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Mixed cyclopentadienyl/dithiolene complexes

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Abstract

Heteroleptic metal complexes with both cyclopentadienyl and dithiolene ligands are organized into four different classes of different Cp/dithiolene ratio: 2:1 complexes, of general formula $Cp_2M(dithiolene)^{0,+1}$ (M = Ti, Zr, Hf, V, Nb, Mo, W); 1:2 complexes, of general formula $CpM(dithiolene)_2^{-1,0}$ (M = Ti, V, Ta, Mo, W, Re); 1:1 complexes, of general formula CpM(dithiolene) (M = Co, Rh, Ir, Ni); bimetallic 1:1 complexes of general formula $[CpM(dithiolene)]_2$ (M = V, Cr, Mo, Fe, Ru). The synthetic procedures, electrochemical properties, structural characteristics, NMR data, magnetic properties and reactivity of those classes of complexes are described and compared, with particular attention to the geometrical changes upon electron count and the effects of the non-innocent character of the dithiolene ligands on the structures and reactivity of the complexes.

Keywords: Coordination modes; Cyclopentadienes; Dithiolenes; Metallacycles; Redox chemistry

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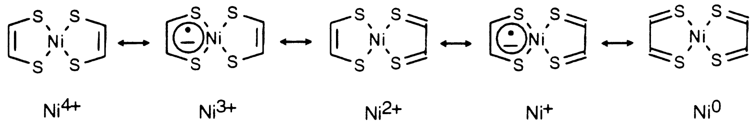
1. Scope and introduction

The remarkable optical, electric and magnetic properties of homoleptic dithiolene complexes, and the wide variety of synthetic and structural possibilities they offer, make them very attractive molecular units. For example, sulfur-rich dithiolenes such as 1,3-dithiole-2-thione-4,5-dithiolate (dmit) have been successfully engaged in Ni, Pt or Pd complexes for the elaboration of conducting and superconducting molecular materials [1,2]. The recent introduction of such ligands in heteroleptic cyclopentadienyl/dithiolene complexes such as $Cp_2Mo(dmit)$, for example, for the elaboration of novel conducting or magnetic materials, offer novel opportunities for the development of this class of compounds. Such heteroleptic complexes have also recently been used as models for the molybdenum cofactor (Moco) found in several molybdenoenzymes, with the dithiolene moiety of a 2-amino-4(3*H*)-pteridinone coordinated to a Cp_2Mo or a CpCo fragment. These novel overhangs justify the comprehensive overview of the literature on those Cp/dithiolene complexes, some of which date back to 1963, which is the purpose of this paper.

As heteroleptic cyclopentadienyl/dithiolene complexes, we understand metal complexes coordinated to, and only to, both one or several cyclopentadienyl rings and one or several dithiolene ligands. Cyclopentadienyl ligands are the prototypical $C_5H_5^-$ ligand (abbreviated Cp) and its alkyl-substituted derivatives such as $MeH_4C_5^-$ (abbreviated Cp′), $(Me_3M)C_5H_4^-$ (M = C, Si, Ge), $Me_5C_5^-$ (abbreviated Cp*) or $Me_4EtC_5^-$ (abbreviated Cp°). As shown throughout this paper, the dithiolene ligands play a major role in the chemical, structural and electrochemical properties of such complexes and it is thus appropriate to start with a short description of some of the homoleptic dithiolene complexes. Their chemistry expanded rapidly after 1962 when Schrauzer and Mayweg [3], Gray and Billig [4] and Davison et al. [5] established the uniqueness of those complexes, which stems from their ability to exist in several clearly defined oxidation states, connected through fully reversible redox steps. The first thorough overview of this field was the seminal paper by McCleverty in 1968 [6]. Homoleptic as well as heteroleptic dithiolene complexes were more recently reviewed by Müller-Westerhoff and Vance, where references to older review papers will be found [7]. The non-innocent character of the dithiolene ligand stems from its ability to be described in several oxidation states in its metal complexes. As shown below for example, the neutral square planar $Ni(S_2C_2H_2)$ complex could be described indistinctly as either an $Ni^{(IV)}$, an $Ni^{(III)}$, an $Ni^{(II)}$, an $Ni^{(I)}$ or an Ni^0 complex!



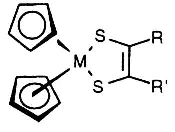
Evaluation of the actual oxidation state of the metal has been done most often indirectly through the characteristics of the ligand, i.e. the C–S and C–C bond lengths, the ^1H NMR chemical shift of the protons of the $S_2C_2H_2$ ligand. Similar questions will arise in the Cp/dithiolene complexes, further complicated by the large geometrical distortions experienced by some of those complexes upon oxidation or reduction.

Throughout this review, the different complexes will be classified according to their composition, i.e. the number of cyclopentadienyl and dithiolene ligands they bear. Four different types have been identified:

(i) complexes with two cyclopentadienyl and one dithiolene ligand, of general formula $\mathbf{Cp_2M(dithiolene)^{0,+1}}$, are common among early transition metals, normally in their IV state. Numerous examples have been described with Group 4 (Ti, Zr, Hf), Group 5 (V, Nb) and Group 6 metals (Mo, W);

(ii) complexes with one cyclopentadienyl and two dithiolene ligands, of general formula $\mathbf{CpM(dithiolene)_2^{-1,0}}$ are found with the same class of metal cations as above, in their IV or V state, with only one example reported with $Re^{(V)}$;

(iii, iv) complexes with one cyclopentadienyl and one dithiolene ligand are normally found with metals in their III oxidation state and can be divided into two classes, (iii) the monomeric complexes, of general formula **CpM(dithiolene)**, described within Group 9 metals (Co, Rh, Ir) as well as with Ni, and (iv) the dimeric complexes, of general formula **[CpM(dithiolene)]$_2$**, with various modes of association (metal–metal bond *vs* metal–chalcogen bond), observed with Group 5 (V), Group 6 (Cr, Mo) as well as a few examples with Group 8 metals (Fe, Ru).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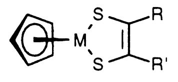
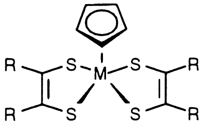
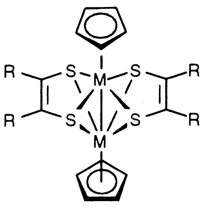
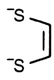

CpM(dithiolene)


CpM(dithiolene)$_2$


[CpM(dithiolene)]$_2$

Within these four classes, the different structural and electronic properties, and different chemical reactivities that are observed will be described in four separate sections. However, the preparation of these complexes involves common synthetic procedures, see Section 2.

In the present review, we will make extensive use of common (and less common) abbreviations for certain dithiolene ligands, regardless of their oxidation state, and whose structural formulae are shown below.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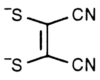
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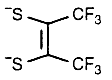
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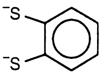
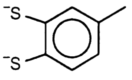

bdt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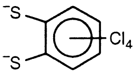
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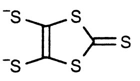
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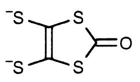
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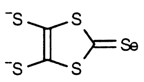
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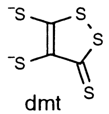
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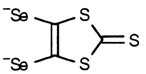
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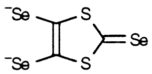
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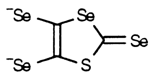
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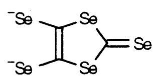
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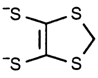
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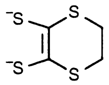
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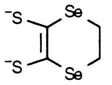
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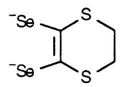
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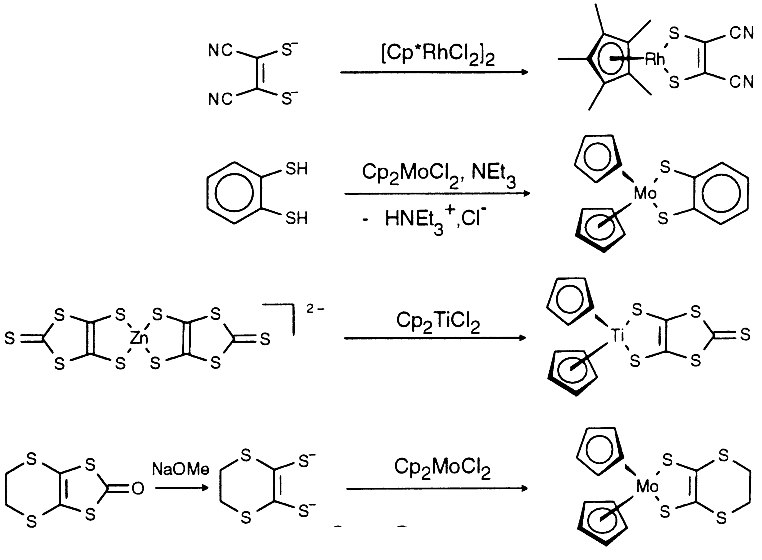
2. Synthetic procedures

2.1. Method A: metallocene halide + dithiolene salt

As illustrated below, this involves the nucleophilic displacement of halides (Cl, Br, I) by the dithiolene salt, existing either as a free-standing salt (Na_2mnt, Na_2edt) or generated in situ from the dithiole or from a protected form of the dithiolene (bis(thioester), dithiocarbonate) and a strong base (KOH, MeONa, CsOH). This very general preparation mode is found in all of the four classes except the dimeric [CpM(dithiolene)$]_2$.

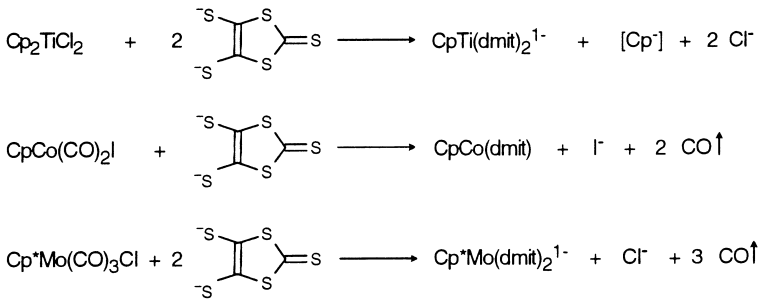


Reactions with the metallocene dichlorides Cp_2MCl_2 are found to be faster and to provide higher yields with the Group 4, 16e$^-$ metals (Ti, Zr, Hf) than with the 18e$^-$ complexes such as Cp_2MoCl_2 [8]. The reactivity of the latter compounds can be enhanced by first oxidizing them to the corresponding 17e$^-$ or 16e$^-$ species before reaction with the desired dithiolene salt, as reported for example with Cp'_2NbCl_2, oxidized to the 16e$^-$ $Cp'_2NbCl_2^+$, PF_6^- to form Cp'_2Nb(dddt)$^+$, PF_6^- after reaction with Na_2dddt [9].

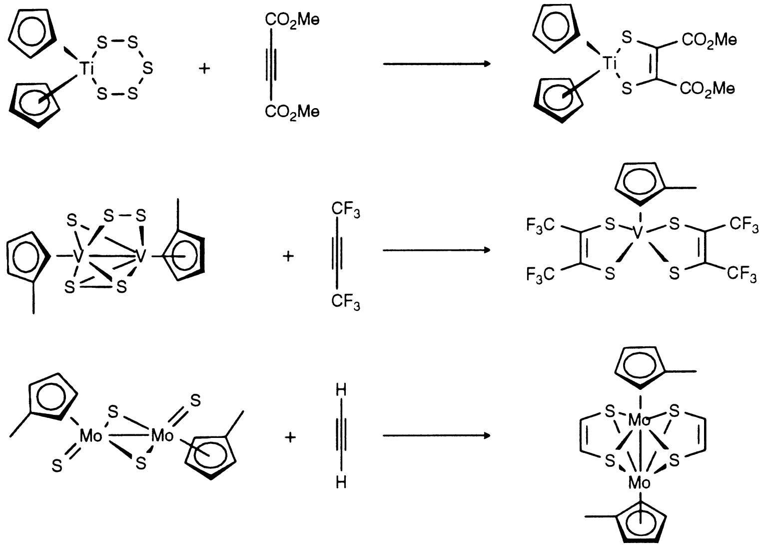
The reactions might also involve the concomitant displacement of other ligands, mainly cyclopentadienyl or carbonyl groups, followed by aerial oxidation.

2.2. Method B: metal sulfido complexes and acetylenes

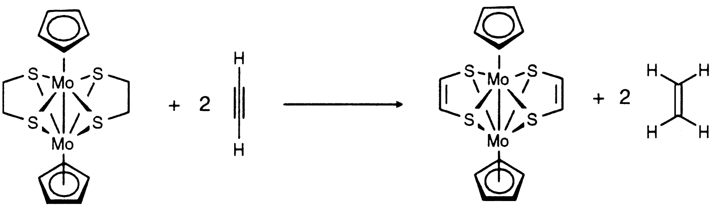
This approach, mainly developed by Rauchfuss and coworkers, involves the reaction of a metallocene chalcogenide with electrophilic acetylenes such as dimethyl

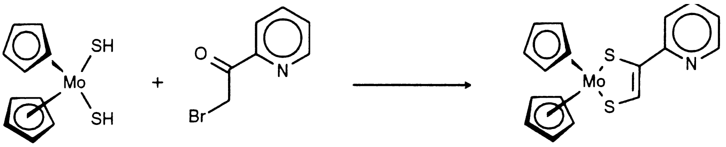


acetylenedicarboxylate (DMAD) or hexafluoro-2-butyne (CF_3–C≡C–CF_3). These reactions, originally described with Cp_2TiS_5 or Cp_2TiSe_5 [10], have been extended to $(MeCp)_2Ti_2S_4$ [11] or to other metal complexes (Mo, Ru, Fe) which were also found to react with non-activated acetylenes. It appears sometimes necessary to eliminate extra sulfur atoms engaged in the metallacycle by using Ph_3P as a desulfurizing agent.



Note that not only metal sulfides but also metal thiolate complexes have been used, as reported by Rakowski DuBois et al., in the reaction of the bimetallic $CpMo(SCH_2CH_2S)_2MoCp$ with acetylene, with concomitant ethylene elimination [12]. Along these lines, it is worth mentioning a recent method reported by Pilato and coworkers who prepared molybdocene dithiolene complexes directly from $Cp_2Mo(SH)_2$ and the readily available α-halogenoketones [13,14].



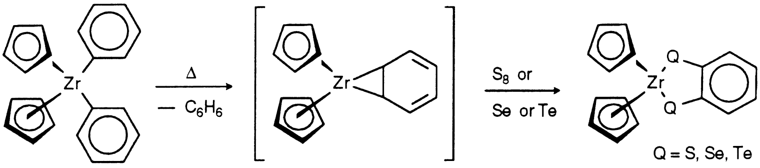


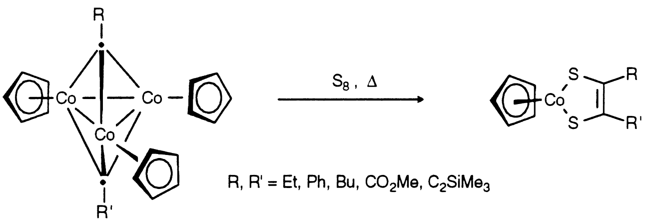
2.3. Method C: oxidative addition

Under this heading are found a wide variety of synthetic preparations which involve different oxidizing sulfurizing agents, as shown in the following sub-sections.

2.3.1. Chalcogen insertion into metal–carbon bond

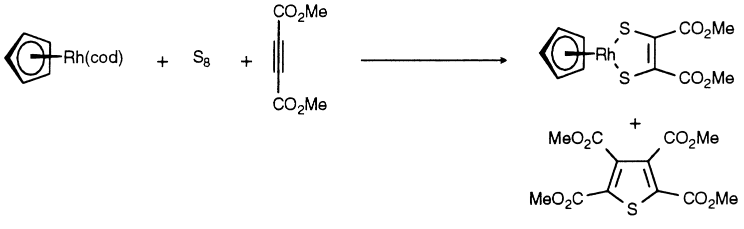
This procedure has been used with two different organometallic derivatives, the aryl zirconium Cp_2ZrR_2 [15] and the trinuclear bis(carbyne) cobalt clusters $(CpCo)_3(CR)_2$ [16]. In the former, it is believed that thermal elimination of one phenyl ring leads to a benzyne complex which inserts S, Se or Te and further rearranges to the dithiolene complex. The latter involves an intramolecular carbyne–carbyne coupling.





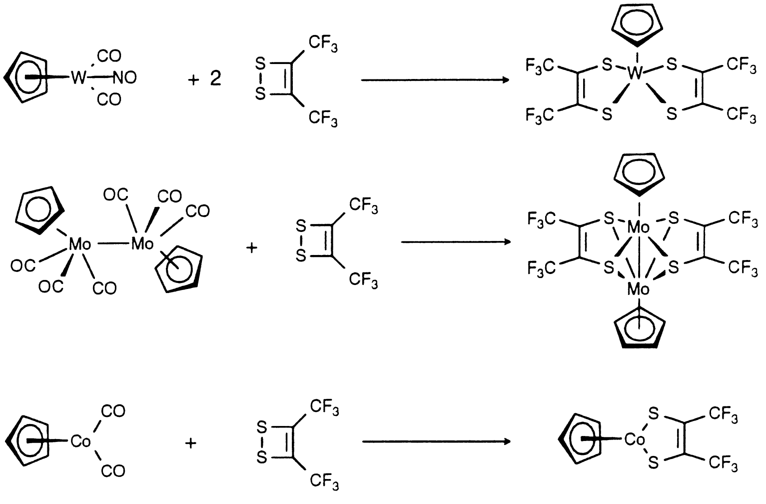
2.3.2. Reaction with chalcogens and acetylenes

This procedure, albeit used extensively in homoleptic dithiolene complex synthesis, has been described only in a few cases for the elaboration of mixed cyclopentadienyl/dithiolene complexes [17], probably because it involves relatively high temperatures and is accompanied with the formation of thiophenes.



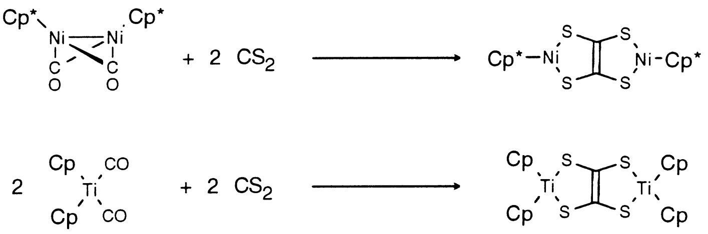
2.3.3. *Reaction with disulfides*

These reactions involve the cyclic dithietene $(CF_3)_2C_2S_2$ and its reactions with a variety of carbonyl complexes [18,19]. It represents the main access to tfd complexes, together with the reactions of the hexafluoro-2-butyne (CF_3–C≡C–CF_3) mentioned above.



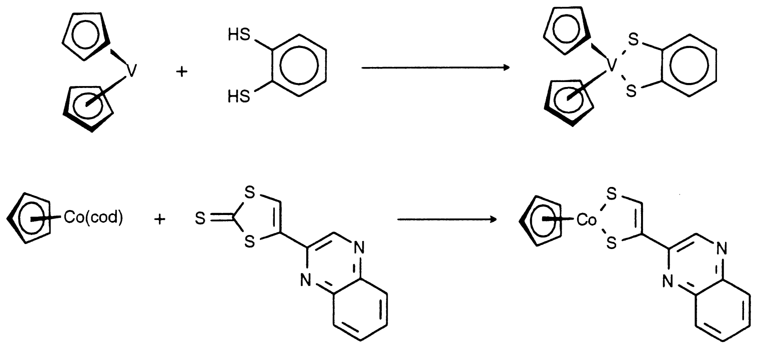
2.3.4. *Reductive dimerization of* CS_2

These reactions, described by Dahl and coworkers, involve the reductive coupling of CS_2 by low-valent metal carbonyl complexes such as $Cp_2Ti(CO)_2$ or $[Cp^*Ni(CO)]_2$ to afford the bimetallic $Cp_2Ti(C_2S_4)TiCp_2$ [20] or $Cp^*Ni(C_2S_4)NiCp^*$ [21]. The genesis of the C_2S_4 unit from two η^2-CS_2 complexes has been discussed in terms of perturbation theory arguments [22]. The homolytic cleavage of the M–C bond would provide two biradical complex species quenching their paramagnetism through the formation of a σ C–C bond and through metal spin pairing within the C_2S_4 π system. In these complexes, geometrical features and electrochemical behavior (see Sections 3.1 and 6.1) point toward an electronic distribution compatible with a tetrathiolene-like ligand, i.e. $C_2S_4^{4-}$, coordinating Ti$^{(IV)}$ or Ni$^{(III)}$ fragments.



2.3.5. *Miscellaneous*

Oxidative additions have also been described with the free dithiols [23], and, more recently, several CpCo(dithiolene) complexes were prepared from CpCo(cod) (cod = cyclooctadiene) and substituted 1,3-dithiol-2-thiones [24,25]. The formal elimination of the thiocarbonyl group may involve the corresponding 1,2-dithiete or the isomeric *o*-dithioquinone [26], as already observed from ultraviolet irradiation of diphenylvinylene dithiocarbonate in the presence of $Mo(CO)_6$ or $Ni(CO)_4$ leading to the formation of homoleptic metal dithiolene complexes [27].



2.4. *Method D: via other mixed cyclopentadienyl/dithiolene complexes*

The chemical stability of these complexes, and their rich electrochemistry, allow some of them to undergo further transformations to novel complexes, as for example by one-electron oxidation or reduction or by chemical modifications of the ligands (reduction, alkylation, acylation). These reactions will be described in subsequent sections: see Sections 3.1.5, 3.2.5, 5.5 and 6.5.

3. Cp_2M(dithiolene) complexes

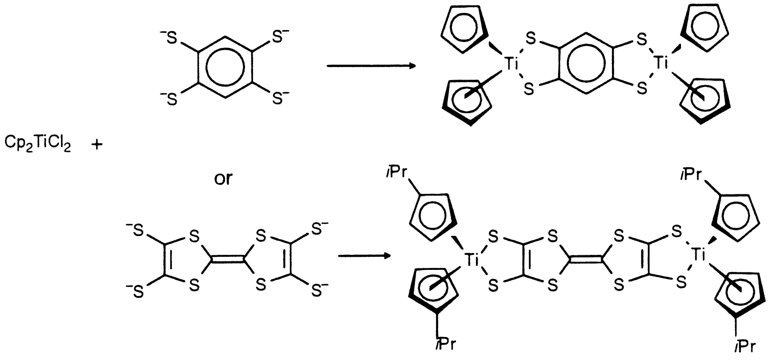
3.1. Cp_2M(dithiolene) complexes of Ti, Zr, Hf

In these diamagnetic complexes, d^0 metals, in the IV state, are complexed by two cyclopentadienyl rings and one dithiolene leading formally to a $16e^-$ complex, if one describes the dithiolene ligand as equivalent to two thiolate ligands.

3.1.1. Synthesis

The first report of a Cp_2Ti(dithiolene) complex appeared in 1965 [28]. Köpf and Schmidt described the reaction of Cp_2TiCl_2 with Na_2(mnt) as well as with benzene-1,2-dithiol in the presence of Et_3N. As seen in Table 1, most of the complexes described have, since then, been prepared by this route (method A). Yields are good to excellent. The stability of the complexes decreases from the Ti to the Zr and Hf complexes (Table 2). While the Ti complexes are highly colored (green to dark blue) and stable under normal conditions, the Zr and Hf analogs are generally yellow–orange and more prone to air and solvent decomposition [51]. Following the development of alkyl-substituted cyclopentadienes, numerous methyl-substituted titanocene dichloride precursors have been engaged in the formation of dithiolene complexes. Of particular note are the preparation of pentamethylcyclopentadienyl derivatives [48] and systematic studies on $(Me_3EC_5H_4)_2Ti$(dithiolene), E = C, Si, Ge [35].

This synthetic route has been extended to bis- and tris(dithiolene) salts such as benzene 1,2,4,5-tetrathiolate [54,55] and tetrathiafulvalene-3,4,3′,4′-tetrathiolate [56], giving rise to several bimetallic complexes, in addition to the C_2S_4 derivative prepared by Dahl and coworkers in 1987, by reductive dimerization of CS_2 with $Cp_2Ti(CO)_2$ [20], as already mentioned in Section 2.



Other routes to these complexes have been described: the reaction of activated alkynes with Cp_2TiS_5 (method B), investigated by Bolinger and Rauchfuss [10], and the insertion of S, Se or Te in Zr–C bonds of organometallic complexes, such as Cp_2ZrPh_2 (method C), reported by Gautheron et al. [15] (Table 3).

A large number of selenium derivatives, Cp_2Ti(diselenolate), was recently prepared

Table 1
Bis(cyclopentadienyl) dithiolene complexes of titanium

Compound	Synth	Information	Ref.
Cp_2Ti(bdt)	A, C	VT-^{1}H-NMR, X-ray	[28–31]
Cp_2Ti(tdt)	A	^{1}H-NMR, IR, VT-^{1}H-NMR, CV	[10,28,29,32–34]
$(Me_3C\text{-}Cp)_2Ti$(tdt)	A	^{1}H-NMR, VT-NMR, IR, MS	[35]
$(Me_3Si\text{-}Cp)_2Ti$(tdt)	A	^{1}H-NMR, VT-NMR, IR, MS	[35]
$(Me_3Ge\text{-}Cp)_2Ti$(tdt)	A	^{1}H-NMR, VT-NMR,IR, MS	[35]
Cp_2Ti(mnt)	A	IR, ^{1}H-NMR, X-ray, CV	[28,32,33,36,37]
$(Me_3C\text{-}Cp)_2Ti$(mnt)	A	^{1}H-NMR, VT-NMR, IR, MS	[35]
$(Me_3Si\text{-}Cp)_2Ti$(mnt)	A	^{1}H-NMR, VT-NMR, IR, MS	[35]
$(Me_3Ge\text{-}Cp)_2Ti$(mnt)	A	^{1}H-NMR, VT-NMR, IR, MS	[35]
Cp_2Ti(edt)	A	IR, ^{1}H-NMR, VT-^{1}H-NMR, X-ray	[29,38–40]
$(Me_3C\text{-}Cp)_2Ti$(edt)	A	^{1}H-NMR, VT-NMR, IR, MS	[35]
$(Me_3Si\text{-}Cp)_2Ti$(edt)	A	^{1}H-NMR, VT-NMR, IR, MS	[35]
$(Me_3Ge\text{-}Cp)_2Ti$(edt)	A	^{1}H-NMR, VT-NMR, IR, MS	[35]
Cp_2Ti(Ph-edt)	A	IR, ^{1}H-NMR	[39]
$Cp_2Ti(Cl_4bdt)$	A	MS, UV	[41]
$Cp_2Ti(S_2C_2(CO_2Me)_2)$	B, C	^{1}H-NMR, IR, MS, VT-NMR, CV	[10,42]
$Cp'_2Ti(S_2C_2(CO_2Me)_2)$	B	^{1}H-, ^{13}C-NMR, IR, MS, X-ray, CV	[10,11]
$Cp_2Ti(S_2C_2H(CO_2Me))$	B	^{1}H-NMR	[43]
$Cp_2Ti(S_2C_6(SMe)_4)$	A	^{1}H-NMR, UV, IR, MS	[44]
$Cp_2Ti(S_2C_6(SMe)_2S_2C_S)$		^{1}H-NMR, UV, IR, MS	[44]
$Cp_2Ti(S_2C_6(SMe)_2S_2CO)$		^{1}H-NMR, UV, IR, MS	[44]
$Cp_2Ti(S_2C_6(S_2CS)_2)$		^{1}H-NMR, UV, IR, MS	[44]
Cp_2Ti(dmit)	A	^{1}H-, ^{13}C-NMR, VT-NMR, IR, MS, CV, X-ray	[45–47]
Cp^*_2Ti(dmit)	A	^{1}H-, ^{13}C-NMR, VT-NMR, IR, CV, X-ray	[48]
$Cp_2Ti(S_2C_2S_3)$	D	UV	[49]
$Cp_2Ti(S_2C_2S_4)$	D	^{1}H-NMR, MS, UV	[49]
$Cp'_2Ti(S_2C_2S_3)$	D	^{1}H-NMR, MS, UV	[49]
$Cp'_2Ti(S_2C_2S_4)$	D	UV	[49]
Cp_2Ti(dmt)	A	^{1}H-, ^{13}C-NMR, VT-NMR, UV, IR, MS	[47,50]
Cp_2Ti(dmid)	A	^{1}H-, ^{13}C-NMR, VT-NMR, MS, IR, CV	[46,47]
Cp_2Ti(dddt)	A	^{1}H-NMR, VT-NMR, MS, IR, CV, X-ray	[46]
Cp^*_2Ti(dddt)	A	^{1}H-, ^{13}C-NMR, VT-NMR, IR, CV	[48]
Cp_2Ti(mdt)	D	^{1}H-NMR, VT-NMR, MS, CV	[46]
Cp_2Ti(dmise)	A	^{1}H-, ^{13}C-NMR, VT-NMR, IR, UV, MS	[47]

(method A) by Olk and coworkers with a series of selenium-containing dmit analogs (dsit, dsise, dsitse, dsis) [58].

3.1.2. Electrochemical behavior

Cyclic voltammetry studies have been reported for several of the d^0 Ti(IV) complexes. They all exhibit similar behavior, i.e. a reversible reduction wave, attributable to the metal-centered $Ti^{(IV)} \rightarrow Ti^{(III)}$ process and two irreversible oxidation waves processes. The irreversible character of the oxidation processes is compatible with the electronic structure of those complexes whose HOMO is strongly metal–ligand bonding. Removal of an electron from this orbital via oxidation is indeed expected to weaken severely the metal-dithiolene interaction [60]. The introduction of alkyl

Table 2
Bis(cyclopentadienyl) dithiolene complexes of zirconium and hafnium (including diselenolates and ditellurolates)

Compound	Synth	Information	Ref.
Cp$_2$Zr(bdt)	A	IR, ^{1}H-NMR	[51]
Cp$_2$Zr(tdt)	A	IR, ^{1}H-NMR	[51]
Cp$_2$Zr(mnt)	A	IR, ^{1}H-NMR	[51]
Cp$_2$Zr(edt)	A	IR, ^{1}H-NMR	[38,39]
(t-Bu-Cp)$_2$Zr(bdt)	C	^{1}H-NMR, VT-NMR	[52]
(t-Bu-Cp)$_2$Zr($S_2C_6H_4$(OMe))	C	^{1}H-NMR, VT-NMR	[52]
Cp$_2$Zr(dmt)	A	^{1}H-, ^{13}C-NMR, IR, UV, MS	[47]
Cp$_2$Zr(dmit)	A	^{1}H-, ^{13}C-NMR, IR, UV, MS	[47]
Cp$_2$Zr(dmid)	A	^{1}H-, ^{13}C-NMR, IR, UV, MS	[47]
Cp$_2$Zr(dmise)	A	^{1}H-, ^{13}C-NMR, IR, UV, MS	[47]
(t-Bu-Cp)$_2$Zr($Se_2C_6H_4$)	C	^{1}H-, ^{77}Se-NMR, MS, X-ray, VT-R	[15,52]
(t-Bu-Cp)$_2$Zr($Se_2C_6H_3$Me)	C	^{1}H-, ^{77}Se-NMR, MS	[15]
Cp$_2$Zr($Se_2C_6H_4$)	A	^{1}H-NMR, MS, IR, VT-NMR	[52,53]
(t-Bu-Cp)$_2$Zr($Te_2C_6H_4$)	C	^{1}H-NMR, VT-NMR	[52]
Cp$_2$Hf($Se_2C_6H_4$)	A	^{1}H-NMR, MS, IR, VT-NMR	[52,53]
(t-Bu-Cp)$_2$Hf($Se_2C_6H_4$)	A	^{1}H-NMR	[52]
Cp$_2$Hf(dmt)	A	^{1}H-, ^{13}C-NMR, UV, IR, MS	[47]
Cp$_2$Hf(dmit)	A	^{1}H-, ^{13}C-NMR, UV, IR, MS	[47]
Cp$_2$Hf(dmid)	A	^{1}H-, ^{13}C-NMR, UV, IR, MS	[47]
Cp$_2$Hf(dmise)	A	^{1}H-, ^{13}C-NMR, UV, IR, MS	[47]

Table 3
Bis(cyclopentadienyl) diselenolate (or ditellurolate) complexes of titanium

Compound	Synth	Information	Ref.
Cp$_2$Ti($Se_2C_2(CO_2Me)_2$)	B	^{1}H-, ^{77}Se-NMR, IR, MS, UV, CV, VT-NMR	[10]
Cp$_2$Ti($Se_2C_2(CF_3)_2$)	B	^{1}H-, ^{19}F-NMR, IR, MS, UV, VT-NMR	[10]
Cp$_2$Ti($Se_2C_6H_4$)	A, C	^{1}H-NMR, MS, IR, VT-NMR	[15,53]
Cp$'_2$Ti($Se_2C_6H_4$)	A	^{1}H-NMR, MS, IR, VT-NMR	[53]
Cp$_2$Ti($Te_2C_6H_4$)	A, C	^{1}H-NMR, MS,IR, VT-NMR	[57]
Cp$_2$Ti($Se_2C_6H_3$(OMe))	C	^{1}H-NMR, VT-NMR	[52]
(t-Bu-Cp)$_2$Ti($Se_2C_6H_4$)	A	^{1}H-NMR	[52]
Cp$^*_2$Ti($Se_2C_6H_4$)	A	^{1}H-NMR	[52]
Cp$_2$Ti(dsit)	A	^{1}H-, ^{13}C-, ^{77}Se-NMR, VT-NMR, IR, MS, CV	[58]
Cp$'_2$Ti(dsit)	A	^{1}H-, ^{13}C-, ^{77}Se-NMR, VT-NMR, IR, MS, CV, X-ray	[58]
Cp$'_2$Ti(dsise)	A	^{1}H-, ^{13}C-, ^{77}Se-NMR, VT-NMR, IR, MS, CV	[58]
Cp$'_2$Ti(dsitse)	A	^{1}H-NMR, VT-NMR, IR, MS, CV	[58]
Cp$'_2$Ti(dsis)	A	^{1}H-NMR, VT-NMR, IR, MS, CV	[58]
Cp$^\circ_2$Ti(dsit)	A	^{1}H-, ^{13}C-, ^{77}Se-NMR, VT-NMR, IR, MS, CV, X-ray	[58]
Cp$^\circ_2$Ti(dsise)	A	^{1}H-, ^{13}C-, ^{77}Se-NMR, VT-NMR, IR, MS, CV, X-ray	[58]
Cp$^\circ_2$Ti(dsitse)	A	^{1}H-, ^{13}C-, ^{77}Se-NMR, VT-NMR, IR, MS, CV	[58]
Cp$^\circ_2$Ti(dsis)	A	^{1}H-, ^{13}C-, ^{77}Se-NMR, VT-NMR, IR, MS, CV, X-ray	[58]
Cp$_2$Ti(ddds)	A		[59]

substituents on the cyclopentadienyl rings induces a cathodic displacement of the $Ti^{(III)}/Ti^{(IV)}$ redox potential by *ca* 0.25 V when going from $Cp_2Ti(dmit)$ to $Cp_2^*Ti(dmit)$ [48] or from $Cp_2Ti(dsit)$ to $Cp_2^\circ Ti(dsit)$ [58]. It was also demonstrated that the Cp* ligand not only influences the metal-centered reduction but also stabilizes the oxidized species. Indeed, the first oxidation wave of $Cp_2^*Ti(dddt)$ was observed to become fully reversible at the higher scan rates, indicating that the lifetime of the electro-oxidized species was increased by at least two orders of magnitude when compared with the unsubstituted $Cp_2Ti(dddt)$ [48].

3.1.3. Structures

In the titanium dithiolene complexes, Ti–S distances are observed between 2.45(1) Å in $Cp_2Ti(mnt)$ and 2.414(2) Å in $Cp_2Ti(dddt)$ with S–Ti–S angles between 82 and 84°. Similar angle values are observed for the titanium diselenene complexes with larger Ti–Se bond distances, between 2.56 and 2.60 Å. Reversible temperature dependence of the C_5H_5 ^1H NMR signals of $Cp_2Ti(edt)$ or $Cp_2Ti(bdt)$, first analyzed by Köpf in 1971 [29], suggested the presence of an inversion process between two folded conformers, in which the TiS_2C_2 plane would fold along the S–S hinge (Fig. 1). This was further confirmed by Kotuglu in 1972 who determined the X-ray crystal structure of $Cp_2Ti(bdt)$ and observed a folding angle of 46° [30]. Such a large folding is actually observed in every reported structure, with folding angles varying between 43° in $Cp_2Ti(mnt)$ and 51° in $Cp_2Ti(dddt)$ in the Ti/S complexes. Similar folding angles, most often even larger, are observed with the analogous diselenolene complexes as in $Cp_2'Ti(dsit)$ with $\theta = 52.4°$ or in $(t\text{-}BuCp)_2Zr(Se_2C_6H_4)$ with $\theta = 56°$ [58].

Note also that steric interactions in pentaalkyl-substituted cyclopentadienyl ligands limit this angle to 38° in $Cp_2^*(dmit)$ [48], and to 40° in $Cp_2^\circ Ti(dsit)$ [58].

3.1.4. NMR studies

The chemical shifts of the $S_2C_2H_2$(edt) ligand in the $Cp_2Ti(S_2C_2H_2)$ and $Cp_2Zr(S_2C_2H_2)$ complexes were observed at δ 7.43 and δ 7.02 respectively [38]. These values lie in the approximate region for ethylenic protons in olefins with somewhat electronegative substituents (in Na_2edt δ 6.8 [61]), thus confirming an

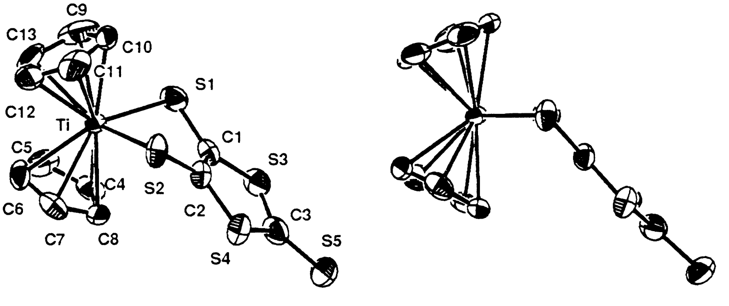


Fig. 1. ORTEP drawing of $Cp_2Ti(dmit)$ and side view showing the strong folding of the TiS_2C_2, plane along the S–S hinge [46].

electronic structure with a d^0 metal, in the IV oxidation state, and a dianionic dithiolene ligand.

As already mentioned above, the occurrence at the lower temperatures of two sharp singlets of equal intensity for the Cp rings and their coalescence at T_c is observed for all complexes of this group, albeit in different temperature ranges. The deduced activation energy $\Delta G^{\ddagger}$ ranges from 40 to 70 kJ mol^{-1}. Guyon and coworkers reported a correlation between the folding angle and the activation energy for this inversion process, as determined by variable-temperature ^{1}H NMR and the nature of the substituents on the dithiolene ligands [46] (Fig. 2). As shown in Table 4, it appears indeed that the largest folding angles are associated with the largest $\Delta G^{\ddagger}$ values, both corresponding to the most electron-rich dithiolene ligands. This electron-

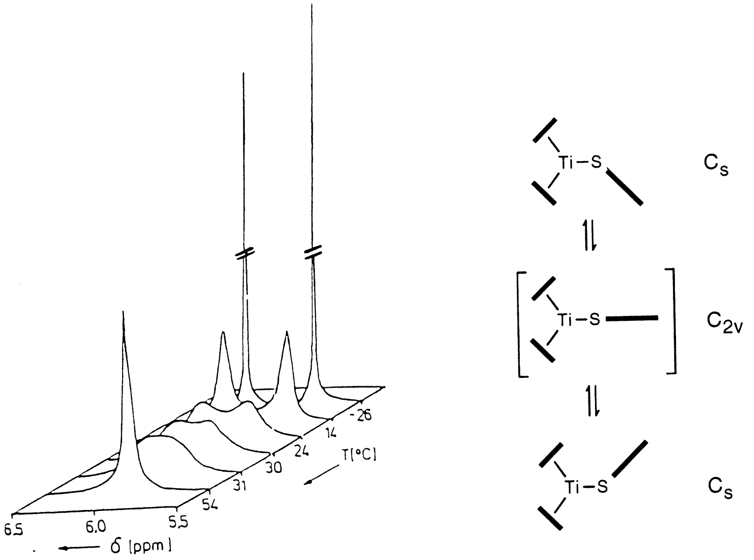


Fig. 2. Variable-temperature ^{1}H NMR spectra of Cp$_2$Ti(dmit) showing the inversion process between the two C_s conformations ($\theta > 0°$), through the C_{2v} conformation ($\theta = 0°$) [47].

Table 4
Evolution of the folding angle θ of the TiS$_2$C$_2$ ring, the activation energy $\Delta G^{\ddagger}$ for the inversion process and the half-wave potential $E^{1/2}_{\mathrm{red}}$ for the Ti$^{(IV)}$→Ti$^{(III)}$ reduction potential (from Ref. [46])

Compound	θ (deg)	$\Delta G^{\ddagger}$ (kJ mol^{-1})	$E^{1/2}_{\mathrm{red}}$ *vs* Ag/AgClO$_4$ (V)	Ref.
Cp$_2$Ti(mnt)	43	40.5 (CD$_2$Cl$_2$)	-0.95	[46]
Cp$_2$Ti[S$_2$C$_2$(CO$_2$Me)]	44	49.7 (CD$_2$Cl$_2$)	-1.20	[10]
Cp$_2$Ti(bdt)	46	58.5 (CS$_2$)		[29]
Cp$_2$Ti(edt)	46.1	61.9 (CS$_2$)		[29]
Cp$_2$Ti(dmit)	47.4	60 (CDCl$_3$)	-1.16	[46]
Cp$_2$Ti(dmid)	49	62 (CDCl$_3$)	-1.27	[46]
Cp$_2$Ti(dddt)	50	67 (CDCl$_3$)	-1.50	[46]

rich character can indeed be evaluated from the evolution of the $E_{\mathrm{red}}^{1/2}$ value associated with the reversible Ti(IV)→Ti(III) reduction process or deduced from the electrochemical series available from the homoleptic square planar complexes such as Ni(dithiolene)$_2^{-2,-1,0}$.

It should also be mentioned here that, despite larger folding angles, the diselenolate complexes seem to exhibit activation energies notably smaller than for their dithiolene analogs. For example, $\Delta G^{\ddagger}$ amounts to 60 kJ mol^{-1} (in $CDCl_3$) for Cp_2Ti(dmit) with a folding angle $\theta = 47.4°$ [46] whereas it decreases to 51 kJ mol^{-1} (in CD_2Cl_2) for Cp_2'(dsit) with $\theta = 52.4°$ [58].

The large folding angle observed in all those Group 4, 16e$^-$ complexes has been rationalized by Lauher and Hoffmann [62] on the basis of an extended Hückel fragment orbital analysis. Fragment orbitals for the Cp_2Ti moiety are shown in Fig. 3, left. In the d^0 Cp_2Ti^{2+} fragment the orbitals, of a_1 or b_2 symmetry, are all empty. On the other hand, the fragment orbital of interest for the dithiolene moiety (Fig. 3, right) is its π-character HOMO, of b_1 symmetry in the C_{2v} symmetry ($\theta = 0°$). Stabilization of this 16e$^-$ complex is only possible if the dithiolene ligand folds, allowing an otherwise symmetry-forbidden interaction between the a_1 fragment orbital of the Cp_2Ti^{2+} and the b_1 fragment orbital of the dianionic dithiolene (Fig. 3, middle). The same analysis explains why the corresponding d^2, 18e$^-$ molybdenum or tungsten complexes are not folded (see Section 3.3). On the basis of this rationale, Guyon and coworkers [46] were also able to explain the evolution of the folding angle with the donor character of the dithiolene ligand. Indeed, as shown in Fig. 3, the energy difference between the empty Cp_2Ti^{2+} a_1 fragment orbital and the π

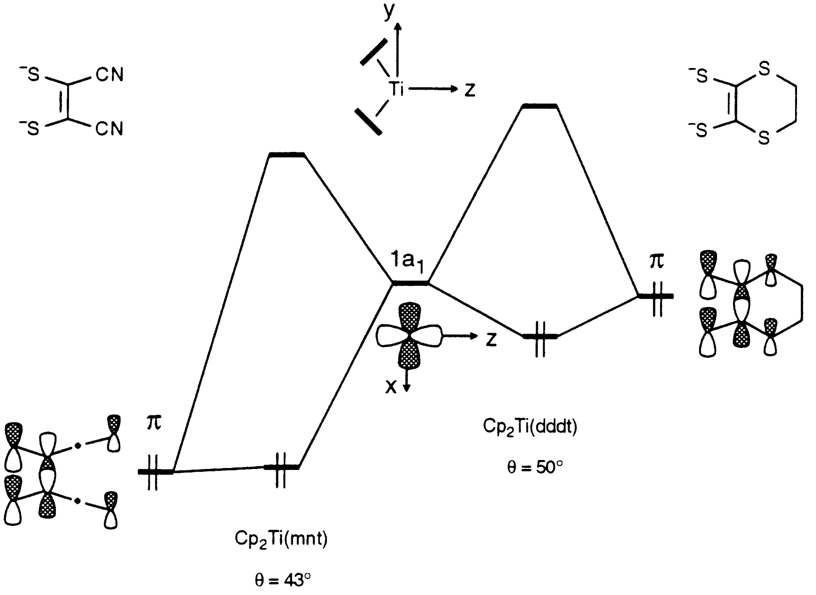
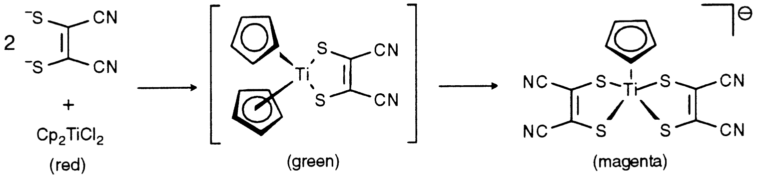


Fig. 3. Fragment orbital interaction diagram for Cp_2Ti(mnt) and Cp_2Ti(dddt) [46].

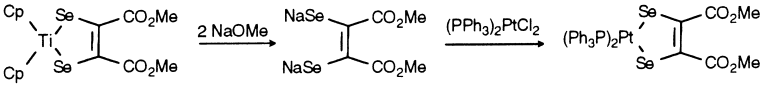
fragment orbital of the dithiolene ligand is largest with those dithiolenes bearing electron-attracting groups (–CN, –CO_2Me), whereas the two fragment orbitals are much closer in energy with electron-releasing dithiolenes such as dddt, thus allowing with the latter a stronger interaction and a larger folding angle. This stronger interaction between the two fragments is further confirmed by the observation of shorter Ti–S bond lengths in the electron-rich Cp_2Ti(dddt) complex, when compared with the Cp_2Ti(mnt) for example.

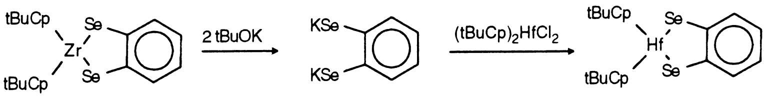
3.1.5. Reactivity

Three types of reaction have described:, (i) the displacement of one of the cyclopentadienyl rings; (ii) the displacement of the dithiolene (or diselenolate) ligand; (iii) the transformation of the dithiolene ligand itself without destroying the complex. As shown below, displacement of one of the Cp rings provides ready access to the second class of compounds to be described in this review, i.e. the **CpM(dithiolene)**$_2^{-1,0}$ complexes (see Section 4) [36,41,46].



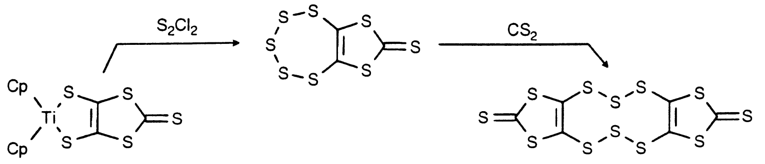
Displacement of the dithiolene ligand from its complex is by far the most common reaction. It has been particularly investigated with diselenenes to afford selenium derivatives otherwise not easily synthetized. As shown below, alcoholysis (NaOMe, t-BuOK) of the complexes provides the free diselenene which can be further derivatized (alkylation, complexation) [10,52].

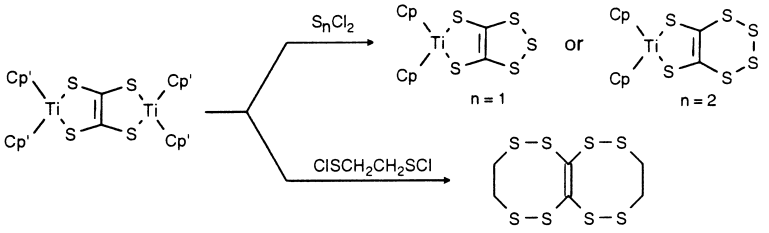




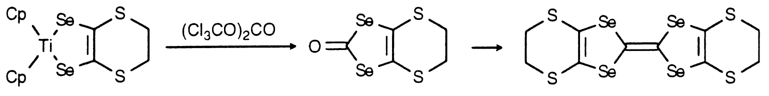
In most of the cases, however, isolation of the free dithiolene or diselenene is not necessary and complexes can be directly reacted with a variety of electrophiles, metal chlorides, alkyl and acyl halides, and sulfur chlorides, with concomitant regeneration of the titanocene (or zirconocene) dichloride. A variety of dichloro compounds L_nMCl_2 were engaged with $(C_5H_4R)_2Ti(E_2C_2Z_2)$ ($E=S$, Se, $Z=CO_2Me$) to give the ligand-exchange product $L_nM(E_2C_2R_2)$ and titanocene dichloride with $L_nMCl_2=(Ph_2PCH_2CH_2CH_2PPh_2)NiCl_2$ or $(AsPh_4)[RhCl_2(CO)_2]$ for example [10], and several alkylation and acylation reactions have been described with $Cp_2Zr(Se_2C_6H_4)$ [63]. Similarly, reactions of the bimetallic $Cp_2Ti(C_2S_4)TiCp_2$ with

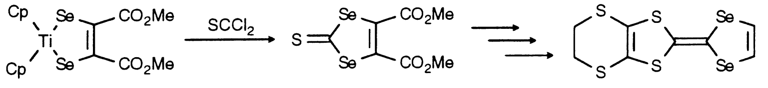
SCl_2, S_2Cl_2 or bis(sulfenyl)chlorides afford the sulfur-rich dithiolene complexes $Cp_2Ti(S_2C_2S_3)$, $Cp_2Ti(S_2C_3S_4)$ [49] or bicyclic unsaturated polysulfides [64].



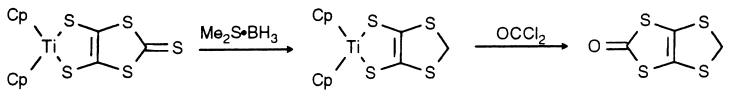


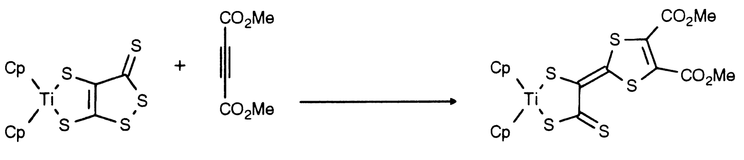
Of particular note is the reaction of diselenene complexes with phosgene or thiophosgene to yield the substituted five-membered ring molecules, 1,3-diselenol-2-one or 1,3-diselenol-2-thione, precursors of selenium analogs of various substituted tetrathiafulvalenes [10,59,65].





Reactions on the dithiolene ligand without destroying the complex are scarce. The reduction of the trithiocarbonate end group of Cp_2Ti(dmit) was accomplished with BH_3/Me_2S to afford Cp_2Ti(mdt) in good yield [46] and 1,3-dipolar addition of DMAD on Cp_2Ti(dmt) afforded the novel complex [50], whose dithiolene character is questionable.



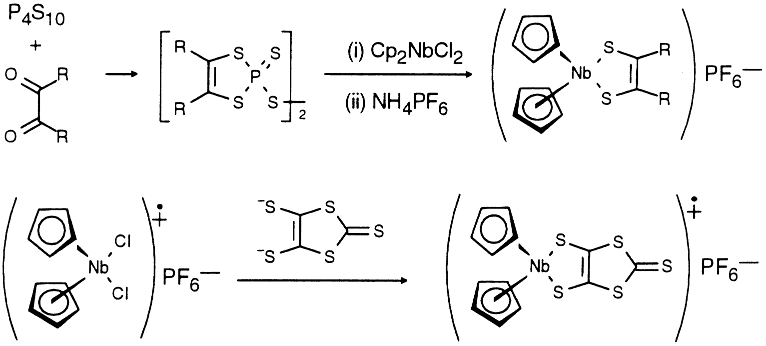


3.2. *Cp_2M(dithiolene) complexes of V and Nb*

Moving from the Group 4 (Ti, Zr, Hf) to the Group 5 (V, Nb, Ta) metal **Cp_2M(dithiolene)** complexes, we now have one more electron in the neutral species with the metal formally in its IV state: d^1 then. These $17e^-$ complexes are paramagnetic, as expected. Their geometry, mainly the possible folding of the MS_2C_2 plane, and their electrochemistry differ markedly from their Group 4 analogs. Of particular interest is also the extent of delocalization of the radical on the dithiolene ligand.

3.2.1. *Synthesis*

All the complexes described so far (Tables 5 and 6) have been prepared from the corresponding metallocene dihalide and the dianionic dithiolene (method A). As already mentioned in Section 2, readily oxidizable niobium complexes of electron-rich dithiolene ligands, such as dddt, $S_2C_2Me_2$ or $S_2C_2Ph_2$, were obtained directly in their oxidized cationic state, $Cp_2Nb(dithiolene)^+$, PF_6^-. Whereas these salts are stable, solutions of the neutral paramagnetic complexes decompose rapidly, particularly in halogenated solvents.



3.2.2. *Electrochemical behavior*

As expected from their electronic configuration, the neutral d^1 complexes exhibit one reduction $M^{(IV)} \rightarrow M^{(III)}$ and one oxidation $M^{(IV)} \rightarrow M^{(V)}$ reversible wave, as well as an irreversible process at more anodic potentials. Introduction of t-Bu or Me_3Si groups on the cyclopentadienyl ligands shifts potentials toward more cathodic values (Fig. 4).

3.2.3. *Structures*

Only two compounds have been characterized by X-ray diffraction: Cp_2V(bdt) [23] and, more recently, $(Me_3SiCp)_2Nb$(dmit) [9] (Fig. 5). As observed in the corresponding Group 4 metal complexes (see above), in both complexes the MS_2C_2 plane is folded, by 38° and 34° respectively. These values are notably smaller than those observed in the d^0 titanium or zirconium analogs, confirming the above-described extended Hückel analysis. Indeed, there are now three electrons to be

Table 5
Bis(cyclopentadienyl) dithiolene complexes of vanadium(IV) and niobium(IV)

			Solution EPR data			
Compound	Synth	Information	g_0	a_0 (mT)	solvent	Ref.
Vanadium dithiolene complexes						
Cp_2V(mnt)	A	IR, UV, CV	1.985(5)	6.0(2)	Me_2CO	[66,67]
			1.9948(5)	6.09(5)	DMSO	[68,69]
Cp_2V(dmt)	A	IR, UV, MS	1.993(2)	6.03(10)	CH_2Cl_2	[47]
Cp_2V(dmit)	A	IR, UV, MS	1.990(2)	5.82(10)	CH_2Cl_2	[47]
Cp_2V(dmid)	A	IR, UV, MS	1.989(2)	5.80(10)	CH_2Cl_2	[47]
Cp_2V(dmise)	A	IR, UV, MS	1.993(2)	6.00(10)	CH_2Cl_2	[47]
Cp_2V(bdt)	D	X-ray, CV	1.998	4.5	THF	[23]
Vanadium diselenene complexes						
$(MeCp)_2V$(dsit)	A	IR, UV, MS	2.013(2)	5.94(10)	CH_2Cl_2	[58]
$(MeCp)_2V$(dsise)	A	IR, UV, MS	2.013(2)	5.86(10)	CH_2Cl_2	[58]
$(MeCp)_2V$(dsitse)	A	IR, UV, MS	2.013(2)	5.80(10)	CH_2Cl_2	[58]
$(MeCp)_2V$(dsis)	A	IR, UV, MS	2.014(2)	5.83(10)	CH_2Cl_2	[58]
Niobium dithiolene complexes						
Cp_2Nb(dmit)	A	IR, MS, CV	1.988		CH_2Cl_2	[70]
$(Me_3SiCp)_2Nb$(dmit)	A	IR, CV, X-ray		8.29	CH_2Cl_2	[9]
(t-BuCp)$_2$Nb(dmit)	A	IR, CV		7.99	CH_2Cl_2	[9]
Cp_2Nb(dmid)	A	IR, CV	1.988	8.32	CH_2Cl_2	[70]
$(Me_3SiCp)_2Nb$(dmid)	A	IR, CV		8.21	CH_2Cl_2	[9]
(t-BuCp)$_2$Nb(dmid)	A	CV		7.96	CH_2Cl_2	[9]
Cp_2Nb(dddt)	A	IR, CV	1.999	7.95	CH_2Cl_2	[70]
$Cp_2Nb(S_2C_2Me_2)$		MS	1.9863	7.6	THF	[71]
$Cp_2Nb(S_2C_2Ph_2)$		MS	1.9863	7.6	THF	[71]

Table 6
Cationic bis(cyclopentadienyl) dithiolene niobium(V) complexes and the activation energy ($\Delta G^{\ddagger}$) for the inversion process

Compound	Synth.	Information	$\Delta G^{\ddagger}$ (kJ mol^{-1})	Ref.
$Cp_2Nb(S_2C_2Me_2)^+$, PF_6^-	A	^{1}H-NMR, IR, CV	63	[71]
$Cp_2Nb(S_2C_2Ph_2)^+$, PF_6^-	A	^{1}H-NMR, IR, CV	54	[71]
$Cp_2Nb(dmit)^+$, I^-		IR, CV		[71]
$Cp_2Nb(dmit)^+$, $TCNQ^{-\cdot}$		IR, ^{1}H-NMR	66.5	[9]
(t-BuCp)$_2$Nb(dmit)$^+$, $TCNQ^{-\cdot}$		IR, ^{1}H-NMR	67	[9]
$(Me_3SiCp)_2Nb(dmit)^+$, $TCNQ^{-\cdot}$		IR, ^{1}H-NMR	64	[9]
$Cp_2Nb(dmid)^+$, I^-		IR, CV		[70]
(t-BuCp)$_2$Nb(dddt)$^+$, PF_6^-	A	^{1}H-NMR	67.5	[9]
$(Me_3SiCp)_2Nb(dddt)^+$, PF_6^-	A	^{1}H-NMR, IR	65	[9]

distributed among the bonding and antibonding combinations of the Cp_2M-centered a_1 fragment orbital and the π-type frontier orbital of the dithiolene ligand. Partial occupation of the antibonding combination thus weakens the inter-

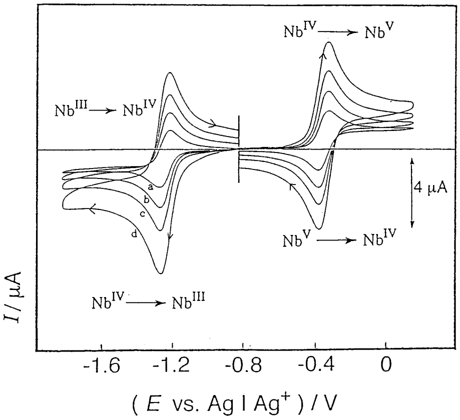


Fig. 4. Cyclic voltammetry of $Cp_2Nb(dmit)$ [70].

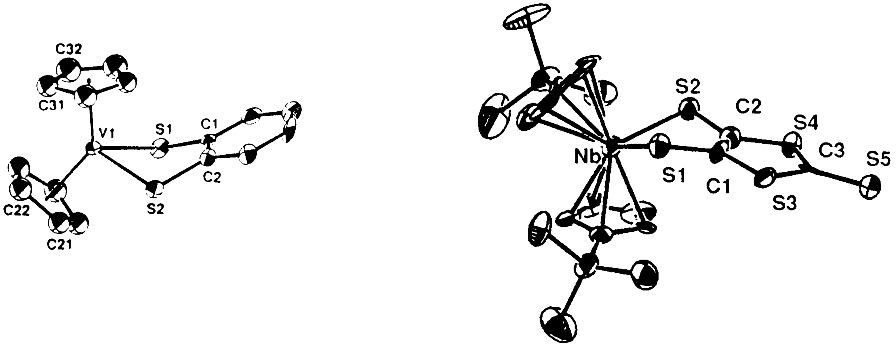


Fig. 5. ORTEP views of $Cp_2V(bdt)$ (left) [23] and $(Me_3SiCp)_2Nb(dmit)$ (right) [9].

action and decreases the folding. No structure has been reported yet for an oxidized d^0 cationic complex, which should exhibit a folding similar to that found in the isoelectronic Group 4 complexes.

3.2.4. EPR and NMR studies

Solution EPR data have been reported for all the neutral paramagnetic d^1 complexes (Table 5). Vanadium complexes show the typical eight-line resonance at g values close to 1.99 with ^{51}V ($I=7/2$) hyperfine coupling constants between 4.5 and 6 mT. Similar a_0 values are found in the vanadium selenolene complexes, but g values increase by 0.02. Niobium complexes show the typical ten-line resonance at g values close to 1.99 with ^{93}Nb ($I=9/2$) hyperfine coupling constants between 7.6 and 8.3 mT. These a_0 values are comparable, albeit smaller than those observed for 1,1-dithiolato complexes, demonstrating that the unpaired electron is mainly localized on the metal center. Anisotropy parameters for a series of vanadium complexes were deduced by Olk and coworkers from the powder diagrams of the corresponding diamagnetic titanium complexes doped (1%) with the vanadium complexes [47]. Note also that, both in the vanadium and niobium complexes, a trend toward smaller a_0 values is systematically observed upon going toward the more electron-rich dithiolenes, once again confirming a stronger interaction between the metal center and the dithiolene ligand and hence a stronger delocalization of the unpaired electron on the dithiolene.

From variable-temperature NMR data, Amaudrut and coworkers were able to identify an inversion process in the diamagnetic d^0 niobium cationic complexes that was very similar to that found in the isoelectronic d^0 titanium complexes [9,71]. Its activation energy, in the range 55–65 kJ mol^{-1}, compares very well with the values reported for analogous titanium complexes, such as Cp_2Ti(dmit) with $\Delta G^{\ddagger} = 60$ kJ mol^{-1}. In the absence of any X-ray crystal structure for the d^0 niobium complexes, however, these data indicate that they are likely to be as folded as the corresponding titanium complexes.

Magnetic susceptibility data have been reported for Cp_2V(mnt), Cp_2Nb(dmit) and Cp_2Nb(dmid) and confirm the presence of one spin per molecule. In the three compounds, Curie-type behavior was observed upon cooling, ruling out the eventuality of any intermolecular interaction in the solid state, in accordance with the unpaired electron localization on the metal atom.

3.2.5. Reactivity

Electrochemical reduction of the cationic $Cp_2Nb(S_2C_2Ph_2)^+$ or $Cp_2Nb(S_2C_2Me_2)^+$ afforded the corresponding neutral paramagnetic d^1 complexes [9,71]. On the other hand, oxidation of the neutral Cp_2Nb(dmit) or Cp_2Nb(dmid) complexes with I_2 or TCNQ afforded the corresponding salts [9].

3.3. Cp_2M(dithiolene) complexes of Mo and W

Coming now to the Group 6 metals (Mo, W), **Cp_2M(dithiolene)** complexes, with M in its IV state, i.e. d^2, exhibit an 18e$^-$ configuration. Compared with the analogous Group 4 (Ti, Zr, Hf) or Group 5 (V, Nb) complexes, they are expected to be more stable, the MS_2C_2 plane should not be folded and the d^2 character of the metal should confer them interesting electrochemical properties, mostly in the oxidation range.

3.3.1. Synthesis

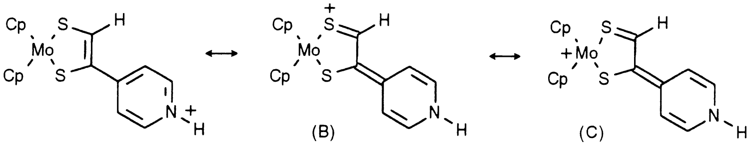
The first complexes of this class were reported in 1967 by Green and Lindsell [72] who described the synthesis of Cp_2M(mnt) and Cp_2M(tdt) (M = Mo, W) from the reaction of Cp_2MoCl_2 and the corresponding dithiolene sodium salt (method A). This procedure has been the only one until recently, when Pilato and coworkers described the direct conversion of α-substituted ketones to bis(cyclopentadienyl)molybdenum dithiolene complexes by the bis(hydrosulfido) complex, $Cp_2Mo(SH)_2$, affording a wide variety of novel compounds [13] (Table 7).

Of particular note is the preparation, by this method, of bis(cyclopentadienyl) molybdenum(S_2C_2(R)Ar), where R = H or Me and Ar is a nitrogen-containing

Table 7
Bis(cyclopentadienyl)molybdenum and tungsten dithiolene complexes

Compound	Synth	Information	Ref.
Molybdenum complexes			
$Cp_2Mo(mnt)$	A	UV, IR, ^1H-NMR	[72]
$Cp_2Mo(tdt)$	A	UV, IR, ^1H-NMR, X-ray	[72–74]
$Cp_2Mo(edt)$	A	IR, ^1H-NMR	[39]
$Cp_2Mo(bdt)$	A	X-ray	[75]
$Cp_2Mo[S_2C_2S(CH_2CH_2O)_4CH_2CH_2S]$	A	^1H-NMR, MS, CV	[76]
$Cp_2Mo(dmit)$	A	IR, ^1H-NMR, CV	[8]
$Cp_2Mo(dmid)$	A	IR, ^1H-NMR, CV	[8]
$Cp_2Mo(dddt)$	A	IR, ^1H-NMR, CV, X-ray	[8]
$Cp_2Mo(dddt)^{+\cdot}$, $TCNQ^{-\cdot}$	D	X-ray, magn. prop.	[8]
$Cp_2Mo(S_2C_2$(2-quinoxalinyl)COMe)	B	X-ray	[77]
$Cp_2Mo[S_2C_2H$(2-quinoxalinyl)]	B	UV, IR, MS, ^1H-NMR, X-ray	[13]
$Cp_2Mo[S_2C_2$(2-quinoxalinium)(H)]$^+$, BF_4^-	D	UV, X-ray	[13]
$Cp_2Mo[S_2C_2Me$(2-quinoxalinyl)]	B	UV, IR, MS, ^1H-NMR	[13]
$Cp_2Mo[S_2C_2H$(2-pyridyl)]	B	UV, IR, MS, ^1H-NMR	[13]
$Cp_2Mo[S_2C_2H$(3-pyridyl)]	B	UV, IR, MS, ^1H-NMR	[13]
$Cp_2Mo[S_2C_2H$(4-pyridyl)]	B	UV, IR, MS, ^1H-NMR	[13]
$Cp_2Mo[S_2C_2H(Ph)]$	B	UV, IR, MS, ^1H-NMR	[13]
$Cp_2Mo(S_2C_2Ph_2)$	B	UV, IR, MS, ^1H-NMR	[13]
$Cp_2Mo[S_2C_2H$(*p*-Cl-Ph)]	B	UV, IR, MS, ^1H-NMR	[13]
$Cp_2Mo[S_2C_2H$(1-pyrenyl)]	B	UV, IR, MS, ^1H-NMR	[13]
$Cp_2Mo\ (Se_2C_6H_4)$	A	IR, MS, ^1H-NMR	[53]
Tungsten complexes			
$Cp_2W(mnt)$	A	UV, IR, ^1H-NMR	[72]
$Cp_2W(tdt)$	A	UV, IR, ^1H-NMR	[72]
$Cp_2W(edt)$	A	IR, ^1H-NMR	[39]
$Cp_2W(bdt)$	A	X-ray	[78]
$Cp_2W(Se_2C_6H_4)$	A	IR, MS, ^1H-NMR	[53]

heterocycle such as 2-quinoxalyl, 2-pyridyl, 3-pyridyl or 4-pyridyl. In these complexes, besides an electronic transition at ≈550 nm, found in every Cp_2Mo(dithiolene) complex and attributable to a weak dithiolene to metal charge-transfer transition, another transition is observed, substantially red-shifted upon protonation of the heterocycle. This is attributed to an intra-ligand charge transfer (ILCT) from the donor dithiolene to the acceptor nitrogen heterocycle orbitals. The dithiolene ligand appears to stabilize the protonated form through resonance forms (B) and (C) [13].



3.3.2. Electrochemical behavior

Cyclic voltammetry data in this class of complexes were first reported by Green et al. for $Cp_2Mo[S_2C_2S(CH_2CH_2O)_3CH_2CH_2S]$ [76]. Two reversible oxidation waves were observed, as also reported later for Cp_2Mo(dmit) or Cp_2Mo(dddt) [8] (Fig. 6). This behavior is consistent with sequential one-electron oxidations of the d^2 Mo(IV) complexes to the formally $Mo^{(V)}$ and $Mo^{(VI)}$ species. Note also that protonation of the complexes bearing a nitrogen heterocycle shifts the first reversible oxidation wave to more anodic values, as expected.

3.3.3. Structures

In these complexes, Mo–S distances amount to 2.435–2.440 Å with S–Mo–S angle values around 82°. Shorter W–S distances (2.421 Å) are found in Cp_2W(tdt) when compared with Mo–S distances (2.437 Å) in the isostructural Cp_2Mo(tdt) complex. As expected from their electronic structures, these neutral d^2 $18e^-$ complexes exhibit no significant folding of the MS_2C_2 plane, which is found to be quasi-planar in every structure described ($\theta = 0$–$9°$), in striking contrast with the analogous $16e^-$ Ti, Zr and Hf complexes mentioned in Section 3.1. Also, in the $17e^-$ $Cp_2Mo(dddt)^{+\cdot}$ radical cation [8], the MoS_2C_2 metallacycle is now folded by 32.3(2)°, a value fully consistent with those observed in the isoelectronic neutral vanadium or niobium complexes described above (Fig. 7). The Mo–S distance is essentially the same, whereas the dithiolene adopts a more dithioketonic form, with much shorter C–S and much larger C–C bonds, consistent with an oxidation

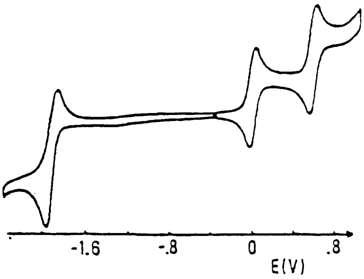
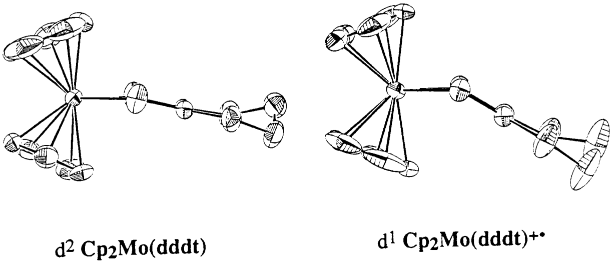


Fig. 6. Cyclic voltammetry of Cp_2Mo(dmit) [8].



d^2 Cp_2Mo(dddt)

d^1 $Cp_2Mo(dddt)^{+\cdot}$

Fig. 7. ORTEP views of the neutral d^2 Cp_2Mo(dddt) and the oxidized d^1 $Cp_2Mo(dddt)^{+\cdot}$ [8].

affecting strongly the dithiolene ligand. In the solid state these radical species were found to interact with each other by pairs through S···S interactions, giving rise to a magnetic susceptibility behavior well-described by the Bleaney–Bower equation.

In the $Cp_2Mo[S_2C_2(H)(2\text{-quinoxalyl})]$ complex recently described by Pilato and coworkers [13], the MoS_2C_2 ring is planar ($\theta = 0°$) and the quinoxaline ring is far from being coplanar with the five-membered MoS_2C_2 plane since the dihedral angle between the two planes amounts to 26.67(7)°. Upon quinoxaline protonation, however, the MoS_2C_2 plane folds slightly ($\theta = 11°$), whereas the quinoxaline ring is approaching planarity with the dithiolene moiety, confirming the interaction between the dithiolene and the quinoxalinium rings.

3.3.4. NMR, EPR and magnetic properties

The chemical shifts of the $S_2C_2H_2$(edt) ligand in the $Cp_2Mo(S_2C_2H_2)$ and $Cp_2W(S_2C_2H_2)$ complexes were observed at δ 6.06 and δ 5.88 respectively [39]. These values, close to those reported for ethylenic protons and those reported above for Cp_2Ti(edt) and Cp_2Zr(edt), confirm the dithiolene character of the structures and the IV oxidation state of the metal in these complexes. In all dithiolene complexes reported so far, only one singlet is observed for the two cyclopentadienyl rings, confirming the unfolded geometry and the absence of the inversion process observed in the d^0 analogs. However, surprisingly enough, Köpf and Klapötke reported the presence of two Cp signals and an inversion process to be observed in $Cp_2M(Se_2C_6H_4)$ (M = Mo, W) with activation energies even larger than in the d^0 complexes [53].

4. CpM(dithiolene)$_2^{-1,0}$ complexes

This class of complexes was inaugurated by McCleverty and coworkers in 1966 with the preparation of the anionic $CpTi(mnt)_2^{-1}$ [33,36]. Known with the early transition metals of Groups 4, 5, 6 and 7, these complexes are close to the above-described Cp_2M(dithiolene) complexes in which one dithiolene has been substituted for a Cp ring. Accordingly, Group 4 anionic complexes, such as $CpTi(dithiolene)_2^{-1}$, relate to d^0 species such as Cp_2Ti(dithiolene); the Group 5 complexes are known only in their d^0 neutral form, as in $Cp^*Ta(edt)_2$; the Group 6 complexes have been described both in d^2 anionic form, $Cp^*Mo(dmit)_2^{-1}$, and in the d^1 neutral species $Cp^*Mo(dmit)_2^{\cdot}$; finally, a few Group 7 d^2 complexes of $Re^{(V)}$ were recently characterized, such as $Cp^*Re(tdt)_2$, although no corresponding cationic d^2 $Cp_2Re(dithiolene)^+$ species has been described. Note, however, that the substitution of a second dithiolene ligand for a cyclopentadienyl modifies the electron count. In Green's Covalent Bond Classification [79], considering the dithiolene as an X_2 ligand (and Cp as L_2X as usual), d^0 Cp_2Ti(dithiolene) complexes are described as $16e^-$, but d^0 $CpTi(dithiolene)_2^{-1}$ as $14e^-$ complexes. Accordingly, $CpTi(dithiolene)_2^{-1}$ complexes are found to be much less stable in solution than their Cp_2Ti(dithiolene) counterparts. The same difference applies between the d^2 Cp_2Mo(dithiolene) ($18e^-$) and $CpMo(dithiolene)_2^{-1}$ ($16e^-$) complexes.

4.1. Synthesis

Preparation of these complexes involves different methods (Table 8). Displacement of chloride and cyclopentadienyl anions (with eventually concomitant displacement of CO groups) from Cp_2TiCl_2, $CpTiCl_3$, Cp^*TaCl_4, $CpMo(CO)_3Cl$, $CpW(CO)_3Cl$ or Cp^*ReCl_4 with the desired dithiolene salt afforded the corresponding complex in good yield (method A). Alternative use of the metal sulfido complexes, such as $Cp^*Re(S_3)(S_4)$ or the bimetallic $(MeCp)_2V_2S_5$, in their reaction with activated acetylenes (DMAD, hexafluoro-2-butyne) affords the $S_2C_2(CO_2Me)_2$ or tfd complexes (method B). Finally, oxidation of $[CpMo(NO)I_2]_2$ or $CpW(CO)_2NO$ with the dithietene $(F_3C)_2C_2S_2$ yields the CpM(tfd)$_2^{\cdot}$ complexes directly in their oxidized d^1 form (method C). Note that the neutral paramagnetic d^1 CpW(tfd)$_2^{\cdot}$ complex has been reduced with hydrazine to the anionic, d^2 complex, CpW(tfd)$_2^{-1}$, isolated as its tetraphenyl phosphonium salt [19], whereas the anionic d^2 Cp*Mo(dmit)$_2^{-1}$ has been electrochemically oxidized to the neutral paramagnetic d^1 Cp*Mo(dmit)$_2^{\cdot}$ [85].

4.2. Electrochemical behavior

These complexes exhibit electrochemical properties which depend on their electron count (d^0, d^1 or d^2) and which compare very well with those of the corresponding Cp_2M(dithiolene) complexes. Thus CpTi(mnt)$_2^{-1}$ reduces reversibly to the Ti(III) species at -0.73 V *vs* SCE, the same potential as Cp_2Ti(mnt). Similarly, a reversible reduction wave is observed for CpMo(mnt)$_2^{-1}$ at -1.42 V *vs* SCE and at a more

Table 8
Cyclopentadienyl bis(dithiolene) complexes

Compound	Synth	Information	Ref.
CpTi(mnt)$_2^-$, Et$_4$N$^+$	A	IR, ^{1}H-NMR, CV	[33,36]
CpTi(Cl$_4$bdt)$_2^-$, Et$_4$N$^+$	A	UV, ^{1}H-NMR	[41]
CpTi(bdt)$_2^-$, Ph$_4$P$^+$	A	IR, MS, ^{1}H-NMR, VT-NMR, X-ray	[80]
CpTi(dmit)$_2^-$, Ph$_4$P$^+$	A	CV, X-ray	[46]
(MeCp)V(tfd)$_2$	B	IR, MS, ^{1}H-, ^{19}F-NMR, UV	[81]
(MeCp)V(S$_2$C$_2$(CO$_2$Me)$_2$)$_2$	B		[81]
Cp*Ta(edt)$_2$	A	^{1}H-NMR, MS, VT-NMR	[82]
(Me$_4$EtCp)Ta(edt)$_2$	A	^{1}H-NMR, MS, VT-NMR	[82]
CpMo(mnt)$_2^{-1}$, Ph$_4$P$^+$	A	IR, ^{1}H-NMR, CV, X-ray	[33,36,83]
CpMo(tfd)$_2^{-1}$, Ph$_4$P$^+$	C	IR, UV, ^{1}H-NMR, CV	[84]
Cp*Mo(dmit)$_2^{-1}$, Ph$_4$P$^+$	A	CV, X-ray	[85]
Cp*Mo(dmit)$_2^{\cdot}$	D	X-ray, EPR	[85]
CpW(mnt)$_2^{-1}$, Ph$_4$P$^+$	A	IR, ^{1}H-NMR, CV	[33,36]
CpW(tfd)$_2^{-1}$, Et$_4$N$^+$	D	IR, UV, ^{1}H-, ^{19}F-NMR	[19]
CpW(tfd)$_2^{\cdot}$	C	IR, UV, magn. suscep.	[19]
CpW(edt)$_2^-$	A	IR, UV, ^{1}H-NMR	[38]
Cp*Re(tdt)$_2$	A	IR, ^{1}H-NMR, MS, X-ray	[86]
Cp*Re[S$_2$C$_2$(CO$_2$Me)$_2$]$_2$	B	IR, MS, ^{1}H-, ^{13}C-NMR, X-ray	[87]

cathodic potential (−1.78 V *vs* SCE) for CpW(mnt)$_2^{-1}$ (whereas the reversible first oxidation wave is observed at the same potential for the two complexes (+0.78 V *vs* SCE), confirming a metal-centered reduction process Mo$^{(IV)}$→Mo$^{(III)}$ whereas the oxidation affects mostly the dithiolene ligands, with little influence of the metal (Mo *vs* W) [33]. Indeed, CpMo(mnt)$_2^{-1}$ oxidizes at +0.78 V *vs* SCE, CpMo(tfd)$_2^{-1}$ at 0.45 V *vs* SCE and the more electron-rich Cp*Mo(dmit)$_2^{-1}$ at only 0.20 V *vs* SCE [85].

4.3. Structures

In these complexes, coordination around the metal atom can be described as square-pyramidal (four-leg piano stool) with the Cp ring at the summit of the pyramid and the four sulfur atoms forming its basal plane. The two metallacycles MS_2C_2 fold along the S–S hinges by different values, depending upon the electron count of the complexes. Whereas the d^2 complexes, such as the anionic CpMo(mnt)$_2^{-1}$ or Cp*Mo(dmit)$_2^{-1}$ and the neutral Cp*Re(tdt)$_2$, adopt an exo–exo configuration with the two dithiolenes rotating toward the Cp ring [46,85], in the d^1 Cp*Mo(dmit)$_2^{\cdot}$ complex one of the dithiolene ligands starts folding away from the Cp* ring and in the d^0 complexes, such as CpTi(bdt)$_2^{-1}$ and CpTi(dmit)$_2^{-1}$, a fully exo–endo structure is reached (Figs. 8 and 9). Extended Hückel calculations [46,82] have shown that a mechanism very similar to the one described by Hoffmann [62] for the Cp$_2$M(dithiolene) complexes can explain these different behaviors.

4.4. NMR, EPR and magnetic properties

Concerning the d^0 complexes, precise NMR data have been reported for CpTi(bdt)$_2^{-1}$ and Cp*Ta(edt)$_2^{-1}$. In the former, one single sharp signal was observed

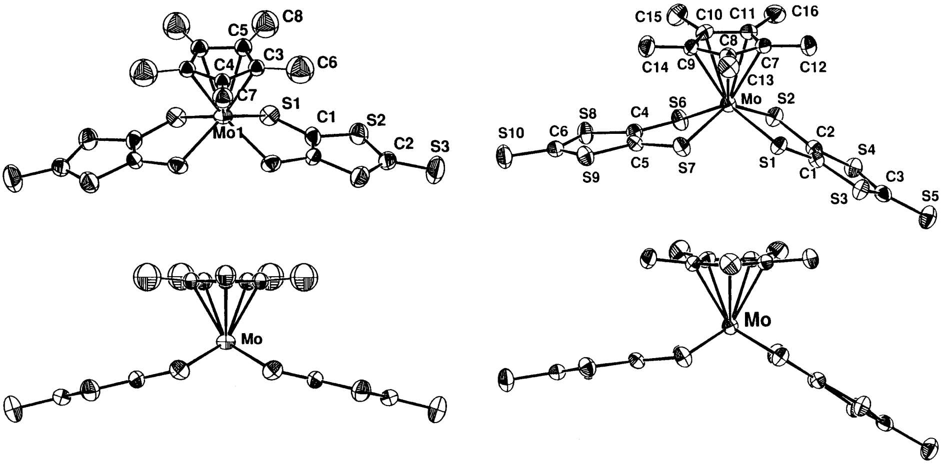


Fig. 8. ORTEP views of the d^2 Cp*Mo(dmit)$_2^{-1}$ (left) and the oxidized d^1 Cp*Mo(dmit)$_2^{\cdot}$ (right) [85].

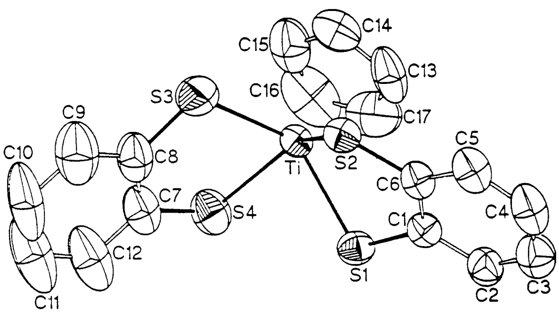


Fig. 9. ORTEP view of $\mathrm{CpTi(bdt)}_2^{-1}$ [80].

for the protons of the Cp ring, whereas the aromatic protons of the bdt ligands were hidden in a complex multiplet together with the protons of the PPh_4^+ cation. No inversion process was observed for the Cp protons, down to −81 °C [80]. In the latter, the methyl groups of the Cp* ligand were observed as a sharp singlet and the broad peak of the edt protons, which sharpens above 40 °C, appears as two singlets (δ 7.14, 7.84) at −50 °C [82]. This behavior indicated the presence of two conformers in equilibrium, each of which contains orientationally non-equivalent dithiolene ligands, as confirmed later on from the X-ray structure determinations of isostructural $\mathrm{Ti}^{(\mathrm{IV})}$ d^0 complexes (Fig. 9). Furthermore, the chemical shift for the protons of one of the edt ligands (at δ 7.84) is significantly larger than the values found for example in the d^0 $\mathrm{Cp_2Ti(edt)}$ or $\mathrm{Cp_2Zr(edt)}$, indicating a stronger interaction with the metal.

On the other hand, in the d^2 $\mathrm{CpW(edt)}_2^{-1}$, edt protons chemical shift is observed at δ 5.35, a value even smaller than those found for $\mathrm{Cp_2Mo(edt)}$ (δ 6.08) or $\mathrm{Cp_2W(edt)}$ (δ 5.88). This shielding is probably attributable to the added negative charge of this d^2 complex.

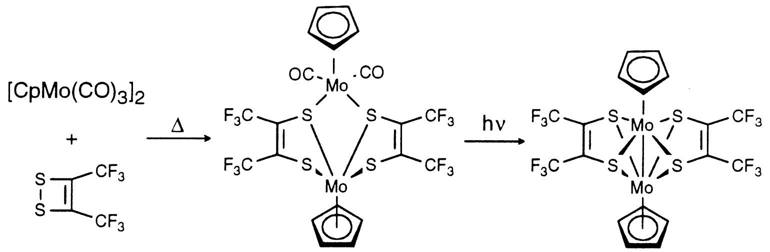
Magnetic properties of the paramagnetic d^1 complexes have been partially investigated. A magnetic moment of 1.68 μ_B mol^{-1} was determined for $\mathrm{CpW(tfd)}_2^{\cdot}$, confirming the presence of one $S = 1/2$ per molecule. Single-crystal EPR data were reported for $\mathrm{Cp^*Mo(dmit)}_2^{\cdot}$. The temperature dependence of the spin susceptibility follows a Curie–Weiss law with $\theta = -38$ K, indicating the presence of strong antiferromagnetic interactions in the solid state. Below $T_{\mathrm{N\acute{e}el}} = 8$ K, the occurrence of an antiferromagnetic ground state is confirmed by the observation of antiferromagnetic resonance [85].

5. Bimetallic [CpM(dithiolene)]$_2$ complexes

Complexes with a 1:1 stoichiometry, i.e. one cyclopentadienyl for one dithiolene ligand can be divided into two classes: the monomeric **CpM(dithiolene)** and the dimeric **[CpM(dithiolene)]$_2$**. The latter class of compounds will be presented first because it mainly involves early transition metals (V, Mo), as in the previous complexes. The monomeric **CpM(dithiolene)** complexes (M = Co, Rh, Ir, Ni) will be described in Section 6.

5.1. Synthesis

Most of these complexes have been prepared by oxidative addition (method C) of the free dithiole or the dithietene on carbonyl complexes (Table 9). Intermediate carbonylated complexes have been isolated in the reactions with $[CpMo(CO)_3]_2$; prolonged refluxing in methylcyclohexane or UV irradiation allows for full carbonyl displacement.



Original cubane-like clusters containing an Fe_4S_4 core (Fig. 10), $Cp_2^{(*)}(S_2C_2Ph_2)_2Fe_4S_4$, have been obtained from the reaction of $Cp_2Fe_2(CO)_4$ or $Cp_2^*Fe_2(CO)_4$ with S_8 and diphenylacetylene, together with the known $Cp_4^{(*)}Fe_4S_4$ clusters which are thought to be intermediates in this reaction [98,99]. Those complexes exhibit four reversible redox waves, indicating the existence of five discrete species, $[Cp_2^{(*)}(S_2C_2Ph_2)_2Fe_4S_4]^n$, $n = -2, -1, 0, +1, +2$. The corresponding cation radical ($n = +1$) was obtained by electrolysis or ferricinium oxidation.

Table 9
Bimetallic $[CpM(dithiolene)]_2$ complexes

Compound	Synth	Information	Ref.
$[CpV(bdt)]_2$	C	X-ray	[23]
$[CpV(tfd)]_2$	C	IR, magn. susc., MS, CV	[18,19,34]
$[CpCr(tfd)]_2$	C	IR, X-ray	[18,88]
$[CpMo(tfd)]_2$	C	IR, ^{19}F-NMR, CV, UV, X-ray	[18,34,89]
$[CpMo(edt)]_2$	B	IR, ^{1}H-NMR, MS, X-ray, CV	[12,90,91]
$[CpMo(S_2C_2(H)Ph)]_2$	B	IR, ^{1}H-NMR, MS	[12]
$[CpMo(S_2C_2(Me)Ph]_2$	B	IR, ^{1}H-NMR, MS	[12]
$[(MeCp)Mo(edt)]_2$	B	^{1}H-, ^{95}Mo-NMR	[92–94]
$[CpMo(tdt)]_2$		^{1}H-NMR, UV, MS, X-ray	[90]
$[CpW(edt)]_2$	B	^{1}H-NMR, MS	[95]
$[CpFe(tfd)]_2$	B	IR, MS, X-ray	[96]
$[CpFe(bdt)]_2$	A	IR, MS, ^{1}H-NMR, X-ray	[97]

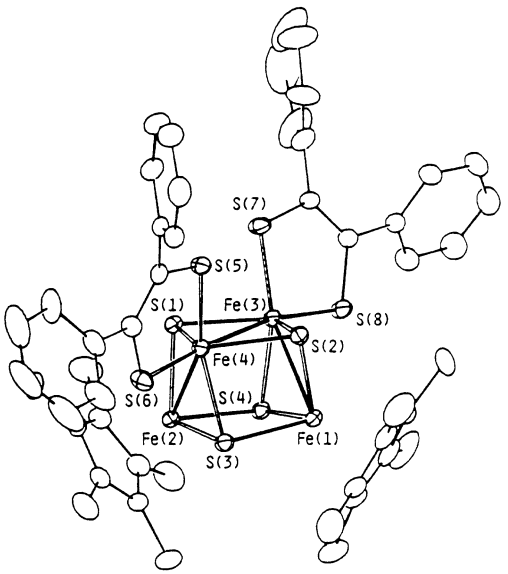


Fig. 10. ORTEP diagram of $Cp^{2*}(S_2C_2Ph_2)Fe_4S_4$ [98].

A specific preparation method of the molybdenum complexes has been extensively described by Rakowski DuBois et al. [12]. It involves the exchange reaction of bimetallic dithiolate (not dithiolene) complexes $CpMo(SCH_2CHRS)_2MoCp$ with acetylenes $R'{-}C{\equiv}C{-}R''$ to provide the ethylenes $H_2C{=}CHR$ and the bimetallic dithiolene complexes $[CpMo(S_2C_2R'R'')]_2$. This reaction has been extended to the hydrosulfido complex $[(MeCp)Mo(S)SH]_2$ [92] as well as the sulfido complex $[(MeCp)MoS(\mu\text{-}S)]_2$ [100] which both afforded $[(MeCp)Mo(edt)]_2$ upon reaction with acetylene. A similar reaction with the tungsten analog $[CpWS(\mu\text{-}S)]_2$ afforded the dimeric $[CpW(edt)]_2$ [95]. Similar reactions are involved in the preparation of iron complexes such as $[CpFe(tfd)]_2$ from $[CpFe(S_2)]_2$ and hexafluorobutyne [96].

5.2. Electrochemistry

Little is known of the electrochemical properties of the vanadium(III) complexes except that $[CpV(tfd)]_2$ reduces reversibly to a paramagnetic dianion whose EPR spectra have been reported [34]. Data in the oxidation range have not been reported.

An irreversible $2e^-$ reduction wave has been reported in $[CpMo(tfd)]_2$ together with a reversible one-electron oxidation wave [34,89]. Substituting the edt ligand for the electron-withdrawing tfd one shifts this oxidation potential in $[CpMo(edt)]_2$ by 0.65 V toward more cathodic potentials, as expected, and allows for the observation of a second irreversible oxidation wave to the dicationic $[CpMo(edt)]_2^{2+}$ [91]. Methyl substitution on the cyclopentadienyl rings shifts the oxidation potential from 0.23 V (*vs* SCE) in $[CpMo(edt)]_2$ to 0.15 V (*vs* SCE) in

[(MeCp)Mo(edt)]$_2$. Of particular note is the electrochemical behavior of the corresponding dithiolate complex [CpMo(SCH$_2$CH$_2$S)]$_2$ which oxidizes reversibly to the cation radical at 0.15 V (*vs* SCE), i.e. at a lower potential than the conjugated [CpMo(edt)]$_2$. It was shown that interaction of the frontier orbitals, of Mo–Mo bonding character, with the conjugated edt ligand led to a stabilization of the HOMO, and hence a higher oxidation potential compared with the analogous dithiolate complexes [94].

5.3. Structures

[CpV(bdt)]$_2$ exhibit a structure characteristic of most of these complexes [23] (Fig. 11). The four bridging sulfur atoms are in a plane which bisects the vanadium–vanadium bond vector. V–V bond length amounts here to 2.520(2) Å, a value slightly shorter than the one observed in (i-PrC$_5$H$_4$)$_2$V$_2$S$_4$ at 2.610(1) Å where two d^1 V$^{(IV)}$ atoms form a single V–V bond [101].

Indeed, as discussed by King for the analogous [CpV(tfd)]$_2$, if those d^2 V$^{(III)}$ complexes were to exhibit a single V–V bond, the two remaining electrons, one on each V, would each contribute 1.7 μ_B to the magnetic susceptibility [18]. The measured magnetic moment of 0.9 μ_B for [CpV(tfd)]$_2$ demonstrates that there must be partial pairing between remaining unpaired electrons, giving the V–V bond partial double-bond character.

The corresponding d^3–d^3 molybdenum(III) complexes exhibit a similar geometry with a single Mo–Mo bond, at 2.584(1) Å in [CpMo(tfd)]$_2$ [89], 2.576(1) Å in [CpMo(edt)]$_2$ [90] and 2.580(1) Å in [CpMo(tdt)]$_2$ [90]. Indeed, extended Hückel calculations have shown that the six available electrons occupy respectively a bonding σ, an antibonding δ* and a bonding δ orbital, giving a net bond order of one [94].

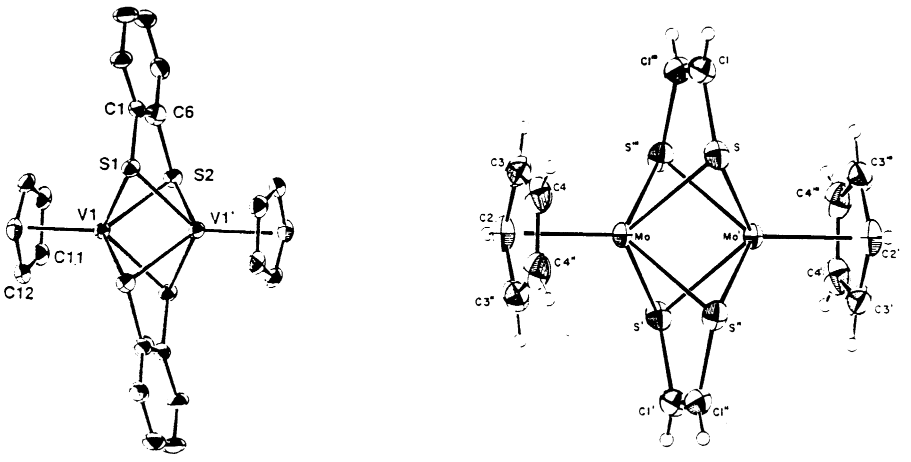


Fig. 11. ORTEP view of [CpV(bdt)]$_2$ (left) [23] and [CpMo(edt)]$_2$ (right) [90].

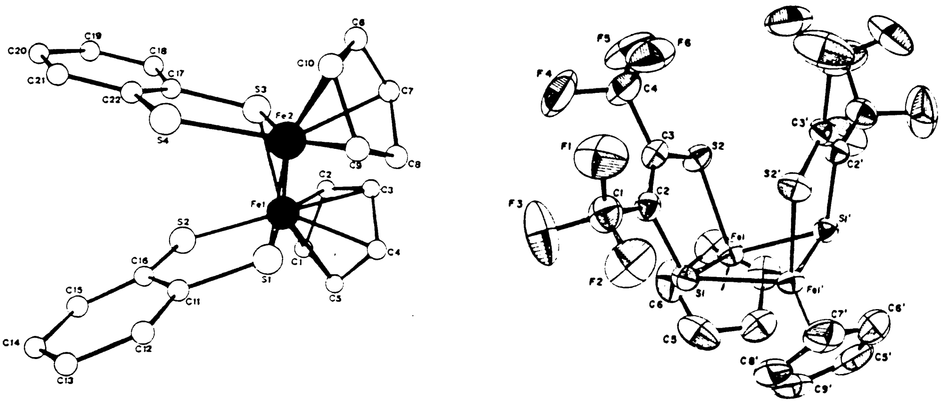


Fig. 12. ORTEP views of $[CpFe(bdt)]_2$ (left) [97], $[CpFe(tfd)]_2$ (right) [96].

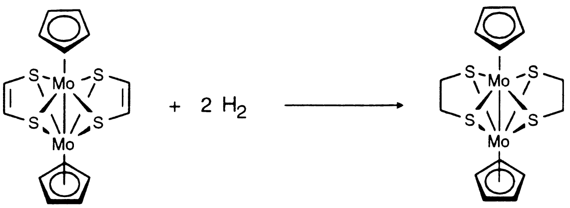
Structures reported for the chromium and iron complexes are similar, and notably different from those described above. As shown in Fig. 12, each dithiolene ligand contains one bridging and one terminally coordinated sulfur atom. The diamagnetism of those compounds implies the presence of a single M–M bond, found at 2.98 Å in the d^3–d^3 chromium complex $[CpCr(tfd)]_2$ [88], and at 2.657 Å in the d^5–d^5 iron complex $[CpFe(S_2C_2CO_2Me)]_2$ [96].

5.4. NMR data

Of particular interest is the chemical shift of the protons of the edt ligand in $[CpMo(edt)]_2$, which gives an indication for the dithiolene or dithioketone character of the ligand. Observed at δ 6.43 in $[CpMo(edt)]_2$ [12] and δ 6.49 in $[(MeCp)Mo(edt)]_2$ [92], these values, close to that reported for the free Na_2edt dithiolene, confirms the dithiolene character of the ligand in these complexes and hence the III oxidation state for the metal. ^{95}Mo NMR has been reported for $[(MeCp)Mo(edt)]_2$. Observed at δ 2327 (rel. to 1 M Na_2MoO_4(aq) at pH 11, high frequency position), it represents a very strong deshielding, observed only in those complexes with conjugated dithiolene ligands. By comparison, the tetrathiolate complex $[CpMo(SMe)_2]_2$ is observed at ^{95}Mo δ 937. This deshielding has been attributed to the strong stabilization of the δ^* and π^* LUMOs when each pair of sulfur atoms is included in a conjugated ligand (such as edt, when compared with the σ-only substituents [94].

5.5. Reactivity

Little has been reported on the reactivity of these complexes, except by Rakowski DuBois et al. who described specific conditions for the hydrogenation of $[CpMo(edt)]_2$ to afford the saturated dithiolate complex $[CpMo(S_2C_2H_4)]_2$ [12].



6. Monomeric CpM(dithiolene) complexes (M = Co, Rh, Ir, Ni)

This class of complexes is observed with d^6 or d^7 metals in their III oxidation state. With the Group 9 metals (Co, Rh, Ir), these formally $16e^-$ complexes exhibit interesting addition reactions with phosphines, ethylenes, etc. Furthermore, a high degree of delocalization in the metallacycle allows for reactions on the dithiolene ligand which are totally unknown in the other classes of complexes.

6.1. Synthesis

Methods A and C have been employed for the preparation of these complexes (Table 10). Method A involves mixed halogen/carbonyl complexes such as $CpCo(CO)_2I$ [36,38] and more recently the halogenated $[CpRhBr_2]_n$ or $[Cp^*RhCl_2]_2$. Oxidative additions have been performed on various substrates such as $CpRh(CO)_2$, $[CpNi(CO)]_2$ or CpCo(cod) in their reaction with the $(CF_3)_2C_2S_2$ dithietene [18,19] or with cyclic trithiocarbonates accompanied by CS elimination [25].

Two other types of oxidative addition have been reported: chalcogen insertion and intramolecular carbyne–carbyne coupling in trinuclear bis(carbyne) cobalt clusters $(CpCo)_3(CR)_2$ [16] and, in a similar way, reaction of the carbonyl complexes $CpCo(CO)_2$ or CpRh(cod) with acetylenes in the presence of elemental sulfur or selenium [17,106]. Of particular note also is the preparation of the bimetallic cobalt [123] and nickel [21] C_2S_4 derivatives through CS_2 reductive coupling of the corresponding carbonyl compound (see Section 2.3.4).

The nickel complexes have been prepared either by oxidative addition of the $(CF_3)_2C_2S_2$ dithietene to $[CpNi(CO)]_2$ [18] or by displacement of a cyclopentadienyl ring in $(Cp_2Ni)^+BF_4^-$ by the dmit ligand [122].

6.2. Electrochemical behavior

Cyclic voltammetry data have been reported for a large selection of cobalt complexes. All of them exhibit a reversible reduction wave, attributable to a one-electron $Co^{(III)} \rightarrow Co^{(II)}$ process. Substitution of a Cp* ring for a Cp ring shifts this reduction potential by 0.2 V toward more cathodic values, as expected [115]. Note also that these complexes become increasingly difficult to reduce when going down the column of the periodic table. Whereas CpCo(tfd) reduces at −1.1 V (*vs* $Ag/AgClO_4$), CpRh(tfd) and CpIr(tfd) reduce at −1.4 V and −1.7 V (*vs* $Ag/AgClO_4$) respectively

Table 10
CpM(dithiolene) complexes (M = Co, Rh, Ir, Ni)

Compound	Synth	Information	Ref.
CpCo(tfd)	C	IR, ^{19}F-NMR, X-ray, CV, ^{59}Co-NQR	[18,19,33,102–104]
CpCo(tfd)$^{-\cdot}$	EPR		[102]
CpCo(mnt)	A	IR, ^{1}H-NMR, X-ray, CV,^{59}Co-NQR	[33,36,104,105]
CpCo(edt)	A	IR, ^{1}H-NMR, ^{59}Co-NQR	[38,104]
CpCo(tdt)	A, C	UV, MS, ^{1}H-NMR, CV, ^{59}Co-NQR	[26,33,106,107]
Cp*Co(tdt)	A	^{1}H-, ^{13}C-NMR, ^{59}Co-NQR	[106]
CpCo(bdt)	A	IR, UV, X-ray	[108,109]
[CpCo(bdt)]$_2$	A	IR, X-ray	[108]
CpCo(SSeC$_6$H$_4$)	A	^{59}Co-NQR	[106]
Cp*Co(SSeC$_6$H$_4$)	A	^{1}H-, ^{13}C-NMR, MS, ^{59}Co-NQR	[106]
CpCo[S$_2$C$_2$H(Ph)]	C	MS, ^{1}H-, ^{13}C-NMR	[16,106]
CpCo[S$_2$C$_2$H(COMe)]	D		[110]
CpCo[S$_2$C$_2$Ph(COMe)]	D		[110]
CpCo[S$_2$C$_2$(Ph)(d^5-Ph)]	C		[16]
CpCo[S$_2$C$_2$(Et)(Ph)]	C		[16]
CpCo[S$_2$C$_2$(*n*-Bu)$_2$]	C		[16]
CpCo[Se$_2$C$_2$(*n*-Bu)$_2$]	C	^{59}Co-NQR	[16,106]
CpCo(S$_2$C$_2$Ph$_2$)	C		[106,111]
CpCo[Se$_2$C$_2$Ph$_2$]	C	^{1}H-, ^{13}C-NMR, ^{59}Co-NQR	[106]
CpCo[S$_2$C$_2$(CO$_2$Me)$_2$]	C		[16]
CpCo[S$_2$C$_2$(H)CO$_2$Me]	C		[112]
CpCo[S$_2$C$_2$(C$_2$SiMe$_3$)$_2$]	C		[16]
(MeCp)Co(S$_2$C$_2$Ph$_2$)	C		[16]
CpCo(S$_2$C$_6$Cl$_4$)	A	^{1}H-NMR, ^{59}Co-NQR	[104]
CpCo(dmit)	A	MS, ^{1}H-NMR, CV, X-ray	[113,114]
Cp*Co(dmit)	A	MS, CV, X-ray	[113,114]
CpCo(dmid)	A	CV	[115]
Cp*Co(dmid)	A	CV	[115]
CpCo[S$_2$C$_2$(S(CS)NMe)]		MS, IR, UV, ^{1}H-, ^{13}C-NMR, X-ray	[116]
CpCo[S$_2$C$_2$H(2-quinoxalinyl)]	C	X-ray, UV, IR, MS, ^{1}H-NMR	[24,25]
CpCo[S$_2$C$_2$H(C$_9$H$_{11}$N$_6$O)]	C	X-ray, UV, IR, MS, ^{1}H-, ^{13}C-NMR	[25,117]
CpRh(tfd)	C	IR, UV, ^{1}H-, ^{19}F-NMR, CV	[19,102]
CpRh(edt)	A	IR, ^{1}H-NMR	[38]
CpRh(S$_2$C$_2$Ph$_2$)	C	MS, UV, ^{1}H-NMR	[16,118]
CpRh[S$_2$C$_2$(CO$_2$Me)$_2$]	C	MS, ^{1}H-, ^{13}C-NMR, UV, IR, MS	[17,119]
Cp*Rh(mnt)	A	MS, UV, IR, ^{1}H-, ^{13}C-NMR, X-ray	[120,121]
Cp*Rh(tdt)	A	MS, ^{1}H-, ^{13}C-NMR	[120]
CpIr(tfd)	C	IR, UV, ^{1}H-, ^{19}F-NMR, CV	[19,34]
Cp*Ir(mnt)	A	MS, UV, IR, ^{1}H-, ^{13}C-NMR	[120,121]
CpNi(tfd)	C	IR, magn. susc., CV	[18,102]
CpNi(dmit)	A	MS, X-ray	[122]

[34,103]. An effect is also observed upon dithiolene substitution: CpCo(tdt) reduces at −0.61 V (*vs* SCE) [26], whereas CpCo(tfd) bearing electron-withdrawing CF_3 substituents reduces at −0.45 V (*vs* SCE). The reversible character of this reduction is further demonstrated by the persistence in solution of the $CpCo(dmit)^{-\cdot}$ [115] and $CpM(tfd)^{-\cdot}$ (M = Co, Rh, Ir) radical anions. Eight-line EPR signals, expected for coupling of the unpaired electron with the ^{59}Co ($I = 7/2$) have been observed for $CpCo(tfd)^{-\cdot}$ ($g_0 = 2.545$, $a_0 = 41$ G) [103] and $CpCo(mnt)^{-\cdot}$ ($g_0 = 2.5$, $a_0 = 40$ G) radical anions [33].

Analysis of the data reported in the anodic range is confusing. Whereas irreversible processes have been reported for CpCo(bdt) [108], two reversible oxidation waves are observed in CpCo(dmit) or CpCo(dmid) complexes [113,115]. Despite this reversibility, electrolytic oxidation of Cp*Co(dmit) leads to the destruction of the complex and formation of a tricyclic organic compound, C_6S_8.

CpNi(tfd) has been reported to exhibit similar behavior to the cobalt complexes with a reversible reduction wave. A sharp single EPR line was observed for the $CpNi(tfd)^{-\cdot}$ radical anion, with $g = 2.0479$ [103]. Similarly, two one-electron reduction waves are also observed in the bimetallic $Cp^*Ni(C_2S_4)NiCp^*$ together with one reversible oxidation wave [21].

6.3. Structures

Several crystal structures have been reported for this class of compounds. They all present the same characteristics, with the dithiolene plane being mostly perpendicular to the Cp plane.

There has been some controversy on the extent of delocalization within the CoS_2C_2 metallacycle in these complexes. Comparison of the C–S and C–C bond distances in the metallacycle with other dithiolene complexes does not allow for a clear description of the ligand, dithiolene or dithioketone. As shown below, ^1H NMR probably provides a better insight on this matter. One Cp* derivative, Cp*Co(dmit) (Fig. 13), has recently been described and does not exhibit extra features. Of particular note is the structure of CpCo(bdt) described by Brill and coworkers [108] (Fig. 14). A reversible single-crystal chemical reaction was discovered to occur when a crystal of CpCo(bdt) converts at room temperature to produce

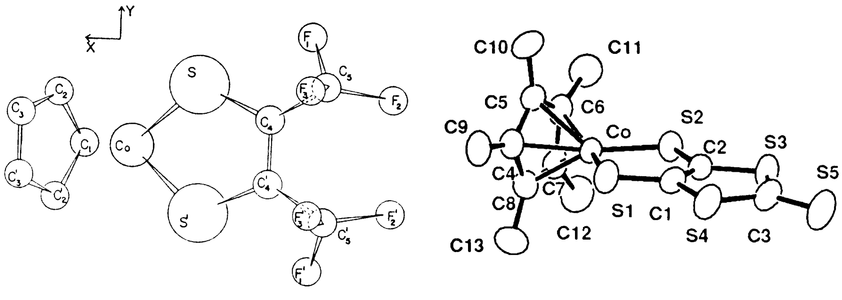


Fig. 13. ORTEP view of CpCo(tfd) (left) [102] and Cp*Co(dmit) (right) [114].

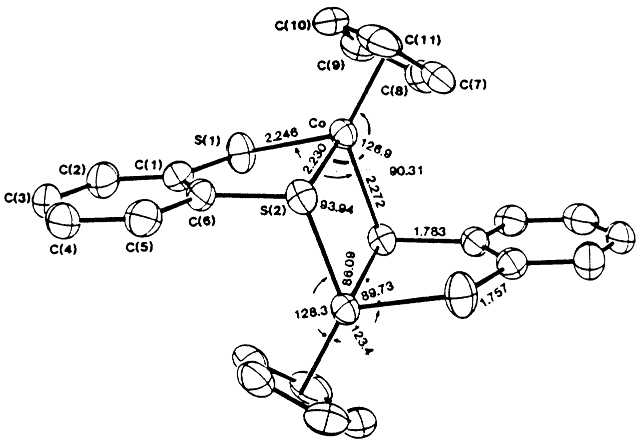
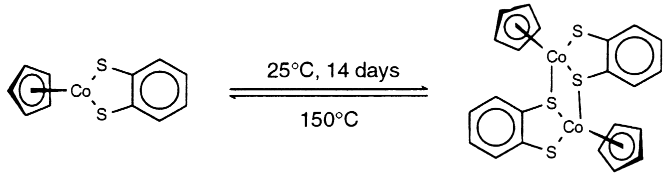


Fig. 14. ORTEP view of the dimeric form of CpCo(bdt), i.e. $[CpCo(bdt)]_2$ [108].

a crystal of a dimeric $[CpCo(bdt)]_2$. Heating the dimer crystal at 150 °C reverts it to the monomer crystal without loss of crystallinity.



In the monomer structure, molecules in the usual geometry adopt a head-to-tail arrangement, whereas in the dimer profound changes occur. The Cp ring undergoes a tilting of about 45° relative to the CoS_2 plane, the formerly planar CoS_2C_2 metallacycle folds along the S–S hinge by 20.9° and each dithiolene ligand now contains one bridging and one terminally coordinated sulfur atom.

Structures of nickel complexes are very similar. A strong delocalization of the π system of the bicyclic $Cp^*Ni(C_2S_4)NiCp^*$ complex was deduced from the C–S and C–C bond lengths as being very similar to those found in neutral nickel bis(dithiolene) complexes [21] (Fig. 15).

6.4. NMR and NQR data

As pointed out by King [38], ^1H NMR data provide a unique opportunity to assess the extent of delocalization of the π system in these metallacycles. Whereas the chemical shift of the protons of the edt ligand was found to lie between δ 5.4 and 7.4 in all the complexes described above, values of δ 8.50 and δ 8.88 are found for CpRh(edt) and CpCo(edt) respectively, to be compared for example with a chemical shift of δ 9.2 in the neutral, formally $Ni^{(IV)}$, $Ni(edt)_2$. This result clearly

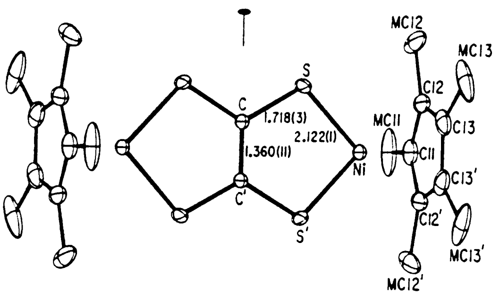


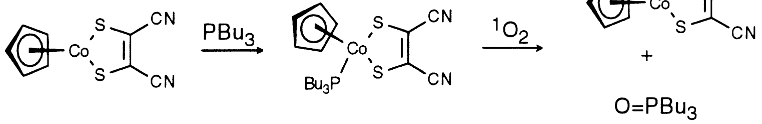
Fig. 15. ORTEP view of Cp*Ni(C_2S_4)NiCp* [21].

demonstrates that there is indeed an important contribution of the dithioketonic form of the dithiolene in the Group 9 CpM(dithiolene) complexes, or in other words an intramolecular charge transfer with a partial metal reduction.

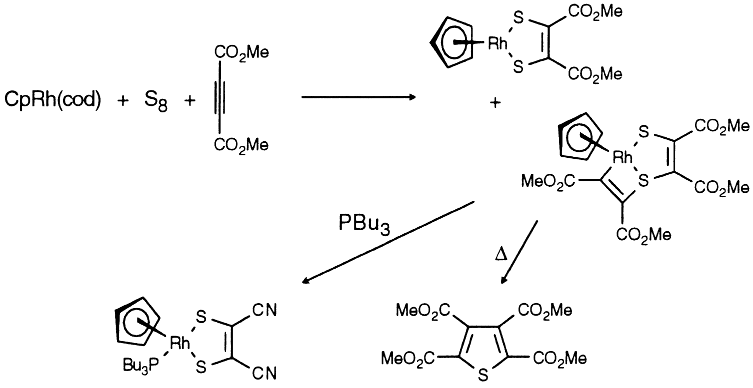
^{59}Co nuclear quadrupole resonance (NQR) has been used to detect relative changes in the electronic distribution on the metal center. It was found, however, that the nature of the substituents on the dithiolene ligand (H in edt, CN in mnt, CF_3 in tfd, bdt, Cl_4bdt) had little influence on the electric field gradient (EFG). The largest values were observed with the phenylene complexes (bdt, Cl_4bdt), where a significant alteration of the π-electron density of the metallacycle might be produced by the extended delocalization [104]. Substitution of selenium atoms for sulfur atoms shows that the EFG at Co is controlled simply by the sum of the electronegativities of the atoms bound to the metal, whereas replacing Cp with Cp* causes the EFG of the complexes to decrease, a variation which is not easily rationalized [106].

6.5. Reactivity

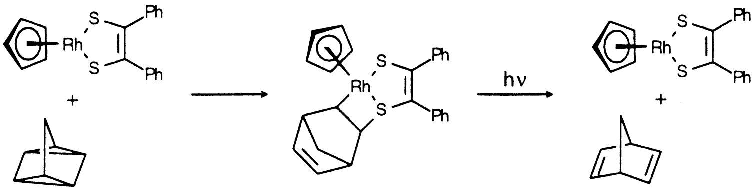
The 16e$^-$ species were found to add a variety of molecules to reach the 18e$^-$ configuration. Reaction with tertiary phosphines and phosphites afforded the corresponding 1:1 adducts [124,125]. The PBu_3 complex, CpCo(mnt)PBu_3, was found to dissociate under the action of singlet oxygen to the CpCo(mnt) and the phosphine oxide $O{=}PBu_3$ [126]. Similarly, the preparation of the triphenylphosphine and t-butylisocyano adducts of Cp*Ir(mnt) has been reported together with their X-ray crystal structures [127].



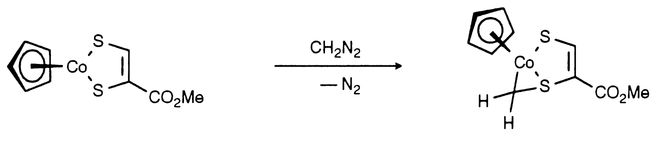
Those cobalt complexes formed upon reaction of $CpCoL_2$, L_2=COD, $(CO)_2$ with S_8 and acetylenes were found by Bönnemann et al. to further react with additional alkynes to afford dithienes which, under more drastic conditions, lose sulfur to give thiophene derivatives [128]. Several other adducts have been described by Sugimori and coworkers and their reactivity investigated in detail. For example, during the preparation of $CpRh[S_2C_2(CO_2Me)_2]$ from CpRh(cod), S_8 and DMAD, an DMAD adduct of $CpRh[S_2C_2(CO_2Me)_2]$, was also reported, which exchanges with PBu_3 [17]. Pyrolysis of the DMAD adduct, in the solid state or in solution, affords tetramethylthiophene tetracarboxylate together $CpRh[S_2C_2(CO_2Me)_2]$ [119].

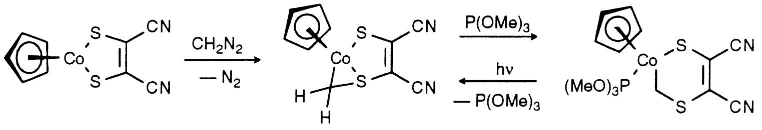


$CpCo(bdt)$ [109] and $CpRh(S_2C_2Ph_2)$ [118] were found to insert the strained hydrocarbon quadricyclane into the metal–sulfur bond. Irradiation of the Rh adduct with a medium pressure mercury lamp yields norbornadiene together with $CpRh(S_2C_2Ph_2)$.

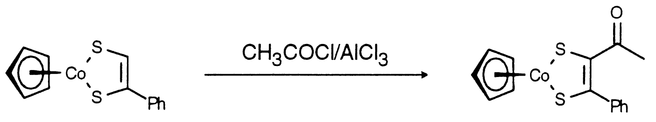


Sugimori and coworkers also reported numerous examples of addition of alkylidene groups between metal and sulfur in the reactions of CpM(dithiolene) complexes with diazo compounds [112]. Attempts to irradiate the diazo solutions in the presence of the cobalt complexes did not yield the addition compound, demonstrating that the adduct forms by reaction, not with the free carbene species, but with the diazo compound, followed by N_2 elimination. Addition of unsymmetrically substituted dithiolene complexes is regioselective: the diazo compound adds on the Co–S bond close to the most electron-withdrawing substituent of the dithiolene. These reactions have been extended to Rh complexes, as well as to dithiolene without electron-withdrawing groups such as bdt or $S_2C_2(H)Ph$ [111]. The diazomethane addition compound to CpCo(mnt) exhibits a reversible carbene insertion into the metallacycle upon treatment with trimethylphosphite [129].





The large degree of delocalization in these CpCo(dithiolene) complexes, or in other words, their aromatic character, has been further demonstrated recently by the occurrence of electrophilic substitution reactions such as Friedel–Crafts acylation. Indeed, reaction of $CpCo[S_2C_2(H)Ph]$ with acetyl chloride and $AlCl_3$ or with acetic anhydride and phosphoric acid afforded at room temperature the acetyl derivatives $CpCo[S_2C_2H(COMe)]$ or $CpCo[S_2C_2Ph(COMe)]$ [110].



7. Outlook

Mixed cyclopentadienyl/dithiolene complexes, first investigated 30 years ago, form a group of air-stable, highly colored, eventually paramagnetic compounds, whose number is increasing rapidly today with the development of novel dithiolene ligands associated with the search for conducting or superconducting homoleptic dithiolene complexes or for models of molybdenum-containing enzymes. The π-donor and non-innocent character of the dithiolene ligands lead to highly covalent complexes exhibiting a notable electronic delocalization in their MS_2C_2 metallacycles, whose extent strongly depends upon the nature of the metal and the electron count. The electron-deficient character of some of these complexes shows itself through structural distortions involving a mixture of metal d and dithiolene π states, as well as through reversible adduct formation, with possible interest for catalysis [128]. On the other hand, the d^2 18-electron structure of some others favors their oxidation to the corresponding paramagnetic d^1 species whose magnetic solid state properties are intimately related to their solid state arrangement and the dimensionality of the intermolecular interactions.

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References

[1] P. Cassoux, L. Valade, H. Kobayashi, A. Kobayashi, R.A. Clark, A.E. Underhill, Coord. Chem. Rev. 110 (1991) 115.
[2] R.-M. Olk, B. Olk, W. Dietzsch, R. Kirmse, E. Hoyer, Coord. Chem. Rev. 117 (1992) 99.
[3] G.N. Schrauzer, V.P. Mayweg, J. Am. Chem. Soc. 84 (1962) 3221.
[4] H.B. Gray, E. Billig, J. Am. Chem. Soc. 85 (1963) 2019.
[5] A. Davison, N. Edelstein, R.H. Holm, A.H. Maki, J. Am. Chem. Soc. 85 (1963) 2029.
[6] J.A. McCleverty, Prog. Inorg. Chem. 10 (1968) 49.
[7] U.T. Müller-Westerhof, B. Vance, in: G. Wilkinson, R.D. Gillard, J.A. McCleverty (Eds.), Comprehensive Coordination Chemistry, Vol. 2, Pergamon Press, Oxford, 1987, pp. 595–631.
[8] M. Fourmigué, C. Lenoir, C. Coulon, F. Guyon, J. Amaudrut, Inorg. Chem. 34 (1995) 4979.
[9] F. Guyon, M. Fourmigué, R. Clérac and J. Amaudrut, J. Chem. Soc. Dalton Trans. (1996) 4096.
[10] C.M. Bolinger, T.B. Rauchfuss, Inorg. Chem. 21 (1982) 3947.
[11] C.M. Bolinger, J.E. Hoots, T.B. Rauchfuss, Organometallics 1 (1982) 223.
[12] M. Rakowski DuBois, R.C. Haltiwanger, D.J. Miller, G. Glatzmaeir, J. Am. Chem. Soc. 101 (1979) 5245.
[13] J.K. Hsu, C.J. Bonangelino, S.P. Kaiwar, C.M. Boggs, J.C. Fettinger, R.S. Pilato, Inorg. Chem. 35 (1996) 4743.
[14] S.P. Kaiwar, J.K. Hsu, A. Vodacek, G. Yap, L.M. Liable-Sands, A.L. Rheingold, R.S. Pilato, Inorg. Chem. 36 (1997) 2406.
[15] B. Gautheron, G. Tainturier, S. Pouly, F. Théobald, H. Vivier, A. Laarif, Organometallics 3 (1984) 1495.
[16] K.P.C. Vollhardt, E.C. Walborsky, J. Am. Chem. Soc. 105 (1983) 5507.
[17] M. Kajitani, T. Suetsugu, R. Wakabayashi, A. Igarashi, T. Akiyama, A. Sugimori, J. Organomet. Chem. 293 (1985) C15.
[18] R.B. King, J. Am. Chem. Soc. 85 (1963) 1587.
[19] R.B. King, M.B. Bisnette, Inorg. Chem. 6 (1967) 469.
[20] H.A. Harris, A.D. Rae, L.F. Dahl, J. Am. Chem. Soc. 109 (1987) 4739.
[21] J.J. Maj, A.D. Rae, L.F. Dahl, J. Am. Chem. Soc. 104 (1982) 4278.
[22] C. Bianchini, C. Mealli, A. Meli, M. Sabat, P. Zanello, J. Am. Chem. Soc. 109 (1987) 185.
[23] D.W. Stephan, Inorg. Chem. 31 (1992) 4218.
[24] E.M. Armstrong, M.S. Austerberry, R.L. Beddoes, M. Helliwell, J.A. Joule, C.D. Gamer, Acta Crystallogr. Sect. C: 49 (1993) 1764.
[25] A. Dinsmore, J.H. Birks, C.D. Garner, J.A. Joule, J. Chem. Soc. Perkin Trans. 1:, (1997) 801.
[26] A.R. Siedle, J. Organomet. Chem. 120 (1976) 369.
[27] W. Kusters, P. de Mayo, J. Am. Chem. Soc. 96 (1974) 4502.
[28] H. Köpf, M. Schmidt, J. Organomet. Chem. 4 (1965) 426.
[29] H. Köpf, Angew. Chem. Int. Ed. Engl. 10 (1971) 134.
[30] A. Kotuglu, Z. Anorg. Allg. Chem. 390 (1972) 195.

[31] M. Draganjac, T.B. Rauchfuss, Angew. Chem. Int. Ed. Engl. 24 (1985) 742 (F.N. Tebbe, personal commun. cited therein)
[32] M.A. Chaudhari, F.G.A. Stone, J. Chem. Soc. A: (1966) 838.
[33] J.A. McCleverty, T.A. James, E.J. Wharton, Inorg. Chem. 8 (1969) 1340.
[34] R.E. Dessy, R.B. King, M. Waldrop, J. Am. Chem. Soc. 88 (1966) 5112.
[35] B. Plincke, H. Köpf, Z. Anorg. Allg. Chem. 620 (1994) 1805.
[36] J. Locke, J.A. McCleverty, Inorg. Chem. 5 (1966) 1157.
[37] A.C. Villa, A.G. Manfredotti, C. Guastini, Acta Crystallogr. Sect. B: 32 (1976) 909.
[38] R.B. King, C.A. Eggers, Inorg. Chem. 7 (1968) 340.
[39] H. Köpf, Z. Naturforsch. Teil B: 23 (1968) 1531.
[40] A. Kotuglu, Acta Crystallogr. Sect. B: 29 (1973) 2891.
[41] T.A. James, J.A. McCleverty, J. Chem. Soc. A: (1970) 3318.
[42] C.M. Bolinger, J.E. Hoots, T.B. Rauchfuss, Organometallics 1 (1982) 223.
[43] D.M. Giolando, T.B. Rauchfuss, A.L. Rheingold, S.R. Wilson, Organometallics 6 (1987) 667.
[44] E. Fanghänel, J. Bierwisch, A. Ullrich, A. Herrmann, Chem. Ber. 128 (1995) 1047.
[45] X. Yang, T.B. Rauchfuss, S.C. Wilson, J. Am. Chem. Soc. 111 (1989) 3465.
[46] F. Guyon, C. Lenoir, M. Fourmigué, J. Larsen, J. Amaudrut, Bull. Soc. Chim. Fr. 131 (1994) 217.
[47] S. Zeltner, W. Dietzsch, R.-M. Olk, R. Kirmse, R. Richter, U. Schröder, B. Olk, E. Hoyer, Z. Anorg. Allg. Chem. 620 (1994) 1768.
[48] F. Guyon, M. Fourmigué, P. Audehert, J. Amaudrut, Inorg. Chim. Acta 239 (1995) 117.
[49] R. Steudel, U. Westphal, J. Organomet. Chem. 388 (1990) 89.
[50] D.D. Doxsee, C.P. Galloway, T.B. Rauchfuss, S.R. Wilson, X. Yang, Inorg. Chem. 32 (1993) 5467.
[51] H. Köpf, J. Organomet. Chem. 14 (1968) 353.
[52] P. Meunier, B. Gautheron, A. Mazouz, J. Organomet. Chem. 320 (1987) C39.
[53] H. Köpf, T. Klapötke, J. Organomet. Chem. 310 (1986) 303.
[54] H. Köpf, H. Balz, J. Organomet. Chem. 387 (1990) 77.
[55] H. Balz, H. Köpf, J. Pickardt, J. Organomet. Chem. 417 (1991) 397.
[56] R.D. McCullough, J.A. Belot, J. Seth, A.L. Rheingold, G.P.A. Yap, D.O. Cowan, J. Mater. Chem. 5 (1995) 1581.
[57] H. Köpf, T. Klapötke, J. Chem. Soc. Chem. Commun. (1986) 1192.
[58] S. Zeltner, R.-M. Olk, M. Pink, S. Jelonek, P. Jörchel, T. Gelbrich, J. Sieler, R. Kirmse, Z. Anorg. Allg. Chem. 622 (1996) 1979.
[59] R. Kato, H. Kobayashi, A. Kobayashi, Synth. Met. 42 (1991) 2093.
[60] H.A. Harris, D.R. Kanis, L.F. Dahl, J. Am. Chem. Soc. 113 (1991) 8602.
[61] N. Schrauzer, V.P. Mayweg, J. Am. Chem. Soc. 87 (1985) 3585.
[62] J.W. Lauher, R. Hoffmann, J. Am. Chem. Soc. 98 (1976) 1729.
[63] P. Meunier, B. Gautheron, A. Mazouz, J. Chem. Soc. Chem. Commun. (1986) 424.
[64] U. Westphal, R. Steudel, Chem. Ber. 124 (1991) 2141.
[65] T. Imakubo, H. Sawa, R. Kato, Synth. Met. 86 (1997) 1883.
[66] A.T. Casey, J.R. Thackeray, Austr. J. Chem. 28 (1975) 471.
[67] O. Hackelberg, R. Kramolowsky, Z. Naturforsch. Teil B: 30 (1975) 219.
[68] A.M. Bond, A.T. Casey, J.R. Thackeray, Inorg. Chem. 13 (1974) 84.
[69] A.T. Casey, J.B. Raynor, J. Chem. Soc. Dalton Trans. (1983) 2057
[70] F. Guyon, J. Amaudrut, M.-F. Mercier, K. Shimizu, J. Organomet. Chem 465 (1994) 187.
[71] B. Viard, J. Amaudrut, J. Sala-Pala, A. Fakhr, Y. Mugnier, C. Moise, J. Organomet. Chem. 292 (1985) 403.
[72] M.L.H. Green, W.E. Lindsell, J. Chem. Soc. A: (1967) 1455.
[73] J.R. Knox, C.K Prout, J. Chem. Soc. Chem. Commun. (1967) 1277.
[74] J.R. Knox, C.K. Prout, Acta Crystallogr. Sect. B: 25 (1969) 2013.
[75] A. Kotuglu, H. Köpf, J. Organomet. Chem. 25 (1970) 455.
[76] M.L.H. Green, W.B. Heuer, G.C. Saunders, J. Chem. Soc. Dalton Trans. (1990) 3789.
[77] R.S. Pilato, K.A. Eriksen, M.A. Greaney, E.I. Stiefel, S. Goswami, L. Kilpatrick, T.G. Spiro, E.C. Taylor, A.L. Rheingold, J. Am. Chem. Soc. 113 (1991) 9372.
[78] T. Debaerdemaeker, A. Kotuglu, Acta Crystallogr. Sect. B: 29 (1973) 2664.

[79] M.L.H. Green, J. Organomet. Chem. 500 (1995) 127.
[80] H. Köpf, K. Lange, J. Pickardt, J. Organomet. Chem. 420 (1991) 345.
[81] C.M. Bolinger, T.B. Rauchfuss, A.L. Rheingold, Organometallics 1 (1982) 1551.
[82] K. Tatsumi, J. Takeda, Y. Sekiguchi, M. Kohsada, A. Nakamura, Angew. Chem. Int. Ed. Engl. 24 (1985) 332.
[83] M.R. Churchill, J. Coake, J. Chem. Soc. A: (1970) 2046.
[84] T.A. James, J.A. McCleverty, J. Chem. Soc. A: (1970) 3308.
[85] M. Fourmigué, C. Coulon, Adv. Mater. 6 (1994) 948.
[86] J. Takacs, P. Kiprof, W.A. Herrmann, Polyhedron 9 (1990) 2211.
[87] M. Herberhold, G.-X. Jin, W. Milius, Z. Anorg. Allg. Chem. 620 (1994) 1295.
[88] J. Locke, J.A. McCleverty, Inorg. Chem. 5 (1966) 1157(footnote citation: S.F. Watkins, L.F. Dahl, Abstr. of Papers, 150th National Meet. Am. Chem. Soc., Atlantic City, NJ, 1965, p. 23)
[89] K. Roesselet, K.E. Doan, S.D. Johnson, P. Nicholls, G.L. Miessler, R. Kroeker, S.H. Wheeler, Organometallics 6 (1987) 480.
[90] W.K. Miller, R.C. Haltiwanger, M.C. VanDerveer, M. Rakowski DuBois, Inorg. Chem. 22 (1983) 2973.
[91] C.J. Casewit, R.C. Haltiwanger, J. Nootdik, M. Rakowski DuBois, Organometallics 4 (1985) 119.
[92] M. Rakowski DuBois, M.C. VanDerveer, D.L. DuBois, R.C. Haltiwanger, W.K. Miller, J. Am. Chem. Soc. 102 (1980) 7456.
[93] M. McKenna, L.L. Wright, D.J. Miller, L. Tanner, R.C. Hatiwanger, M. Rakowski DuBois, J. Am. Chem. Soc. 105 (1983) 5329.
[94] C.J. Casewit, M. Rakowski DuBois, R.A. Grieves, J. Mason, Inorg. Chem. 26 (1987) 1889.
[95] O.A. Rajan, M. McKenna, J. Noordik, R.C. Haltiwanger, M. Rakowski DuBois, Organometallics 3 (1984) 831.
[96] R. Welberg, R.C. Haltiwanger, M. Rakowski DuBois, Organometallics 4 (1985) 1315.
[97] D. Sellmann, E. Unger, Z. Naturforsch. Teil B: 33 (1978) 1438.
[98] S. Inomata, H. Tobita, H. Ogino, J. Am. Chem. Soc. 112 (1990) 6145.
[99] S. Inomata, H. Tobita, H. Ogino, Inorg. Chem. 31 (1992) 723.
[100] M. Rakowski DuBois, D.L. DuBois, M.C. VanDerveer, R.C. Haltiwanger, Inorg. Chem. 20 (1981) 3064.
[101] C.M. Bolinger, T.B. Rauchfuss, A.L. Rheingold, J. Am. Chem. Soc. 105 (1983) 6321.
[102] H.W. Baird, B.M. White, J. Am. Chem. Soc. 88 (1966) 4744.
[103] R.E. Dessy, F.E. Stary, R.B. King, M. Waldrop, J. Am. Chem. Soc. 88 (1966) 471.
[104] E.J. Miller, T.B. Brill, Inorg. Chem. 22 (1983) 2392.
[105] M.R. Churchill, J.P. Fennessey, Inorg. Chem. 7 (1968) 1123.
[106] E.J. Miller, S.J. Landon, T.B. Brill, Organometallics 4 (1985) 533.
[107] R.F. Heck, Inorg. Chem. 7 (1968) 1513.
[108] E.J. Miller, T.B. Brill, A.L. Rheingold, W.C. Fultz, J. Am. Chem. Soc. 105 (1983) 7580.
[109] M. Kajitani, H. Hatano, T. Fujita, T. Okumachi, H. Nagao, T. Akiyama, A. Sugimori, J. Organomet. Chem. 430 (1992) C64.
[110] M. Kajitani, G. Hazgino, M. Tamada, T. Fujita, M. Sakurada, T. Akiyama, A. Sugimori, J. Am. Chem. Soc. 118 (1996) 489.
[111] M. Sakurada, M. Kajitani, K. Dohki, T. Akiyama, A. Sugimori, J. Organomet. Chem. 423 (1992) 141.
[112] M. Kajitani, M. Sakurada, K. Dohki, T. Suetsugu, T. Akiyama, A. Sugimori, J. Chem. Soc. Chem. Commun. (1990) 19.
[113] H. Ushijima, S. Sudoh, M. Kajitani, K. Shimizu, T. Akiyama, A. Sugimori, Inorg. Chim. Acta 175 (1990) 11.
[114] M. Fourmigué, V. Perrocheau, Acta Crystallogr. Sect. C: 53 (1997) 1213.
[115] H. Ushijima, S. Sudoh, M. Kajitani, K. Shimizu, T. Akiyama, A. Sugimori, Appl. Organomet. Chem. 5 (1991) 221.
[116] H. Werner, L. Xiaolan, O. Nürnberg, Organometallics 11 (1992) 432.
[117] R.L. Beddoes, A. Dinsmore, M. Helliwell, C.D. Garner, J.A. Joule, Acta Crystallogr. Sect. C: 53 (1997) 213.

[118] M. Kajitani, Y. Eguchi, R. Abe, T. Akiyama, A. Sugimori, Chem. Lett. (1990) 359.
[119] M. Kajitani, T. Suetsugu, T. Takagi, T. Akiyama, A. Sugimori, K. Aoki, H. Yamazaki, J. Organomet. Chem. 487 (1995) C8.
[120] M.J.H. Russel, C. White, A. Yates, P. M. Maitlis, J. Chem. Soc. Dalton Trans. (1978) 849.
[121] R. Ziessel, M.-T. Youinou, F. Balegroune, D. Grandjean, J. Organomet. Chem. 441 (1992) 143.
[122] C. Faulman, F. Delpech, I. Malfant, P. Cassoux, J. Chem. Soc. Dalton Trans. (1996) 2261.
[123] M.H. Englert, J.J. Maj, A.D. Rae, K.T. Jordan, H.A. Harris, L.F. Dahl, Abstr. of Papers, 187th National Meet. Am. Chem. Soc., St Louis, MO, American Chemical Society, Washigton, DC, 1984, INOR 280.
[124] S.D. Henderson, T.A. Stephenson, E.J. Wharton, J. Organomet. Chem. 179 (1979) 43.
[125] M. Kajitani, A. Igarashi, H. Hatano, T. Akiyama, A. Sugimori, S. Matsumoto, Y. Iguchi, H. Bönnemann, K. Shimizu, G.P. Sato, J. Organomet. Chem. 485 (1995) 31.
[126] H. Hatano, M. Kajitani, T. Akiyama, Y. Sakaguchi, J. Nazkamura, H. Hayashi, A. Sugimori, Chem. Lett. (1990) 1089.
[127] K. Yang, M.-J. Don, D.K. Sharma, S.G. Bott, M.G. Richmond, J. Organomet. Chem. 495 (1995) 61.
[128] H. Bönnemann, B. Bogdanovic, W. Brijoux, R. Brinkmann, M. Kajitani, R. Mynott, G.S. Natarajan, M.G. Samson, in: J.R. Kosak (Ed.), Catalysis in Organic Chemistry, Marcel Dekker, New York, 1984, pp. 31–62.
[129] M. Sakurada, M. Kajitani, H. Hatano, Y. Matsudaira, T. Suetsugu, S. Ono, T. Akiyama, A. Sugimori, Organometallics 11 (1992) 2337.