CH_2OH$, $HSCH_2CH_2CO_2H$, $CH_3CH(SH)CO_2H$ and $HSCH_2CH_2SH$ [28,29]. In a subsequent study [29], similar reactions of tridentate ketamines such as $RCO_2CHC(Me)NHCH_2CH_2SH$ were studied. In both cases complexes of the form $Ti(O\text{-}i\text{-}Pr)_2L$ **31–37** and TiL_2 **38–44** were reported [28,29], although these products were poorly characterized. Choukroun and Gervais [30] employed a similar reaction of $Ti(O\text{-}i\text{-}Pr)_4$ with EtSH to prepare $Ti(O\text{-}i\text{-}Pr)_3(SEt)$ **45** while Jones and Douek have more recently characterized a series of dithiolate derivatives of formulae $Ti(O\text{-}i\text{-}Pr)_2$(dithiolate) **46**, **47**, $Ti(O\text{-}i\text{-}Pr)_2(\text{dithiolate})_2$ **48**, **49** and $Ti(O\text{-}i\text{-}Pr)_2(\text{dithiolate})L_2$ ($L_2 = (py)_2$, bipy, phen) **50–58** [31]. In addition, the derivative of aminobenzenethiol (abt) $Ti(O\text{-}i\text{-}Pr)_2(abt)_2$ **59** was also described. The intermediacy of related titanium derivatives of the form $RCH{=}C(NMe_2)STi(O\text{-}i\text{-}Pr)_3$ and $[RCH{=}C(NMe_2)STi(O\text{-}i\text{-}Pr)_4]^-$ in 1,2 and 1,4 additions of α-enenes has been shown by Goasdoue et al. [81].

In a recent study Verkade and coworkers [32] have prepared thiolate derivatives of titantranes by thiolysis of the amido derivative $(Me_2N)Ti(OCH_2CH_2)_3N$ (Eq. (4)). In this way the compounds $[(RS)Ti(OCH_2CH_2)_3N]_2$ (R = Et, i-Pr, CMe_2Et, allyl, Ph) **60–64** were prepared.

Mixed halide–thiolate complexes of Ti are rare. While an early report suggested compounds of the form $TiCl_2(SCH_2CH_2S)L_2$ **65–68** [33], the only well-characterized examples known are $Ti(S\text{-}t\text{-}Bu)_2Cl_2(L)$ (L = diars, dmpe, dppe) **69–71**. These com-



(4)

pounds were prepared via the reaction of $TiCl_4$ with LiS-*t*-Bu in the presence of the chelating ligand. In the case of **69** the compound was structurally characterized by Jones et al. [34]. This compound has a distorted octahedral geometry (Fig. 9) in which the thiolate ligands are in a *cis* orientation.

A series of studies have examined compounds which incorporate ligands which are derivatives of mercaptophenol and benzenedithiol [82]. As these are closely related to dithiolene derivatives, these species are not discussed here.

Only a single Ti(III) coordination compound containing a thiolate ligand is known. Marchon et al. [35] reported that the reaction of the tetraphenylphorphyrin (TPP) Ti(III) species (TPP)TiF with NaSPh yields the paramagnetic compound (TPP)Ti(SPh) **72**. This species is readily oxidized to the Ti(IV) oxide:

$$2(\mathrm{TPP})\mathrm{Ti(SPh)} + O_2 \rightarrow 2(\mathrm{TPP})\mathrm{Ti{=}O} + (\mathrm{PhS})_2 \qquad (5)$$

3.2. *Zirconium*

Zirconium coordination complexes containing thiolate ligands are rare. In fact to our knowledge the only reports of such compounds have been made by Coucouvanis and coworkers [36,37]. In 1985, the synthesis of the compound $Zr_3S_3(t\text{-BuS})_2(BH_4)_4(THF)_2$ **73** (Fig. 10) in 70% yield (Eq. (6)) was reported. On standing in CD_2Cl_2 **73** yields yellow crystals of **74** formulated as $Zr_6S_6(S\text{-}t\text{-Bu})_4(BH_4)_8(THF)_2$ (Fig. 10). In a related reaction Coucouvanis et al. [37] also reported the synthesis of $Zr_3(S)(t\text{-BuS})_{10}$ **75** (Fig. 11) from the reaction of $Zr(Bz)_4$ and *t*-BuSH. Although the observation of S—C bond cleavage is reminiscent of reactions in V-related chemistry (*vide infra*), the mechanism of S—C bond cleavage was not addressed in these preliminary reports.

$$\begin{aligned}&3Zr(BH_4)_4 + 13t\text{-BuSH} + 2THF\\ &\quad\rightarrow Zr_3S_3(t\text{-BuS})_2(BH_4)_4(THF)_2 + (8/3)(t\text{-BuSBH}_2)_3 + 13H_2 + 3t\text{-BuH} \qquad (6)\end{aligned}$$

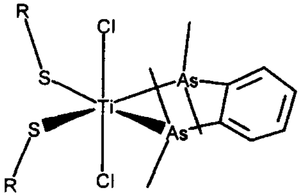


Fig. 9. The structure of the compound $TiCl_2(S\text{-}t\text{-Bu})_2(diars)$ **69**.

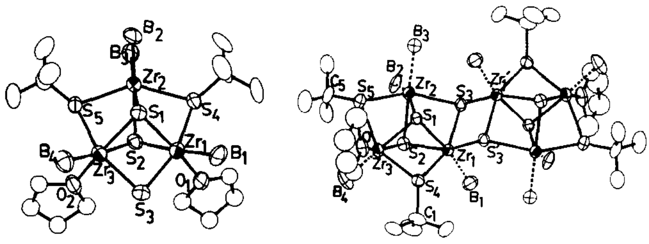


Fig. 10. ORTEP drawings of $Zr_3S_3(t\text{-}BuS)_2(BH_4)_4(THF)_2$ **73** and $Zr_6S_6(S\text{-}t\text{-}Bu)_4(BH_4)_8(THF)_2$ **74**. Reproduced with permission from Ref. [37]. Copyright 1985 American Chemical Society.

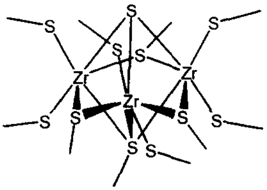


Fig. 11. The structure of the compound $Zr_3S(t\text{-}BuS)_{10}$ **75**. *t*-Bu groups are omitted for clarity.

3.3. *Hafnium*

No thiolate coordination compounds of Hf have been reported to date.

3.4. *Vanadium*

3.4.1. *Vanadyl derivatives*

Early studies of thiolate coordination complexes of vanadium centered about vanadyl species. A number of compounds of the general form VOL_2 where L is a bidentate aminothiolate have been described (compounds **76–81**, Table 2). In the early papers, spectroscopic characterization is limited to IR and visible spectra [38–40,45] while others described EPR [41], electrochemistry [42], magnetic properties [43] and condutivity studies [44]. The pyridine adducts **82** and **83** have also been described [39], while the related thiosalicylate compound **84** and its pyridine adduct **85** are also known [45].

Studies of compounds of similar structure and properties were subsequently prompted by the discovery of a physiological role of vanadium ion in the blood of ascidians as well as the inhibitory effect of V on Na, K ATPase. This bioinorganic interest led to the study of compounds $[VO(SCH_2C(CO_2)NH_2)_2]^{2-}$ **86** and $[VO(SCH_2C(CO_2Me)NH_2)_2]$ **87**. These species were prepared either from vanadylsulfate [47] or directly via reduction of vanadate(V) by cysteine [46]. Electrochemical studies of these [48] and the related penicillamine–ester complex, $[VO(SC(CH_3)_2C(CO_2Me)NH_2)_2]$ **88** [49] have been described. A crystallographic study of **87** reveals the pseudo-square-pyramidal nature of the V coordination sphere **87** [50]. Stability constants of the related complexes **89–92** have been determined

[51]. More recently, tetradentate N_2S_2 Schiff base [52] (Fig. 12) or diaminodithiol ligands [53,54] have been used to prepare related vanadyl complexes **93–97** [52]. Structural studies confirm a similar distorted square pyramidal geometry for both **93** and **97**.

Christou and coworkers [55] have reported that the reaction of VCl_3 with $Me_2NCH_2CH_2SNa$ yielded the complex $V_2O(SCH_2CH_2NMe_2)_4$ **98**. The presence of the bridging oxygen atom is attributed to adventitious water or O_2. The structural data reveal a nearly linear V—O—V vector (177.84(25)°). Each of the V atoms adopts an approximate trigonal bipyramidal geometry with the O and two thiolate S atoms in the equatorial planes (Fig. 13). In a similar manner the complex $V_2O(SCH_2CH_2NH_2)_4$ **99** was prepared. The complex **99** can also be prepared via the reduction of **77** with sodium acenaphthylenide. Christou suggests that this chemistry may be related to the fate of vanadyl impurities in crude oil when placed under the reducing conditions of hydrodesulfurization.

The simple V(V) vanadyl derivative $VO(SEt)_3$ **100** was prepared in 1978 via

$$VO(NR_2)(OR')_2 + EtSH \rightarrow (1/3)VO(SEt)_3 + (2/3)VO(OR')_3 + HNR_2 \qquad (7)$$

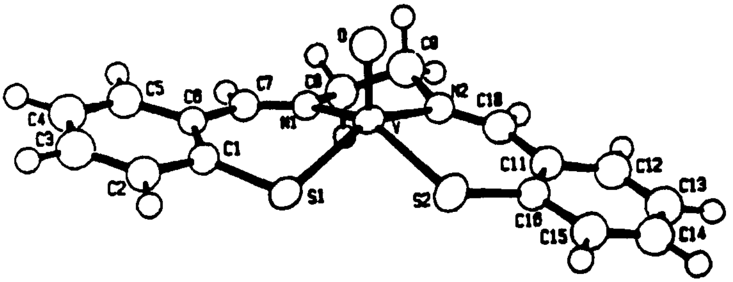


Fig. 12. ORTEP drawings of $VO(SC_6H_4CHN(CH_2))_2$ **93**. Reproduced with permission from Ref. [52]. Copyright 1988 American Chemical Society.

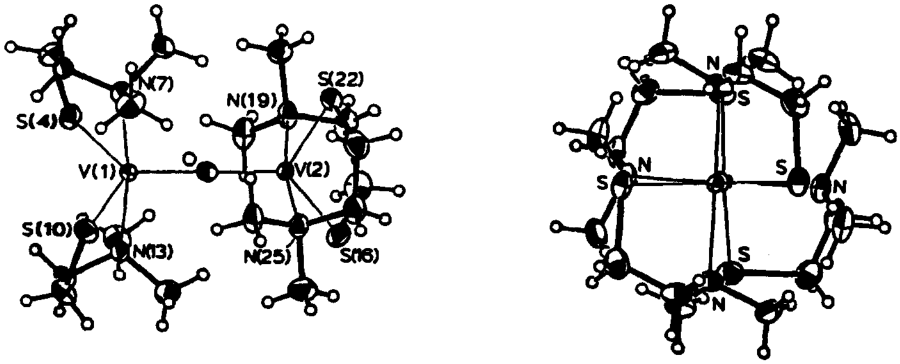


Fig. 13. ORTEP drawings of $V_2O(SCH_2CH_2NMe_2)_4$ **98**. Reproduced with permission from Ref. [55]. Copyright 1987 American Chemical Society.

Alternatively, **100** could be prepared via the ligand exchange reaction of thiol with $VO(OR)_3$ with the concurrent elimination of alcohol [56]. An analog of the intermediate in these ligand redistribution reactions, i.e. $VO(S\text{-i-Pr})(O\text{-i-Pr})_2$ **101**, is formed from $VOCl(O\text{-i-Pr})_2$ and the sodium thiolate. Although the ^{51}V NMR signal for **101** can be observed [57], it is not stable photochemically, degrading via ligand redistribution to $VO(S\text{-i-Pr})_3$ **102** and $VO(O\text{-i-Pr})_3$ [57]. A series of related complexes has been prepared by Preuss and Noichl [17]. These complexes $VO(S\text{-}t\text{-Bu})_n(O\text{-}t\text{-Bu})_{3-n}$ ($n = 1$ **103**, 2 **104**, 3 **105**) as well as $VO(SSiPh_3)_3$ **106** are prepared by thiolate substitution on the appropriate vanadyl halide. Compound **103** undergoes an interesting reaction on heating to give the species $VS(O\text{-}t\text{-Bu})_3$. Alternatively, on reaction of **103** with Lawesson's reagent or by oxidation with sulfur the species $VS(S\text{-}t\text{-Bu})(O\text{-}t\text{-Bu})_2$ **107** is formed. Monitoring solutions of **107** via ^{51}V NMR revealed the presence of several species including $VO(O\text{-}t\text{-Bu})_3$, **103**, **104**, **107** and $VS(S\text{-}t\text{-Bu})_2(O\text{-}t\text{-Bu})$ **108**. In a similar fashion $VS(SSiPh_3)_3$ **109** is prepared from **106** [17].

The preparation of vanadyl derivatives of bidentate dithiols occurred almost concurrently in two researchs groups. In the 1983 communication where Christou and coworkers [13] reported the preparation of the dimeric homoleptic species **7**, the synthesis of the V(IV) anion $[VO(SCH_2CH_2S)_2]^{2-}$ **110** from $VO(acac)_2$ was also reported (Fig. 14). Likewise, in the 1984 report from the Henkel group [58] the synthesis of **110** as a byproduct from a reaction of **7**, presumably formed by scavenging of adventitious oxygen, was described. Structural studies of salts of **110** in both papers defined the approximate square pyramidal geometry about V(IV). The V—O distance in **110** is 1.625(5) Å and the V—S distances range from 2.371(1) to 2.388(1) Å. Christou's group also showed that the related complex $[VO(SCH_2CH_2CH_2S)_2]^{2-}$ **111** could be prepared by the reactions of the disodium dithiolate with either $VO(acac)_2$ or $VOSO_4$ [59,60].

3.4.2. *Thiolate derivatives of vanadium sulfides and selenides*

The alkyl migration reactions observed in the formation of **107–109** were among the first preparations of simple VS thiolate derivatives. The related species $[VS(SCH_2CH_2S)_2]^{2-}$ **112** was synthesized via the reaction of VS_4^{3-} with **7** [58]. In this case, the species **110** and **112** cocrystallized with sodium cations. The structural data for **112** showed a similar structure to that seen for **110**, with a V=S bond length of 2.098(2) Å and V—S(thiolate) distances of 2.348(2)–2.386(2) Å. Christou's group subsequently showed that **110** could be cleanly converted to **112** via the reaction with excess $(Me_3Si)_2S$ [59]. In addition, an intermediate species $[V(OSiMe_3)(SCH_2CH_2S)_2]^-$ **113** was isolated in the presence of excess $(Me_3Si)_2S$

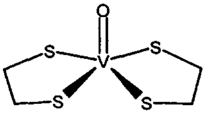


Fig. 14. The structure of the compound $[VO(SCH_2CH_2S)_2]^{2-}$ **110**.

[60]. Structural data for **113** revealed a V—O distance of 1.7608 Å and the mean V—S distance of 2.322 Å.

Related compounds of the form $[VE(SPh)_4]^{2-}$ (E = S **114**, Se **115**) are prepared via the reaction of VCl_3–thiolate and elemental sulfur or selenium. Using a similar procedure the compound $[VSe(SCH_2CH_2S)_2]^{2-}$ **116** was prepared. Structural data show that the V=S distance of **114** at 2.078(2) Å is slightly shorter than the V=Se distance of 2.196(3) Å seen in **116** [61]. Adjustment of the V:thiolate:S ratio leads to the isolation of the species $[VS_2(S_2)(SPh)]^{2-}$ **117** in which an S_2 unit, a thiolate and two terminal S atoms are bound to V (Fig. 15) [62].

3.4.3. Higher-order aggregates

The synthesis of higher order V—O and V—S aggregates has been achieved primarily by Christou's research group. In contrast to the above reaction of $(Me_3Si)_2S$, treatment of **110** with a single equivalent of Me_3SiCl leads to attack at sulfur affording the species $[V_2O_2(SCH_2CH_2S)_3]^{2-}$ **118**:

$$\begin{aligned} &2[VO(SCH_2CH_2S)_2]^{2-} + 2Me_3SiCl \\ &\quad \rightarrow [V_2O_2(SCH_2CH_2S)_3]^{2-} + 2Cl^- + (Me_3SiSCH_2)_2 \end{aligned} \tag{8}$$

The two VO units are bridged by two thiolate sulfur atoms and adopt a *syn* arrangement (Fig. 16) [18]. Reactions with more Me_3SiCl are reported to yield larger aggregates but have yet to be characterized. Related aggregations in which V=S is incorporated are derived from systematic variations in the stoichio-

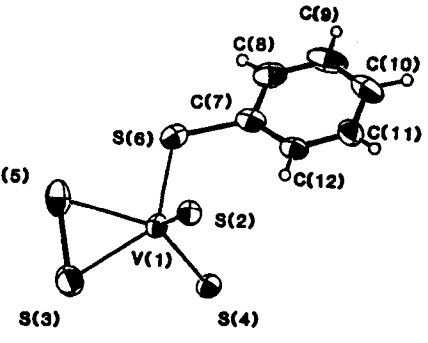


Fig. 15. ORTEP drawing of $[VS_2(S_2)(SPh)]^{2-}$ **117**. Reproduced with permission from Ref. [62]. Copyright 1986 American Chemical Society.

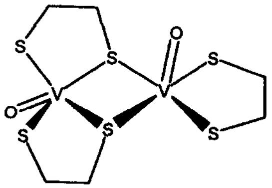


Fig. 16. The structure of the compound $[V_2O_2(SCH_2CH_2S)_3]^{2-}$ **118**.

metry of the reactions of VCl_3–thiolate and sulfur. In this way the species $[V_2S_5(SCH_2CH_2S)]^{3-}$ **119**, $[V_2OS_4(SCH_2CH_2S)]^{3-}$ **120** and $[V_3S_4(SCH_2CH_2S)_3]^{3-}$ **121** are isolated. In the case of **120** the structural data can be viewed as VS_4^{3-} coordinated to a $[VO(SCH_2CH_2S)]^{2+}$ fragment (Fig. 17). In **121**, the V_3S_4 core forms a partial cube-type structure with dithiolate ligands on each of the three V atoms (Fig. 18) giving the anion an idealized C_{3v} symmetry [16]. This species exhibits two reversible processes at −1.51 and −0.63 V vs. the normal hydrogen electrode (NHE) which are attributed to a one-electron reduction and a one-electron oxidation of **121**. A third redox process attributed to the second oxidation anion is irreversible (Eq. (9)). In a similar sense complex **120** undergoes a reversible one-electron reduction at −1.23 V vs. NHE.

$$\begin{aligned}
[V_3S_4(SCH_2CH_2S)_3]^{4-} &\xrightleftharpoons{-1.51\ \mathrm{V}} [V_3S_4(SCH_2CH_2S)_3]^{3-}\\
&\xrightleftharpoons{-0.63\ \mathrm{V}} [V_sS_4(SCH_2CH_2S)_3]^{2-}\\
&\xrightarrow{0.00\ \mathrm{V}} [V_3S_4(SCH_2CH_2S)_3]^{-} \qquad (9)
\end{aligned}$$

Christou and coworkers [63] also showed that modification of the sulfide source has a dramatic effect. Reaction of VCl_3, Li_2S and dithiolate in a 3:4:3 ratio affords the species $[V_4S_2(SCH_2CH_2S)_6]^{2-}$ **122**. The structural data (Fig. 19) showed that two sulfide atoms are triply bridging while six thiolate sulfur atoms are bridging. Christou points out the similarity of the V_4S_{14} core to VS lattice in Li_xVS_2, a material related to the battery electrode material Li_xTiS_2.

In a similar procedure, Christou and coworkers [64] have examined the reaction of VCl_3 with dithiolate and NBu_4Cl in a 2:1:1 ratio. This results in the isolation of the species $[V_4O(SCH_2CH_2S)_2Cl_8]^{2-}$ **123**. The source of O is apparently adventitious oxygen. Complex **123** is the first example of a square planar oxide in a molecular species (Fig. 20). This structure has been rationalized in terms of a MO scheme in

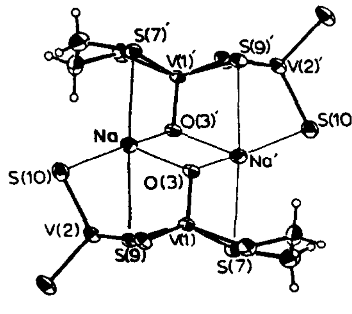


Fig. 17. ORTEP drawing of $[V_2OS_4(SCH_2CH_2S)]^{3-}$ **120**. Reproduced with permission from Ref. [16]. Copyright 1988 American Chemical Society.

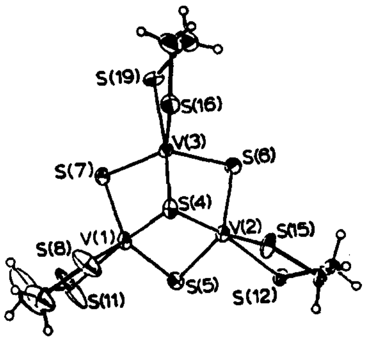


Fig. 18. ORTEP drawing of $[V_3S_4(SCH_2CH_2S)_3]^{3-}$ **121**. Reproduced with permission from Ref. [16]. Copyright 1988 American Chemical Society.

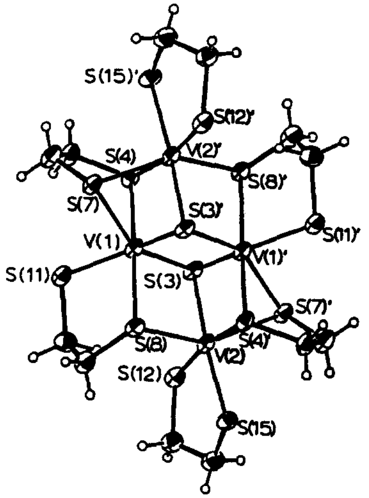


Fig. 19. ORTEP drawing of $[V_4S_2(SCH_2CH_2S)_6]^{2-}$ **122**. Reproduced with permission from Ref. [63]. Copyright 1987 American Chemical Society.

which the O s and p orbitals overlap with V d orbitals. This scheme also is consistent with the observed paramagnetism of **123**.

3.4.4. Imido derivatives

In a preparative route similar to that used for vanadyl analogs, the reaction of t-BuN=VCl$_3$ and t-BuN=V(O-t-Bu)$_n$Cl$_{3-n}$ with LiSR (R = t-Bu, SiPh$_3$) affords a variety of imido–thiolate derivatives **124–129** [65]. The structural study of the species t-BuN=V(SSiPh$_3$)$_3$ **129** revealed that V—N and V—S(avearge) bond lengths of 1.622(2) Å and 2.246(2) Å respectively. The imido derivatives **124–129** were found to be susceptible to hydrolysis by H_2O. In the case of **124** the resulting hydrolysis

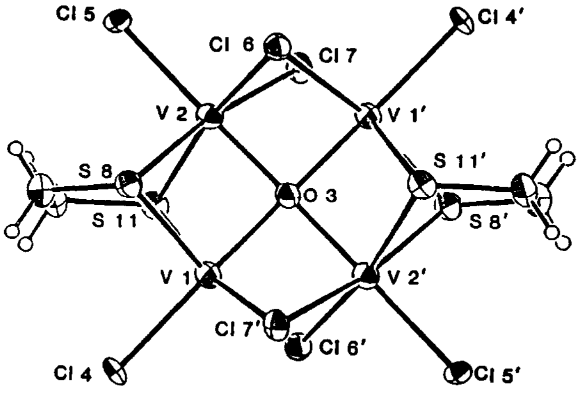


Fig. 20. ORTEP drawing of $[V_4O(SCH_2CH_2S)_2Cl_8]_4^{2-}$ **123**. Reproduced with permission from Ref. [64]. Copyright 1989 American Chemical Society.

product $(t\text{-BuN}{=}V(S\text{-}t\text{-Bu})_2)_2O$ **130** (Eq. (10)) was crystallographically characterized [65].

$$2t\text{-BuN}{=}V(S\text{-}t\text{-Bu})_3 + H_2O \rightarrow (t\text{-BuN}{=}V(S\text{-}t\text{-Bu})_2)_2O \qquad (10)$$

3.4.5. *Low valent derivatives*

The reactions of V(II) and V(III) with cysteine and other biologically relevant thiols in neutral and weakly acidic solutions have been studied. In both cases the reactions appear to proceed through several steps in the formation of complexes. In the case of V(II), the reducing agent $[V(SCH_2C(CO_2)NH_2)_3]^{4-}$ **131** has been inferred, while for V(III) the nature of the species is less well defined. Nonetheless, electrochemical and thermodynamic data have been reported for these equilibria [66]. A Schiff base complex of V(III) undergoes straightforward substitution to give the corresponding thiolate derivative $[V(OC(CH_3)CHC(CH_3){=}NCH_2)_2(SPh)]_n$ **132** [67].

Randall and Armstrong have reported the isolation of the V(III) species $V(SC_6H_2\text{-}2,4,6\text{-i-Pr})_3(THF)_2$ **133** [68]. The sterically demanding nature of the thiolate substituents results in the formation of the simple mononuclear pseudo-trigonal-bipyramidal structure. V—S distances in **133** average 2.320(1) Å (Fig. 21) [68].

Although related to dithiolene derivatives, we do mention here the synthesis of the species $[V_3(SC_6H_4O)_6]^-$ **134**. This paramagnetic compound is prepared from VCl_3 and thiolate and has a novel linear V_3 fragment in which oxygen atoms bridge the V centers [69].

Christou and coworkers [19] in attempting to prepare $V(S\text{-}t\text{-Bu})_3(\text{bipy})$ observed the products of a ligand redistribution. The V(III) cation, $[V(S\text{-}t\text{-Bu})_2(\text{bipy})_2]^+$ **135**, and the anion **10** were obtained and characterized crystallographically (Fig. 22).

In 1992, Henkel et al. reported the reactions of VCl_2 with several N,S bidentate ligands. In this way, the V(II) species, $[V(SNC_5H_4)_3]^-$ **136** was isolated [70]. This was reportedly the first structurally characterized V(II)-thiolate derivative. This

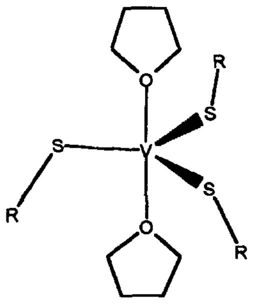


Fig. 21. The structure of the compound $V(SC_6H_2\text{-}2,4,6\text{-i-Pr})_3(THF)_2$ **133**.

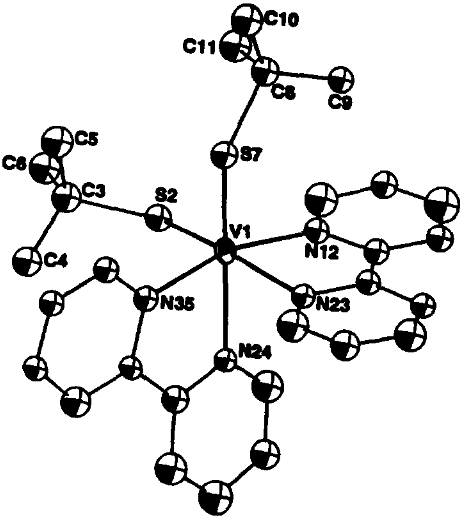


Fig. 22. ORTEP drawing of $[V(S\text{-}t\text{-}Bu)_2(bipy)_2]^+$ **135**. Reproduced with permission from Ref. [19]. Copyright 1991 American Chemical Society.

species exhibits a distorted octahedral geometry in which the three sulfur atoms are facial. Employing similar conditions, the V(III) complex anion species $[V(SNH_2C_6H_4)_2(SNHC_6H_4)]^-$ **137** was derived from the reaction of sodium aniline–thiolate [70]. In this anion, the presence of one amido nitrogen is clearly evidenced by the V—N bond lengths as the V—N(amide) distance is 1.94 Å and the mean V—N(amide) distance is 2.18 Å. In a similar sense, the V(III) species $V(SC_9H_6N)_3$ **138** was obtained from the analogous reaction employing sodium quinoline–thiolate.This species also exhibits a pseudo-octahedral geometry with mean V—S and V—N bond distances of 2.364 Å and 2.18 Å respectively.

3.5. Niobium

Christou and coworkers [71] reported that the reaction of $Nb_2Cl_6(Me_2S)_3$ with an excess of LiSPh results in C—S bond cleavage and leads to the formation of the species $[Nb_4S_2(SPh)_{12}]^{4-}$ **139**. This anion contains a square of Nb atoms with quadruply bridging sulfur atoms above and below the Nb_4 plane. Each Nb atom is also bound to four bridging and one terminal thiolate ligands yielding a Nb_4S_{14} core of near D_{4h} symmetry [71] (Fig. 23). Two structurally related compounds were subsequently reported by Cotton and coworkers [72]. In reactions of $(PhS)_2$, phosphine, $NbCl_5$ and reducing agent, the compounds $[Nb_4S_2(SPh)_8(PMe_3)_4]$ **140** and $[Nb_4S_2(SPh)_8(PMe_2Ph)_4]$ **141** were isolated. In these compounds the NbS core is similar to that seen in **139** while the terminal thiolate ligands are replaced by phosphine donors [72]. A related but less complex formation of a niobium sulfide via C—S bond cleavage has been described above for the synthesis of **13**.

In a 1990 communication Coucouvanis and coworkers [25] reported the preparation of the species $Nb_2(\mu\text{-}SPh)_4(SPh)_2Cl_2(NCEt)_2$ **142** from $NbCl_5$ and thiolate in propionitrile. The two centers in **142** are bridged by four thiolate ligands while a terminal thiolate, nitrile and chloride complete the coordination spheres of the Nb atoms (Fig. 24) [25]. In a subsequent communication Coucouvanis et al. [73] described the reactions of $NbCl_5$ and *t*-BuSNa in acetonitrile. Modification of the ratios afforded the compounds $[NbS(S\text{-}t\text{-}Bu)_4]^-$ **143** and $[NbS_2(S\text{-}t\text{-}Bu)_2]^-$ **144** (Fig. 25) [73]. The former species adopts a distorted trigonal bipyramidal structure while the latter is pseudotetrahedral at Nb. Here again, the ability of Nb to induce

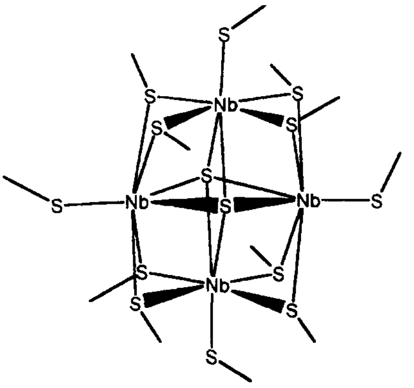


Fig. 23. The structure of the compound $[Nb_4S_2(SPh)_{12}]^{4-}$ **139**. Phenyl rings are omitted for clarity.

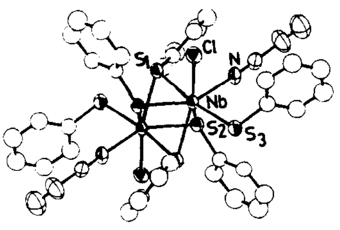


Fig. 24. ORTEP drawing of $Nb_2(SPh)_4(SPh)_2Cl_2(NCEt)_2$ **142**. Reproduced with permission from Ref. [25]. Copyright 1990 American Chemical Society.

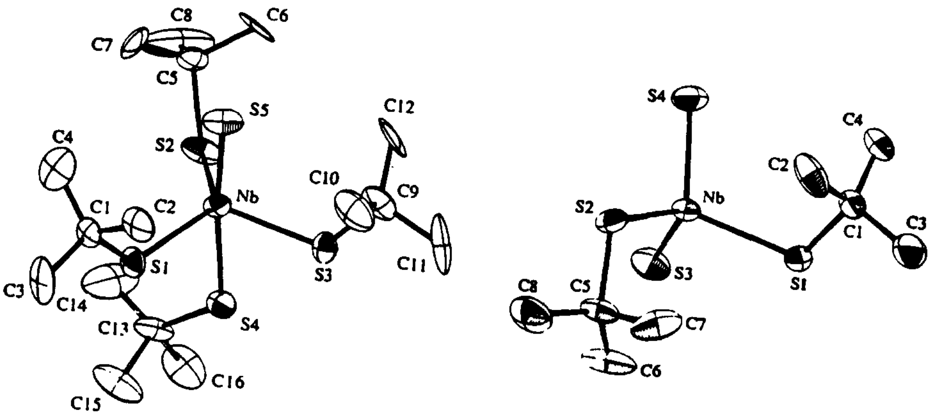


Fig. 25. ORTEP drawings of $[NbS(S\text{-}t\text{-}Bu)_4]^-$ **143** and $[NbS_2(S\text{-}t\text{-}Bu)_2]^-$ **144**. Reproduced with permission from Ref. [73]. Copyright 1992 American Chemical Society.

C—S bond cleavage is exhibited. It was proposed that this process proceeds homolytically and that the *t*-Bu radical abstracts a proton from the solvent [73].

Christou and coworkers [74] had previously reported the preparation of the mononuclear Nb–thiolate species $[NbS(SPh)_4]^-$ **145** from the reaction of $[NbSCl_4]^-$ and thiolate. The terminal Nb—S distance was determined to be 2.171(2) Å while the Nb—S thiolate distances averaged 2.442(2) Å. The thiolate ligands were readily removed via reaction of **145** with benzoylchloride [74]:

$$[NbS(SPh)_4]^- + 4PhCOCl \rightarrow [NbSCl_4]^- + 4PhCOSPh \qquad (11)$$

Low valent Nb thiolate derivatives have been reported by Green et al. [75]. The compounds $[(\eta^6\text{-}C_6H_5Me)Nb(SMe)_2]_2$ **146**, $[(\eta^6\text{-}C_6H_5Me)Nb(SBu)_2]_2$ **147** and $[(\eta^6\text{-}C_6H_5Me)Nb(SBz)_2]_2$ **148** were derived from the reaction of $(RS)_2$ and $(\eta^6\text{-}C_6H_5Me)_2Nb$. Although unconfirmed the structure was proposed to be isostructural with $[(\eta^6\text{-}C_6H_5Me)Mo(SMe)]_2^{2+}$ [75].

3.6. Tantalum

The oxidative addition of $(PhS)_2$ to Ta=Ta double bond of $[TaCl_2(SMe_2)]_2(\mu\text{-}Cl)(\mu\text{-}SMe_2)$ [83] was described by Cotton and coworkers [76]. The product $[TaCl_3(Me_2S)]_2(SPh)_2$ **149** is a d^1—d^1 thiolate bridged dimer whose geometry is best described as an edge-sharing bioctahedron. Fenske–Hall MO (FHMO) calculations support the presence of a metal–metal bond in **149**, a result that is also consistent with spectroscopic data [76]. In analogous reaction of $(EtS)_2$ the compound $[TaCl_2(SMe)]_2(\mu\text{-}SEt)_2(\mu\text{-}Cl)$ **150** is formed. This Ta(III)–Ta(IV) species exhibits a face-sharing bioctahedral structure in which the two thiolate ligands and a chloride bridge the two metal centers [77].

Schrock and coworkers [78] have described Ta derivatives of bulky thiolates. The species $Ta(S\text{-}2,4,6\text{-}C_6H_2\text{-}i\text{-}Pr_3)_3(THF)(CH\text{-}t\text{-}Bu)$ **151** is readily prepared by metathetical displacement of Cl^- by lithium thiolate. Unlike the phenoxide analog, **151** does not react with ordinary olefins and will not polyrize them. Addition of pyridine results in the displacement of THF from **151** affording $Ta(S\text{-}2,4,6\text{-}C_6H_2\text{-}i\text{-}Pr_3)_3(py)(CH\text{-}t\text{-}Bu)$ **152**. This compound reacts with norbornene resulting in displacement of pyridine and polymerization. The living polymer has been shown to be an alkylidene complex and can be cleaved with benzaldehyde [79]. Complex **151** reacts with SEt_2 to give $Ta(S\text{-}2,4,6\text{-}C_6H_2\text{-}i\text{-}Pr_3)_3(SEt_2)(CH\text{-}t\text{-}Bu)$ **153** in which structural data show that the sulfide ligand is *trans* to the axial alkylidene ligand (Fig. 26). This geometry is in contrast to that seen for an analogous phenoxide complex in which the donor ligand is *cis* to the alkylidene moiety. This difference in geometry is presumed to account for the inability of **153** to metathesize olefins.

The dinitrogen complexes $[Ta(S\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)_3(THF)]_2(N_2)$ **154** and

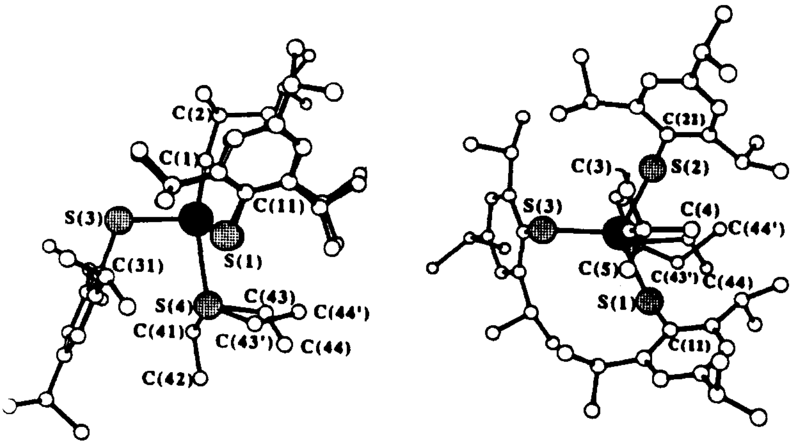


Fig. 26. ORTEP drawings of $Ta(S\text{-}2,4,6\text{-}C_6H_2\text{-}i\text{-}Pr_3)_3(SEt_2)(CH\text{-}t\text{-}Bu)$ **153**. Reproduced with permission from Ref. [79]. Copyright 1990 American Chemical Society.

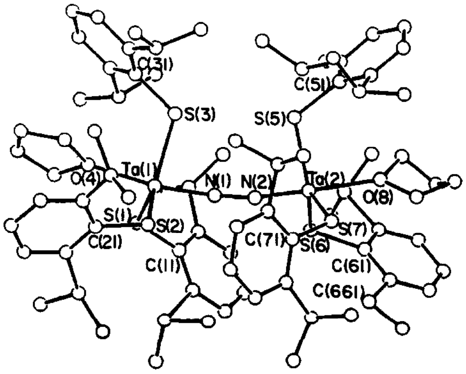


Fig. 27. ORTEP drawing of $[Ta(S\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)_3(THF)]_2(N_2)$ **154**. Reproduced with permission from Ref. [80]. Copyright 1988 American Chemical Society.

$[Ta(S\text{-}2,4,6\text{-}C_6H_2\text{-i-}Pr_3)_3(THF)]_2(N_2)$ **155** were prepared from $[TaCl_3(THF)_2]_2(N_2)$ by methathesis with the appropriate thiolate. A structural study of **154** showed that the dinitrogen bridge was *trans* to the axial THF ligand on each Ta center (Fig. 27). This, again, is in contrast to the analogous phenoxide species in which the bridging N_2 moiety is *cis* to THF [80].

4. Cyclopentadienyl metal thiolate complexes

A summary of monocyclopentadienyl thiolate complexes is listed in Table 3.

4.1. Titanium

The first monocyclopentadienyl titanium thiolate derivative reported was the preparation of $CpTi(SPh)Cl_2$ **156** by Kopf and Block [84] in 1968. Subsequently, Coutts and Wailes [85] described the syntheses of the compounds $CpTi(SR)Cl_2$ (R = Me **157**, Ph **156**) via oxidative addition of the corresponding disulfides RS—SR to $CpTiCl_2$ in THF (Eq. (12)) [85]. This reaction, however, does not proceed when benzene is used as the solvent, presumably because of the inability of benzene to coordinate and break the Ti(III) oligomer. Similar reactions employing CpTi(OAr)Cl and RS—SR were not successful in obtaining the chiral complexes CpTi(OAr)(SR)Cl [115].

$$2(CpTiCl_2)_n + RS{-}SR \rightarrow 2nCpTi(SR)Cl_2 \qquad (12)$$

The related complexes $CpTi(SR)Cl_2$, (R = Et **158**, C_6H_{11} **159**, C_6H_4X **160–163**, C_6F_5 **164**) and $(C_5H_4Me)Ti(SR)Cl_2$ (R = Ph **165**, C_6H_4X **166–169**) have been prepared in high yields (70%–85%) using either the salt elimination approach starting from the metal halide and alkali metal thiolate or by the reaction of free thiols with a metal halide in the presence of triethylamine [86]. Similarly, the related *bis* or *tris* thiolate substituted derivatives of monocyclopentadienyl titanium have been reported. Species $CpTi(SPh)_2Cl$ **170** [86], $CpTi(SMe)_3$ **171** [87] and $CpTi(SPh)_3$ **172** [86] were prepared employing the appropriate stoichiometry of sodium or lithium thiolate and $CpTiCl_3$.

In general, the above thiolate derivatives are orange in color and very sensitive to hydrolysis. Thus often the characterizations of these compounds have been limited to NMR and mass spectrometry data.

The Schiff base complexes CpTi(SMe)(SB) where SB = *N,N'*-ethylenebis-(salicylideneimine) **173** and *N,N'*-*o*-phenylenebis(salicylideneimine) **174** have been synthesized from CpTi(SB)Cl and MeSH in the presence of triethylamine [88,89]. Based on NMR arguments, these compounds are suggested to have a pseudo-octahedral environment around the titanium center with the thiolate group *trans* to the Cp ligand (Fig. 28).

Recently, several systems which contain monocyclopentadienyl titanium thiolato metallocycles have been reported. Reaction of $CpTiCl_3$ with 1,3 propanedithiol in

Table 3
Monocylopentadienyl thiolate complexes of the early metals

No.	Compound	Information	Ref.
Titanium			
156	$CpTi(SPh)Cl_2$	Synthesis, NMR	[84,85]
157	$CpTi(SMe)Cl_2$	Synthesis, NMR	[85]
158	$CpTi(SEt)Cl_2$	Synthesis, NMR, MS	[86]
159	$CpTi(SC_6H_{11})Cl_2$	Synthesis, NMR, MS	[86]
160	$CpTi(p\text{-}SC_6H_4Cl)Cl_2$	Synthesis, NMR, MS	[86]
161	$CpTi(p\text{-}SC_6H_4Br)Cl_2$	Synthesis, NMR, MS	[86]
162	$CpTi(o\text{-}SPhMe)Cl_2$	Synthesis, NMR, MS	[86]
163	$CpTi(p\text{-}SPhMe)Cl_2$	Synthesis, NMR, MS	[86]
164	$CpTi(SC_6F_5)Cl_2$	Synthesis, NMR, MS	[86]
165	$(C_5H_4Me)Ti(SPh)Cl_2$	Synthesis, NMR, MS	[86]
166	$(C_5H_4Me)Ti(p\text{-}SC_6H_4Cl)Cl_2$	Synthesis, NMR, MS	[86]
167	$(C_5H_4Me)Ti(o\text{-}SPhMe)Cl_2$	Synthesis, NMR, MS	[86]
168	$(C_5H_4Me)Ti(p\text{-}SPhMe)Cl_2$	Synthesis, NMR, MS	[86]
169	$(C_5H_4Me)Ti(p\text{-}SPhBr)Cl_2$	Synthesis, NMR, MS	[86]
170	$CpTi(SPh)_2Cl$	Synthesis, NMR, MS	[86]
171	$CpTi(SMe)_3$	Synthesis, NMR	[87]
172	$CpTi(SPh)_3$	Synthesis, NMR, MS	[86]
173	$CpTi(SMe)(o\text{-}OC_6H_4CH{=}NCH_2)_2$	Synthesis, NMR	[88,89]
174	$CpTi(SMe)[(o\text{-}OC_6H_4CH{=}N)_2(o\text{-}C_6H_4)]$	Synthesis, NMR	[88,89]
175	$CpTi(SCH_2CH_2CH_2S)Cl$	Synthesis, NMR, MO, X-ray	[90]
176	$[CpTi(SCH_2CH_2S)Cl]_2$	Synthesis, NMR, X-ray	[91]
177	$CpTi(SCH_2CH_2CH_2S)Ph$	Synthesis, NMR, MO, X-ray	[90]
178	$[CpTi(SCH_2CH_2S)(SPh)]_2$	Synthesis, NMR, X-ray	[91]
179	$[CpTi(SCH_2CH_2CH_2S)]_2O$	Synthesis, NMR, MO, X-ray	[90]
180	$[CpTi(o\text{-}(SCH_2)_2C_6H_4)]_2O$	Synthesis, NMR, X-ray	[92]
181	$[CpTi(SCH_2CH_2CH_2S)(SPh)_2]^-$	Synthesis, NMR	[90]
182	$[CpTi(SCH_2CH_2CH_2S)_2Na(THF)]_n$	Synthesis, NMR, X-ray	[90]
183	$[CpTi(SCH_2CH_2CH_2S)_2Na(THF)_2]_n$	Synthesis, NMR, X-ray	[90]
184	$[CpTi(SCH_2CH_2CH_2S)Cl]_2(\mu\text{-dmpe})$	Synthesis, NMR, MO, X-ray	[90]
185	$CpTi(SCH_2CH_2CH_2S)Cl(dmpe)$ (dangling)	Synthesis, NMR	[90]
186	$CpTi(SCH_2CH_2CH_2S)Cl(dmpe)$ (chelate)	Synthesis, NMR	[90]
187	$CpTi(SCH_2CH_2SCH_2CH_2S)Cl$	Synthesis, NMR, MO, X-ray	[90]
188	$[CpTi(SCH_2CH_2NH)Cl]_n$	Synthesis, NMR	[93]
189	$[CpTi(SCH_2CH(NH_2)OCO)Cl]$	Synthesis, NMR, IR	[94]
190	$CpTi(o\text{-}OC_6H_4CH{=}N\text{-}o\text{-}C_6H_4S)Cl$	Synthesis, NMR, IR, MS	[95]
191	$[CpTi(ASP)Cl]$ $(H_2ASP =$ $o\text{-}HSC_6H_4N{=}C(Me)CH{=}C(Me)OH)$	Synthesis, NMR, IR	[96]
Vanadium			
192	$[CpV(SMe)_2]_2$	Synthesis	[97,98]
193	$[CpV(SPh)_2]_2$	Synthesis, Variable temperature magnetic susceptibility, MS, IR, EPR	[99–101]
194	$[CpV(SCH_2CH_2S)]_2$	Synthesis, MS, Electrochemistry, X-ray	[102,103]
195	$[CpV(SCH(Me)CH_2S)]_2$	Synthesis, MS	[102]
196	$[CpV(CO)_2SMe]_2$	Synthesis, NMR, IR	[104]

Table 3 (continued)

No.	Compound	Information	Ref.
197	[CpV(CO)$_2$SEt]$_2$	Synthesis, NMR, IR	[105]
198	[CpV(CO)$_2$S-*n*-Pr]$_2$	Synthesis, NMR, IR	[105]
199	[CpV(CO)$_2$S-*t*-Bu]$_2$	Synthesis, NMR, IR	[105]
200	[CpV(CO)$_2$SPh]$_2$	Synthesis, NMR, IR	[98,105]
201	[CpV(CO)(CN-*t*-Bu)(SMe)]$_2$	Synthesis, NMR, IR	[105]
202	[CpV(CO)(CN-xylyl)(SMe)]$_2$	Synthesis, NMR, IR	[105]
203	[Cp$_2$V$_2$(CO)$_3$(CN-*t*-Bu)(SMe)]$_2$	Synthesis, NMR, IR	[105]
204	[Cp$_2$V$_2$(CO)$_3$(CN-xylyl)(SMe)]$_2$	Synthesis, NMR, IR	[105]
205	[Cp*V(CO)$_2$(SMe)]$_2$	Synthesis, NMR, IR, X-ray	[98]
206	[Cp*V(CO)$_2$(SPh)]$_2$	Synthesis, NMR, IR, X-ray	[98]
207	CpVO(SPh)$_2$	Synthesis, NMR, IR, X-ray	[106,107]
208	Cp*VO(SPh)$_2$	Synthesis, NMR, IR, MS	[106,107]
209	CpV(S-*t*-Bu)(O-*t*-Bu)(N-*t*-Bu)	Synthesis, NMR	[108]
210	CpV(S-*t*-Bu)$_2$(N-*t*-Bu)	Synthesis, NMR	[108]
211	CpV(SBz)$_2$(N-*t*-Bu)	Synthesis, NMR	[108]
212	CpV(SPh)$_2$(N-*t*-Bu)	Synthesis, NMR	[108]
213	CpV(S-*p*-PhMe)$_2$(N-*t*-Bu)	Synthesis, NMR	[108]
214	CpV(SCy)$_2$(N-*t*-Bu)	Synthesis, NMR	[108]
215	CpV(SCH$_2$CH$_2$CH$_2$SH)$_2$(N-*t*-Bu)	Synthesis, NMR	[108]
216	CpV(SCH$_2$CH$_2$CH$_2$S)(N-*t*-Bu)	Synthesis, NMR, X-ray	[108]
Niobium			
217	[CpNb(CO)$_2$(SMe)]$_2$	Synthesis, IR, X-ray	[109]
218	[CpNb(CO)$_2$(SH)]$_2$	Synthesis, IR, X-ray	[110]
219	[CpNb(CO)$_2$(SH)]$_2$(S)	Synthesis, IR, X-ray	[110]
220	CpNb(PhC$_2$Ph)(S-i-Pr)$_2$	Synthesis, NMR, MS	[111]
Tantalum			
221	Cp*Ta(SCH$_2$CH$_2$S)$_2$	Synthesis, NMR	[112]
222	Cp*Ta(S$_2$C$_7$H$_{10}$)$_2$	Synthesis, NMR	[113]
223	MeCpTa(SPh)$_4$	Synthesis, NMR, X-ray, MO calculations	[114]

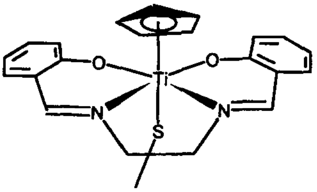
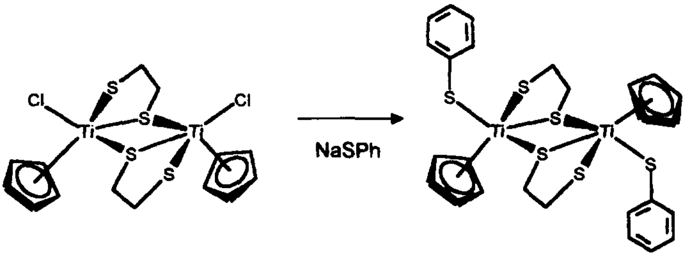


Fig. 28. Proposed structure of CpTi(SMe)(SB) where SB = *N,N'*-ethylenebis(salicylideneimine) **173**.

the presence of excess imidazole yields the bright orange mononuclear Ti(IV) chelate complex CpTi(SCH$_2$CH$_2$CH$_2$S)Cl **175** [90]. The analogous reaction utilizing 1,2-ethanedithiol leads to the dimeric compound [CpTi(SCH$_2$CH$_2$S)Cl]$_2$ **176** [91]. While compound **175** is a simple pseudotetrahedral complex, the species **176** is a dimeric species in which two thiolate sulfur atoms bridge the metal centers. The Cl atoms in **175** and **176** can be displaced by thiolate ligands. Reactions of **175** and **176** with NaSPh proceed immediately to give the complexes $CpTi(SCH_2CH_2CH_2S)SPh$ **177** and $[CpTi(SCH_2CH_2S)(SPh)]_2$ **178** respectively. Compounds **176** and **178** exhibit differing conformations in that the cyclopentadienyl ligands of **176** are *cis* with respect to the Ti_2S_2 core, while in **178** they adopt a *trans* disposition (Eq. (13)) [90,91]:



(13)

176 **178**

Controlled hydrolysis of compound **175** affords the oxo-bridged complex $[CpTi(SCH_2CH_2CH_2S)]_2O$ **179**. Both **179** [90] and the analogous *o*-xylenedithiol complex **180** [92] have been structurally characterized. Reaction of **177** with an additional equivalent of NaSPh gives $[CpTi(SCH_2CH_2CH_2S)(SPh)_2]Na$ **181**. Similarly, the reaction of **175** with the disodium salt of 1,3-propanedithiol affords the dark red products $[CpTi(SCH_2CH_2CH_2S)_2Na(THF)_x]_n$ ($x = 1$ **182**, $x = 2$ **183**) depending on the conditions of crystallization. Crystallographic characterization shows that in both cases the titanium atom adopts a four-legged piano-stool geometry with four sulfur atoms acting as the legs of the cyclopentadienyl stool. The sodium atoms bridge the anionic titanium units forming infinite polymeric structures (Fig. 29) [90].

In addition to substitution reactions, compound **175** also interacts with phosphorus donors to form adducts. Low temperature $^{31}P(^1H)$ NMR shows the reaction of **175**

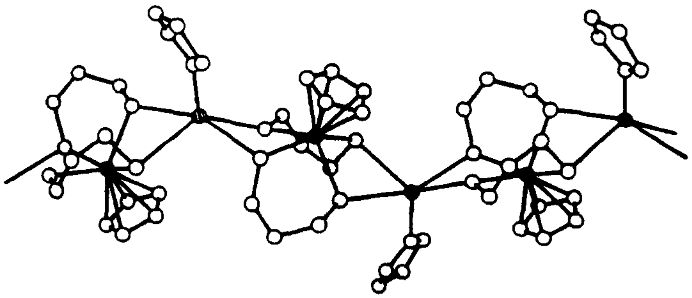


Fig. 29. Polymeric structures of $[CpTi(SCH_2CH_2CH_2S)_2Na(THF)_x]_n$ $x = 1$ **182**, $x = 2$ **183**. Reproduced with permission from Ref. [90]. Copyright 1993 American Chemical Society.

with dmpe to yield three species **184–186**. The most abundant species, 60% of the products, is the dmpe-bridged product $[CpTi(SCH_2CH_2CH_2S)Cl]_2(\mu\text{-dmpe})$ **184** which has been structurally characterized. The other products are mononuclear species in which the diphosphine is either dangling (**185**) or chelated (**186**) (Fig. 30). In a similar case, an additional donor has been built into the backbone of a dithiolate chain. Reaction of $S(CH_2CH_2SSiMe_3)_2$ with $CpTiCl_3$ affords orange crystals of the complex $CpTi(SCH_2CH_2SCH_2CH_2)Cl$ **187**. A structural study of **187** reveals that the geometry about titanium is pseudotrigonal bipyramidal with the thioether sulfur taking up a position approximately *trans* to the cyclopentadienyl ring (Fig. 31) [90].

The nature of the Lewis acidity in the monocyclopentadienyl titanium thiolates has been addressed using a series of FHMO calculations [90]. The low-lying vacant orbitals in the 12-electron compound $CpTiCl_3$ are the $1a_1$ and 1e orbitals. These orbitals are largely metal based comprised primarily of d_{z^2}, d_{xy} and $d_{x^2-y^2}$ character. FHMO calculations reveal only a small energy gap between these orbitals and, interestingly, calculations on the model $CpTi(SH)_3$ indicate a reversal in their order. Removal of the 3-fold symmetry at Ti, as in the case of **175**, results in a splitting of the pair of e orbitals [90].

A few examples of dissymmetric chelate thiolate complexes of titanium also have been reported. Reaction of Cp_2TiCl_2 with excess $HSCH_2CH_2NH_2$ in boiling THF proceeds to give a violet–red, air-sensitive powder formulated as $[CpTi(SCH_2CH_2NH)Cl]_n$ **188** [93]. The compound $Cp_2Ti(SCH_2CH_2NH_3^+Cl^-)$-

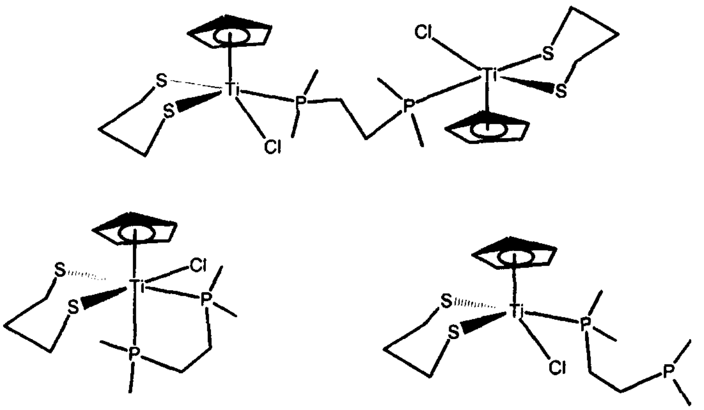


Fig. 30. Structures of compounds **184**, **185** and **186**.

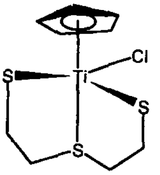


Fig. 31. The structure of $CpTi(SCH_2CH_2SCH_2CH_2)Cl$ **187**.

Cl is also isolated when the reagents are reacted in a 1:1 molar ratio. This suggests that in the presence of excess ligand the reactive intermediate $Cp_2Ti(SCH_2CH_2NH_2)Cl$ is formed which undergoes rapid inter- and intramolecular attack of the dangling amine on a Cp—Ti bond to form **188** and CpH. The value of *n* has not been determined, although the appearance of a single Cp resonance in the ^1H NMR rules out the possibility of **188** being a short chain polymer or a dissymmetric dimer. In a related reaction, the compound $[CpTi(SCH_2CH(NH_2)CO_2)Cl].H_2O$ **189** was obtained from the equimolar reaction of Cp_2TiCl_2 and L-cystine in the presence of pyridine [94]. While this complex was presumed to have a monomeric structure, no attempt was made to discount the possibility of a dimeric or higher oligomeric structure. Both of the above examples, **188** and **189**, illustrate a preference for Ti—Cl bond scission when a soft nucleophilic base such as sulfur is used whereas Cp—Ti bond rupture can take place in the reactions with hard atoms such as nitrogen and oxygen. The complexes $CpTi(o\text{-}OC_6H_4CH{=}N\text{-}o\text{-}C_6H_4S)Cl$ **190** [95] and $CpTi[o\text{-}SC_6H_4N{=}C(Me)CH{=}C(Me)O]Cl$ **191** [96] have been prepared from the reactions of $CpTiCl_3$ and the appropriate tridentate thiol–alcohol ligands.

4.2. *Zirconium*

No cyclopentadienyl zirconium thiolate derivatives have been described to date.

4.3. *Hafnium*

No cyclopentadienyl hafnium thiolate derivatives have been described to date.

4.4. *Vanadium*

In 1963, the species $[CpV(SMe)_2]_2$ **192** was prepared via the thermal reaction of $CpV(CO)_4$ with $(MeS)_2$ [97]. Employing a similar method the species $[CpV(SPh)_2]_2$ **193** was later prepared and the magnetic properties studied in detail [99–101]. Rakowski-Dubois and coworkers have prepared related chelated V dimers, $[CpV(SCH_2CH_2S)]_2$ **194** and $[CpV(SCH(Me)CH_2S)]_2$ **195**, and crystallographically characterized compound **194** [102]. These dimers are reported to undergo a one-electron oxidation to give the salts of the form $[CpV(SCH(R)CH_2S)]_2BF_4$, although these products were not characterized [102]. Compound **194** can also be prepared via the reaction of Cp_2V and ethanedithiol [103]. It was subsequently shown that photoinduced addition of $(MeS)_2$ to $CpV(CO)_4$ afforded the species $[CpV(CO)_2(SMe)]_2$ **916** [104]. This methodology was later extended to a series of related compounds of the form $[CpV(CO)_2(SR)]_2$ (R = Et **197**, Pr **198**, *t*-Bu **199**, Ph **200**) [105]. Reactions of **196** with isonitriles afford compounds of the form $[CpV(CO)(CNR)(SMe)]_2$ (R = *t*-Bu **201**, xylyl **202**) and $[Cp_2V_2(CO)_3(CNR)(SMe)_2]$ (R = *t*-Bu **203**, xylyl **204**) [105]. Crystallographic studies of the related species $[Cp^*V(CO)_2(SR)]_2$ (R = Me **205**, Ph **206**) have been reported. In these compounds the Cp* groups are *cis* to each other and the substituents on sulfur occupy *exo,exo* positions (Fig. 32) [98].

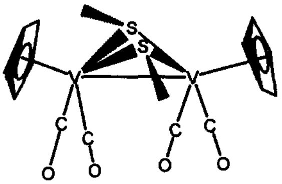


Fig. 32. Structure of $[Cp^*V(CO)_2(SMe)]_2$ **205**.

The vanadium(V) complexes $CpVO(SPh)_2$ **207** and $Cp^*VO(SPh)_2$ **208** were readily prepared by halide ion metathesis (Eq. (14)) [106,107]. As expected, crystallographic data for compound **207** showed that it exhibits a distorted tetrahedral geometry at V [106,107].

$$CpVOCl_2 + 2NaSPh \rightarrow CpVO(SPh)_2 + NaCl \tag{14}$$

A series of related imido derivatives including CpV(N-*t*-Bu)(O-*t*-Bu)(S-*t*-Bu) **209**, species of the form $CpV(N\text{-}t\text{-}Bu)(SR)_2$ (R = *t*-Bu **210**, Bz **211**, Ph **212**, PhMe **213**, Cy **214**, $CH_2CH_2CH_2SH$ **215**) and $CpV(N\text{-}t\text{-}Bu)(SCH_2CH_2CH_2S)$ **216** have been prepared by metathetical reactions of thiolates with $CpV(N\text{-}t\text{-}Bu)Cl_2$ [108]. The structure of the species **216** was confirmed by X-ray methods (Fig. 33), revealing the expected distorted tetrahedral geometry at vanadium [108].

4.5. *Niobium*

The product of the reaction of MeSH with $CpNb(CO)_3(THF)$ has been confirmed by X-ray methods as $[CpNb(CO)_2(SMe)]_2$ [109]. The related complexes $[CpNb(CO)_2(SH)_2]_2$ **218** and $[CpNb(CO)_2(SH)]_2(S)$ **219** have also been isolated and crystallographically characterized [110]. The Nb—Nb distances in **217** and **218** are 3.143 Å and 3.164 Å respectively, indicative of the presence of metal–metal bonds. In contrast, the metal–metal separation in **219** of 3.555 Å suggests the absence of a direct Nb—Nb bond and thus is consistent with the observed diamagnetism.

The compound $CpNb(S\text{-}i\text{-}Pr)_2(PhCCPh)$ **220**, reported by Curtis and coworkers, represents the only example of a mononuclear CpNb thiolate derivative known [111]. This species is prepared via the metathetical reaction of $CpNb(PhCCPh)Cl_2$ with LiS-i-Pr. This species has been subsequently employed to prepare thiolate-bridged heterobimetallics (vide infra) [111].

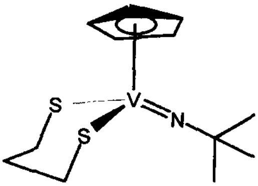


Fig. 33. Structure of $CpV(SCH_2CH_2S)(N\text{-}t\text{-}Bu)$ **216**.

4.6. *Tantalum*

The "piano-stool" type complexes such as $Cp^*Ta(SCH_2CH_2S)_2$ **221** [112], $Cp^*Ta(S_2C_7H_{10})_2$ **222** [113] and $(C_5H_4Me)Ta(SPh)_4$ **223** [114] have been prepared via metathetical reactions employing the appropriate $CpTaCl_4$ starting material. In the case of **223** crystallographic data have been reported (Fig. 34) [114]. EHMO calculations on the model compound $CpTa(SH)_4$ showed that the distortion in four-legged piano-stool geometry of **223** is largely electronic in nature involving pπ–dπ Ta—S interaction [114].

5. Metallocene thiolate derivatives

Table 4 lists bis-cyclopentadienyl thiolate complexes of the early metals.

5.1. *Titanium*

Although numerous examples of titanocene derivatives of thiolates **224–308** [93,116–170,185,187,213–217] have appeared in the literature (Table 4), only a few distinct synthetic methods have been employed. Monosubstituted titanocene thiolates can be obtained from the oxidative addition of dialkyl or diaryl disulfides to $(Cp_2TiCl)_2$ in a bimolecular process (Eq. (15)). In a brief report this method has been employed to prepare complexes of the form CpCp′Ti(OAr)(SR) [115].

$$(Cp_2TiCl)_2 + (RS)_2 \rightarrow 2Cp_2Ti(SR)Cl \qquad (15)$$

In this manner the compounds $Cp_2Ti(SR)Cl$ (R = Me **224**, Et **225**, Bz **226**, Ph **227**) have been prepared in high yield [116]. Alternatively, metathesis employing an

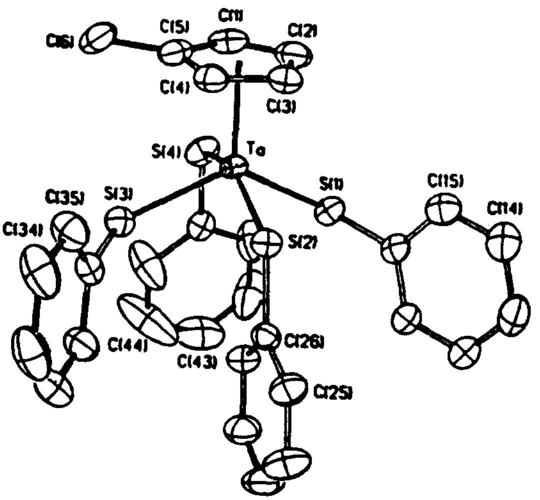


Fig. 34. ORTEP drawing of $(C_5H_4Me)Ta(SPh)_4$ **223**. Reproduced with permission from Ref. [114]. Copyright 1991 American Chemical Society.

Table 4
Bis-cyclopentadienyl thiolate complexes of the early metals

No.	Compound	Information	Ref.
Titanium			
224	$Cp_2Ti(SMe)Cl$	Synthesis, NMR	[116]
225	$Cp_2Ti(SEt)Cl$	Synthesis, NMR	[116]
226	$Cp_2Ti(SBz)Cl$	Synthesis, NMR	[116]
227	$Cp_2Ti(SPh)Cl$	Synthesis, NMR	[116]
228	$Cp_2Ti(SCH_2CH_2NH_3^+Cl^-)Cl$	Synthesis, NMR	[93]
229	$Cp_2Ti(o\text{-}SPhMe)Cl$	Synthesis, NMR, IR, MS	[117]
230	$Cp_2Ti(p\text{-}SPhMe)Cl$	Synthesis, NMR, IR, MS	[117]
231	$Cp_2Ti(p\text{-}SC_6H_4OH)Cl$	Synthesis, NMR, IR, MS	[118]
232	$Cp_2Ti(o\text{-}SC_6H_4NH_2)Cl$	Synthesis, NMR, IR, MS	[119]
233	$Cp_2Ti(p\text{-}SC_6H_4NH_2)Cl$	Synthesis, NMR, IR, MS	[119]
234	$Cp_2Ti(p\text{-}SC_6H_4NH_3^+Cl^-)Cl$	Synthesis, IR, AT	[120]
235	$Cp_2Ti[SCH_2(CO)NHPh]_2Cl$	Synthesis, NMR, IR, UV, EC	[121]
236	$(C_5H_4Me)_2Ti[SCH_2(CO)NHPh]_2Cl$	Synthesis, NMR, IR, UV, EC	[122]
237	$Cp(C_9H_7)Ti[SCH(CH_3)_2]Cl$	Synthesis, NMR	[123]
238	$Cp_2Ti(o\text{-}SPhMe)CH_3$	Synthesis, NMR, IR, MS	[117]
239	$Cp_2Ti(p\text{-}SPhMe)CH_3$	Synthesis, NMR, IR, MS	[117]
240	$Cp_2Ti(o\text{-}SC_6H_4NH_2)CH_3$	Synthesis, NMR, IR, MS	[119]
241	$Cp_2Ti(p\text{-}SC_6H_4NH_2)CH_3$	Synthesis, NMR, IR, MS	[119]
242	$(C_5H_4Me)_2Ti(SPh)CH_3$	Synthesis, NMR (CIDNP)	[124]
243	$CpCp''Ti(SPh)(NCO)$ $(Cp'' = 1\text{-}Me(2\text{-}CHMe_2)C_5H_3)$	Synthesis, NMR	[125]
244	$CpCp''Ti(SPh)(NCS)$ $(Cp'' = 1\text{-}Me(2\text{-}CHMe_2)C_5H_3)$	Synthesis, NMR, X-ray	[126]
245	$Cp_2Ti(SMe)_2$	Synthesis, NMR, X-ray, SC	[127–133]
246	$(C_5H_4Me)_2Ti(SMe)_2$	Synthesis	[129]
247	$(C_5H_4PPh_2)_2Ti(SMe)_2$	Synthesis, NMR, IR	[134]
248	$[C_5H_4P(p\text{-}PhMe)_2]_2Ti(SMe)_2$	Synthesis, NMR, IR	[134]
249	$Cp_2Ti(SEt)_2$	Synthesis, NMR, IR, SC, X-ray, MO	[128,130,135]
250	$Cp_2Ti(S\text{-}n\text{-}Pr)_2$	Synthesis, NMR, IR, SC	[130,136–138]
251	$Cp_2Ti(S\text{-}t\text{-}Bu)_2$	Synthesis, SR transfer	[116,127,130,139]
252	$Cp_2Ti(SBz)_2$	Synthesis, NMR, IR	[130,131,136]
253	$Cp_2Ti(SCH_2CH_2Ph)_2$	Synthesis, NMR, IR	[130]
254	$Cp_2Ti(SCH_2CH_2PPh_2)_2$	Synthesis, NMR, UV	[140]
255	$Cp_2Ti(SCH_2CH_2CH_2PPh_2)_2$	Synthesis, NMR, UV	[141]
256	$Cp_2Ti[S(CH_2)_{11}CH_3]_2$	Synthesis	[127]
257	$Cp_2Ti(SCH_2CH_2SEt)_2$	Synthesis, NMR	[142]
258	$Cp_2Ti(SCH_2CH_2SBz)_2$	Synthesis, NMR	[142]
259	$Cp_2Ti[SCH_2(CO)NHPh]_2$	Synthesis, NMR, IR, UV, EC	[121]
260	$(C_5H_4Me)_2Ti[SCH_2(CO)NHPh]_2$	Synthesis, NMR, IR, UV, EC	[122]
261	$Cp_2Ti(SPh)_2$	Synthesis, X-ray, IR, NMR, He(I)—He(II) spectroscopy, UV, CV	[127,129–131, 138,142–150]
262	$(C_5H_4Me)_2Ti(SPh)_2$	Synthesis	[129]
263	$Cp_2Ti(o\text{-}SPhMe)_2$	IR, NMR, MS	[117]
264	$Cp_2Ti(m\text{-}SPhMe)_2$	IR, NMR, MS	[117]
265	$Cp_2Ti(p\text{-}SPhMe)_2$	Synthesis, NMR, IR, MS, UV, CV	[117,130,131, 138,142,147]

Table 4 (continued)

No.	Compound	Information	Ref.
266	$Cp_2Ti(p\text{-}SC_6H_4Cl)_2$	Synthesis, NMR, IR, UV, CV	[130,142]
267	$Cp_2Ti(p\text{-}SC_6H_4OCH_3)_2$	Synthesis, NMR, UV, CV	[142]
268	$Cp_2Ti(o\text{-}SC_6H_4NH_2)_2$	IR, MS, NMR	[119]
269	$Cp_2Ti(p\text{-}SC_6H_4NH_2)_2$	IR, MS, NMR	[119]
270	$Cp_2Ti(p\text{-}SC_6H_4NH_3^+Cl^-)_2$	Synthesis, IR, AT	[120]
271	$Cp_2Ti(SC_6F_5)_2$	Synthesis, NMR, MS, AT, SSES	[133,147,151, 152]
272	$Cp_2Ti(o\text{-}SC_6H_4NH).2HSC_6H_4NH_2$	Synthesis, IR, MS, TGA	[153]
273	$Cp_2Ti(OC_{10}H_{16}S)$	Synthesis, NMR	[154]
274	$Cp_2Ti(o\text{-}SC_6H_4COO)$	Synthesis, IR, NMR, MS, AT	[118,153]
275	$Cp_2Ti(SCH_2CH_2S)$	Synthesis, IR, MS	[153,155,156]
276	$(Cp_2TiSMe)_2$	Synthesis, EPR	[157]
277	$(Cp_2TiSEt)_2$	Synthesis, MS, Magnetic susceptibility	[131]
278	$(Cp_2TiSPh)_2$	Synthesis, MS, IR, Magnetic susceptibility	[131,158]
279	$[Cp_2Ti(p\text{-}SPhMe)]_2$	Synthesis, MS, Magnetic susceptibility	[131]
280	$Cp_2Ti(SBz)(C_4H_3S)$	Synthesis, NMR, IR, MS	[159]
281	$Cp_2Ti(o\text{-}S{-}C_4H_3S)(C_4H_3S)$	Synthesis, NMR, IR, MS	[159]
282	$Cp_2Ti(SPh)[C(Ph){=}N\text{-}2,6(CH_3)_2C_6H_3]$	Synthesis, IR, NMR, Magnetic susceptibility	[160]
283	$Cp_2Ti(SPh)[C(o\text{-}PhMe){=}N\text{-}2,6(CH_3)_2C_6H_3]$	Synthesis, IR, NMR, Magnetic susceptibility	[160]
284	$Cp_2Ti(SPh)[C(CH_2CH{=}CHCH_3){=}N{-}C_6H_5]$	Synthesis, NMR, IR	[161]
285	$Cp_2Ti(SPh)[C(CH_2CH{=}CHCH_3){=}N\text{-}2,6(CH_3)_2C_6H_3]$	Synthesis, NMR, IR	[161]
286	$Cp_2Ti(S\text{-}i\text{-}Pr)(SS\text{-}i\text{-}Pr)$	Synthesis, NMR	[139]
287	$Cp_2Ti(S\text{-}t\text{-}Bu)(SS\text{-}t\text{-}Bu)$	Synthesis, NMR	[139]
288	$(C_5H_4Me)_2Ti(SCMe_3)(SSCMe_3)$	Synthesis, NMR	[139]
289	$Cp_2Ti(SBz)(SSBz)$	Synthesis, NMR	[139]
290	$Cp_2Ti(S\text{-}p\text{-}PhMe)(SS\text{-}p\text{-}PhMe)$	Synthesis, NMR	[139]
291	$Cp_2Ti(SPh)(SSSPh)$	Synthesis, NMR, IR, X-ray	[162]
292	$Cp_2Ti(S\text{-}p\text{-}PhMe)(SSS\text{-}p\text{-}PhMe)$	Synthesis, NMR, IR	[162]
293	$(C_5H_4Me)_2Ti(SCH_2SSS)$	Synthesis, NMR	[163]
294	$Cp_2Ti(S\text{-}i\text{-}Pr)Br$	NMR	[136]
295	$Cp_2Ti(SPh)Br$	NMR	[136]
296	$Cp_2Ti(\mu\text{-}SCH_2CH_2S)_2TiCp_2$	Synthesis, NMR, CV	[164]
297	$Cp_2Ti(SCH_2CH_2CH_2S)$	Synthesis, NMR, MS	[156,165–168]
298	$Cp_2Ti(\mu\text{-}SCH_2CH_2CH_2S)_2TiCp_2$	Synthesis, NMR, CV	[164]
299	$Cp_2Ti(SCH_2CH_2)_2S$	Synthesis, NMR	[169]
300	$[Cp_2Ti(SCH_2CH_2)_2S]_2$	Synthesis, NMR	[169]
301	$Cp_2Ti(SCH_2CH_2CH_2)_2S$	Synthesis, NMR	[169]
302	$[Cp_2Ti(SCH_2CH_2CH_2)_2S]_2$	Synthesis, NMR	[169]
303	$Cp_2Ti(SCH_2CH_2SCH_2)_2(CH_2)$	Synthesis, NMR	[169]
304	$[Cp_2Ti(SCH_2CH_2SCH_2)_2(CH_2)]_2$	Synthesis, NMR	[169]
305	$[Cp_2TiCl]_2(SCH_2CH_2)_2S$	Synthesis, NMR	[169]
306	$Cp_2Ti[SCH_2CH_2PPh_2(Me)^+I^-]_2$	Synthesis, NMR	[130]

Table 4 (continued)

No.	Compound	Information	Ref.
307	Cp$_2$Ti(CH$_2$S)(PMe$_3$)	Synthesis, NMR, X-ray	[170]
308	Cp$_2$Ti(SCH$_2$CH$_2$CH$_2$CH$_2$)	Synthesis, NMR	[170]
Zirconium			
309	Cp$_2$Zr(SCH$_2$CONHPh)Cl	Synthesis, NMR, IR, UV	[171]
310	Cp$_2$Zr[SCH$_2$CONH(*o*-C$_6$H$_4$Me)]Cl	Synthesis, NMR, IR, UV	[171]
311	Cp$_2$Zr[SCH$_2$CONH(*m*-C$_6$H$_4$Me)]Cl	Synthesis, NMR, IR, UV	[171]
312	Cp$_2$Zr[SCH$_2$CONH(*p*-C$_6$H$_4$Me)]Cl	Synthesis, NMR, IR, UV	[171]
313	Cp$_2$Zr[SCH$_2$CONH(3,5-PhMe$_2$)]Cl	Synthesis, NMR, IR, UV	[171]
314	Cp$_2$Zr[SCH$_2$CONH(α-C$_{10}$H$_7$)]Cl	Synthesis, NMR, IR, UV	[171]
315	Cp$_2$Zr(SMe)[CH(SiMe$_3$)Ph]	Synthesis, NMR	[172]
316	Cp$_2$Zr(SMe)[CH(SiMe$_3$)*p*-C$_6$H$_4$OMe]	Synthesis	[172]
317	Cp$_2$Zr(SEt)Me	Synthesis, NMR, IR, MS	[173,174]
318	Cp$_2$Zr(S-*t*-Bu)(Et)	Synthesis, NMR	[175]
319	Cp$_2$Zr(SBz)Me	Synthesis, NMR, IR, MS	[173,174]
320	Cp$_2$Zr[SCH$_2$(*p*C$_6$H$_4$CF$_3$)]Me	Synthesis, NMR, IR, MS	[174]
321	Cp$_2$Zr[SCH$_2$(*p*-C$_6$H$_4$Cl)]Me	Synthesis, NMR, IR, MS	[174]
322	Cp$_2$Zr[SCH$_2$(*p*-C$_6$H$_4$NMe$_2$)]Me	Synthesis, NMR, IR, MS	[174]
323	Cp$_2$Zr[SCH$_2$(*p*-C$_6$H$_4$OMe)]Me	Synthesis, NMR, IR, MS	[174]
324	Cp$_2$Zr(SPh)Me	Synthesis	[176]
325	Cp$_2$Zr(SPh)[CH(SiMe$_3$)Ph]	Synthesis, NMR	[172]
326	Cp$_2$Zr(SPh)[CH(SiMe$_3$)(*p*-C$_6$H$_4$Cl)]	Synthesis, NMR	[177]
327	Cp$_2$Zr(SPh)[CH(SiMe$_3$)(*p*-PhMe)]	Synthesis, NMR	[177]
328	Cp$_2$Zr(SPh)[CH(SiMe$_3$) (*p*-C$_6$H$_4$OMe)]	Synthesis, NMR	[177]
329	Cp$_2$Zr(SPh)(η^2-COPh)	Synthesis	[178]
330	[Cp$_2$Zr(Et)]$_2$(μ-SCH$_2$CH$_2$S)	Synthesis, NMR	[179]
331	[Cp$_2$Zr(S-*t*-Bu)]$_2$(μ-O)		[180]
332	[Cp$_2$Zr(SPh)]$_2$(μ-O)	Synthesis, IR, X-ray, MO	[180]
333	Cp$_2$Zr(SMe)$_2$	Synthesis, NMR, MS	[181]
334	Cp$_2$Zr(SEt)$_2$	Synthesis, NMR, IR	[182]
335	Cp$_2$Zr(S-*t*-Bu)$_2$	Synthesis	[183]
336	Cp$_2$Zr(SPh)$_2$	Synthesis, NMR, IR	[176,178,181, 183,184]
337	(*t*-BuC$_5$H$_4$)$_2$Zr(SPh)$_2$	He(I)—He(II) spectroscopy	[185]
338	Cp$_2$Zr(SCH$_2$CON-Ph)$_2$	Synthesis, NMR, IR, UV	[171]
339	Cp$_2$Zr[SCH$_2$CONH(*o*-C$_6$H$_4$Me)]$_2$	Synthesis, NMR, IR, UV	[171]
340	Cp$_2$Zr[SCH$_2$CONH(*m*-C$_6$H$_4$Me)]$_2$	Synthesis, NMR, IR, UV	[171]
341	Cp$_2$Zr[SCH$_2$CONH(*p*-C$_6$H$_4$Me)]$_2$	Synthesis, NMR, IR, UV	[171]
342	Cp$_2$Zr[SCH$_2$CONH(3,5-PhMe$_2$)]$_2$	Synthesis, NMR, IR, UV	[171]
343	Cp$_2$Zr[SCH$_2$CONH(α-C$_{10}$H$_7$)]$_2$	Synthesis, NMR, IR, UV	[171]
344	(C$_5$H$_4$Me)$_2$Zr(SBz)$_2$	Synthesis, NMR, MS	[181]
345	(*t*-BuC$_5$H$_4$)$_2$Zr(SBz)$_2$	Synthesis, MS	[181]
346	[Cp$_2$Zr(S-*t*-Bu)(THF)][BPh$_4$]	Synthesis, NMR, X-ray	[184]
347	[Cp$_2$Zr(S-*t*-Bu)(DMAP)][BPh$_4$] (DMAP = 4-(*N*,*N*-dimethylaminopyridine))	Synthesis, NMR	[186]
348	[Cp$_2$Zr(SPh)]$_2$	Synthesis, NMR, IR	[182]
349	[CpZr(SPh)(η^1:η^5-C$_5$H$_4$)]$_2$	Synthesis, NMR	[173]
350	[η^5:η^5-C$_{10}$H$_8$][CpZr(μ-SPh)]$_2$	Synthesis, NMR, X-ray	[173]
351	[η^5:η^5-C$_{10}$H$_8$][CpZr(SPh)$_2$]$_2$	Synthesis, NMR	[173]

Table 4 (continued)

No.	Compound	Information	Ref.
352	$[\eta^1{:}\eta^5\text{-}C_5H_4][\mu\text{-}NSiMe_3][CpZrSPh]\text{-}[Cp(C_5H_4SPh)Zr]$	Synthesis, NMR, X-ray	[174]
353	$Cp_2Zr(\mu\text{-}SCH_2CH_2S)_2ZrCp_2$	Synthesis, NMR, X-ray	[187]
354	$Cp_2Zr(\mu\text{-}SCH_2CH_2CH_2S)_2ZrCp_2$	Synthesis, NMR, X-ray	[187]
355	$Cp_2Zr(\mu\text{-}SCH_2CH_2CH_2CH_2S)_2ZrCp_2$	Synthesis, NMR	[187]
356	$Cp_2Zr(\mu\text{-}o\text{-}SCH_2C_6H_4CH_2S)_2ZrCp_2$	Synthesis, NMR	[187]
357	$Cp_2Zr(\mu\text{-}m\text{-}SCH_2C_6H_4CH_2S)_2ZrCp_2$	Synthesis, NMR	[187]
358	$Cp_2Zr(\mu\text{-}SCH_2CH_2SCH_2CH_2S)_2ZrCp_2$	Synthesis, NMR, X-ray	[169]
359	$Cp_2Zr(\mu\text{-}OCH_2CH_2S)_2ZrCp_2$	Synthesis, NMR, X-ray	[154]
360	$Cp_2Zr(OC_{10}H_{16}S)$	Synthesis, NMR	[154]
361	$Cp_2Zr(o\text{-}SC_6H_4O)$	Synthesis	[154]
362	$[Cp_2Zr(\mu\text{-}O)(\mu\text{-}OC_{10}H_{16}S)ZrCp_2]$	Synthesis, NMR, X-ray	[154]
363	$Cp_2Zr(SCHMe)PMe_3$	Synthesis, NMR, MS, X-ray	[188]
364	$Cp_2Zr(SCHPh)PMe_3$	Synthesis, NMR, MS	[188]
365	$Cp_2Zr[SCH(p\text{-}C_6H_4CF_3)]PMe_3$	Synthesis, NMR	[189]
366	$Cp_2Zr[SCH(p\text{-}C_6H_4Cl)]PMe_3$	Synthesis, NMR	[189]
367	$Cp_2Zr[SCH(p\text{-}C_6H_4NMe_2)]PMe_3$	Synthesis, NMR	[189]
368	$Cp_2Zr[SCH(p\text{-}C_6H_4OMe)]PMe_3$	Synthesis, NMR	[189]
369	$Cp_2Zr(SCH_2CH{=}CH)$	Synthesis, NMR	[190]
370	$Cp_2Zr[SCH_2C(Me){=}C(Me)]$	Synthesis, NMR	[190]
371	$Cp_2Zr[SCH_2C(Ph){=}C(Ph)]$	Synthesis, NMR	[190]
Hafnium			
372	$Cp_2Hf[SCH_2CONH(C_{10}H_7)]Cl$	Synthesis, NMR, IR, UV	[191]
373	$Cp_2Hf(SCH_2CONHPh)Cl$	Synthesis, NMR, IR, UV	[191]
374	$Cp_2Hf[SCH_2CONH(o\text{-}PhMe)]Cl$	Synthesis, NMR, IR, UV	[191]
375	$Cp_2Hf[SCH_2CONH(m\text{-}PhMe)]Cl$	Synthesis, NMR, IR, UV	[191]
376	$Cp_2Hf[SCH_2CONH(p\text{-}PhMe)]Cl$	Synthesis, NMR, IR, UV	[191]
377	$Cp_2Hf[SCH_2CONH(3{,}5\text{-}PhMe_2)]Cl$	Synthesis, NMR, IR, UV	[191]
378	$Cp_2Hf[SCH_2CONH(C_{10}H_7)]_2$	Synthesis, NMR, IR, UV	[191]
379	$Cp_2Hf(SCH_2CONHPh)_2$	Synthesis, NMR, IR, UV	[191]
380	$Cp_2Hf[SCH_2CONH(o\text{-}PhMe)]_2$	Synthesis, NMR, IR, UV	[191]
381	$Cp_2Hf[SCH_2CONH(m\text{-}PhMe)]_2$	Synthesis, NMR, IR, UV	[191]
382	$Cp_2Hf[SCH_2CONH(p\text{-}PhMe)]_2$	Synthesis, NMR, IR, UV	[191]
383	$Cp_2Hf[SCH_2CONH(3{,}5\text{-}PhMe_2)]_2$	Synthesis, NMR, IR, UV	[191]
384	$Cp_2Hf(SPh)_2$	Synthesis, NMR, IR, MS	[192]
385	$Cp_2Hf(o\text{-}SPhMe)_2$	Synthesis, NMR, IR, MS	[192]
386	$Cp_2Hf(p\text{-}SPhMe)_2$	Synthesis, NMR, IR, MS	[192]
387	$Cp_2Hf(p\text{-}SC_6H_4NH_2)_2$	Synthesis, NMR, IR, MS	[192]
Vanadium			
388	Cp_2VSMe	Synthesis, IR, MS	[193–195]
389	Cp_2VSEt	Synthesis, MS	[194]
390	$Cp_2VS\text{-}i\text{-}Pr$	Synthesis, MS	[194]
391	Cp_2VSPh	Synthesis, MS, X-ray	[193–196]
392	Cp_2VSBz	Synthesis, MS	[194]
393	$Cp_2VSC_6H_2(CMe_3)_2OH$	Synthesis, X-ray	[196]
394	$Cp^*_2V(S\text{-}p\text{-}PhMe)$	Synthesis, Magnetic susceptibility	[197]

Table 4 (continued)

No.	Compound	Information	Ref.
395	$Cp_2VSC{=}C(t\text{-}Bu)$	Synthesis, EPR	[198]
396	$Cp_2VSC{=}C(CF_3)_2$	Synthesis, EPR, X-ray	[198]
397	$Cp_2VSC{=}C(SiMe_3)_2$	Synthesis, EPR, X-ray	[198]
398	$Cp_2VSC{=}C(Me_2CCH_2CH_2CH_2CMe_2)$	Synthesis, EPR	[198]
399	$(Cp_2V)_2(m\text{-}S_2C_6H_4)$	Synthesis, X-ray	[103]
400	$Cp_2V(SMe)(CO)$	Synthesis, IR	[195]
401	$Cp_2V(SPh)(CO)$	Synthesis, IR	[195]
402	$Cp^*_2V(S\text{-}p\text{-}PhMe)(CO)$	Synthesis, IR	[197]
403	$Cp_2V(SMe)_2$	Synthesis, EPR, MO X-ray	[128,148]
404	$Cp_2V(SPh)_2$	Synthesis, EPR, MO	[148]
405	$Cp_2VS_2C_6H_4$	Synthesis, X-ray	[103]
406	$Cp_2V(SCH_2CH_2CH_2S)$	Synthesis, EPR, X-ray	[103]
407	$[Cp_2V(SCH_2CH_2CH_2S)]_2$	Synthesis, EPR	[103]
Niobium			
408	$Cp_2Nb(SPh)(C_4H_3S)$	Synthesis, MS, IR, EPR	[199]
409	$Cp_2Nb(SC_4H_3S)(C_4H_3S)$	Synthesis, MS, IR, EPR	[199]
410	$Cp_2Nb(SPh)(C_4H_3S)I$	Synthesis, MS, IR, EPR	[199]
411	$Cp_2Nb(SC_4H_3S)(C_4H_3S)I$	Synthesis, MS, IR, EPR	[199]
412	$Cp_2Nb(SPh)I_2$	Synthesis, MS, IR, EPR	[199]
413	$Cp_2Nb(SC_4H_3S)I_2$	Synthesis, MS, IR, EPR	[199]
414	$Cp_2Nb(SMe)(MeO_2CC_2CO_2Me)$	Synthesis, MS, IR, EPR	[200]
415	$Cp_2Nb(SMe)(F_3CC_2CF_3)$	Synthesis, MS, IR, EPR	[200]
416	$Cp_2Nb(SMe)_2$	Synthesis, IR, Magnetic susceptibility, EPR	[201–203]
417	$Cp_2Nb(SEt)_2$	Synthesis, IR, Magnetic susceptibility	[201]
418	$Cp_2Nb(S\text{-}i\text{-}Pr)_2$	Synthesis, IR, Magnetic susceptibility	[201]
419	$Cp_2Nb(S\text{-}n\text{-}Pr)_2$	Synthesis, IR, Magnetic susceptibility	[201]
420	$Cp_2Nb(S\text{-}n\text{-}Bu)_2$	Synthesis, IR, Magnetic susceptibility	[201]
421	$Cp_2Nb(S\text{-}i\text{-}Bu)_2$	Synthesis, IR, Magnetic susceptibility	[201]
422	$Cp_2Nb(S\text{-}i\text{-}Pentyl)_2$	Synthesis, IR, Magnetic susceptibility	[201]
423	$Cp_2Nb(SPh)_2$	Synthesis, X-ray, MS, UV–visible, CV, MO	[204–206]
424	$Cp_2Nb(SPh\text{-}p\text{-}Me)_2$	Synthesis, MS, UV–visible, CV, X-ray	[205]
425	$Cp_2Nb(SPh\text{-}p\text{-}OMe)_2$	Synthesis, MS, UV–visible, CV, X-ray	[205]
426	$Cp_2Nb(SPh\text{-}p\text{-}Cl)_2$	Synthesis, MS, UV–visible, CV, X-ray	[205]
427	$Cp_2Nb(SCOPh)_2$	Synthesis, MS, IR, EPR	[207]
428	$In_2Nb(SMe)_2$	Synthesis, IR, Magnetic susceptibility	[201]
429	$In_2Nb(SEt)_2$	Synthesis, IR, Magnetic susceptibility	[201]

Table 4 (continued)

No.	Compound	Information	Ref.
430	$In_2Nb(S\text{-i-}Pr)_2$	Synthesis, IR, Magnetic susceptibility	[201]
431	$In_2Nb(S\text{-}n\text{-}Pr)_2$	Synthesis, IR, Magnetic susceptibility	[201]
432	$In_2Nb(S\text{-}n\text{-}Bu)_2$	Synthesis, IR, Magnetic susceptibility	[201]
433	$In_2Nb(S\text{-i-}Bu)_2$	Synthesis, IR, Magnetic susceptibility	[201]
434	$In_2Nb(S\text{-i-Pentyl})_2$	Synthesis, IR, Magnetic susceptibility	[201]
435	$[Cp_2Nb(SMe)_2]I$	Synthesis, IR, Magnetic susceptibility	[201–203]
436	$[Cp_2Nb(SPh)_2]^+$	Synthesis, MS, NMR, X-ray	[204]
437	$[Cp_2Nb(SPh\text{-}p\text{-}Me)_2]^+$	Synthesis, MS, NMR	[205]
438	$[Cp_2Nb(SPh\text{-}p\text{-}NH_2)_2]^+$	Synthesis, MS, NMR	[205]
439	$[Cp_2Nb(SPh\text{-}p\text{-}NO_2)_2]^+$	Synthesis, MS, NMR	[205]
440	$[Cp_2Nb(SPh\text{-}p\text{-}Cl)_2]^+$	Synthesis, MS, NMR, X-ray	[205]
441	$Cp_2Nb(SCH{=}C(t\text{-}Bu)_2)(SC{=}C(t\text{-}Bu)_2)$	Synthesis, NMR, X-ray	[208]
442	$Cp_2Nb(SCH{=}C(C_9H_{18})(SC{=}C(C_9H_{18}))$	Synthesis, NMR	[208]
443	$[Cp_2Nb(SC{=}C(t\text{-}Bu)_2)]^+$	Synthesis, NMR	[208]
444	$[Cp_2Nb(SCH{=}C(t\text{-}Bu)_2)_2]^+$	Synthesis, NMR	[208]
445	$[Cp_2Nb(SC{=}C(C_9H_{18}))_2]^+$	Synthesis, NMR	[208]
446	$Cp_3Nb(SMe)_2$	Synthesis, IR, MW	[209]
447	$Cp_3Nb(SEt)_2$	Synthesis, IR, MW	[209]
448	$Cp_3Nb(S\text{-i-}Pr)_2$	Synthesis, IR, MW	[209]
449	$Cp_3Nb(S\text{-}n\text{-}Pr)_2$	Synthesis, IR, MW	[209]
450	$Cp_3Nb(S\text{-}n\text{-}Bu)_2$	Synthesis, IR, MW	[209]
451	$Cp_3Nb(S\text{-i-}Bu)_2$	Synthesis, IR, MW	[209]
452	$Cp_3Nb(SPh)_2$	Synthesis, IR, MW	[209]
453	$In_3Nb(SMe)_2$	Synthesis, IR, MW	[209]
454	$In_3Nb(SEt)_2$	Synthesis, IR, MW	[209]
455	$In_3Nb(S\text{-i-}Pr)_2$	Synthesis, IR, MW	[209]
456	$In_3Nb(S\text{-}n\text{-}Pr)_2$	Synthesis, IR, MW	[209]
457	$In_3Nb(SPh)_2$	Synthesis, IR, MW	[209]
458	$In_3Nb(S\text{-}n\text{-}Bu)_2$	Synthesis, IR, MW	[209]
459	$In_3Nb(S\text{-i-}Bu)_2$	Synthesis, IR, MW	[209]
460	$[Cp_2Nb(SPh)]_n$	Synthesis	[109]
461	$[Cp_2Nb(S\text{-}t\text{-}Bu)]_2$	Synthesis	[109]
Tantalum			
462	$Cp_2Ta(SMe)_2$	Synthesis, EPR, MO	[210,211]
463	$Cp_2Ta(SPh)_2$	Synthesis, EPR	[210]
464	$Cp_2Ta(SC(O)Ph)_2$	Synthesis, MS, IR, EPR, X-ray	[207]
465	Cp_2^*TaSMe		[212]

AT, anti-tumor activity; EC, electrochemistry; SC, scanning calorimetry; CIDNP, chemical induced dynamic nuclear polarization; SR, thiolate; SSES, solid state electron spectroscopy; TGA, thermogravimetric analysis.

alkali metal salt of a thiolate or the reaction of thiol with Cp_2MCl_2 in the presence of base may be used to obtain compounds of the form $Cp_2TiCl(SR)$ **228–237** [117–124], $Cp_2TiMe(SR)$ **238–242** [117,119,124], $Cp_2Ti(NCX)(SPh)$ **243–244** [125,126], and $Cp_2Ti(SR)_2$ **245–275** [127–130,134,140–142,151,153]. Oxidative addition of disulfides to Ti(II) precursors affords an alternate route to complexes of the form $Cp_2Ti(SR)_2$ (Eq. (16)) [131,143,144] as well as Ti(III) products of the form $[Cp_2Ti(SR)]_2$ **276–279** [131].

$$Cp_2TiL_2 + (RS)_2 \rightarrow Cp_2Ti(SR)_2 + 2L \qquad (16)$$

$$L = CO,\ PMe_3$$

Alternatively the Ti(III) species $[Cp_2Ti(SMe)]_2$ **276** is also derived from the metathesis reaction involving $[Cp_2TiCl]_2$ and NaSMe [157] while the species $[Cp_2Ti(SPh)]_2$ **278** is derived from the thermal decomposition of **261** [158]. Several simple titanocene thiolates also have been prepared through the addition of an alkyl- or arylthiotrimethylsilane to Cp_2TiCl_2 coupled with the elimination of Me_3SiCl [145]. The acidiolysis of a Ti—C bond by thiol has also been used to form thiolate derivatives of the form $Cp_2Ti(SR)(C_4H_3S)$ **280**, **281** [155,159] and **275** [155].

Oxidative addition of disulfides to compounds of the form $Cp_2Ti(CR'{=}NR'')$ can also be employed to access the species $Cp_2Ti(CR'{=}NR'')(SR)$ **282–285** [160,161]. Similarly, oxidative additions of trisulfides RSSSR to Ti(II) yield the compounds $Cp_2TiSR(SSR)$ **286–290** [139]:

$$Cp_2Ti(CO)_2 + RSSSR \rightarrow Cp_2Ti(SR)(SSR) + 2CO \qquad (17)$$

Alternatively, reaction of $Cp_2Ti(SH)_2$ with RS imide affords analogous compounds $Cp_2Ti(SR)SSSR$ **291**, **292** [162]. The compound **291** was crystallographically characterized (Fig. 35) [162]. The related compound $Cp_2Ti(SCH_2SSS)$ **293** was derived from the reaction of Cp_2TiS_5 and CH_2Br_2 [163]. Reaction of $Cp_2Ti(SR)_2$ with Br_2 proceeds slowly through the species $Cp_2TiBr(SR)$ **294**, **295** ultimately resulting in the elimination of disulfide and the formation of Cp_2TiBr_2 [136], while transfer of thiolate ligands from Ti to other metals has also been demonstrated [128,139,146,157].

A number of studies have examined the properties of these titanocene dithiolate complexes. Reaction–solution calorimetric studies of the compounds $Cp_2Ti(SR)_2$ where R = Me, Et, *n*-Pr and Ph [135] support previous work on molybdenum thiolate systems [137] which show that the M—SR bond strengths increase with the length of the alkyl chain. Studies show that metal—sulfur bond enthalpies are about 10^2 kJ mol^{-1} weaker than related metal—oxygen bond enthalpies [133,135,137,138]. Solid state electron spectroscopy has been reported [156], while extended Hückel MO (EHMO) calculations [142,148] support the preference of the thiolate substituents on titanocene dithiolates for an endo disposition.

The discovery in 1979 by Köpf and Köpf-Maier that Cp_2TiCl_2 exhibits cancerostatic activity has heightened interest in titanocene derivatives [213]. It has been demonstrated that two unmodified cyclopentadienyl rings are required to maintain a high level of antitumor activity [149,150] and that the chloride ligands can

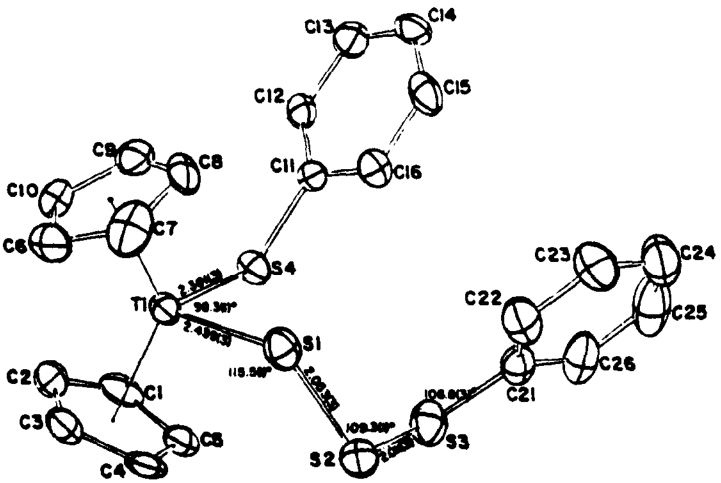


Fig. 35. ORTEP drawing of $Cp_2Ti(SPh)SSSPh$ **291**. Reproduced with permission from Ref. [162]. Copyright 1983 American Chemical Society.

be substituted for other halide or pseudohalide ligands [152]. This suggests that the best site for molecular modification is the chloride ligands and, consequently, work has been undertaken which involves studying the antitumor activity of titanocene thiolates. The compounds $Cp_2Ti(p\text{-}SC_6H_4NH_3^+Cl^-)Cl$ **234**, $Cp_2Ti(p\text{-}SC_6H_4NH_3^+Cl^-)_2$ **270** [120] and $Cp_2Ti(SC_6F_5)_2$ **271** [152] have been tested for antiproliferative activity against Ehrlich ascites tumors in mice. These complexes show a reduction in the toxicity, an increase in the therapeutic range and an increase in the water solubility while procuring cure rates of 100%.

Physicochemical studies of these compounds have been limited; however, several crystallographic reports of simple titanocene dithiolates have been published [128,129,132,160]. In the case of **245** the coordination sphere of Ti is the expected distorted tetrahedron with Ti—S bond distances of 2.403(1) Å (Fig. 36). Photoelectron spectroscopy (PES) [185] and electrochemical studies [214] of titanocene dithiolates have drawn limited attention. Although studies of the reactivity of simple titanocene thiolate complexes have not been extensive, industrial interest has

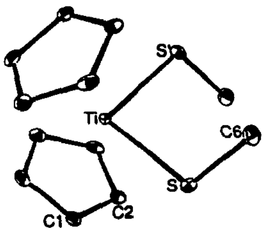


Fig. 36. ORTEP drawing of $Cp_2Ti(SMe)_2$ **245**. Reproduced with permission from Ref. [128]. Copyright 1989 American Chemical Society.

been stimulated by the applications of titanocenedithiolates as homogeneous hydrogenation catalysts [215] while early reports of such compounds led to a patent for applications as additives in furniture finishes [216]. Early attempts to synthesize titanocene thiolates using titanocene dichloride and dithiols in the presence of NEt_3 led to unstable oligomers reported still to contain chlorine [156]. An equivalent reaction using the disodium salt of 1,2-ethanedithiol was reported to give a 41% yield of a red material which analyzed to be a 1:1 ratio of the dithiolate and titanocene [155]. Similar results have been obtained when the dithiol is reacted with Cp_2TiCl_2 in the presence of gaseous ammonia [153]. Other studies claimed that the polymeric compounds $[Cp_2TiS(CH_2)_xS]_n$ [165–167] and related dithiolates were prepared by the reactions of Cp_2TiCl_2 and the appropriate dithiol, in the presence of base, under aqueous conditions. The characterization of these insoluble yellow–orange products was limited to IR spectroscopy. In view of more recent results and the hydrolytic sensitivity of early metal thiolates, these early studies are suspect. The reaction of 1,2-ethanedithiol with Cp_2TiCl_2 in the presence of excess imidazole has been shown to yield the titanium-based macrocyclic compound $Cp_2Ti(\mu\text{-}SCH_2CH_2S)_2TiCp_2$ **296** [164]. This compound exhibits a fluxional ^1H NMR spectrum which can be interpreted as being either the twisting and untwisting of a macrocyclic compound or a monomer–dimer equilibrium (Fig. 37). Complexation studies (vide infra) of **296** suggest that the former is the case as has been established for related titanocene alkoxide systems [217] and the analogous Zr compounds [187]. The 12-membered open macrocycle $Cp_2Ti(\mu\text{-}SCH_2CH_2CH_2S)_2TiCp_2$ **298** has been prepared using several synthetic methods (Fig. 38) [164]. A series of titanocene thiolatometallocycles which have additional thioether donors also have been prepared **299–304** [169]. While the macrocyclic nature of these complexes has been confirmed it is noteworthy

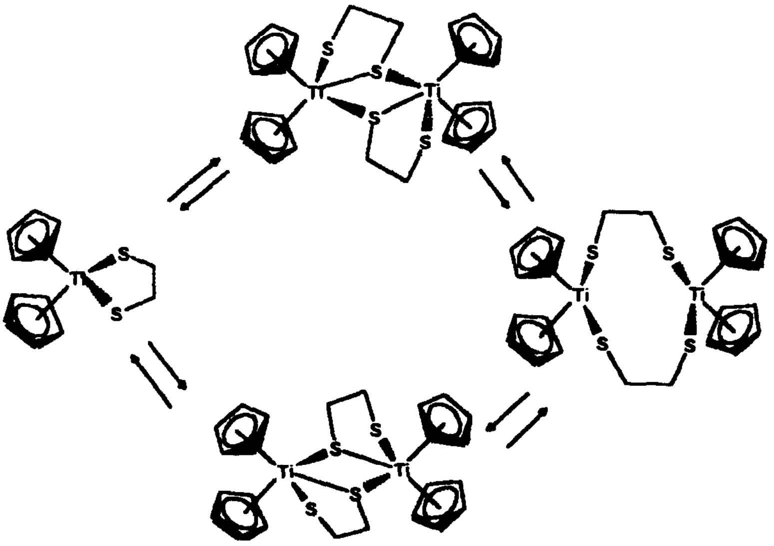


Fig. 37. Fluxionality of $[Cp_2Ti(SCH_2CH_2S)]_2$ **296**.

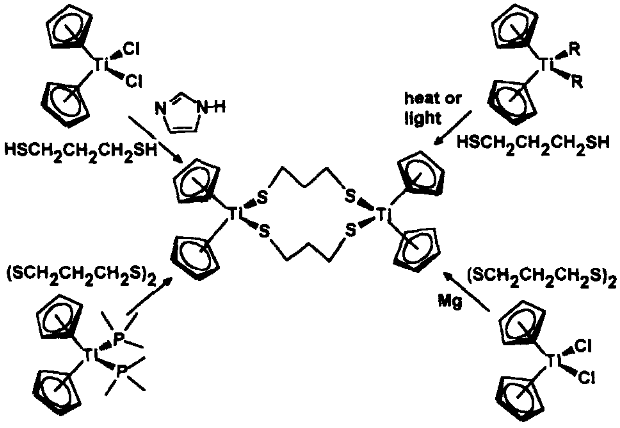


Fig. 38. Synthetic routes to $[Cp_2Ti(SCH_2CH_2CH_2S)]_2$ **298**.

that the mononuclear species $Cp_2Ti(SCH_2CH_2CH_2S)$ **297** has also been reported [168]. Attempts to make related titanium mixed alkoxide–thiolate macrocycles yields exclusively mononuclear products [154].

Several other heterofunctional metallocycles which contain metal—sulfur and metal–carbon bonds have been reported. The structurally characterized PMe_3 adduct of titanocene η^2-thioformaldehyde **307** (Fig. 39) has been prepared from the reactions of the PMe_3 adduct of titanocene–methylidene and either sulfur-containing compounds such as alkene sulfides and triphenylphosphine sulfide or elemental sulfur [170]. The related compound $Cp_2Ti(SCH_2CH_2CH_2CH_2)$ **308** was prepared in a similar manner using trimethylene sulfide as the sulfur reagent. The reactivity of **307** has been investigated via several reactions. It is found to react with H_2 to give $Cp_2Ti(SMe)_2$ and what is presumably a disproportionation product. Reaction of **307**

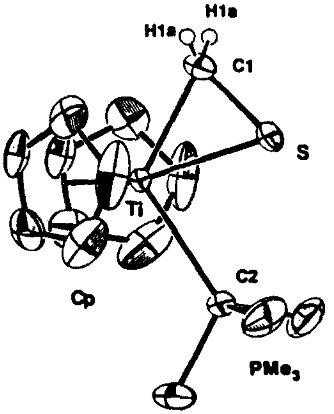


Fig. 39. ORTEP drawing of $Cp_2Ti(SCH_2)(PMe_3)$ **307**. Reproduced with permission from Ref. [170]. Copyright 1990 American Chemical Society.

with acetyl chloride gave the product $Cp_2Ti(CH_2S(CO)Me)Cl$. The reaction of **307** and MeI leads to a cationic titanocene η^2-thiomethoxymethyl PMe_3 complex. Attempts to isolate insertion products of various CC and CN triple bonds as well as C=C, C=O and C=S with **307** were unsuccessful.

5.2. Zirconium

Synthetic routes to thiolate derivatives of zirconocene **309–371** often parallel those employed for the analogous titanocene species. This is particularly true for metatheses of halide ion by thiolate [139,171,180–183], while Zr–C acidolysis by thiol also provides a convenient route to zircononene thiolate derivatives [172,175–179,187,218]. In the case of oxidative additions, the limited number of discrete Zr(II) and Zr(III) starting materials has restricted the utility of this approach; nonetheless, some interesting examples have been reported. For example, the compound $[Cp_2Zr(Et)]_2(\mu\text{-}SCH_2CH_2S)$ **330** has been synthesized by the reaction of the complex $Cp_2Zr(C_2H_4)(PMe_3)$ and 1,2-ethanedithiol [179]:

$$\begin{aligned}&Cp_2Zr(C_2H_4)(PMe_3) + HSCH_2CH_2SH\\&\quad\rightarrow Cp_2Zr(Et)SCH_2CH_2SZr(Et)Cp_2 + 2PMe_3\end{aligned} \tag{18}$$

The compound $Cp_2ZrEt(S\text{-}t\text{-}Bu)$ **318** has been prepared in a similar fashion [175]. The oxidative addition of RS–SR to $Cp_2Zr(CO)_2$ has led to $Cp_2Zr(SR)_2$ (R = Ph **336**, Et **334**) while the redox–disproportionation reaction of $Cp_2Zr(CO)_2$ and **336** gives the dimeric compound $[Cp_2Zr(SPh)]_2$ **348** [182]:

$$Cp_2Zr(SR)_2 + Cp_2Zr(CO)_2 \rightarrow [Cp_2Zr(SR)]_2 + 2CO \tag{19}$$

Gambarotta and coworkers have isolated the reactive Zr(IV) intermediate $[CpZr(SPh)(\eta^1{:}\eta^5\text{-}C_5H_4)]_2$ **349** (Fig. 40) from the reaction of $[CpZr(PMe_3)(\eta^1{:}\eta^5\text{-}C_5H_4)]_2$ with $(PhS)_2$ in toluene at room temperature [173]. A reductive coupling takes place in boiling THF, or at room temperature on the addition of pyridine, to give the fulvalene-bridged Zr(III) species $(\eta^5{:}\eta^5\text{-}C_{10}H_8][CpZr(\mu\text{-}SPh)]_2$ **350**. The compound $[\eta^5{:}\eta^5\text{-}C_{10}H_8][CpZr(SPh)_2]_2$ **351** is formed on the addition of $(PhS)_2$ to a pyridine solution of **350**, while the related species $[\eta^5{:}\eta^5\text{-}C_5H_4][\mu\text{-}NSiMe_3][CpZr(SPh)][Cp(C_5H_4SPh)Zr]$ **352** is formed in a similar reaction with $[CpZr(\eta^5{:}\eta^5\text{-}C_5H_4)]_2[\mu\text{-}NSiMe_3]$ [174].

A convenient method for the preparations of macrocyclic zirconocene thiolates **353–358** is derived from the reactions of Cp_2ZrMe_2 with dithiols which proceed with the evolution of methane [187]. In the case of $HS(CH_2)_nSH$, where $n = 2, 3$, the products can also be synthesized via reaction of Cp_2ZrMe_2 or $[Cp_2ZrHCl]_n$ with $HS(CH_2)_nSSiMe_3$ ($n = 2, 3$). Crystallographic studies of $Cp_2Zr(\mu\text{-}SCH_2CH_2S)_2ZrCp_2$ **353** and $Cp_2Zr(\mu\text{-}SCH_2CH_2CH_2S)_2ZrCp_2$ **354** show that the reagents react in a 1:1 ratio forming macrocyclic dimers [187]. The geometry of compound **353** is best described as a twisted dimer while **354** forms an open macrocycle.

The related 6-S donor macrocycle $Cp_2Zr(\mu\text{-}SCH_2CH_2SCH_2CH_2S)_2ZrCp_2$ **358**

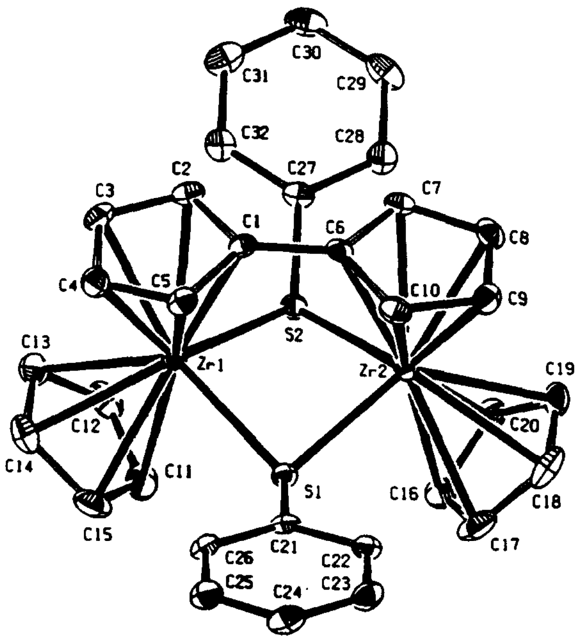


Fig. 40. ORTEP drawing of $[CpZr(SPh)(\eta^1{:}\eta^5\text{-}C_5H_4)]_2$ **349**. Reproduced with permission from Ref. [173]. Copyright 1990 American Chemical Society.

(Fig. 41), which contains a thioether sulfur in the macrocyclic backbone, has recently been reported [169]. The alkoxide–thiolate analog of **353** also has been reported together with several other metallocene complexes of oxygen- and sulfur-containing heterodifunctional ligands [154]. Variable concentration ^1H NMR experiments on **359** suggest that, in solution, an equilibrium exists between monomer and dimer.

As with Ti, small ring thiazirconacycles are accessible via elimination of alkane from precursors of the form $Cp_2ZrR(SR')$ [188,189]. In contrast, however, the related zirconocene thioaldehyde complexes $Cp_2Zr(SCHR)PMe_3$ (Fig. 42) **363–368** are quite reactive. Reaction with butyronitrile gives an imine metallocycle which tautomerizes to an enamine macrocycle [188]:

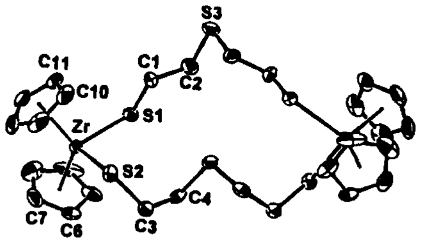


Fig. 41. ORTEP drawing of $Cp_2Zr(\mu\text{-}SCH_2CH_2SCH_2CH_2S)_2ZrCp_2$ **358**. Reproduced with permission from Ref. [169]. Copyright 1993 American Chemical Society.

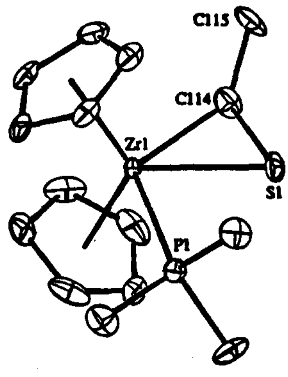
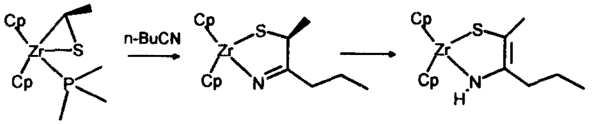
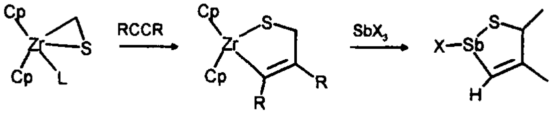


Fig. 42. ORTEP drawing of $Cp_2Zr(SCHMe)PMe_3$ **363**. Reproduced with permission from Ref. [188]. Copyright 1987 American Chemical Society.



(20)

The mechanism of formation of the zirconocene thioaldehyde complexes by heating alkylthiomethylzirconocenes has been studied [189]. Kinetic studies suggest that the transformation goes by a concerted four-center cyclometallation process as opposed to a stepwise β-hydrogen elimination–reductive elimination mechanism. Insertion reactions with acetylenes result in the expanded metallocycles **369–371** while subsequent metal atom exchange chemistry of these species affords a novel synthetic route to thiastibacycles or thiastibolanes [190]:



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Recently, Piers et al. have described C—S bond cleavage in complex cations of the form $[Cp_2Zr(SR)(THF)]^+$. They conclude that the electrophilic nature of the Zr center induces C—S bond cleavage under thermal duress, affording $[Cp_2ZrS]_2$ according to Eq. (22) [186]. During the course of this work the species $[Cp_2Zr(S\text{-}t\text{-}Bu)(THF)][BPh_4]$ **346** was structurally characterized (Fig. 43). Related thermolysis studies of complexes of the form $Cp_2Zr(SR)_2$ have been reported to proceed to similar products [181].

5.3. *Hafnium*

Hafnocene thiolates have been relatively unexplored. A majority of the work has appeared in a single publication reporting the binding modes of nitrogen–oxygen–

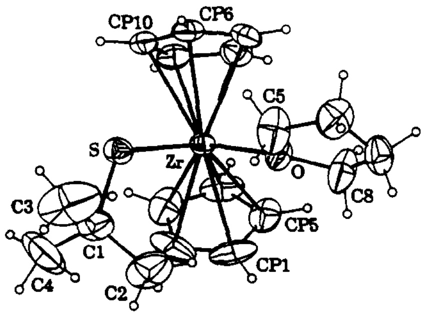
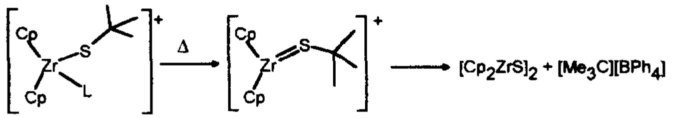


Fig. 43. ORTEP drawing of $[Cp_2Zr(S\text{-}t\text{-}Bu)(THF)][BPh_4]$ **346**. Reproduced with permission from Ref. [186]. Copyright 1992 American Chemical Society.



(22)

suflur chelating ligands [191]. Cp_2HfCl_2 was reacted with a series of ligands of the type $RNH(CO)CH_2SH$, in the presence of triethylamine, to yield the complexes $Cp_2Hf(L)Cl$ and Cp_2HfL_2 **372–383**. IR and ^1H NMR data suggest that the ligands coordinate in a bidentate fashion via a thiolate bond and a carbonyl oxygen donation to the metal center. Simple dithiolate derivatives of halfnocene, $Cp_2Hf(SR)_2$, are limited to **384–387** which have been prepared from Cp_2HfCl_2 and the appropriate lithium thiolate salt [192]. A single report describing polymeric hafnocene polythioethers has also appeared although characterization of these species is incomplete [219].

5.4. Vanadium

Nucleophilic substitution reactions of thiolate with Cp_2VX afford complexes of the form $Cp_2V(SR)$ (R = Me **388**, Et **389**, i-Pr **390**, Ph **391**, Bz **392**) [193,194]. The fragmentation of these species and related compounds have been studied in detail by mass spectral analyses [194]. These V(III) vanadocene thiolates react with CO to form the adducts $Cp_2V(SR)(CO)$ **400**, **401** [195]. Oxidative addition of thiol to vanadocene has also been exploited to prepare the compounds Cp_2VSR (R = Ph **391**, $C_6H_2(CMe_3)_2OH$ **393**) [196] and $Cp^{*}_{2}V(S\text{-}p\text{-}C_6H_4Me)$ **394** [197]. Similarly, vanadocene reacts with thioketenes to give complexes of the form $Cp_2V(SR)$ **395–398** [198]. Structural data for these compounds reveal the η^2 binding mode of the thioketene (Fig. 44). Oxidative addition of dithiols to Cp_2V yields either V(III) or V(IV) products such as $(Cp_2V)_2(m\text{-}S_2C_6H_4)$ **399** (Fig. 45) and $Cp_2V(SCH_2CH_2CH_2S)$ **406** (Fig. 46) [103]. Analogous oxidative addition of the bis-disulfide $(SCH_2CH_2CH_2S)_2$ affords the macrocyclic bimetallic species $[Cp_2V(SCH_2CH_2CH_2S)]_2$ **407** [103]. Simple dithiolate derivatives of V(IV) vanadocene such as $Cp_2V(SR)_2$ (R = Me **403**, Ph **404**) can also be prepared via the standard substitution methods employing

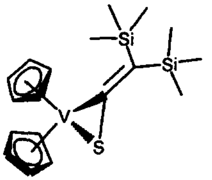


Fig. 44. Structure of $Cp_2VSC{=}C(SiMe_3)_2$ **397**.

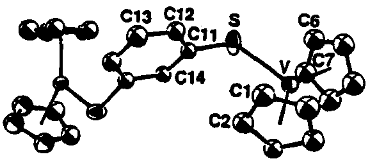


Fig. 45. ORTEP drawing of $(Cp_2V)_2(m\text{-}S_2C_6H_4)$ **399**. Reproduced with permission from Ref. [103]. Copyright 1992 American Chemical Society.

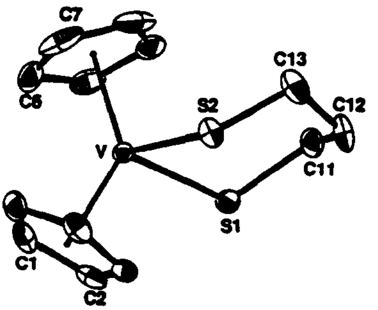


Fig. 46. ORTEP drawing of $Cp_2V(SCH_2CH_2CH_2S)$ **406**. Reproduced with permission from Ref. [103]. Copyright 1992 American Chemical Society.

Cp_2VCl_2 and thiolate salts [128,148]. Spectral [148], structural [128,148] and theoretical [148] studies of these paramagnetic species have been compared with the isoelectronic, diamagnetic, group 4 compounds with a view to examining the stereochemical role of the unpaired electron on the d^1 vanadium center.

5.5. *Niobium*

Monothiolate derivatives of niobocene $Cp_2Nb(C_4H_3S)(SR)$ **408**, **409** have been prepared via the reaction of thiolate with $Cp_2Nb(C_4H_3S)Cl$ [199]. These species undergo oxidation with I_2 to give $Cp_2Nb(C_4H_3S)(SR)I$ **410**, **411** and $Cp_2Nb(SR)I_2$ **412**, **413** [199]. Related monothiolate derivatives $Cp_2Nb(RCCR)(SR)$ **414**, **415** are synthesized by reaction of Cp_2NbH_3 with $(SR)_2$ in the presence of acetylenes [200]. A number of reports described the preparation of niobocene thiolate derivatives $Cp_2Nb(SR)_2$ **416–427** [201–209] and $In_2Nb(SR)_2$ **428–434** [201] via methods analogous to those used for the other early metals.

Oxidation of such Nb(IV) thiolates to the related Nb(V) cations $[Cp_2Nb(SR)_2]^+$ **435–440** can be achieved by reaction with I_2 or $NOPF_6$ [201–204,206]:

$$Cp_2NbCl_2 \xrightarrow[-2NaCl]{2NaSR} Cp_2Nb(SR)_2 \xrightarrow{I_2} [Cp_2Nb(SR)_2]^+ I \tag{23}$$

Redox chemistry of the Nb(IV) niobocenedithiolates has also been studied electrochemically [204]. These species exhibit reversible one-electron oxidations and reductions, although the Nb(III) anions have not been isolated [207]. Structural studies of Nb(IV) and Nb(V) analogs (Fig. 47) have been reported by Darensbourg and coworkers [204,205]. The conformation of the thiolate substituents has been shown to be responsive to changes in the oxidation state of the metal. Ab initio MO calculations also support this view [206].

Reactions of Cp_2NbH_3 with thioketenes yield Nb(IV) complexes of the form $Cp_2Nb(SCR)(SR')$ **441**, **442**, while oxidation of these complexes yields the corresponding Nb(V) cations **443–445** [208]. An X-ray structure of **441** confirmed the π bonding nature of the binding of the thioketene fragment:

A brief report [209] describes the preparation of the Nb(V) complexes $Cp_3Nb(SR)_2$ **446–452** and $In_3Nb(SR)_2$ **453–459** via the reaction of $NbCl_3(SR)_2$ and NaCp or NaIndenyl. Characterization of these compounds is limited to IR and elemental analyses.

Nb(III) derivatives are less common. The reaction of Cp_2NbBH_4 with NEt_3 and PhSH is reported to yield the species $[Cp_2Nb(SPh)]_n$ **460** which is presumed to have a polymeric structure [109]. The related compound $[Cp_2Nb(S\text{-}t\text{-}Bu)]_2$ **461** is suggested as an intermediate en route to $[Cp_2NbS]_2$ [109].

5.6. Tantalum

The number of tantalocene thiolate derivatives known is very limited. The species $Cp_2Ta(SR)_2$ (R = Me **462**, Ph **463**) have been prepared by the standard nucleophilic substitution methods and characterized by EPR [210,211,220,221]. An X-ray structure of the related species $Cp_2Ta(SCOPh)_2$ **464** has been reported [207]. The complex Cp^*_2TaSMe **465** undergoes β-hydrogen activation to give the Ta(V) hydride intermediate which undergoes subsequent S—C bond cleavage affording the species $Cp^*_2Ta(S)Me$. The energetics of this process has been studied permitting the construction of a partial free energy surface [212].

6. Thiolato-bridged heterobimetallic complexes

These are summarized in Table 5.

6.1. Titanium

The lone pairs on sulfur of transition metal thiolates have been employed to form bridges to other metal centers. Such heterobimetallics were reviewed as part of a

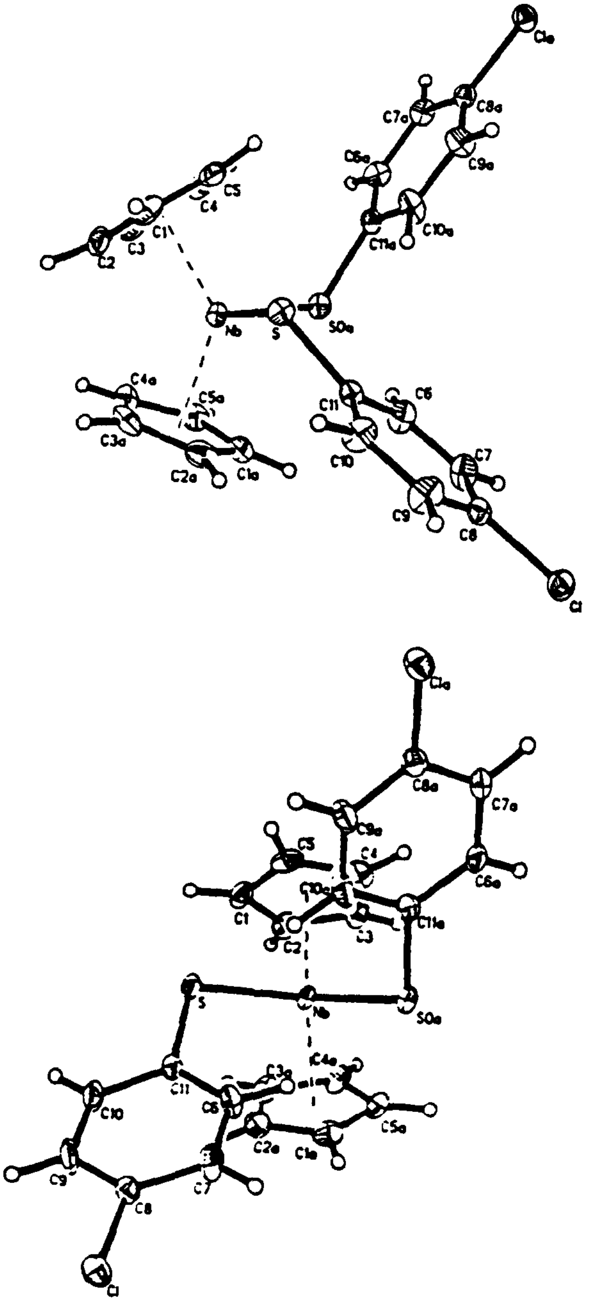
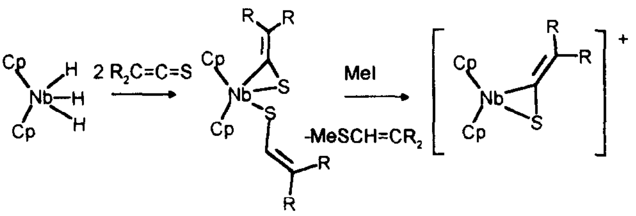


Fig. 47. ORTEP drawing of $[Cp_2Nb(S\text{-}p\text{-}C_6H_4Cl)_2]^+$ **440**. Reproduced with permission from Ref. [205]. Copyright 1990 American Chemical Society.



(24)

larger survey of the subject. Thus, in the present review of the chemistry of early metal thiolates descriptions of the early work will not be repeated. Only work subsequent to 1989 will be presented herein.

In work similar to that previously described, the systems $Cp_2Ti(\mu\text{-}SC_6H_4X)_2Mo(CO)_4$ (X = Cl **467**, Me **468**, OMe **469**) have been synthesized by reaction of the early metal thiolates with a labile Mo complex [142]. These complexes also exhibit temperature-dependent ^1H NMR spectra indicative of a dynamic process. Comparison of $\Delta G^\ddagger$ values for these fluxional processes with those of the displacement of the metalloligands $Cp_2Ti(p\text{-}SC_6H_4X)_2$ from **467–469** by CO argues in favor of a mechanism involving pyramidal inversion at sulfur.

In a related series of compounds, $[Cp_2Ti(\mu\text{-}SMe)_2CuPCy_3]PF_6$ **479** and $[Cp_2Ti(\mu\text{-}SR)_2Cu(NCMe)_2]PF_6$ (R = Me **478**, R = Et **481**) have been synthesized via the metalloligand approach [225]. Although the crystal structure of **478** shows that the methyl substituents on sulfur adopt a *cis* disposition in the solid state, variable-temperature ^1H NMR studies reveal that a dynamic process is taking place at room temperature in solution. These results have been interpreted in terms of a *cis–trans* isomerism. Inversion at sulfur has been proposed as the mechanism that leads to the time-averaged signals at ambient temperatures. Reaction of **478** with a second equivalent of $Cp_2Ti(SMe)_2$ leads to the trimetallic species **480** (Eq. (25)). Although the structure was not confirmed crystallographically, the crystal structure of the NI(0) analog **477** has been determined (Fig. 48) [128].

$$Cp_2Ti(SMe)_2 + [Cu(NCMe)_4]^+ \rightarrow [Cp_2Ti(SMe)_2Cu(NCMe)_2]^+ \rightarrow [(Cp_2Ti(SMe)_2)_2Cu]^+ \quad (25)$$

Related compounds in which the early metal metalloligand incorporated pendent donor groups were previously described. CV studies of $[Cp_2Ti(\mu\text{-}SCH_2CH_2CH_2PPh_2)_2Rh]BF_4$ **475** reveal reversible Ti(IV)/Ti(III) redox couples [141]. It is noteworthy that the bimetallic complexes exhibit reversible Ti(IV)/Ti(III) redox couples while the corresponding metalloligands do not [141,142].

An extension of the metalloligand approach to synthesizing heterometallic systems is the incorporation of early metals into the backbone of a sulfur macrocycle thus leading to macrocyclic metalloligands. The complexation chemistry of such titanium-based metalloligands with various transition metals has been studied. For example, complexation of Cu(I) by the S_4 macrocycles has been confirmed crystallographically in the cases of the complexes $[Cp_2Ti(SCH_2CH_2SCH_2)_2CH_2Cu][PF_6]$ **485** (Fig. 49)

Table 5
Thiolate-bridged early–late heterobimetallics

No.	Compound	Information	Ref.
Titanium			
467	$Cp_2Ti(\mu\text{-}p\text{-}SC_6H_4Cl)_2Mo(CO)_4$	Synthesis, NMR, UV, CV, X-ray	[142]
468	$Cp_2Ti(\mu\text{-}p\text{-}SC_6H_4CH_3)_2Mo(CO)_4$	Synthesis, NMR, UV, CV	[142]
469	$Cp_2Ti(\mu\text{-}p\text{-}SC_6H_4OCH_3)_2Mo(CO)_4$	Synthesis, NMR, UV, CV	[142]
470	$(SMe)Ti(\mu\text{-}C_5H_4PPh_2)_2(\mu\text{-}SMe)Mo(CO)_3$	Synthesis, NMR, IR	[222]
471	$(SMe)Ti(\mu\text{-}C_5H_4PR_2)_2(\mu\text{-}SMe)Mo(CO)_3$ $(R = p\text{-}C_6H_4CH_3)$	Synthesis, NMR, IR	[222]
472	$(p\text{-}SPhMe)_2Ti[\mu\text{-}C_5Me_4(PPh_2)]_2Mo(CO)_4$	Synthesis, NMR, IR	[223]
473	$(SMe)Ti(\mu\text{-}C_5H_4PPh_2)_2(\mu\text{-}SMe)W(CO)_3$	Synthesis, NMR, IR	[222]
474	$(SMe)Ti(\mu\text{-}C_5H_4PR_2)_2(\mu\text{-}SMe)W(CO)_3$ $(R = p\text{-}C_6H_4CH_3)$	Synthesis, NMR, IR	[222]
475	$[Cp_2Ti(\mu\text{-}SCH_2CH_2CH_2PPh_2)_2Rh]BF_4$	Synthesis, NMR, X-ray, UV, CV, MO calculations	[141,224]
476	$Cp_2Ti(\mu\text{-}SMe)_2NiPCy_3$	Synthesis, NMR	[128]
477	$Cp_2Ti(\mu\text{-}SMe)_2Ni(\mu\text{-}SMe)_2TiCp_2$	Synthesis, NMR, CV, X-ray, MO calculations	[128,223]
478	$[Cp_2Ti(\mu\text{-}SMe)_2Cu(NCMe)_2]PF_6$	Synthesis, NMR, CV, X-ray, MO calculations	[224,225]
479	$[Cp_2Ti(\mu\text{-}SMe)_2CuPCy_3]PF_6$	Synthesis, NMR, CV	[225]
480	$[Cp_2Ti(\mu\text{-}SMe)_2Cu(\mu\text{-}SMe)_2TiCp_2]PF_6$	Synthesis, NMR, CV	[225]
481	$[Cp_2Ti(\mu\text{-}SEt)_2Cu(NCMe)_2]PF_6$	Synthesis, NMR, CV	[225]
482	$[(Cp_2Ti(\mu\text{-}SCH_2CH_2S)_2TiCp_2)Cu]BF_4$	Synthesis, NMR, CV	[164]
483	$[(Cp_2Ti(\mu\text{-}SCH_2CH_2S)_2TiCp_2)Cu]^0$	Synthesis, EPR	[164]
484	$[Cp_2Ti(SCH_2CH_2SEt)_2Cu][PF_6]$	Synthesis, NMR	[169]
485	$[Cp_2Ti(SCH_2CH_2SCH_2)_2CH_2Cu][PF_6]$	Synthesis, NMR, X-ray, CV, MO calculations	[169]
486	$[(Cp_2Ti(SCH_2CH_2SCH_2)_2CH_2)_2Cu][PF_6]$	Synthesis, NMR	[169]
487	$[(Cp_2Ti(\mu\text{-}SCH_2CH_2CH_2S)_2TiCp_2)Ag]BPh_4$	Synthesis, NMR, CV, X-ray, MO calculations	[164,224]
488	$[(Cp_2Ti(\mu\text{-}SCH_2CH_2CH_2S)_2TiCp_2)Ag]^0$	Synthesis, EPR	[164]
Zirconium			
489	$(SMe)Zr(\mu\text{-}C_5H_4PPh_2)_2(\mu\text{-}SMe)Mo(CO)_3$	Synthesis, NMR, IR	[222]
490	$(SMe)Zr(\mu\text{-}C_5H_4PR_2)_2(\mu\text{-}SMe)Mo(CO)_3$ $(R = p\text{-}PhMe)$	Synthesis, NMR, IR	[222]
491	$Cp_2ZrCl(\mu\text{-}SCH_2CH_2)WCp(CO)_3$	Synthesis, NMR	[226]
492	$Cp_2ZrCl(\mu\text{-}SCH_2CH_2)WCp(CO)_2PMe_3$	Synthesis, NMR, IR, UV–visible	[226]
493	$Cp_2ZrCl(\mu\text{-}SCH(Me)CH_2)WCp(CO)_2PMe_3$	Synthesis, NMR, IR, UV–visible	[226]
494	$(SMe)Zr(\mu\text{-}C_5H_4PR_2)_2(\mu\text{-}SMe)W(CO)_3$ $(R = p\text{-}PhMe)$	Synthesis, NMR, IR	[222]
495	$(t\text{-}BuC_5H_4)_2Zr(SPh)(C_5H_4FeC_5H_4SPh)$	Synthesis, NMR, MS	[227]
496	$[Cp_2Zr(\mu\text{-}SCH_2CH_2S)_2ZrCp_2]Pd$	Synthesis, NMR, X-ray	[228]
497	$[(Cp_2Zr(\mu\text{-}SCH_2CH_2S)ZrCp_2)Ag]BPh_4$	Synthesis, NMR, X-ray MO calculations	[187,224]
498	$[(Cp_2Zr(\mu\text{-}SCH_2CH_2CH_2S)_2ZrCp_2)Ag]BPh_4$	Synthesis, NMR, X-ray MO calculations	[187,224]
Vanadium			
499	$CpVO((SC_5H_4)_2Fe)$	Synthesis, NMR, IR	[229]
500	$Cp^*VO((SC_5H_4)_2Fe)$	Synthesis, NMR, IR, X-ray	[229]

Table 5 (continued)

No.	Compound	Information	Ref.
Niobium			
501	$CpNbCl_2(SEt)_2NiCp$	Synthesis, NMR, X-ray	[230]
502	$CpNb(PhC_2Ph)(S\text{-}i\text{-}Pr)_2Mo(CO)_4$	Synthesis, NMR, X-ray	[230]
503	$[Cp_2Nb(SPh)_2M(CO)_4]^+$	Synthesis, NMR, X-ray	[204]
504	$Cp_2Nb(SC_{10}H_9Fe)_2$	Synthesis, EPR	[231]
505	$[Cp_2Nb(SC_{10}H_9Fe)_2]^+$	Synthesis, NMR	[231]

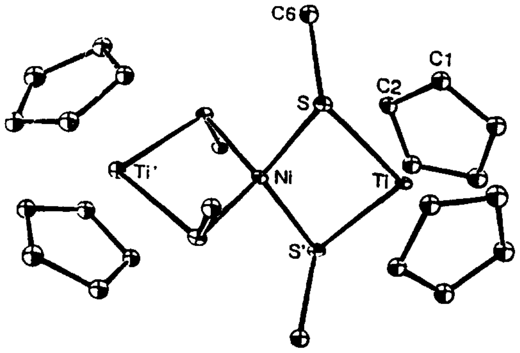


Fig. 48. ORTEP drawing of $(Cp_2Ti(SMe)_2)_2Ni$ **477**. Reproduced with permission from Ref. [128]. Copyright 1989 American Chemical Society.

[169] and $[(Cp_2Ti(\mu\text{-}SCH_2CH_2CH_2S)_2TiCp_2)Ag]BPh_4$ **487** (Fig. 50) [164]. Both **487** and **485** undergo chemical reduction leading to the species $[(Cp_2Ti(\mu\text{-}SCH_2CH_2CH_2S)_2TiCp_2)Ag]^0$ **488** and $[(Cp_2Ti(\mu\text{-}SCH_2CH_2S)_2TiCp_2)Cu]^0$ **483**.

The bonding and conformational aspects of thiolata-bridged early–late heterobimetallic compounds have been studied using extended Hückel and Fenske–Hall

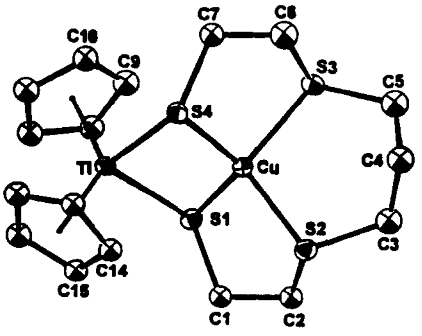


Fig. 49. ORTEP drawing of $[Cp_2Ti(SCH_2CH_2SCH_2)_2CH_2Cu][PF_6]$ **485**. Reproduced with permission from Ref. [169]. Copyright 1993 American Chemical Society.

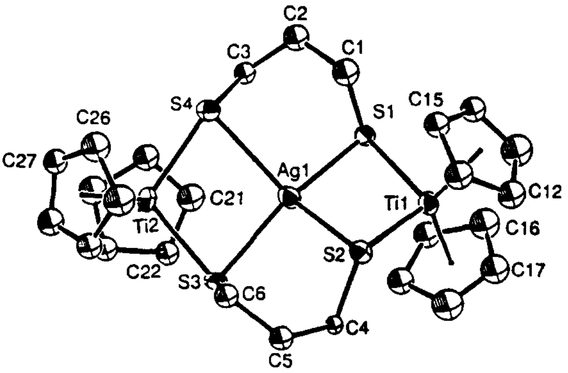
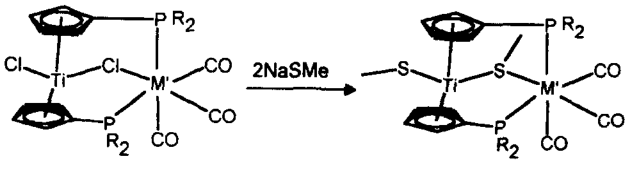


Fig. 50. ORTEP drawing of $[(Cp_2Ti(\mu\text{-}SCH_2CH_2CH_2S)_2TiCp_2)Ag]BPh_4$ **487**. Reproduced with permission from Ref. [164]. Copyright 1992 American Chemical Society.

calculations [224]. These results support the postulate of a weak dative interaction between the electron-rich late metal and the electron-deficient early metal. In cases where the late metal has a trigonal or square planar coordination sphere the MS_2M' core is folded and the R groups on the bridging S atoms adopt an *endo–cis*oid conformation. Alternatively, if the late metal has a pseudotetrahedral coordination environment, the MS_2M' core is planar and the R groups on the bridging S atoms adopt an *endo-trans*oid conformation [224].

Several other heterometallic systems have been reported which are not solely supported by thiolato bridges. The triply bridging systems $(SMe)Ti(\mu\text{-}C_5H_4PR_2)_2(\mu\text{-}SMe)M(CO)_3$ (R = Ph, M = Mo **470**, W **473**; R = PhMe, M = Mo **471**, W **474**) have been prepared by the replacement of both the terminal and the bridging chloride ligands in $ClTi(\mu\text{-}C_5H_4PR_2)_2(\mu\text{-}Cl)M(CO)_3$ with MeS^- (Eq. (26)) or by utilizing the metalloligand approach involving the reaction of $(C_5H_4PR_2)_2Ti(SMe)_2$ and $M'(CO)_3(C_7H_8)$ [222]. The related bimetallic complex $(p\text{-}SPhMe)_2Ti[\mu\text{-}C_5Me_4(PPh_2)]_2Mo(CO)_4$ **472** in which only terminal thiolates are present has been prepared by the reaction of NaS(*p*-PhMe) and $Cl_2Ti[\mu\text{-}C_5Me_4(PPh_2)_2]Mo(CO)_4$ [223].

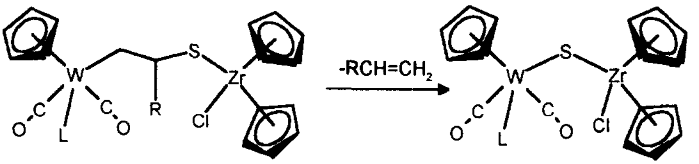


(26)

6.2. Zirconium

Zirconium analogs of **470** and **471** were prepared in a similar fashion [222]. Complexation of zirconium-based macrocycles has also been described and the structure of $[(Cp_2Zr(\mu\text{-}SCH_2CH_2CH_2S)_2ZrCp_2)Ag]BPh_4$ **498** reported [187]. The metal centers in the similar species $[(Cp_2Zr(\mu\text{-}SCH_2CH_2S)_2ZrCp_2)Pd]$ **496** adopt pseudotetrahedral coordination spheres. This species was prepared via the reaction of Cp_2ZrH_2 and $[Pd''(PPh_3)(\mu\text{-}SCH_2CH_2S)]_2$ [228].

The complexes $Cp_2ZrCl(\mu\text{-}SCH_2CH_2)WCp(CO)_2L$ (L = CO **491**, PMe_3 **492**) and $Cp_2ZrCl(\mu\text{-}SCH(Me)CH_2)WCp(CO)_2PMe_3$ **493** have been prepared by the addition of either ethylene or propylene sulfide to a mixture of $Li^+[Cp(CO)_2(L)W]^-$ and Cp_2ZrCl_2 [226]. Both **492** and **493** are transient intermediates which eliminate alkene to form sulfide-bridged bimetallic species (Eq. (27)). Compound **491** has been isolated and spectroscopically characterized; however, attempts to isolate sulfide-bridged bimetallic species from the decomposition of **491** were unsuccessful.



(27)

6.3. Vanadium

The reaction of $CpVOCl_2$ or Cp^*VOCl_2 with 1,1-ferrocene-dithiolates yields the heterobimetallic complexes $CpVO((SC_5H_4)_2Fe)$ **499** and $Cp^*VO((SC_5H_4)_2Fe)$ **500** [229]. The complex **500** was characterized crystallographically, revealing an Fe—V distance of 4.014(2) Å (Fig. 51).

6.4. Niobium

In the complex $[(Cp_2Nb(SPh)_2Mo(CO)_4]^+$ **503**, the thiolate ligands bridge the metal centers. Crystallographic data reveal an Nb—Mo distance of 3.116(2) Å and a structure very similar to that described for isoelectronic analogs [204]. Curtis and coworkers have described the reaction of $Cp_2Nb_2Cl_2(\mu\text{-}Cl)_2(CO)_4$ with $Cp_2Ni_2(\mu\text{-}SEt)_2$ which yields the paramagnetic species $CpNbCl_2(\mu\text{-}SEt)_2NiCp$ **501** [230]. Employing $CpNb(S\text{-}i\text{-}Pr)_2(PhCCPh)$ and $Mo(NCMe)_3(CO)_3$ the species $CpNb(PhC_2Ph)(S\text{-}i\text{-}Pr)_2Mo(CO)_4$ **502** was prepared. Crystal structures of both **501** (Fig. 52) and **502** (Fig. 53) indicate respective metal–metal separations of 2.759(1)

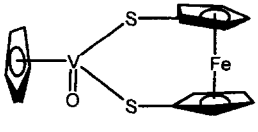


Fig. 51. Structure of $Cp^*VO((SC_5H_4)_2Fe)$ **500**.

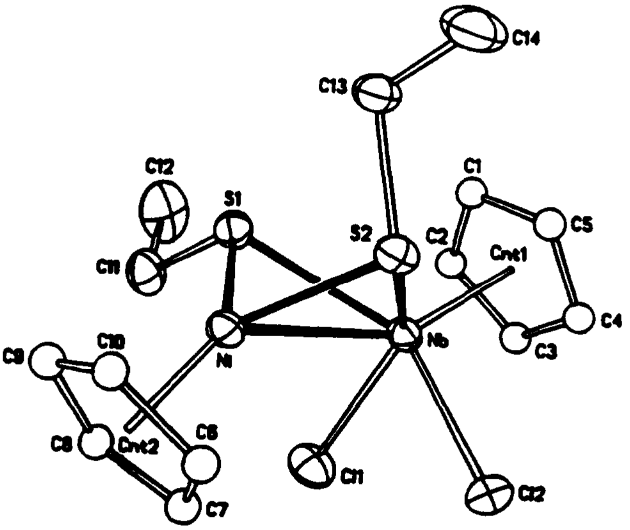


Fig. 52. ORTEP drawing of $CpNbCl_2(\mu\text{-}SEt)_2NiCp$ **501**. Reproduced with permission from Ref. [230]. Copyright 1992 American Chemical Society.

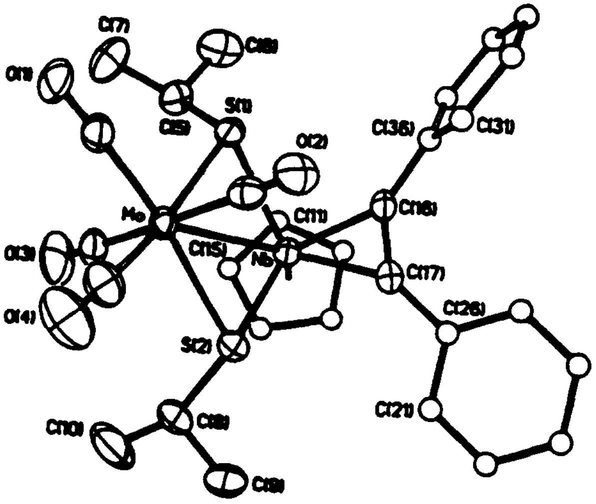


Fig. 53. ORTEP drawing of $CpNb(PhC_2Ph)(S\text{-}i\text{-}Pr)_2Mo(CO)_4$ **502**. Reproduced with permission from Ref. [230]. Copyright 1992 American Chemical Society.

and 2.996(1) Å. EHMO calculations support the localizations of the odd electron of **501** on Nb, but with a substantial Nb—Ni bond.

A brief report has described 1,1-ferrocene dithiolate derivatives of niobocene prepared by reaction of the ferrocenyldisulfide and Nb(II) precursors generated in situ [231].

7. Conclusion

This review has described the progress to date in the area of thiolate chemistry of the early metals. Much of this work has focused on the synthesis and characterization of such compounds. Despite this, few thiolate derivatives of the heavier early metals are known. Clearly, this presents a synthetic challenge as such species are expected to be sensitive and reactive. More recently examinations of the chemistry of early metal thiolates have been spurred by relevance to biological systems, MOCVD, materials, hydrodesulfurization and applications of the early metal systems in organic chemistry. It is clear that the development of the chemistry of early metal thiolates will continue to be an area of focus for many inorganic and organometallic chemists. Undoubtedly, rich and interesting reactivity awaits those who take up the challenge of early transition metal–thiolate chemistry.

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