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Dinuclear molybdenum thiolato-bridged compounds: syntheses, reactivities and electrochemical studies of site–substrate interactions

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Abstract

The synthesis, reactivity, structures and electrochemistry of dimolybdenum complexes jointly stabilized by cyclopentadienyl and bridging thiolate ligands are reviewed. The complexes involved are principally those of molybdenum(II) and molybdenum(III) and they contain from one to four thiolate bridges. It is shown that their reactivity can be controlled by varying the electronic and steric properties of the ancillary ligands and that they provide bimetallic sites for the activation and transformation of various substrates.

Keywords: Dimolybdenum; Cyclopentadienyl; Thiolate; Transition metal site; X-ray structure; Electrochemistry

1. Introduction

This review has been prompted by our accumulation of novel results on dimolybdenum thiolate complexes. However, it is well to emphasize that the past 20 years have seen an intense and wide-ranging chemical investigation of compounds in which transition-metal centres are exposed to a sulfur environment. Though some of these studies were aimed at establishing metal–sulfur compounds as convenient synthons for the construction of clusters of high nuclearity, most have been prompted by the need for a better understanding of key biological and catalytic processes. Transition-metal complexes with sulfide, thiolate, or thioether ligands have long been regarded as models for the sulfur-rich metal centres of the metalloenzymes involved in the nitrogen cycle (nitrogenases, nitrate reductase) or for the species involved in catalytic processes of industrial importance, such as desulfurization [1–16]. The search for functional models of the active centre in nitrogenase has contributed much to the development of the chemistry of complexes in which molybdenum, tungsten, vanadium or iron atoms are associated with sulfur ligands. Most of these studies relate to mononuclear complexes; less attention has been devoted to reactions at dinuclear-sulfur sites. However, it has been established that many mono- or di-nuclear M–S centres can coordinate hydrazines and unsaturated ligands which are alternative substrates of nitrogenase, such as nitriles, cyanides, isocyanides, or alkynes [3,5,13]. In contrast, very few of these systems have the ability to bind dinitrogen itself [17,18].

This observation led us to investigate fundamental aspects of ligand-binding processes at electrogenerated sulfur-ligated dinuclear metal sites, paying particular

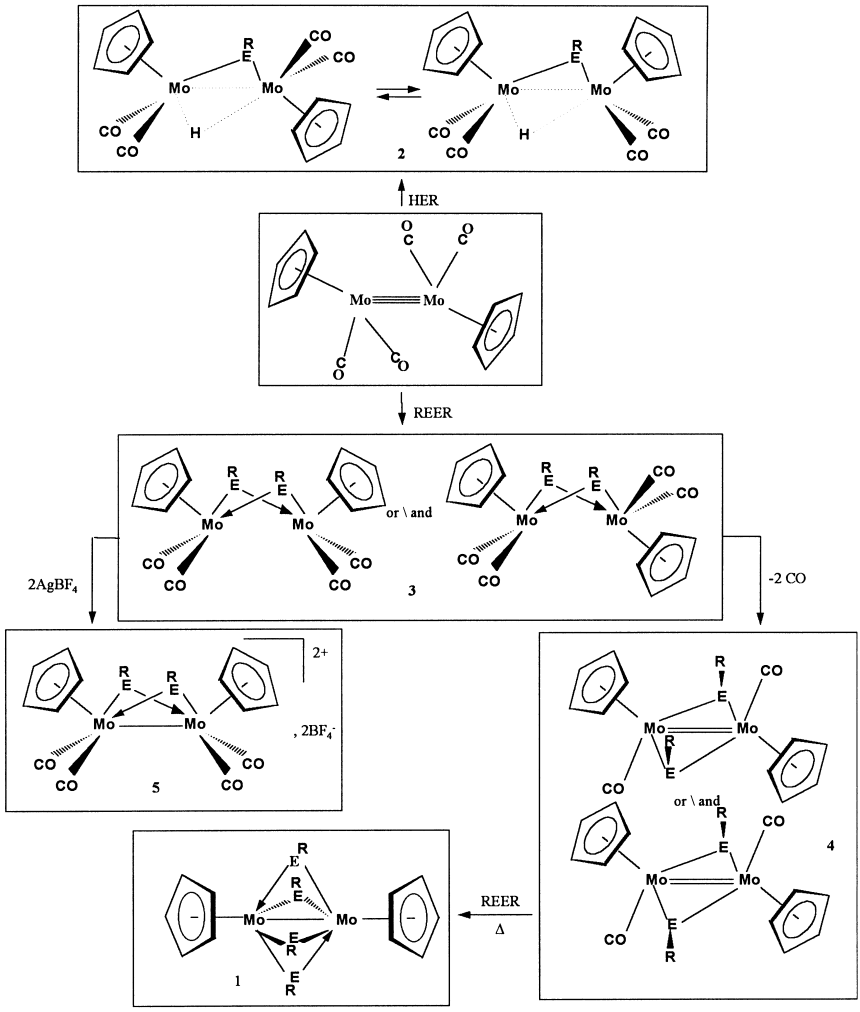
attention to the nature of site–substrate interactions and recognition phenomena in these systems. An understanding of the parameters which control the reactivity and the selectivity of coordinatively unsaturated metal centres might allow the rational design of sites either with high selectivity, adapted to a given substrate, or with low selectivity so that a variety of substrates with different σ/π donating/accepting properties, including dinitrogen, could be accommodated. To achieve this it is necessary to examine the electronic and steric effects of the ligands on the different steps of a substrate activation process (i.e. generation of the site, substrate-binding and transformation at the site). Consequently, it became necessary to prepare new dinuclear complexes possessing an $[M_2(\mu\text{-}SR)_n]$ core (M = Mo, W, V; $n = 1$–3) and different co-ligands (CO, $Cp' = \eta^5\text{-}C_5R_5$, R = H or Me). Section 2 describes the synthetic routes to the desired $\{[M_2(\mu\text{-}SR)_n]\}$ compounds, their structural characterization and reactivity. It concludes with a section on systems with bridging nitrogen-donor ligands where the parallels with metalloenzymes are particularly striking. Section 3 is devoted to the electrochemical behaviour of dimolybdenum thiolate systems, focusing on the reactivity at the metal centres and its often subtle dependence on the steric and electronic properties of the surrounding ligands [19–41].

No attempt has been made to cover comprehensively the significant and valuable contributions of Rakowski DuBois to the chemistry of dinuclear sulfur-bridged complexes. The reader interested in all facets of the reactivity of dinuclear complexes bridged by sulfide, hydrosulfide or thiolate is referred to her original publications [7,42] and should note particularly that the cleavage of nitrile and isocyanide C≡N triple bonds as a result of their insertion into the S–H bond of a hydrosulfide bridge, the cyclic reduction (hydrogenation) of azobenzene to 1,2-diphenylhydrazine and of alkynes to alkenes [43–45] may be relevant to the reduction of similar substrates by the sulfur-rich active centre of nitrogenase, even though these reactions do not take place at the metal centres.

2. Synthetic aspects, reactivities and structural considerations

2.1. Preparation of cyclopentadienyl thiolate-bridged dimolybdenum [Mo(II)–Mo(II)], [(Mo(III)–Mo(III)] complexes

Group 6 metal carbonyl compounds, such as $[MCp(CO)_3]_2$, $[MCp(CO)_2]_2$, or $[MCpX(CO)_3]$ (M = Cr, Mo, W; X = H, Cl), are known to react with REER or REH (E = S, Se, Te), and under vigorous conditions non-carbonyl complexes $[MCp(ER)_x]_2$ ($x = 1.5$ (Cr) or 2 (Mo,W)) **1** are formed [46–49]. It has been shown that dimeric intermediates, $[MCp(ER)(CO)_n]_2$, are involved in these reactions, though only those with $n = 1$ and 2 have so far been characterized [19,47,50–63]. The oxidative addition of HER or REER across the Mo_2 centre of $[Mo_2Cp_2(CO)_4]$, according to a mechanism originally proposed by Curtis et al. for reactions with the halides HX (X = Cl, Br) [64], yields respectively the thiolato-bridged compounds $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}ER)(CO)_4]$ **2** [31] and $[Mo_2Cp_2(\mu\text{-}ER)_2(CO)_4]$ **3** [19] (Scheme 1). Decarbonylation of **3** affords the derivative $[Mo_2Cp_2(\mu\text{-}ER)_2(CO)_2]$ **4** and its oxidation by two equivalents of $AgBF_4$ gives



Scheme 1.

the dicationic species $[Mo_2Cp_2(\mu\text{-}ER)_2(CO)_4](BF_4)_2$ **5** (Scheme 1) [22]. The fluxional nature of complexes **2** in solution has been shown from variable-temperature NMR experiments to involve a cis–trans isomerization. In the solid state, molecules of **2** contain a planar $Mo_2(\mu\text{-}H)(\mu\text{-}S)$ core and the Cp ligands are cis with respect to the Mo–Mo axis (3.237(1) Å) (Fig. 1), whereas the trans configuration is found in phosphido and arsenido analogues [65–68]. The Mo–H–Mo unit contains a three-centre two-electron bond and, if the Mo–Mo bond is disregarded, each Mo atom has a four-legged piano-stool coordination. Various isomers are known for complexes $[Mo_2Cp_2(\mu\text{-}ER)_2(CO)_4]$ **3** and $[Mo_2Cp_2(\mu\text{-}ER)_2(CO)_2]$ **4** which are based on cis- or trans-configurations of the cyclopentadienyl ligands with respect to the

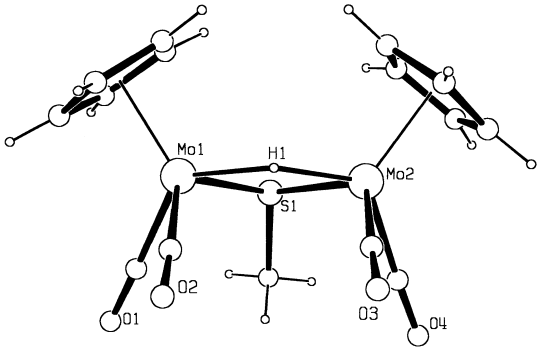


Fig. 1. A view of a molecule of $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}SMe)(CO)_4]$ **2**. The Mo1–Mo2 separation is 3.237(1) Å. Carbon and hydrogen atoms (apart from the μ-H hydride) are not explicitly labelled but are shown as spheres of different sizes. Labels are shown for all other atoms. Similar conventions are used in Figs. 2–11.

Mo_2S_2 ring and on the mutually syn or anti orientations of the chalcogen R substituents. Complex **4** exists as two isomers in solution, with trans–anti and trans–syn geometries (Scheme 1). The principal feature of these molecules is a planar Mo_2S_2 core with an Mo=Mo double bond (2.569(6)–2.616(2) Å) [55,63]. Although *trans*-$[Mo_2Cp_2(\mu\text{-}SR)_2(CO)_2]$ complexes have been known for about 20 years [19,55] their reactivity has only recently been studied [28,69,70]. Thus $[Mo_2Cp_2(\mu\text{-}SCF_3)_2(CO)(CNMe)]$ is the first isocyanide complex derived from such a reaction to be characterized by X-ray crystallography (Fig. 2) [38]. The CO and CNMe ligands are trans with respect to the Mo_2S_2 core, with the isocyanide ligand situated on the same side of the core as the syn CF_3 groups. The Mo–Mo separation (2.597(1) Å) is consistent with a metal–metal bond of order two which confers a closed shell configuration on the metal centres and is similar to that found in other *trans*-$[M_2Cp_2(\mu\text{-}SR)_2(CO)_2]$ complexes [55,60]. As in the structure of

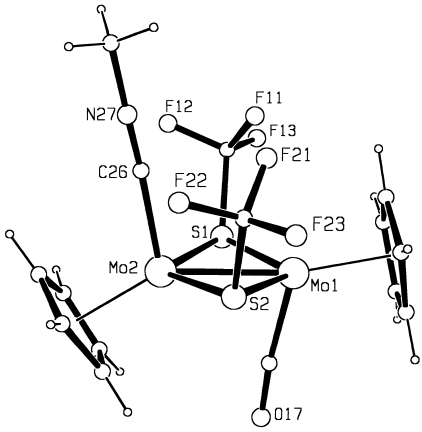


Fig. 2. A view of a molecule of $[Mo_2Cp_2(\mu\text{-}SCF_3)_2(CO)(CNMe)]$. The Mo1–Mo2 separation is 2.597 Å.

trans, *syn*-[$Mo_2Cp_2(\mu\text{-}S^tBu)_2(CO)_2$] [55], there is a pseudo-mirror plane of symmetry in the molecule of *trans, syn*-[$Mo_2Cp_2(\mu\text{-}SCF_3)_2(CO)(CNMe)$]. The trans, anti complexes adopt a centrosymmetric arrangement, with a planar Mo_2S_2 core.

The existence of geometric isomers of **3** is also well known [49,55,56,60]. In the solid state these complexes adopt a trans–anti geometry with a non-planar Mo_2S_2 core and Mo–Mo distances (3.916(1)–4.23 Å) [47,55] which preclude metal–metal bonding. In solution a mixture of trans and cis isomers is observed (Scheme 1), the cis/trans ratio depending on the nature of the sulfur substituents. Syn and anti isomerism can be detected provided the inversion at the sulfur is slowed sufficiently by cooling. [$Mo_2Cp_2(\mu\text{-}SR)_2(CO)_4$] complexes undergo a two-electron oxidation which is reversible only for the cis isomer. The transfer of two electrons in a single reversible step requires that addition of the first electron destabilizes the singly occupied HOMO, which, in turn, triggers the transfer of a second electron at the same potential as the first. In the case of *cis*-[$Mo_2Cp_2(\mu\text{-}SR)_2(CO)_4$], the single-step two-electron process is due to a modification of the geometry of the Mo_2S_2 core [22,25,71–76]. The geometrical change of the butterfly $Mo_2(\mu\text{-}S)_2$ unit upon two-electron oxidation is demonstrated by the X-ray structural analysis of *cis*-$[Mo_2Cp_2(\mu\text{-}SR)_2(CO)_4]^{2+}$ **5** (R = ^{t}Bu) (Fig. 3) [22]. The Mo–Mo distance (3.008(2) Å) [22] is considerably shorter than corresponding values for the neutral *trans*-[$Mo_2Cp_2(\mu\text{-}SPh)_2(CO)_4$] (Mo…Mo = 3.940 Å [55]) and the M–S–M angles are, in consequence, more acute. The irreversible two-electron oxidation of the trans isomer of [$Mo_2Cp_2(\mu\text{-}SR)_2(CO)_4$] induces a trans–cis isomerization process (Scheme 2). Although the radical cation $[Mo_2Cp_2(\mu\text{-}SR)_2(CO)_4]^{\cdot +}$ is thermodynamically unstable with respect to disproportionation into the neutral and dicationic compounds, it will be shown in Section 2.2.2 to be a key-intermediate in substitution reactions.

The reaction of [$MoCpH(CO)_3$] with MeSSMe also leads to **3**, but in presence of allyl halides this molybdenum(II) product can be further oxidized with

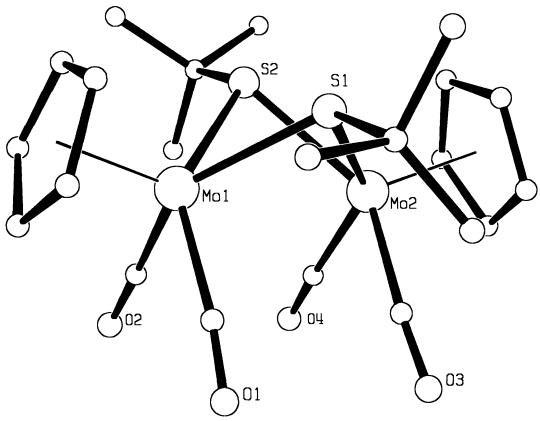
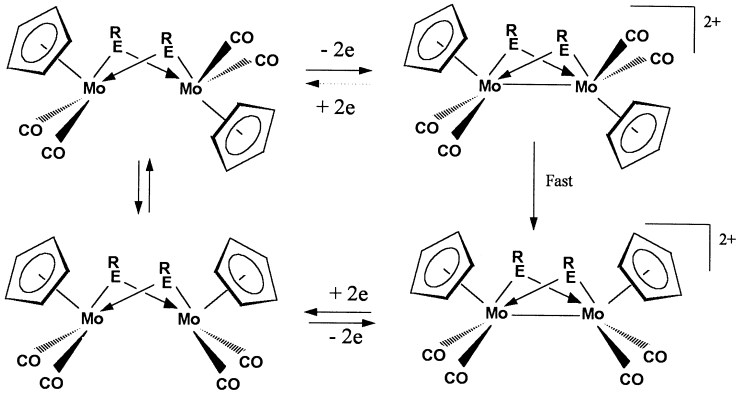
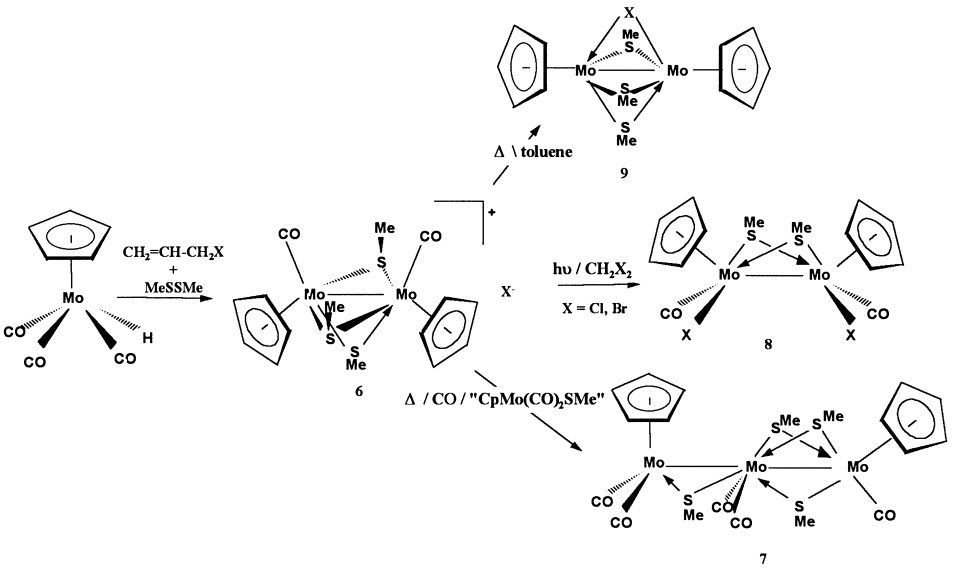


Fig. 3. A view of the dication *cis*-$[Mo_2Cp_2(\mu\text{-}S^tBu)_2(CO)_4]^{2+}$ **5** as found in crystals of its BF_4^- salt. The Mo1–Mo2 separation is 3.008 Å. Hydrogen atoms are not shown.



Scheme 2.

MeSSMe to give the tris-thiolato-bridged dimolybdenum(III) derivatives $[Mo_2Cp_2(\mu\text{-}SMe)_3(CO)_2]X$ **6** (X = Cl, Br) (Scheme 3) [21]. In addition to the cationic species **6**, and depending on the experimental conditions, a trinuclear co-product $[CpMo(CO)(\mu\text{-}SMe)_3Mo(CO)_2(\mu\text{-}SMe)Mo(CO)_2Cp]$ **7** is obtained and has been identified by an X-ray diffraction study [32]. The photolysis of **6** in dihalomethane, CH_2X_2, affords, through a ligand exchange reaction, neutral molybdenum(III) dimers formulated as $[Mo_2Cp_2X_2(\mu\text{-}SMe)_2(CO)_2]$ **8** (X = Cl, Br). The thermolysis of **6** in toluene yields the decarbonylated derivatives $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}X)]$ **9** (X = Cl, Br) (Scheme 3) [21]. The structure of the bromide salt $[Mo_2Cp_2(\mu\text{-}SMe)_3(CO)_2]Br$



Scheme 3.

6 (Fig. 4) involves two strongly distorted $MoS_3(CO)$ pyramids connected via three sulfur bridges. A notable feature of this structure is the near linearity of the Cp–Mo–Mo–Cp axis. The Mo–Mo separation (2.785 Å), is consistent with an Mo–Mo single bond [77]. **7** contains a $(C_5H_5)(CO)Mo(\mu\text{-}SMe)_3Mo(CO)_2$ core in which the triply-bridged Mo–Mo bond is of normal length [2.800(1) Å). This core is linked to the $C_5H_5Mo(CO)_2SMe$ unit via its sulfur atom and through an unusually weak Mo–Mo bond of 3.115(2) Å, the Mo–Mo–Mo angle being 144.5(1)° (Fig. 5). Recently, the structure of an analogue of **9**, namely $[Mo_2Cp_2(\mu\text{-}Cl)(S_2CH_2)(\mu\text{-}SMe)]$, was described [78] and the results of this crystallographic study indicated that these mixed quadruply-bridged molybdenum(III) complexes are very similar to the dinuclear species $[Mo_2Cp_2(\mu\text{-}SMe)_4]$ [48].

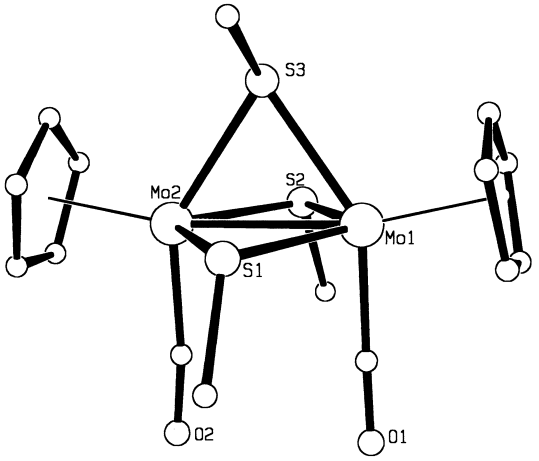


Fig. 4. A view of the cation $[Mo_2Cp_2(\mu\text{-}SMe)_3(CO)_2]^+$ **6** as found in its bromide salt. The Mo1–Mo2 separation is 2.784 Å. Hydrogen atoms are not shown.

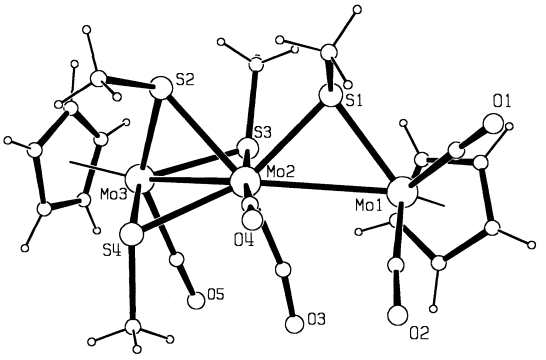


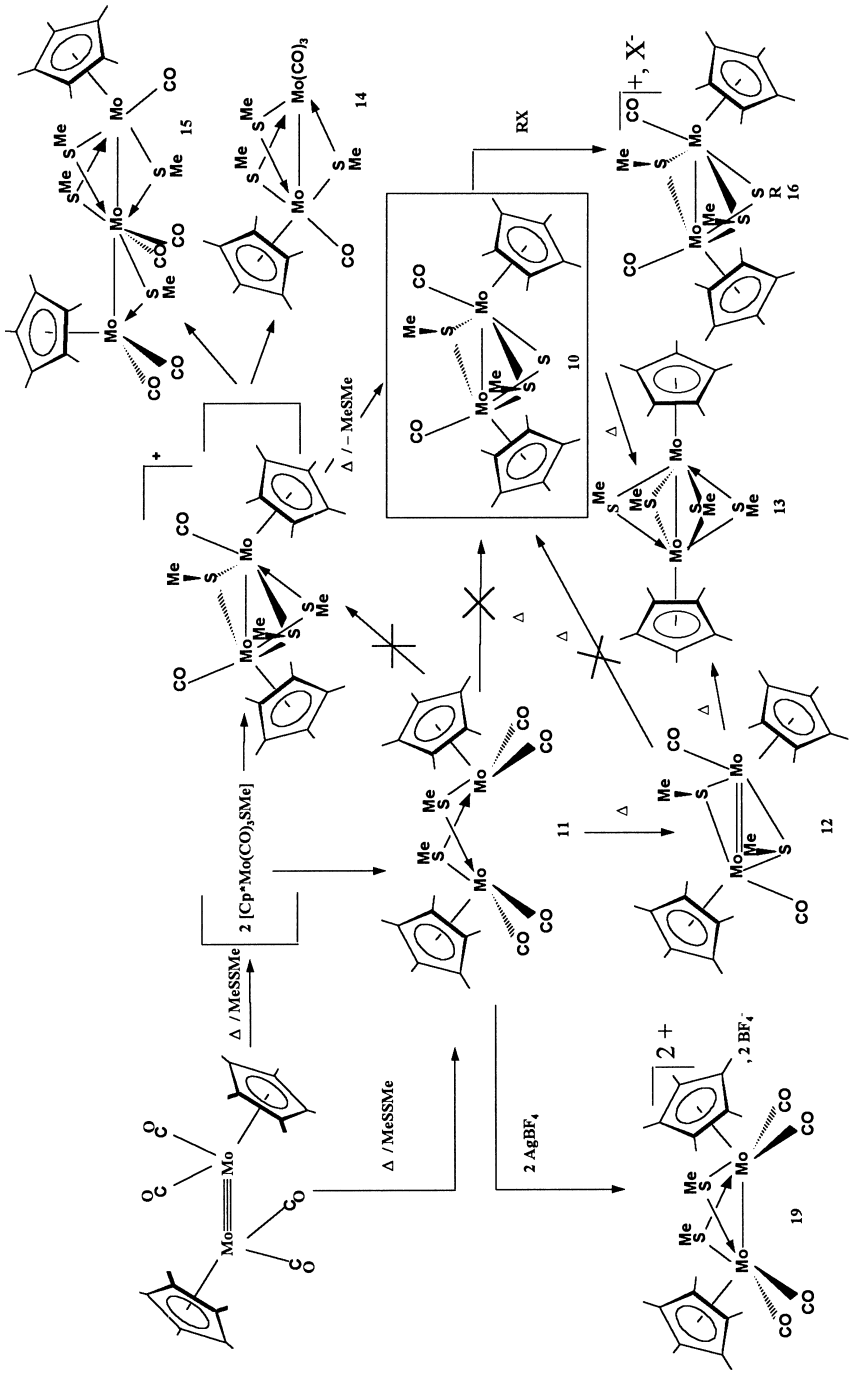
Fig. 5. A view of a molecule of $[CpMo(CO)(\mu\text{-}SMe)_3Mo(CO)_2(\mu\text{-}SMe)Mo\text{–}(CO)_2Cp]$ **7**. The Mo1–Mo2 and Mo2–Mo3 distances are 3.115(2) and 2.800(1) Å.

2.2. Pentamethylcyclopentadienyldimolybdenum [Mo(II)–Mo(II)], [Mo(III)–Mo(III)] compounds: substitution of cyclopentadienyl by pentamethylcyclopentadienyl

2.2.1. Reaction of MeSSMe with $[Mo_2Cp^*_2(CO)_4]$

The replacement of Cp by the more electron-rich pentamethylcyclopentadienyl (Cp*) influences both the ease and the course of the decarbonylation reactions. The thermal or photochemical reactions of $[Mo_2Cp^*_2(CO)_4]$ with dialkyl or diaryl dichalcogenides, REER, or with thiol or selenol, HER, give products which depend on the nature of E and R (Scheme 4 with ER = SMe) [30]. As in their reaction with the analogous cyclopentadienyl complex, the dialkyl or diaryl chalcogenides, REER, can directly couple to the dimolybdenum site in $[Mo_2Cp^*_2(CO)_4]$ to produce the corresponding chalcogenato-bridged molybdenum complexes $[Mo_2Cp^*_2(\mu\text{-ER})_2(CO)_4]$ by oxidative addition, but the reaction with HER does not afford the complexes $[Mo_2Cp^*_2(\mu\text{-H})(\mu\text{-ER})(CO)_4]$.

The two main products of the oxidation of $[Mo_2Cp^*_2(CO)_4]$ with dimethyl disulfide are $[Mo_2Cp^*_2(\mu\text{-SMe})_2(\mu\text{-S})(CO)_2]$ **10** [Mo(III)–Mo(III)] and $[Mo_2Cp^*_2(\mu\text{-SMe})_2(CO)_4]$ **11** [Mo(II)–Mo(II)]. The reaction also gives significant amounts of four side-products: $[Mo_2Cp^*_2(\mu\text{-SMe})_2(CO)_2]$ **12**, $[Mo_2Cp^*_2(\mu\text{-SMe})_4]$ **13**, $[Cp^*Mo(CO)(\mu\text{-SMe})_3Mo(CO)_3]$ **14** and $[Cp^*Mo(CO)(\mu\text{-SMe})_3Mo(CO)_2(\mu\text{-SMe})Mo(CO)_2Cp^*]$ **15** (Scheme 4). In solution the compound $[Mo_2Cp^*_2(\mu\text{-SMe})_2(CO)_4]$ **11** has a cis–syn geometry which contrasts with that of the Cp analogue. Only the trans–syn form is observed in solution of $[Mo_2Cp^*_2(\mu\text{-SMe})_2(CO)_2]$ **12**, and $[Mo_2Cp^*_2(\mu\text{-SMe})_2(\mu-S)(CO)_2]$ **10** was assigned a cis–syn geometry. The μ-sulfido complex **10** is only obtained when ER = SMe. Complex **10** reacts through the nucleophilic sulfido bridge with electrophilic and alkylating agents. Addition of either HX (X = BF_4, Cl, F) or $[Me_3O][BF_4]$, MeI and other alkyl halides to a dichloromethane solution of **10** rapidly produces the tris-thiolato-bridged complexes $[Mo_2Cp^*_2(\mu\text{-SMe})_2(\mu\text{-SR})(CO)_2]X$ **16** (Scheme 4). One of these, $[Mo_2Cp^*_2(\mu\text{-SMe})_2(\mu\text{-SH})(CO)_2](BF_4)$ (**16**, R = H, X = BF_4; Fig. 6) contains a cation whose structure is closely analogous to that found in the cyclopentadienyl complex $[Mo_2Cp_2(\mu\text{-SMe})_3(CO)_2]Br$ [21]. It contains two nearly identical Cp*Mo(CO) units which eclipse each other when viewed along the Mo–Mo vector. The Mo–Mo bond (Mo–Mo = 2.772(2) Å) is supported by two bridging μ-SMe groups and a bridging μ-SH unit. The metal coordination can be described as a $Cp^*Mo(CO)S_3$ piano stool and the cation approximates quite closely to C_{2v} geometry. $[Mo_2Cp^*_2(\mu\text{-SMe})_2(\mu\text{-SH})(CO)_2](BF_4)$ **16** can be deprotonated with bases such as triethylamine to regenerate the sulfido complex **10**. Decarbonylation of **11** by heating in toluene solution (110°C) gives the dinuclear product $[Mo_2Cp^*_2(\mu\text{-SMe})_2(CO)_2]$ **12**, but no **10** is formed in this reaction. Complete decarbonylation of these complexes by prolonged heating gives the tetra-bridged product $[Mo_2Cp^*_2(\mu\text{-SMe})_4]$ **13** (Scheme 4). It therefore follows that complexes **11** and **12** are not precursors of **10**. Of the candidates which have been considered for the role, the cationic tris-thiolato-bridged complex $[Mo_2Cp^*_2(\mu\text{-}SMe)_3(CO)_2]^+$ appears to be the most plausible choice for a precursor of **10**: heating an authentic sample of this



Scheme 4.

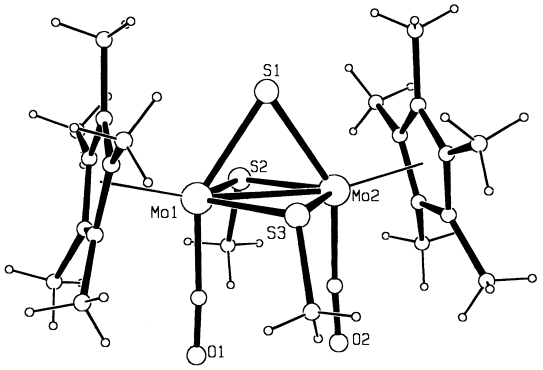
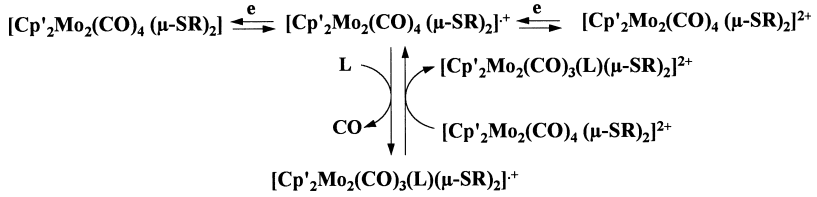


Fig. 6. A view of the cation in $[Mo_2Cp^*_2(\mu\text{-}SMe)_2(\mu\text{-}SH)(CO)_2](BF_4)$ **16**. The Mo1–Mo2 separation is 2.772(2) Å. The hydrogen atom attached to S1 was not located.

complex, obtained by a different route, gives **10** quantitatively. Dealkylation of one thiolato group of the cationic intermediate provides a μ-S ligand. There have been a few reports of the dealkylation of thiolato ligands at mono- and di-nuclear molybdenum centres, but in each case the presence of a hydride ligand has been considered significant [79,80]. In the present case the alkyl group could be eliminated as Me_2S. No Cp analogue of **10** is known, and it is possible that the greater electron release from the Cp* ring stabilizes this (μ-sulfido)dicarbonyldimolybdenum(III) compound toward decarbonylation. It has been shown that CpCr analogues of **11** and **12**, e.g. $[Cr_2Cp_2(\mu\text{-}SPh)_2(CO)_4]$ and $[Cr_2Cp_2(\mu\text{-}SPh)_2(CO)_2]$, are the precursors of the carbonyl-free unsaturated sulfido compound $[Cr_2Cp_2(\mu\text{-}SPh)_2(\mu\text{-}S)]$, but no carbonyl-containing sulfido compound was detected in the thermolytic reaction of the thiolato chromium complexes. Similarly, complete thermal decarbonylation of $[CrCpTePh(CO)_3]$ to $[Cr_2Cp_2(\mu\text{-}TePh)_2(\mu\text{-}Te)]$ has been observed [81].

2.2.2. *Carbonyl-substitution reactions in* $[Mo_2Cp'_2(\mu\text{-}SMe)_2(CO)_4]^{2+}$ *and* $[Mo_2Cp'_2(NCO)(\mu\text{-}SMe)_2(CO)_3]^+$ $(Cp' = C_5H_5,\ C_5Me_5)$

The $[Mo_2Cp_2(\mu\text{-}SR)_2(CO)_4]^{z+}$ complexes have the interesting property of forming substituted derivatives via electrochemically induced processes. Many reactions of this type, which may or may not be catalytic [82], have been reported for mono- [83–88], di- [89–98], and poly-nuclear [99–108] complexes. In the case of $[Mo_2(\mu\text{-}SR)_2(CO)_8]^{2-}$, oxidatively induced substitution of MeCN for CO has been reported to yield the disubstituted complexes $[Mo_2(\mu\text{-}SR)_2(CO)_6(MeCN)_2]$ [76,109]. The singly substituted derivatives were identified electrochemically but could not be isolated. The electrochemical oxidation of the neutral dimers $[Mo_2Cp_2(\mu\text{-}SR)_2(CO)_4]$ performed at the potential of the trans→cis^{2+} process in neat MeCN or in THF containing added MeCN or ^{t}BuNC ($T \sim 40°C$), leads to the formation of singly substituted nitrile or isocyanide complexes $[Mo_2Cp_2(\mu\text{-}SR)_2(CO)_3L]^{2+}$, which can also be obtained from the reduction of *cis*-$[Mo_2Cp_2(\mu\text{-}SR)_2(CO)_4]^{2+}$ in the presence of these ligands, according



Scheme 5.

to an electron-transfer chain catalysed (ETC) process [24]. Neither $[Mo_2Cp_2(\mu\text{-}SR)_2(CO)_4]$ nor $[Mo_2Cp_2(\mu\text{-}SR)_2(CO)_4]^{2+}$ react with the ligand (L) at room temperature (nor even at 40°C on the time scale of the electrochemical experiment). It follows that the substitutionally labile species which leads from either the neutral or the dicationic parent to the acetonitrile or isocyanide complexes must be the radical cation $[Mo_2Cp_2(\mu\text{-}SR)_2(CO)_4]^{\cdot +}$ (Scheme 5). EHMO calculations suggested that the substrate-binding site may be formed by opening a thiolate bridge at the radical cation stage [26]. The sulfur substituents R have a substantial effect on both the readiness of the complex to undergo substitution and on the cis/trans isomer ratio for the neutral complex; the effect can be rationalized on the basis that M–SR bonds are more readily broken when R is electron-withdrawing [110].

Monosubstituted cyclopentadienyl derivatives $[Mo_2Cp_2(\mu\text{-}SR)_2(CO)_3L](BF_4)_2$ (L = MeCN) **17** can also be obtained on refluxing an acetonitrile solution of the tetracarbonyl dimer **5** [24]. X-ray analysis of $[Mo_2Cp_2(\mu\text{-}SPh)_2(CO)_3(CH_3CN)](BF_4)_2$ (**17**, R = Ph; Fig. 7) shows that the dimeric structure of the cation is based on a butterfly $Mo_2(\mu\text{-}S)_2$ core. A comparison of the bond lengths and angles in the substituted complex with those in the related tetracarbonyl parent

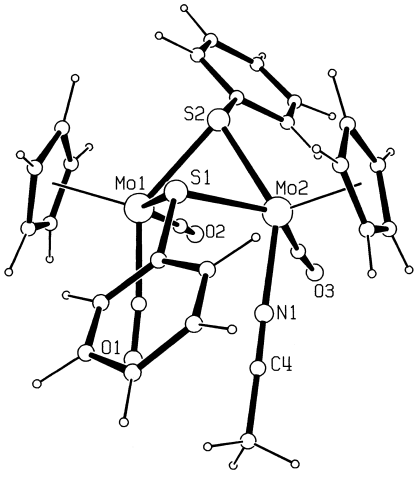
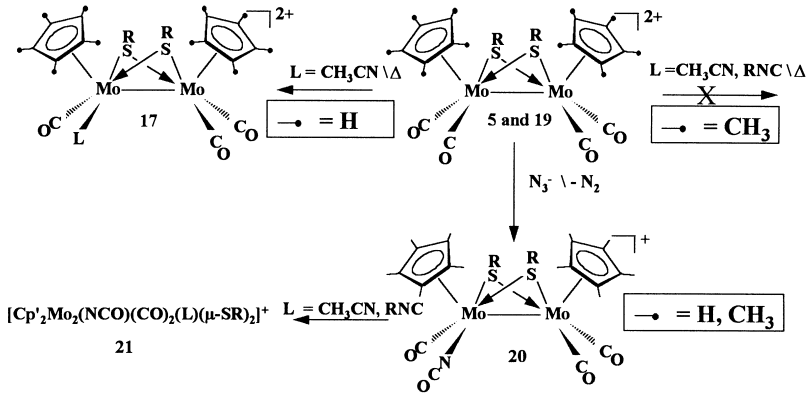


Fig. 7. A view of the cation in $[Mo_2Cp_2(\mu\text{-}SPh)_2(CO)_3(CH_3CN)](BF_4)_2$ 18. The Mo1–Mo2 separation is 3.006(3) Å.

$[Mo_2Cp_2(\mu\text{-}S\text{–}^tBu)_2(CO)_4](BF_4)_2$ [22] indicates that the $Mo_2(\mu\text{-}5)_2$ cores have very similar geometries. The observed Mo–Mo bond length (3.006(3) Å) is typical of the values found in other complexes of similar structure [21]. The Mo–S–Mo angles subtended at the μ-S atoms are acute (75°) and are comparable with those required for a structure in which metal–metal interaction exists [111,112]. The cyclopentadienyl rings, and, therefore, the two pairs of carbonyl and carbonyl/acetonitrile ligands, adopt a mutually cis configuration. The two phenyl rings are syn with respect to the S…S vector. Thermal treatment of the dimers **3** with $AgBF_4$ in acetonitrile yields mono- and tri-substituted derivatives $[Mo_2Cp_2(\mu\text{-}SMe)_2(CO)_{4-n}L_n](BF_4)_2$ (L = MeCN) (n = 1, **17**; 3, **18**) depending on the experimental conditions. Attempts to substitute ^{t}BuNC for CO by reacting the neutral dimers $[Mo_2Cp_2(\mu\text{-}SMe)_2(CO)_4]$ with $AgBF_4$ and ^{t}BuNC proved unsuccessful.

The Mo–Mo distances in *cis*-$[Mo_2Cp_2(\mu\text{-}SR)_2(CO)_3L](BF_4)_2$ (L = CO, R = ^{t}Bu, L = MeCN, R = Ph) are significantly longer than those found in other Mo^{III}–Mo^{III} complexes. This appears to be associated with the number of bridging groups; thus, a survey of the literature for dimeric Mo complexes containing μ-SMe units [21,41,70,113–118] suggests that the Mo–Mo distance shortens as the number of bridging ligands increases; complexes containing an $Mo_2(\mu\text{-}S)_4$ core have Mo–Mo bond lengths in the range 2.573–2.626 Å with acute Mo–S–Mo angles of 62–65°; species with three bridging groups show slightly less acute Mo–S–Mo angles of 68–70° and longer Mo–Mo distances of 2.755–2.800 Å.[2]

Like its cyclopentadienyl analogue, complex **11** was readily oxidized by $Ag[BF_4]$ to yield the dicationic product cis, syn-$[Mo_2Cp^*_2(\mu\text{-}SMe)_2(CO)_4](BF_4)_2$ **19**, but no substitution of carbonyl by acetonitrile was observed when **19** was stirred in refluxing MeCN; this again accords with Cp* compounds showing greater resistance to decarbonylation than their Cp analogues (Scheme 6). Inert carbonyl complexes of this type can be activated by introducing a halide or a pseudo-halide ligand into the



Scheme 6.

[2]These conclusions are confirmed by a survey of the most recent (October, 1997) version of the Cambridge Structural Database.

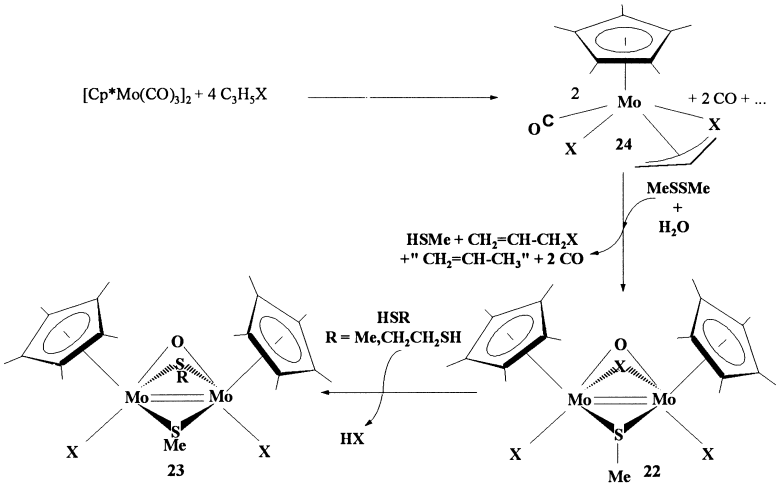
metallic framework [119]. For example, the unreactive pentamethylcyclopentadienyl complex $[Mo_2Cp^*_2(\mu\text{-}SR)_2(CO)_4](BF_4)_2$ **19** can be activated towards further CO substitution if a single carbonyl is replaced by an isocyanate ligand. The reaction of N_3^- with the dinuclear tetracarbonyl complexes $[Mo_2Cp'_2(\mu\text{-}SR)_2(CO)_4]^{2+}$ leads to the isocyanate products $[Mo_2Cp'_2(NCO)(\mu\text{-}SMe)_2(CO)_3](BF_4)$ **20** via a mechanism analogous to the Curtius rearrangement proposed by Beck for monometallic carbonyl compounds [LnMCO] [120,121]. Other examples of di- or poly-metallic isocyanate products are known, eg. see Refs. [122–124]. In contrast to their dicationic precursor $[Mo_2Cp'_2(\mu\text{-}SR)_2(CO)_4]^{2+}$, the NCO–cyclopentadienyl complexes **20** easily undergo carbonyl substitution by unsaturated substrates, such as acetonitrile or isocyanide, under mild conditions (room temperature) to give $[Mo_2Cp'_2(NCO)(\mu\text{-}SMe)_2(CO)_2L](BF_4)$ (L = MeCN, RNC) **21** [39] (Scheme 6). Thermal or electrochemical activation is required to achieve a similar CO labilization in the tetracarbonyl complexes $[Mo_2Cp_2(\mu\text{-}SR)_2(CO)_4]^{2+}$ [24]. The role of the isocyanate ligand can be explained by its semi-labile character. NCO can act as a three-electron donor bridging ligand [122], moving to a terminal position on coordination of a substrate (CO, CH_3CN or R′NC). Halide bridges in some dinuclear complexes behave in a similar fashion [35].

2.2.3. Pentamethylcyclopentadienyl μ-oxo dinuclear molybdenum(IV) thiolato-bridged compounds

The presence of Cp* instead of Cp both facilitates the addition of oxygen and helps to stabilize the increased oxidation state of the metal in the resulting mononuclear and dinuclear oxide complexes [125–128]. An unexpected formation of the dinuclear molybdenum(IV) compounds $[Mo_2Cp^*_2X_2(\mu\text{-}O)(\mu\text{-}X)(\mu\text{-}SMe)]$ (X = Cl, Br) **22** and $[Mo_2Cp^*_2X_2(\mu\text{-}O)(\mu\text{-}SMe)_2]$ (X = Cl, Br) **23** is observed, from reactions of $[MoCp^*(CO)_3]_2$ with halogenating (allyl halide: C_3H_5X) and thioalkylating (dimethyldisulfide) reagents, in moderate but reproducible yields under conditions supposed anhydrous and oxygen-free (Scheme 7) [37].

22 (X = Br) contains an $Mo_2(\mu\text{-}Br)(\mu\text{-}O)(\mu\text{-}SMe)$ core and its Cp* ligands are cis with respect to the Mo–Mo axis, as are the terminal Br groups (Fig. 8). An approximate plane of symmetry normal to the Mo–Mo bond passes through the bridging O, Br and S donor atoms and relates the two Cp*MoBr units. The formally double Mo–Mo bond is relatively long (2.755(1) Å). Although normal electron counting rules would require the presence of an Mo(IV)=Mo(IV) double bond in **22**, there are good reasons for regarding a metal–metal bond order of one as more appropriate: bonding schemes for Mo(III) and Mo(IV) complexes with $[Mo_2Cp_2(\mu\text{-}X)_4]$ or $[Mo_2Cp_2X_2(\mu\text{-}X)_3]$ geometries indicate that in all these species a single frontier orbital is mainly responsible for the Mo–Mo bonding [126,129]. In conformity with this view, the Mo–Mo distance in **22** appears long compared with a mean length of 2.60 Å for 61 formally double Mo–Mo bonds found in the Cambridge Structural Database;[3] 80% of these bonds lie in the range 2.45–2.77 Å [129]. Relatively few

[3]Using the versions of the programs QUEST and VISTA mounted at the Daresbury National Laboratory, Warrington, UK.



Scheme 7.

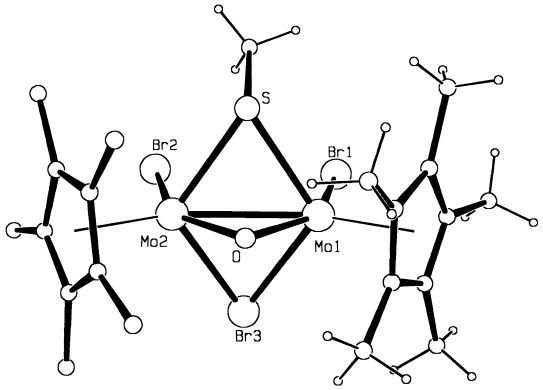


Fig. 8. A view of a molecule of $[Mo_2Cp^*_2Br_2(\mu\text{-}O)(\mu\text{-}Br)(\mu\text{-}SMe)]$ **22**. The Mo1–Mo2 separation is 2.755(1) Å. The Cp* ligand bound to Mo2 is disordered and its hydrogen atoms are not shown.

molybdenum complexes with the $[Mo_2Cp_2X_2(\mu\text{-}X)_3]$ geometry exemplified by **22** have been structurally characterized, but, as expected, all have been found to contain long Mo–Mo bonds irrespective of the metal oxidation state: $[Mo_2^{IV}Cp^*_2Cl_2(\mu\text{-}O)(\mu\text{-}Cl)_2]$ 2.72 Å and $[Mo_2^{IV}Cp^*_2Cl_2(\mu\text{-}Cl)(\mu\text{-}CO_3H)(\mu\text{-}O)]$ 2.799(4) Å [126]; $[Mo_2^{II}Cp_2(\mu\text{-}SMe)_3(CO)_2]^+$ 2.784 (1) Å [21]; $[Mo_2^{IV}Cp^*_2Cl_2(\mu\text{-}Cl)_3]^+$ 2.870(4) Å [129].

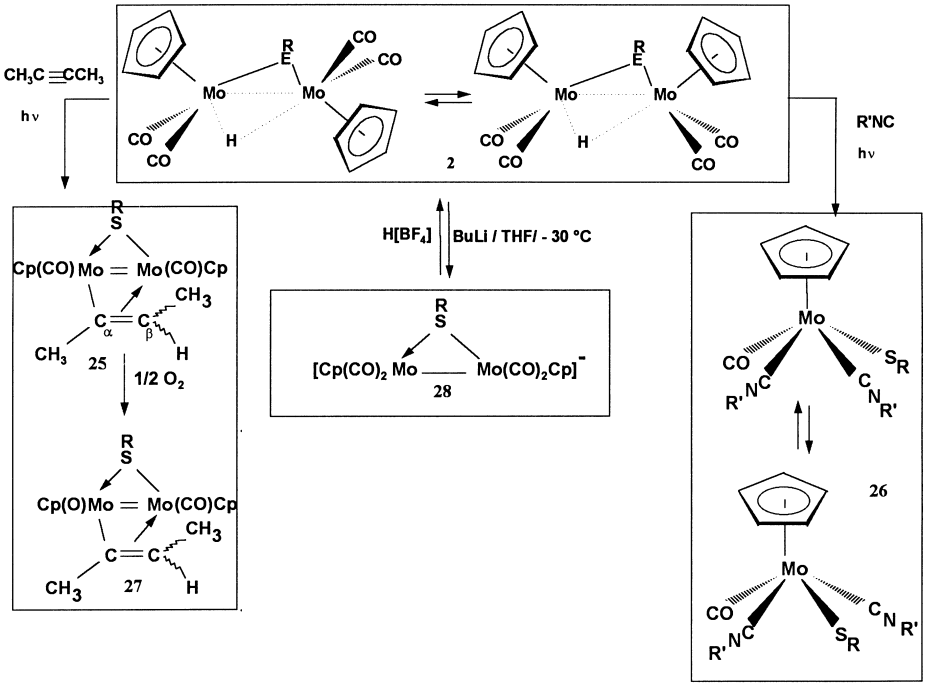
The dinuclear complex $[MoCp^*(CO)_3]_2$ reacts with allyl halide to give $[MoCp^*X_2(\eta^3\text{-}C_3H_5)(CO)]$ **24** via the intermediate $[MoCp^*X(CO)_3]$. It has been shown that the photolytic transformation of $[MoCpX(CO)_3]$ into $[MoCpX_2(\eta^3\text{-}C_3H_5)(CO)]$ in the presence of allyl halide involves two intermediates, $[MoCpX_2(\eta^1\text{-}C_3H_5)(CO)_2]$ and $[MoCpX(\eta^2\text{-}C_3H_5X)(CO)_2]$ [130,131], neither of

which have been observed here. In the presence of dimethyldisulfide and allyl halide, the initial formation of $[MoCpX(CO)_3]$ and $[MoCpX_2(\eta^3\text{-}C_3H_5)(CO)]$ is again observed and the reaction can be stopped at this stage under mild conditions. Formally, the transformation of two molecules of the allylic complex $[MoCp^*X_2(\eta^3\text{-}C_3H_5)(CO)]$ into the oxo-product $[Mo_2Cp^*X_2(\mu\text{-}O)(\mu\text{-}X)(\mu\text{-}SMe)$ requires (i) the addition of an oxygen atom and an SMe group, and (ii) the loss of both two CO groups and of two C_3H_5X units (X = Cl or Br and H) (Scheme 7). The reaction may proceed via the hydrolysis of $[MoCp^*X_2(\eta^3\text{-}C_3H_5)(CO)]$ in the presence of MeSSMe.

2.3. Reactivity of μ-hydrido dimolybdenum complexes

The compounds $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}ER)(CO)_4]$ **2** display a specific reactivity since the presence of the hydride bridge and of only a single μ-thiolate ligand may not be sufficient to inhibit fragmentation and decarbonylation of the dinuclear framework [33]. However, the reactivity of **2** appears rather limited when it is compared with that of the phosphido-bridged analogues [132,133]. Among their possible reactions, insertion of alkyne into the metal–hydrogen bond is one of the most important because it is a key step in catalytic processes involving hydrogenation and polymerization of alkynes [134,135]. Moreover, it provides a convenient route to σ–π alkenyl complexes [132,136,137].

The μ-vinylic complexes $[Mo_2Cp_2\{\mu\text{-}\sigma\text{:}\eta^2\text{-}C(CH_3)=CHCH_3\}(\mu\text{-}SR)(CO)_2]$ (R = Me, Ph) **25** can be obtained by reaction of the hydrido-, thiolato-compounds $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}SR)(CO)_4]$ (R = Me, Ph) **2** with 2-butyne (Scheme 8). The structure of **25** (R = Ph) contains a $\mu\text{-}\sigma\text{:}\eta^2\text{-}C(CH_3)=CHCH_3$ ligand which bridges an Mo=Mo double (Mo–Mo = 2.644(1) Å) (Fig. 9). Electron counting rules require an order of two for the Mo–Mo bond. Its length is close to the average value of 2.61 Å for 62 such distances obtained from the Cambridge Structural Database. Although there are other examples of structurally characterized complexes containing a simple $\mu\text{-}\sigma\text{:}\eta^2\text{-}CR=CR_2$ ligand bridging two molybdenum atoms, such as $[Mo_2Cp_2\{\mu\text{-}\sigma\text{:}\eta^2\text{-}C(CH_3)=CHCH_3\}(\mu\text{-}PMe_2)(CO)_3]$ [132], $[Mo_2Cp_2(\mu\text{-}\sigma\text{:}\eta^2\text{-}CH=CH_2)(CO)_4]$ [138] and $[Mo_2Cp_2(\mu\text{-}\sigma\text{:}\eta^2\text{-}CH=CHPh)(CO)_4(H_2O)]^+$ [139], all involve Mo–Mo bonds with orders less than two and Mo–Mo distances greater than 3 Å. In $[Mo_2Cp_2\{\mu\text{-}C(CO_2Me)=CHCO_2Me\}(\mu\text{-}S^iPr)(CO)_2]$, formally an exact analogue of **25**, the Mo–Mo bond order is reduced to one through coordination of CO_2Me oxygen to one of the metal atoms and the Cp rings appear to be trans with respect to the Mo–Mo bond [140] in contrast to the nearly linear Cp–Mo–Mo–Cp arrangement in **25**. Attempts were made to extend this reaction to other symmetrical and unsymmetrical alkynes, $(MeO_2C)CC(CO_2Me)$, PhCCPh, MeCCH, PhCCH, CF_3CCH, but no photochemical insertion occurred with consistent yields, and no well-defined product was characterized. This lack of reactivity of the thiolato-complexes seems surprising, considering how easily the alkynes insert into the Mo–H bond of the analogous phosphido-bridged compounds [132]. Presumably the phosphido bridge is more effective in stabilizing polynuclear species. This view is consistent with the observation that the thiolate group was unable to



Scheme 8.

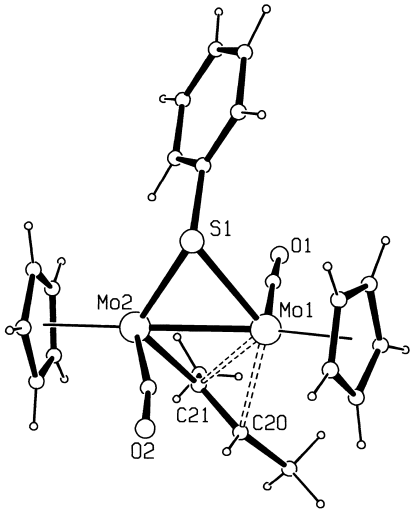


Fig. 9. A view of a molecule of $[Mo_2Cp2\{\mu\text{-}\sigma\text{:}\eta^2\text{-}C(CH_3)=CHCH_3\}(\mu\text{-}SPh)\text{–}(CO)_2]$ **25**. The Mo1–Mo2 separation is 2.644(1) Å.

prevent the break up of the dinuclear framework when attempts were made to insert either alkenes or isocyanide into the M–H bonds of **2** [141]. Thus, the photolytic reaction leads to a mixture of cis and trans isomers of the mononuclear product $[MoCpSR(CO)(R'NC)_2]$ (R′ = ^{t}Bu, Xylyl; R = Me, Ph) **26** [141] when R′NC was used (Scheme 8). Similar mechanisms may be suggested for the initial steps in the formation of the μ-σ:η^2 vinylic products $[Mo_2Cp_2\{\mu\text{-}\sigma\text{:}\eta^2\text{-}C(CH_3)=CHCH_3\}(\mu\text{-}PMe_2)(CO)_3]$ [132] and $[Mo_2Cp_2\{\mu\text{-}\sigma\text{:}\eta^2\text{-}C(CH_3)=CHCH_3\}(\mu\text{-}SR)(CO)_2]$ [142]. However, the final phosphido and thiolato products contain respectively three and two carbonyl groups. Evidently, the electronic properties of the phosphido bridge inhibit decarbonylation of $[Mo_2Cp_2\{\mu\text{-}\sigma\text{:}\eta^2\text{-}C(CH_3)=CHCH_3\}(\mu\text{-}PMe_2)(CO)_3]$, whereas the analogous thiolato-bridged species undergoes photo-induced loss of CO. Partial oxidation of **25** with traces of dioxygen gives the mixed oxidation state Mo(II)/Mo(IV) complex $[Mo_2Cp_2(O)\{\mu\text{-}\sigma\text{:}\eta^2\text{-}C(CH_3)=CHCH_3\}(\mu\text{-}SR)(CO)]$ **27**. Similar oxo compounds have been obtained by exposure of molybdenum(II) derivatives $[Mo_2Cp_2(\mu\text{-}X)_2(CO)_2]$ (X = PPh_2 [143], SR (R = Me, Ph [144])) to atmospheric dioxygen, and as a co-product in the synthesis of $[Mo_2Cp_2\{\mu\text{-}\sigma\text{:}\eta^2\text{-}C(R')=CHR''\}(\mu\text{-}PMe_2)(CO)_3]$ [132].

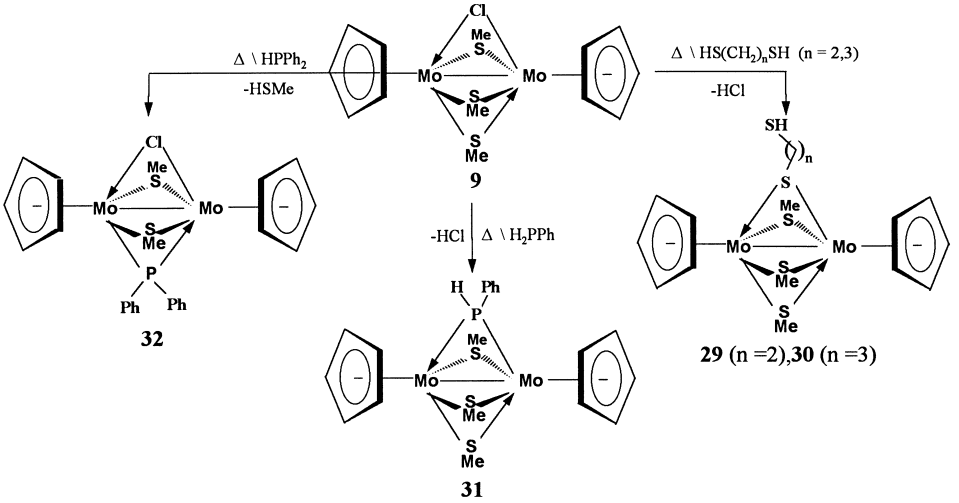
Like their phosphido analogues $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PRR')(CO)_3]$ (R = R′ = Me [145], R = Ph, R′ = H [146]) and other homo- and hetero-bimetallic hydrides [147–149], complexes **2** are acidic, and therefore react readily with bases. Reaction of **2** with BuLi affords green solutions which contain two highly air-sensitive anionic compounds, $[MoCp(CO)_3]^-$ and $[Mo_2Cp_2(\mu\text{-}SR)(CO)_4]^-$ (R = Me, Ph) **28**, the latter also being obtained by two-electron reduction of **2** [33]. Conversely, complexes **28** are easily protonated to regenerate **2** (Scheme 8). The formation of the known mononuclear species $[MoCp(CO)_3]^-$ [150,151] indicates that there is significant decomposition of **2** in the presence of base and that the thiolate bridge is unable to inhibit fragmentation of the dimeric compound under these conditions. Variable-temperature NMR experiments suggest that at low temperature the Cp and CO groups are trans relative to the Mo–Mo axis in **28** and that an enantiomeric interconversion is operative at room temperature [147–149,152].

*2.4. Reactivity of μ-chloro-tris-thiolato-bridged $[Mo_2Cp_2(\mu\text{-}Cl)(\mu\text{-}SMe)_3]$ **9***

The stability of the dinuclear tris-thiolato-bridged $\{Mo_2Cp_2(\mu\text{-}SMe)_3\}$ frame in compound **9**, contrasting with facile cleavage of compounds containing an $\{M_2(\mu\text{-}Cl)\}$ core [153] or M–Cl bonds [154–156], suggested to us that the dinuclear framework $\{Mo_2(\mu\text{-}Cl)(\mu\text{-}SMe)_3\}$ might be used to activate various substrates and to synthesize novel quadruply bridged molybdenum systems through replacement of the chloro-bridge.

*2.4.1. Reactions of **9** with dithiols and phosphines*

The reactions of the chloro-bridged molybdenum(III) complex $[Mo_2Cp_2(\mu\text{-}Cl)(\mu\text{-}SMe)_3]$ **9** with nucleophiles, such as the dithiols $HS(CH_2)_nSH$ (n = 2 or 3) and phosphines H_2PPh and $HPPh_2$, demonstrate its ability to generate new quadruply bridged compounds, the dinuclear structure being maintained by three



Scheme 9.

or two thiolate groups. Thus, the thermal reaction **9** with the dithiols $HS(CH_2)_nSH$ ($n=2, 3$) affords the quadruply thio-bridged complexes $[Mo_2Cp_2(\mu\text{-}S(CH_2)_nSH)(\mu\text{-}SMe)_3]$ (**29**, $n=2$; **30**, $n=3$) (Scheme 9). Complex **29** has been shown by X-ray diffraction to contain the $\mu\text{-}\eta^1$-dithiolate ligand $HS(CH_2)_2S^-$ bridging an Mo–Mo single bond (Fig. 10). It thus belongs to a well-characterized group of structures which contain a $Cp_2Mo_2(\mu\text{-}S)_4$ moiety, where Cp can be a substituted or unsubstituted cyclopentadienyl ring and the bridging sulfur atom may come *inter alia* from ligands such as S_2^-, MeS^-, Me_2S, $CH_2S_2^{2-}$, $^-SCH{=}CHS^-$ or $^-SCHMeCH_2S^-$ [78,115,157,158]. In general, ligands with two

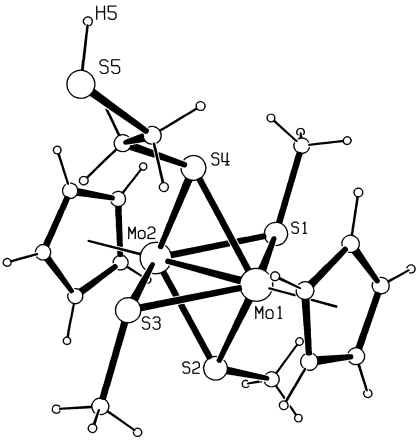


Fig. 10. A view of a molecule of $[Mo_2Cp_2(\mu\text{-}S(CH_2)_2SH)(\mu\text{-}SMe)_3]$ **29**. The Mo1–Mo2 separation is 2.606(1) Å. Disorder of the μ-S atoms, which affects about one molecule in eight, is not shown.

sulfur atoms bind in a μ-η^2-mode, with both S atoms in bridging roles. The few exceptions contain S–S bonds (e.g. S_2Ph [153]) with only one sulfur atom attached to the metal. The Mo–Mo distance in **29** (2.606(1) Å) is virtually identical to the mean of 2.603 Å for **21** such bonds in $Mo_2Cp_2(\mu\text{-}S)_4$ species, the individual values falling in the narrow range 2.573–2.628 Å.[4] Substitution of the chloro bridge in **9** also occurs with phenylphosphine (H_2PPh), giving the μ-phosphido compound $[Mo_2Cp_2(\mu\text{-}HPPh)(\mu\text{-}SMe)_3]$ **31**. However, when diphenylphosphine ($HPPh_2$) is used as the nucleophile, it is the thiolate ligand trans to the chloro bridge which is replaced by a PPh_2 group to give the μ-chloro complex $[Mo_2Cp_2(\mu\text{-}Cl)(\mu\text{-}PPh_2)(\mu\text{-}SMe)_2]$ **32** (Scheme 9).

*2.4.2. Reactions of **9** with hydrazines and azide*

Current interest in the organometallic chemistry of azo and diazo compounds has been stimulated by the realization that derivatives with partially reduced dinitrogenous ligands can be considered as models for the intermediates in the reduction of N_2 by metalloenzymes [5,159]. Furthermore, the generation of nitrogen-containing organic compounds, either directly from molecular nitrogen or from precursors such as hydrazido (2-) or diazenido complexes, through C–N bond-forming reactions is a promising field for organic synthesis [5,160,161]. In this context, an interesting approach to catalytic or stoichiometric processes involving dinitrogen substrates becomes accessible through the activation and subsequent transformation of nitrogenous substrates by a bimetallic centre [36,162].

Cleavage of the N–N bond of hydrazine by the dimolybdenum centre in $[Mo_2Cp_2(\mu\text{-}Cl)(\mu\text{-}SMe)_3]$ **9** gives rise to the amido-bridged complex $[Mo_2Cp_2(\mu\text{-}NH_2)(\mu\text{-}SMe)_3]$ **33** (Scheme 10) [36]. The molecular structure of **33** is based on an $Mo_2(\mu\text{-}SMe)_3(\mu\text{-}N)$ core with a nearly linear CpMo–MoCp group (Fig. 11). The coordination geometry around each Mo atom can be described as a four-legged piano stool supplemented by a metal–metal bond. The Mo–N distances (2.152(3) and 2.150(3) Å) and the acute Mo–N–Mo angle (73.3(1)°) suggest an order of unity for the Mo–N bonds. Normal electron counting rules require the presence of an Mo(III)–Mo(III) single bond in **33**. The Mo–Mo distance (2.566(1) Å) is typical for a tetra-bridged dimer of molybdenum(III) [41,163–165]. The mechanistic details of this reaction are not yet clearly established. The coordination of hydrazine is required before it can be further transformed. This step may be concomitant with opening of the chloro bridge. Later steps, leading to the release of NH_4Cl and N_2, could involve a diazene intermediate, as recently reported for the disproportionation of hydrazine by the dinuclear ruthenium complex $[Ru_2Cp^*_2(\mu\text{-}SR)_2]$ ($Cp^* = C_5Me_5$) [162]. The reaction of phenylhydrazine with $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}Cl)]$ **9** leads to a mixture of μ-η^1- and μ-η^2-phenyldiazenido complexes $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}\eta^1\text{-}N_2Ph)]$ **34** and $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}\eta^2\text{-}N_2Ph)]$ **35** (Scheme 10). $\eta^1 \Leftrightarrow \eta^2$ isomerization of these species occurs under thermal or photolytic activation [166]. **34** is readily protonated to give, at least formally,

[4]Using the versions of the programs QUEST and VISTA mounted at the Daresbury National Laboratory, Warrington, UK.

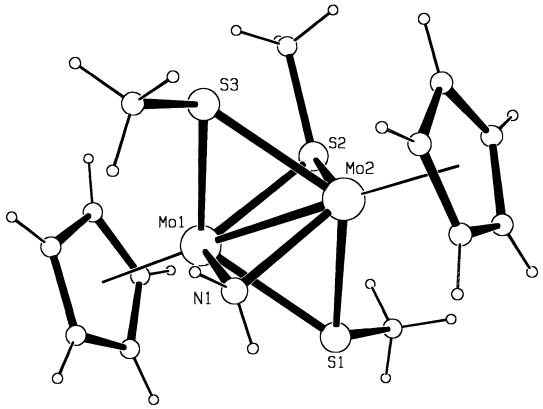
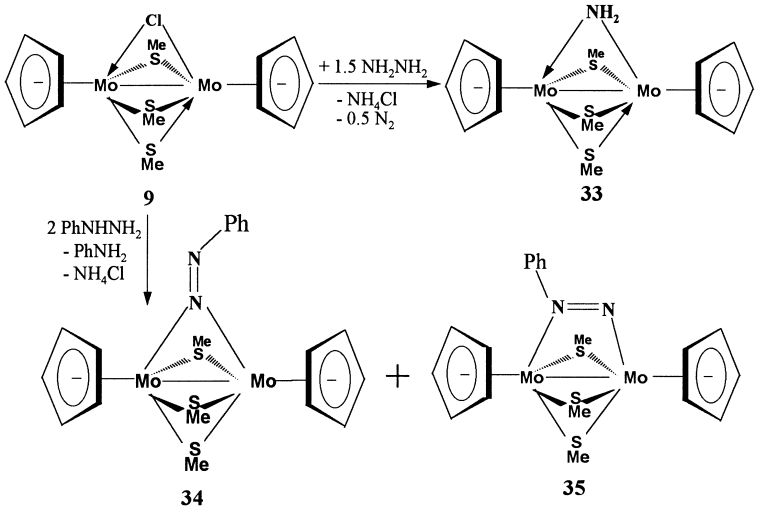


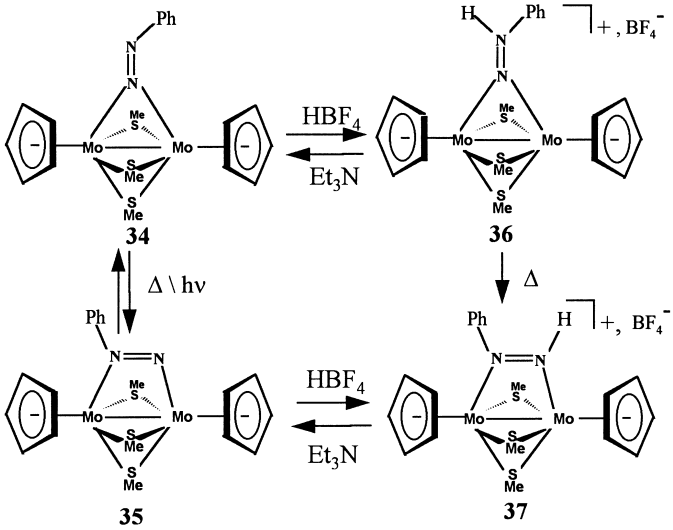
Fig. 11. A view of a molecule of $[Mo_2Cp_2(\mu\text{-}NH_2)(\mu\text{-}SMe)_3]$ **33**. The Mo1–Mo2 separation is 2.566(1) Å. Disorder of the μ-S atoms, which affects about one molecule in eight, is not shown.



Scheme 10.

a μ-η^1-phenylhydrazido(2-) (or isodiazene) product, $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}\eta^1\text{-}NNHPh)]BF_4$ **36**, which easily rearranges into the μ-η^2-phenyldiazene compound $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}\eta^2\text{-}NHNPh)]BF_4$ **37** (Scheme 11).

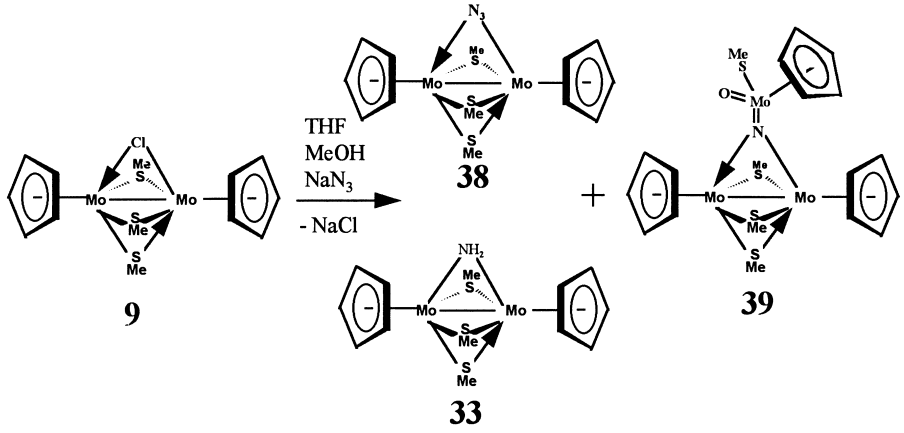
These results demonstrate that the dimolybdenum(III) system $[Mo_2Cp_2(\mu\text{-}Cl)(\mu\text{-}SMe)_3]$ **9** provides a bimetallic site capable of cleaving the N–N bond of NH_2NH_2, a process which may parallel the activation and transformation of dinitrogen and related nitrogenous substrates by thiopolymetallic systems. The μ-η^1- and μ-η^2-phenyldiazenido species and their related protonated species, which are formally μ-η^1-hydrazido (2-) (isodiazene) and μ-η^2-diazene complexes, are also



Scheme 11.

relevant to the study of the reduction of an NNR fragment at a thiopolymetallic centre [5,167–171].

The synthesis of azido compounds provides a route to imido derivatives and permits the introduction of a nitrido ligand into the metallic core by heterolytic cleavage of the $MN–N_2$ bond [121,172]. The thermal reaction of $[Mo_2Cp_2(\mu\text{-}Cl)(\mu\text{-}SMe)_3]$ **9** with NaN_3 in THF/EtOH gives a mixture of three compounds: $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}N_3)]$ **38**, $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}NH_2)]$ **33** and $[Mo_3(O)(N)Cp_3(SMe)_4]$ **39** (Scheme 12) [173]. When the time permitted for thermolysis of **9** is brief, only the μ-azido derivative **38** is isolated. In the presence of



Scheme 12.

ethanol, **38** reacts to give the amido complex **33** and the trinuclear product **39**. **39** contains an $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}N)]$ core which is linked by its nitrogen atom to a CpMo(O)(SMe) unit and is thus a rare example of a nitrido complex containing molybdenum atoms in both relatively low (III) and high (VI) formal oxidation states.

3. Selected aspects of the electrochemistry of dinuclear thiolate-bridged complexes

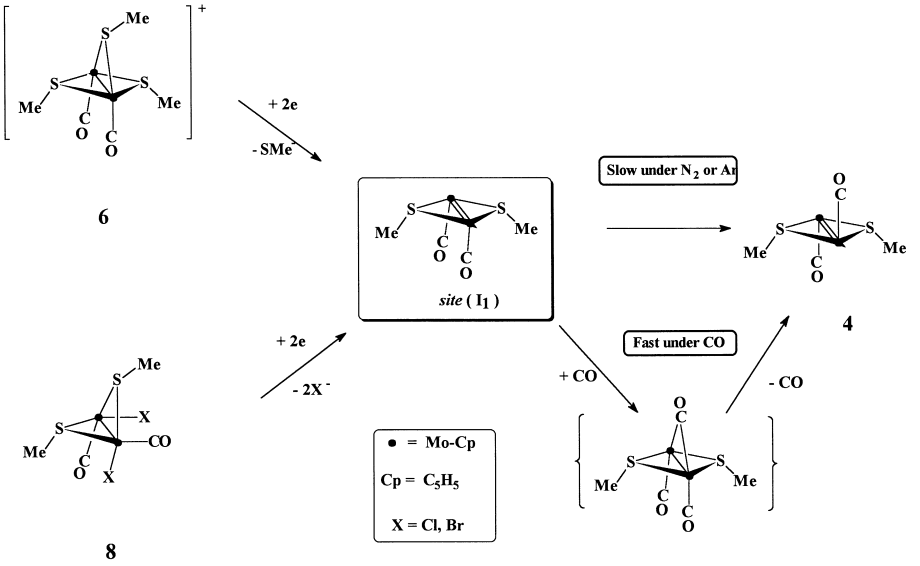
We now review electrochemical studies whose main aim was to establish the factors which control the reactivity and selectivity of substrate-binding sites in dinuclear, thiolate-bridged complexes. Our approach involved detailed investigation of three different steps. (i) The generation of a vacant site. In most cases this was achieved electrochemically. It is a crucial step in any catalytic process, either industrial or biological. (ii) The coordination of the substrate. (iii) The transformation of the coordinated substrate. Since it is not easy to study steps (i) and (ii) independently, especially when the site is generated in the presence of a substrate, they will be presented together in the following discussion. The influence of the steric and electronic properties of the ligands attached to the metal centres on the reactivity of vacant sites will then be illustrated by a few examples. After substrate-binding, large complexes may offer alternative reactive centres susceptible to protonation or alkylation. In order to achieve step (iii), it is essential that the incoming electrophile (proton or alkyl cation) is eventually forced to attack the coordinated substrate rather than other reactive centres within the molecule, such as metal atoms or sulfur lone pairs. An example showing how the ligands control the orientation of the attack by an electrophile will be discussed.

3.1. Generation of the site and substrate binding

Electrochemical cleavage of metal–ligand bonds is a convenient way of generating substrate-binding sites at coordinatively saturated metal centres and is often used with mononuclear complexes [174–177]. Examples of its application to dinuclear thiolate-bridged compounds are presented below.

3.1.1. Reductive cleavage of two Mo–X bonds (X = SMe, Cl, Br)

The irreversible two-electron reduction of the III complexes $[Mo_2Cp_2(\mu\text{-}SMe)_3(CO)_2]^+$ **6** and $[Mo_2Cp_2(\mu\text{-}SMe)_2(CO)_2X_2]$ (X = Cl or Br) **8** under an inert atmosphere produces a common species (Scheme 13: $\mathbf{I}_1$) which could not be isolated, although it was detected by cyclic voltammetry (cv). However, the stable complex *trans*-$[Mo_2Cp_2(\mu\text{-}SMe)_2(CO)_2]$ **4** was formed and characterized at the end of controlled-potential electrolysis (cpe) [28]. All the experimental data support the hypothesis that the cleavage of two Mo–S or two Mo–X bonds initially produces *cis*-$[Mo_2Cp_2(\mu\text{-}SMe)_2(CO)_2]$ ($\mathbf{I}_1$), a kinetic isomer of the final product **4**. However, under an atmosphere of CO, the redox couples associated with *cis*-$[Mo_2Cp_2(\mu\text{-}SMe)_2(CO)_2]$ were replaced by those of its trans isomer, indicating



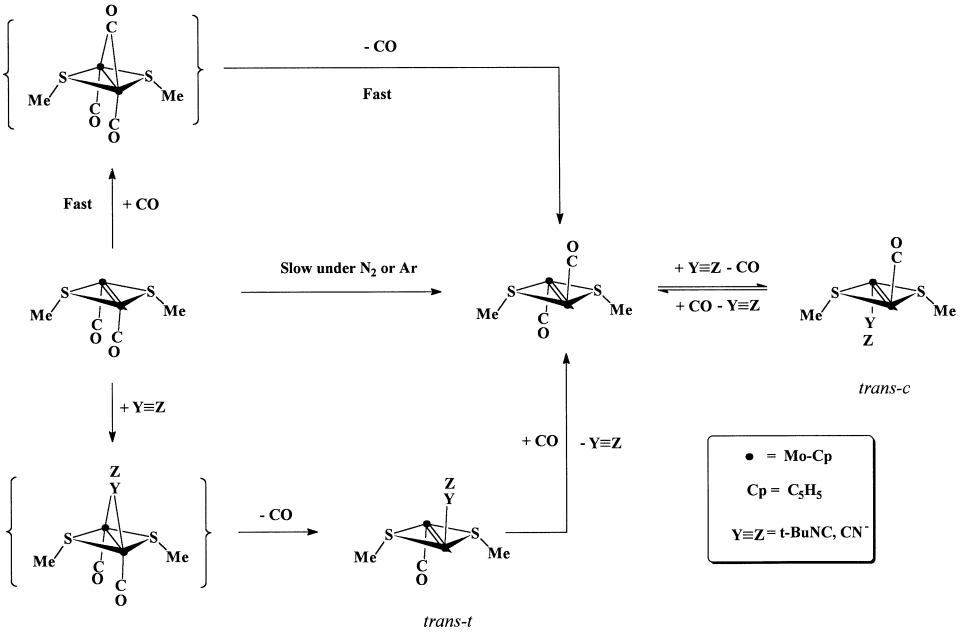
Scheme 13.

that the cis/trans isomerization of $[Mo_2Cp_2(\mu\text{-}SMe)_2(CO)_2]$ is catalysed by CO; this probably occurs via a very unstable $[Mo_2Cp_2(\mu\text{-}SMe)_2(\mu\text{-}CO)(CO)_2]$ intermediate (or transition state) which would decay to *trans*-$[Mo_2Cp_2(\mu\text{-}SMe)_2(CO)_2]$ and carbon monoxide (Scheme 13).

EHMO calculations performed on the reactants, products and possible intermediates of the reactions shown in Scheme 13 are in good agreement with the proposed mechanism [29]. Thus, steric and electronic factors combine to make *cis*-$[Mo_2Cp_2(\mu\text{-}SMe)_2(CO)_2]$ a good substrate-binding site: it has an uncongested Mo_2S_2 face and our calculations show that it has a low-lying LUMO available to hold an incoming nucleophile. The proposed mechanism remains valid if the CO substrate is replaced by other two-electron donor ligands such as isocyanide or cyanide. Indeed, the electrogenerated site, *cis*-$[Mo_2Cp_2(\mu\text{-}SMe)_2(CO)_2]$, reacts rapidly with RNC [28] or CN^- [38] to yield new complexes, assigned as *trans*-$[Mo_2Cp_2(\mu\text{-}SMe)_2(CO)(Y{\equiv}Z)]^z$ ($Y{\equiv}Z{=}RNC$, $z=0$; $Y{\equiv}Z{=}CN^-$, $z=-1$), *trans-t* in Scheme 14, via a mechanism similar to that described above for CO. As in the case of CO, a different isomer of *trans*-$[Mo_2Cp_2(\mu\text{-}SMe)_2(CO)(Y{\equiv}Z)]^z$ ($Y{\equiv}Z{=}RNC$, $z=0$; $Y{\equiv}Z{=}CN^-$, $z=-1$), *trans-c* in Scheme 14 (also see Fig. 2 and Section 3.2.2), is formed due to a CO-induced isomerization process on the longer time scale of electrolyses [28,38].

3.1.2. Reductive cleavage of an Mo–L bond (L = CH_3CN) or of an Mo–X bond (X = NCO)

The Mo^{III} complex *cis*-$[Mo_2Cp_2(\mu\text{-}SMe)_2(CO)_3(MeCN)]^{2+}$, **17**, undergoes an irreversible two-electron reduction under argon or N_2 even at low temperature [25].

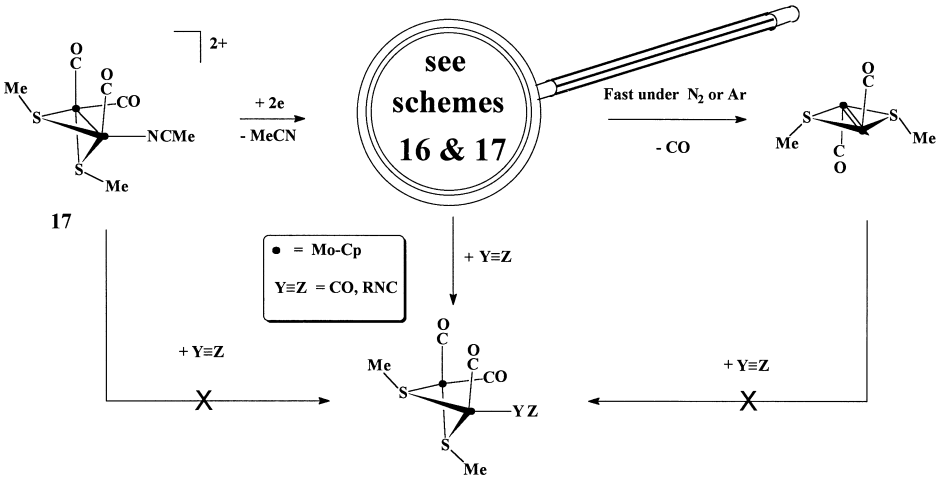


Scheme 14.

The reduction leads to the formation of *trans*-$[Mo_2Cp_2(CO)_2(\mu\text{-}SMe)_2]$, and no intermediate could be detected by cv under the experimental conditions used ($v \leqslant 1$ V s^{-1}). However, trapping experiments demonstrated the transient formation of a previously undetected intermediate: cv in the presence of CO showed the formation of the stable product *cis*-$[Mo_2Cp_2(\mu\text{-}SMe)_2(CO)_4]$ (a minor amount of the trans isomer is also detected); cpe under these conditions produced an equilibrium mixture of the cis and trans isomers of $[Mo_2Cp_2(\mu\text{-}SMe)_2(CO)_4]$ [22,25].

Since neither *cis*-$[Mo_2Cp_2(\mu\text{-}SMe)_2(CO)_3(MeCN)]^{2+}$ **17** nor *trans*-$[Mo_2Cp_2(\mu\text{-}SMe)_2(CO)_2]$ react with CO to generate the tetracarbonyl complex (Scheme 15), these experiments demonstrated the formation of a short-lived substrate-binding site whose reaction with CO is faster than its decay to *trans*-$[Mo_2Cp_2(\mu\text{-}SMe)_2(CO)_2]$. Trapping experiments in the presence of RNC provided further information concerning the site: the formation of *cis*-$[Mo_2Cp_2(\mu\text{-}SMe)_2(CO)_3(CN^tBu)]$ from the reduction of **17** in the presence of CN^tBu (Scheme 15) demonstrated that the unsaturated site retains three carbonyl groups, probably in a cis arrangement [25]. Later studies of *cis*-$[Mo_2Cp^*_2(\mu\text{-}SMe)_2(CO)_3(MeCN)]^{2+}$ [40] (see Section 3.2.3) established that the reduction occurs by an ECE mechanism and that the MeCN ligand is actually lost at the radical cation stage, that is after the transfer of one electron. This should also hold for the Cp analogue; the second electron-transfer step would then consist in the reduction of the unsaturated *cis*-tricarbonyl radical cation to the neutral site.

The reduction of *cis*-$[Mo_2Cp_2(\mu\text{-}SMe)_2(CO)_3(NCO)]^+$ is somewhat similar to that of **17** in that the products formed in the absence and in the presence of Y≡Z (CO



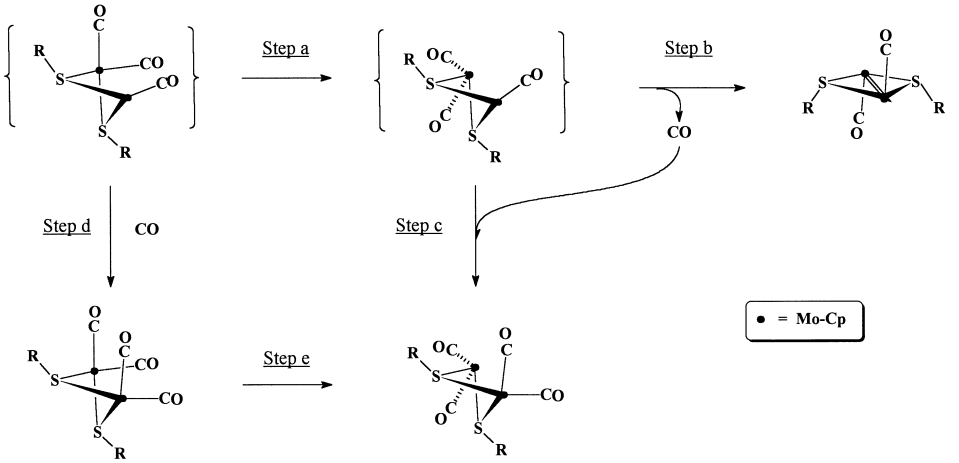
Scheme 15.

or CN^{t}Bu) are such as indicated in Scheme 15. However, instead of the irreversible two-electron reduction observed for **17**, the isocyanate complex undergoes two one-electron reduction steps. The cv in the presence of CN^{t}Bu clearly demonstrated that the isocyanate ligand is lost, and the isocyanide substrate bound, after the transfer of two electrons [40].

The electrochemical behaviour of *cis*-$[Mo_2Cp_2(\mu\text{-}SPh)_2(CO)_3(MeCN)]^{2+}$ under an inert atmosphere is slightly different from that of its methylthiolate analogue **17**, in that the quasi-reversible two-electron reduction leads to the detection of an unsaturated intermediate, assigned as *trans*-$[Mo_2Cp_2(\mu\text{-}SPh)_2(CO)_3]$, on the short time scale of cv. However, this species could not be isolated, since cpe under argon afforded a mixture of *trans*-$[Mo_2Cp_2(\mu\text{-}SPh)_2(CO)_4]$ and *trans*-$[Mo_2Cp_2(\mu\text{-}SPh)_2(CO)_2]$, whereas *cis*-$[Mo_2Cp_2(\mu\text{-}SPh)_2(CO)_4]$ is observed when the cv is run in the presence of CO [25].

3.1.3. The tricarbonyl intermediates

The reduction mechanism of *cis*-$[Mo_2Cp_2(\mu\text{-}SR)_2(CO)_3(MeCN)]^{2+}$ **17** is dependent on the nature of the R groups (Me, Ph), although a tricarbonyl intermediate is involved in both cases. The formation of *cis*-$[Mo_2Cp_2(\mu\text{-}SR)_2(CO)_3(Y{\equiv}Z)]$ in the presence of Y≡Z (CO or RNC) (Scheme 15) suggested a cis geometry of the reactive site, whereas the trans geometry of the final products obtained in the absence of substrate indicated the occurrence of an isomerization step. In the case where R = Ph, the products formed in the presence and in the absence of CO are consistent with the reactions in Scheme 16; this involves the reasonable expectation that CO binding to the first formed, undetected *cis*-$[Mo_2Cp_2(\mu\text{-}SPh)_2(CO)_3]$ (step d) is faster than isomerization of the site (step a). The formation of the trans isomer after electrolysis under CO is expected, since the cis and trans isomers of



Scheme 16.

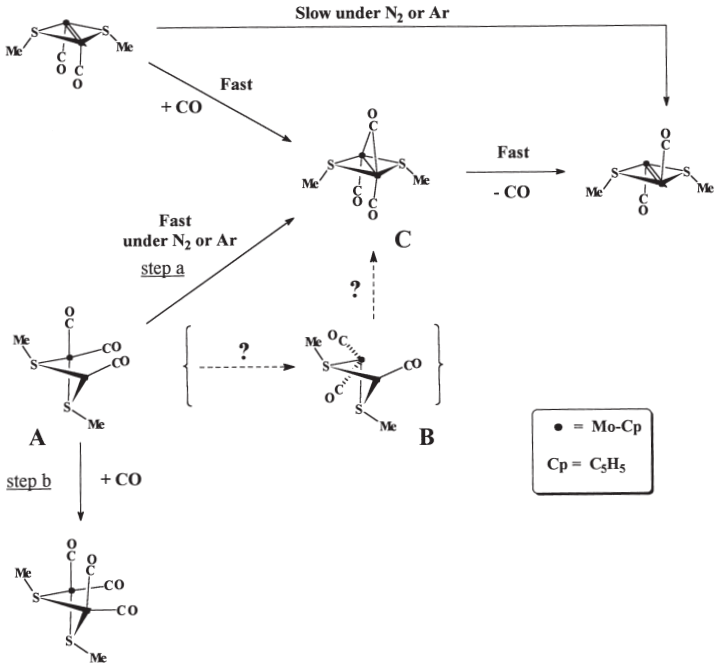
$[Mo_2Cp_2(\mu\text{-}SPh)_2(CO)_4]$ [22,25] are known to interconvert readily (Scheme 16, R = Ph, step e).

In the case of the methylthiolate derivatives, the formation of a single product in the absence of CO [178,179] suggested a different mechanism for the decay of the cis intermediate, which may not involve *trans*-$[Mo_2Cp_2(\mu\text{-}SMe)_2(CO)_3]$. An A to C rearrangement of $[Mo_2Cp_2(\mu\text{-}SMe)_2(CO)_3]$ (Scheme 17, step a), which can be seen as the intramolecular counterpart of the CO-catalysed isomerization of *cis*-$[Mo_2Cp_2(\mu\text{-}SMe)_2(CO)_2]$ described in Section 3.1.1, would account for the observed results.

The different fate of the unsaturated intermediate $[Mo_2Cp_2(\mu\text{-}SR)_2(CO)_3]$ for R = Me and R = Ph is our first illustration of the effect of the sulfur substituents on the reactivity of dinuclear thiolate-bridged complexes. Further examples are presented in Sections 3.2.1 and 3.2.2.

So far, we have demonstrated that reductive cleavage of Mo–X (X = halide, thiolate, isocyanate) or of Mo–L (L = MeCN) bonds can be used to generate reactive sites which can bind unsaturated ligands (CO, cyanide, isocyanide). These reactive sites must therefore possess a set of σ- and π-type orbitals which are suitable for bonding to CO and RNC. Evidently their match with the orbitals of MeCN or N_2 is less good, since these ligands bind only weakly or not at all to the reduced $\{Mo_2(\mu\text{-}SR)_2\}$ centres. The effect of the sulfur substituents (R = Me, Ph) on the reversibility of the reduction of *cis*-$[Mo_2Cp_2(\mu\text{-}SR)_2(CO)_3(MeCN)]^{2+}$ indicated that a modification of the electron density at the metal centres of the parent complexes, which is tuned by the attached ligands, could lead to a stronger interaction of the electrogenerated intermediates with substrates which are moderate π-acids.

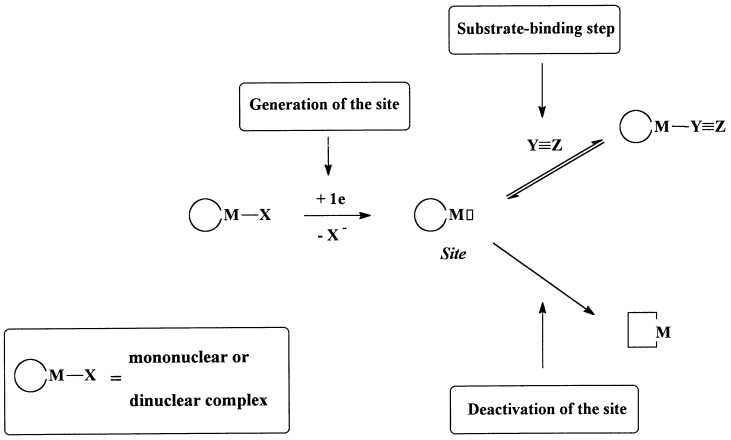
We also observed that, in the absence of a substrate, the electrogenerated sites decay to *trans*-$[Mo_2Cp_2(\mu\text{-}SMe)_2(CO)_2]$ (Scheme 17), which can be seen as a deacti-



Scheme 17.

vation (Scheme 18), although the trans dicarbonyl complex shows an interesting reactivity (see Sections 2 and 3.2.2).

All the different reactions involving a reactive site and a substrate Y≡Z (Y≡Z= CO, CNR, RCN, CN^- or N_2) can be viewed as shown in Scheme 18. Deactivation can occur either by rearrangement to a different isomer in which the site is concealed



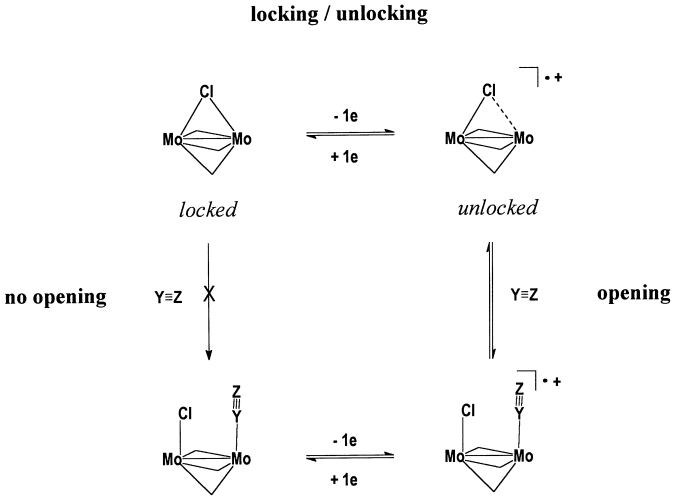
Scheme 18.

or through a destructive reaction which gives a stable product. It competes with the formation of the [site–Y≡Z] complex, particularly when the substrate-binding step is slow or reversible. Two different strategies favour formation of the [site–Y≡Z] complex. (i) Modification of the electronic structure of the site (via that of its precursor) so as to improve the fit between the frontier orbitals of the two partners of the reaction, site and substrate. In this case it is the reactivity and the selectivity of the site which are concerned. Examples showing the influence of the ligands (Cp′, sulfur bridges) on the reactivity and the selectivity of sites is presented in Section 3.2. (ii) The alternative approach is to prevent deactivation by stabilization (protection) of the site, which might involve steric factors. In this case, a compromise between the stability of the site and its reactivity towards substrates must be found. A representative example of this strategy is presented now.

3.1.4. Timing deprotection of the site in the presence of a substrate: the chloro-bridged system [$Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}Cl)$]

In this case the generation of the substrate-binding site by opening the chloride bridge arises from an electrochemical one-electron oxidation step instead of the two-electron reduction process described in previous examples. The originality of the system is that a protective device (the bridging chloride ligand) prevents premature exposure of the site which, as shown above, can be destructive. In the present case, the reactive site becomes available only when a potential substrate is present: in the absence of substrate the radical cation retains the quadruply bridged structure of the neutral complex [35]. However, in the presence of Y≡Z (MeCN, CO, CNR) the one-electron oxidation follows an EC mechanism, the chemical step C of which is the opening of the chloride bridge, concerted with Y≡Z binding at the neighbouring Mo centre [35]. In the neutral complex the chloride bridge is locked, as shown by the absence of reaction with CO or isocyanides; the formation of $[Mo_2Cp_2(\mu\text{-}SMe)_3(Cl)(Y{\equiv}Z)]$ (Y≡Z = CN^tBu or CO), which are stable complexes, requires an oxidation/reduction sequence. The one-electron oxidation of the complex unlocks the chloride bridge. The actual opening of the bridge of $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}Cl)]^{\cdot +}$ is triggered by the substrate (Y≡Z = MeCN, CN^tBu or CO) (Scheme 19).

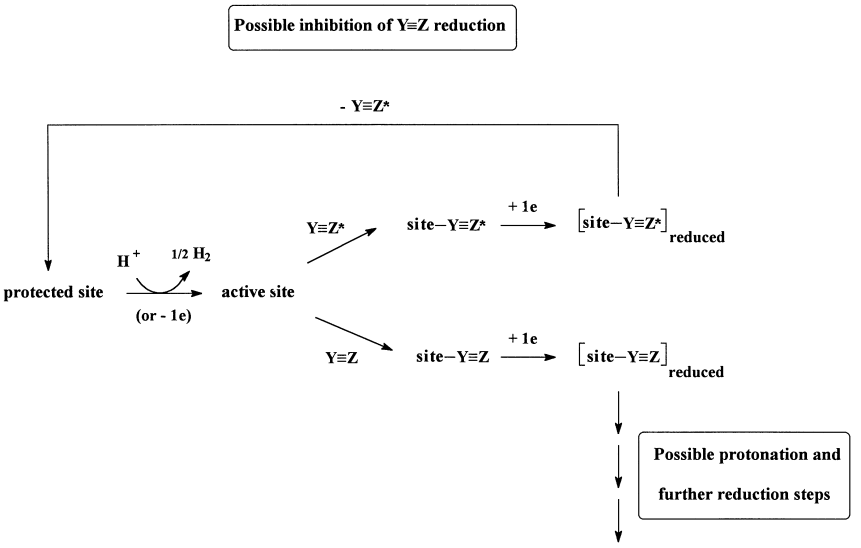
There are different levels of site selectivity. The first results from the nature and the rates of the reactions of the different substrates with $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}Cl)]^{\cdot +}$; cyanide reduces the site (with the regeneration of the neutral μ-Cl complex), CO reacts more slowly than CN^tBu and MeCN, and MeCN is bound less tightly than CO and CN^tBu. The reduction of $[Mo_2Cp_2(\mu\text{-}SMe)_3(Cl)(Y{\equiv}Z)]^{\cdot +}$ gives rise to second-order selectivity; among the substrates studied, only CO and CN^tBu could possibly be reduced by such a complex since the $[Mo_2Cp_2(\mu\text{-}SMe)_3(Cl)(Y{\equiv}Z)]$ assembly survives the one-electron reduction only for Y≡Z = CO and CN^tBu; MeCN is lost upon reduction of $[Mo_2Cp_2(\mu\text{-}SMe)_3(Cl)(MeCN)]^{\cdot +}$, but the protective device operates to prevent destructive deactivation: the protected site $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}Cl)]$ is recovered. This observation suggested how the reduction of a substrate Y≡Z (CO or CN^tBu in this case) could be inhibited by the presence of a non-reducible substrate, Y≡Z*



Scheme 19.

(MeCN in this case), provided the rates of the reactions of Y≡Z and Y≡Z* with the site are similar (Scheme 20).

The electrochemical site deprotection process described above is reminiscent of redox-induced partial decoordination of chelating organic ligands [180–183]. This original mechanism for the well-timed deprotection of a coordination site is interesting in the context of site–substrate interactions and recognition phenomena.



Scheme 20.

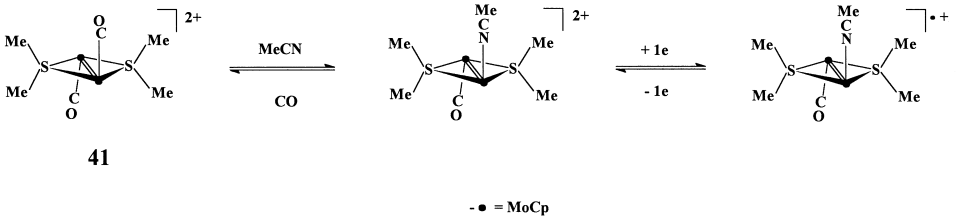
3.2. Reactivity and selectivity of substrate-binding sites: influence of the ancillary ligands

It is obvious that the ligands attached to a metal centre help to define the local electronic and steric conditions; modifications of these ligands may therefore be used to change the electron density at, and access to, the metal centre, thereby controlling its reactivity and selectivity. Here we show how the reactivity of complexes can be altered by modification of the ancillary ligands.

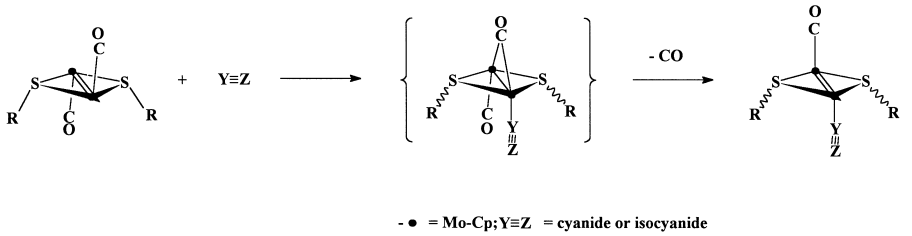
3.2.1. Influence of the bridging ligands: thiolate versus thioether

The dicarbonyl complexes *trans*-$[Mo_2Cp_2(\mu\text{-}SMe)_2(CO)_2]$, **4**, *trans*-$[Mo_2Cp_2(\mu\text{-}SMe)(\mu\text{-}SMe_2)(CO)_2]^+$ **40** [70] and *trans*-$[Mo_2Cp_2(\mu\text{-}SMe_2)_2(CO)_2]^{2+}$ **41** [70], were used to investigate the effects on the electrochemistry and on the reactivity of $\{Mo_2(\mu\text{-}E)_2\}$ complexes of substituting one or two anionic thiolate bridges by neutral bridging thioether ligands [34]. These substitutions do not fundamentally affect the nature of the redox processes, since all three compounds undergo at least two reversible reduction steps and one irreversible oxidation step. As expected, the increase of the positive charge on the Mo_2S_2 framework causes a positive shift, by 0.55 V (average) for each substitution of SMe_2 for SMe^-, of the reversible reduction processes of these formally Mo^{II}–Mo^{II} compounds. The reactions of the dicarbonyl complexes **4**, **40**, **41** with one equivalent of CN^tBu or CN^- all give similar products in which one carbonyl group has been replaced by the isocyanide or cyanide ligand. However, increasing the positive charge on the Mo_2S_2 core via the substitution of the bridging ligands significantly modifies the affinity of the metal centres for the CO, isocyanide and cyanide substrates. This is illustrated by the reactions of $[Mo_2Cp_2(\mu\text{-}SMe)(\mu\text{-}SMe_2)(CO)(CN^tBu)]^+$ and $[Mo_2Cp_2(\mu\text{-}SMe_2)_2(CO)(CN^tBu)]^{2+}$ with CO in which the dicarbonyl complexes **40** and **41** are not regenerated quantitatively, in contrast to what is observed for $[Mo_2Cp_2(\mu\text{-}SR)_2(CO)(CN^tBu)]$ [28,29,38]. Furthermore, both carbonyls in **41** can be replaced by CN^tBu. Thus, as expected from the change in electron density illustrated by the shift of the redox potentials, comparatively good donor ligands such as isocyanide and cyanide are retained more strongly than CO by the metal centres of the thioether-substituted complexes, contrary to what is observed for the bis(thiolate)-bridged analogues. The electronic conditions in **41** also allow the slow substitution of one CO ligand by MeCN, whereas **4** and **40** do not react with this substrate. The acetonitrile ligand in $[Mo_2Cp_2(\mu\text{-}SMe_2)_2(CO)(MeCN)]^{2+}$ is labile: treatment with CO regenerates **41** (Scheme 21), whereas the reaction with one equivalent of CN^- produces $[Mo_2Cp_2(\mu\text{-}SMe_2)_2(CO)(CN)]^+$ [34].

The binding of MeCN to **41** is consistent with the observation that this step is favoured by oxidation of complexes which do not react with MeCN: although **4**, **40** and **41** are all formally Mo^{II}–Mo^{II} complexes, the latter reduces at a potential which is more positive than those of **4** and **40** by 1.16 V and 0.53 V respectively. In the case of *cis*-$[Mo_2Cp_2(\mu\text{-}SR)_2(CO)_3(MeCN)]^{2+}$ and $[Mo_2Cp_2(\mu\text{-}SMe)_3(Cl)(MeCN)]^{\cdot +}$, rapid loss of the MeCN ligand was observed upon (irreversible) reduction (see above and Refs. [25,35]). In the present case, MeCN is still retained at the radical cation



Scheme 21.



Scheme 22.

stage (formally Mo^{I}–Mo^{II}) since the first reduction of $[Mo_2Cp_2(\mu\text{-}SMe_2)_2(CO)(MeCN)]^{2+}$ is a reversible process [34], Scheme 21.

Although the point is somewhat beyond the scope of this review, it is worth noting that reduction of the thioether-substituted complexes $[Mo_2Cp_2(\mu\text{-}SMe)(\mu\text{-}SMe_2)(CO)(Y{\equiv}Z)]^n$ and $[Mo_2Cp_2(\mu\text{-}SMe_2)_2(CO)(Y{\equiv}Z)]^m$ ($Y{\equiv}Z{=}CO$ or CN^-; $n=1$ or 0, $m=2$ or 1) leads to S–C bond(s) cleavage. Examples of electrochemical S–C bond cleavage have been reported, but they are still rare [184,185]. The increase of the electron density in the complex arising from the CO/CN^- substitution favours S–C bond cleavage both kinetically and thermodynamically [34], whereas this process is favoured by a decrease of the electron density in the Mo_2S_4 core of complexes with 1,1-dithiolate ligands [186,187].

3.2.2. Influence of the R groups on the attack of trans-$[Mo_2Cp_2(\mu\text{-}SR)_2(CO)_2]$ *by CN^- and RNC: a discriminating effect*

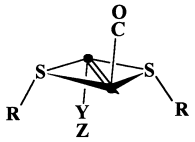
Though it can be viewed as a product of the deactivation of electrogenerated substrate-binding sites (Scheme 17), *trans*-$[Mo_2Cp_2(\mu\text{-}SR)_2(CO)_2]$ possesses its own interesting reactivity [38]. Different *trans, syn*-$[Mo_2Cp_2(\mu\text{-}SR)_2(CO)_2]$ complexes (trans refers to the mutual disposition of the Cp (or CO) ligands, syn to the relative orientation of the sulfur substituents) have been used to study the effects of the R groups on the reaction shown in Scheme 22, which is thought to involve an undetected CO-bridged intermediate [29] (the position of the syn R groups in the intermediate and product shown in Scheme 22 may be up–up or down–down, see below).

To differentiate steric and electronic effects, R groups with similar electronic properties (R = Me, ^{i}Pr, ^{t}Bu) were used to study the steric effects, whereas those of

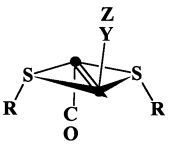
similar size (R = alkyl and CF_3) allowed the electronic influence of the sulfur substituents to be estimated.

Its ^{t}Bu substituents completely prevent the reaction of *trans, syn*-$[Mo_2Cp_2(\mu\text{-}S^tBu)_2(CO)_2]$ with Y≡Z (CN^tBu or CN^-): otherwise the size of the R groups (Me, ^{i}Pr, Ph) was found not to effect the formation or nature of the product, *trans, syn*-$[Mo_2Cp_2(\mu\text{-}SR)_2(CO)(Y{\equiv}Z)]^z$ ($Y{\equiv}Z = CN^tBu$, $z = 0$; $Y{\equiv}Z = CN^-$, $z = -1$).

Since the two faces of the Mo_2S_2 core are not equivalent in *trans, syn*-$[Mo_2Cp_2(\mu\text{-}SR)_2(CO)(Y{\equiv}Z)]$, two isomers which differ in the relationship of the Y≡Z ligand to the R groups may exist, i.e. *trans-c* and *trans-t* (*-c* and *-t* respectively indicate that Y≡Z and R are cis and trans).

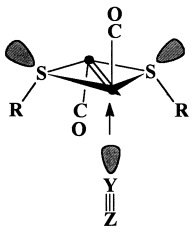


trans-c



trans-t

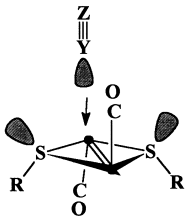
All the products obtained on reacting *trans, syn*-$[Mo_2Cp_2(\mu\text{-}SR)_2(CO)_2]$ (R = Me, ^{i}Pr, Ph) with isocyanides or with cyanide have a *trans-c* geometry. Therefore, the attack of Y≡Z on the more crowded face of the complex is favoured (see **I**).



I

The attack shown in **II**, which would produce a *trans-t* derivative, might be impeded by the repulsion of the incoming nucleophile by the sulfur lone pairs. It is worth noting that when **I** is hampered for steric reasons (R = ^{t}Bu), then no cyanide or isocyanide complex is formed at all. Consequently, the *trans-t* isomer, much less

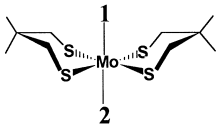
frequently found than its *trans-c* analogue, results essentially from the reaction of CNR or CN^- at the exposed face of the electrogenerated *cis,* syn-$[Mo_2Cp_2(\mu\text{-}SMe)_2(CO)_2]$ complex (see Scheme 14) [28,38].



II

The reaction of *trans, syn*-$[Mo_2Cp_2(\mu\text{-}SCF_3)_2(CO)_2]$ with CN^tBu also produces a derivative with a *trans-c* geometry, showing that the strongly electron-withdrawing substituents on sulfur do not change the course of the reaction with isocyanide. However, the reaction with cyanide yields both isomers of *trans,* syn-$[Mo_2Cp_2(\mu\text{-}SCF_3)_2(CO)(CN)]^-$. In this case, situation **II** appears to be even more favourable than **I** since the ratio *trans-t*/*trans-c* is about 60/40 and it thus appears that cyanide and isocyanide prefer different binding-sites in *trans,* syn-$[Mo_2Cp_2(\mu\text{-}SCF_3)_2(CO)_2]$ [38]. Of the different trans, syn- dicarbonyl complexes studied, only the $R=CF_3$ complex is able to discriminate between cyanide and isocyanide: the sulfur substituents must play an essential part in this site–substrate recognition phenomenon. It can plausibly be argued that an anionic substrate ($Y\equiv Z=CN^-$) would be repelled nearly equally by the fluorine atoms of the CF_3 substituents on one side of the Mo_2S_2 plane (**I**) and by the sulfur lone pairs on the other side (**II**). The nature of the sulfur substituents is important in determining the magnitude of the interactions between the CN^- nucleophile and the sulfur lone pairs (**II**). As mentioned above, the steric bulk of the ^{t}Bu substituents prevented the formation of the *trans-c* isomer, but the fact that no *trans-t* isomer is formed suggests that repulsion of the incoming CN^- by the sulfur lone pairs is stronger when $R=^t$Bu (electron-releasing group) than when the bridging sulfur substituents are electron-withdrawing ($R=CF_3$).

An interesting example of a similar effect in the {Mo(*syn*-Me_8[16]aneS_4)} moiety has been reported by Yoshida and co-workers [188,189]. Owing to the "all up" conformation of the carbon ring atoms of the crown thioether, the axial sites **1** and **2** (Scheme 23) are not equivalent. The complex can therefore discriminate between



Scheme 23.

ligands at the axial sites. For example, the two PhNC ligands in $[Mo(PhNC)_2(S_4)]$ adopt different geometries: the isocyanide ligand at site **1** is severely bent (C–N–C = 139.3(8)°) whereas the one at site **2** is nearly linear (C–N–C = 167.4(7)°) (S_4 = *syn*-Me_8[16]aneS_4) [188]. In the bis(phenylisocyanate) complex $[Mo(PhNCO)_2(S_4)]$ the coordination of the η^2-PhNCO ligands is one PhNCO is bound through the C=O, the second is bound through the C=N through the C=O bond at site **1** but through the C=N bond at site **2** [189]. The bending of the PhNC ligand was attributed to electronic effects, whereas the discrimination between the C=N and C=O bonds of PhNCO was shown to be steric in origin [188,189].

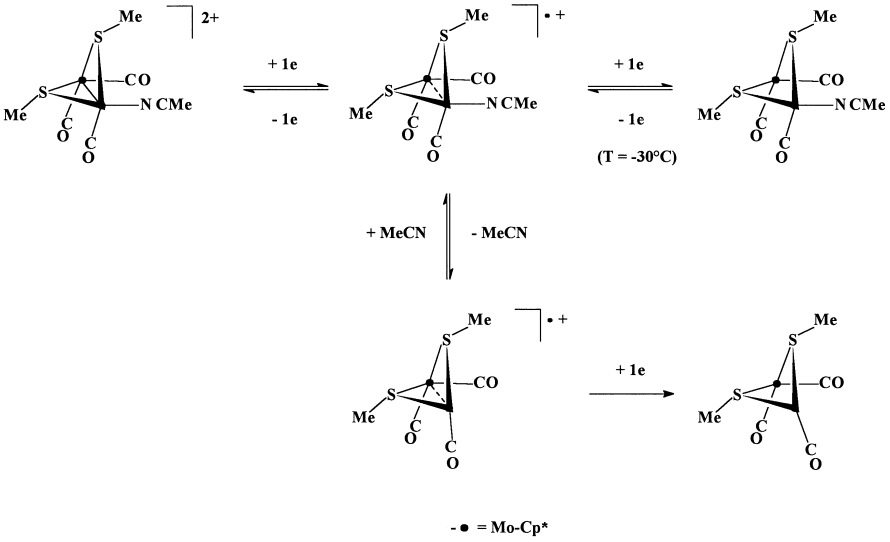
3.2.3. *Influence of the C_5R_5 rings, R = H (Cp) or Me (Cp*)*

Since the C_5Me_5 (Cp*) ring is more electron-releasing [190–192] and bulkier than C_5H_5 (Cp), a $C_5H_5 \rightarrow C_5Me_5$ substitution should modify both the electron density and the steric constraints at the metal centres. Both factors could affect the formation of the [site–Y≡Z] complex (Scheme 18).

As expected from the electronic properties of the rings, C_5Me_5 complexes are harder to reduce than their C_5H_5 counterparts. However, the magnitude of the negative shift of the redox potentials is strongly dependent on the complex considered. The electronic effect of the substitution, as estimated from the redox potentials, appears to be buffered in the case of *cis*-$[Mo_2Cp'_2(\mu\text{-SMe})_2(CO)_4]^{2+}$ ($\Delta E^{red}_{1/2} = 0.11$ V) compared with *trans*-$[Mo_2Cp'_2(\mu\text{-SMe})_2(CO)_2]$ ($\Delta E^{red}_{1/2} = 0.42$ V) (Cp′ = Cp or Cp*). This is not imputable only to a delocalization of the electron density on the four CO ligands of the former since $\Delta E^{red}_{1/2} = 0.33$ V for $[Mo_2Cp'_2(CO)_4]$ [40]. In the case of *cis*-$[Mo_2Cp'_2(\mu\text{-SMe})_3(CO)_2]^+$, the substitution of Cp* for Cp causes a negative shift of the irreversible two-electron reduction by *ca*. 0.3 V, whereas the potential of the reversible one-electron oxidation is almost unaffected [193]. The energy change of the orbitals of the complex, illustrated by the shift of the redox potentials, is dependent on factors such as the geometry of the molecule, the nature of the co-ligands, etc. In *cis*-$[Mo_2Cp'_2(\mu\text{-SMe})_2(CO)_4]^{2+}$ the contribution of the rings orbitals to the LUMO is probably less than in *trans*-$[Mo_2Cp'_2(\mu\text{-SMe})_2(CO)_2]$, whereas in *cis*-$[Mo_2Cp'_2(\mu\text{-SMe})_3(CO)_2]^+$, the LUMO presumably receives a stronger contribution from the Cp′ ring than the HOMO. Both electronic and steric effects of the Cp′ rings are observable in the latter complex. The reduction mechanism of the Cp* derivative, similar to that of the Cp′ analogue **6** (Scheme 14), affords a product assigned as $\boldsymbol{I}^*_1$ [193] by analogy with the Cp system. The cis/trans isomerization of the site (deactivation, see Scheme 18), which was quantitative on the electrolysis time scale for the Cp complexes (Section 3.1.1) [28], occurs more slowly with the Cp* analogue, presumably because of steric hindrance by the Cp* rings. The cost of the (kinetic) stabilization, in terms of reactivity of the site, is moderate: the reactions of *cis*-$[Mo_2Cp'_2(\mu\text{-SMe})_2(CO)_2]$ with CO and CN^tBu still take place for Cp′ = Cp* although they are slower than for Cp′ = Cp′ [193]. It is reasonable to assume that this effect on the reaction rates results essentially from the steric bulk of the Cp* ligands which screen the exposed face of *cis*-$[Mo_2Cp^*_2(\mu\text{-SMe})_2(CO)_2]$.

The increase of the steric demand of the Cp* rings can also be manifested by a change in the preferred geometry of a complex, as is the case for $[Mo_2Cp'_2(\mu\text{-}SR)_2(CO)_4]$: the Cp complex prefers the trans geometry for R = Ph and ^{t}Bu (for R = Me, the cis/trans ratio is about 50/50) [22], whereas $[Mo_2Cp^*_2(\mu\text{-}SMe)_2(CO)_4]$ is found exclusively with the cis geometry [40]. The effect of the Cp* ligands on the reactivity and selectivity of substrate-binding sites is further exemplified by differences in the electrochemistry of *cis*-$[Mo_2Cp'_2(\mu\text{-}SMe)_2(CO)_3(MeCN)]^{2+}$ for Cp′ = Cp (see Section 3.1.2) and Cp*. Thus, the Mo^{II}–NCMe bond is considerably more stable towards reductive cleavage in the Cp* complex which shows two one-electron reduction steps, both reversible at low temperature (Scheme 24) [40]. The neutral (formally Mo^{II}–Mo^{II}) acetonitrile-substituted complex is detectable at −30°C. This must be compared with the irreversible two-electron reduction of the Cp counterpart showing that even the MeCN-substituted radical cation escaped cv detection under similar conditions (low temperature, identical scan rate) [25].

The study of the first reduction step of *cis*-$[Mo_2Cp^*_2(\mu\text{-}SMe)_2(CO)_3(MeCN)]^{2+}$ at room temperature under an inert atmosphere demonstrated the occurrence of an ECE process, involving the reversible decoordination of MeCN (Scheme 24) [40]. Whether the formation of *cis*-$[Mo_2Cp^*_2(\mu\text{-}SMe)_2(CO)_3(Y{\equiv}Z)]$ in the presence of a substrate (Y≡Z = CO or RNC) arises from an ECCE mechanism (coordination of Y≡Z to the tricarbonyl radical cation and subsequent reduction of the product), an ECEC mechanism (reduction of the tricarbonyl radical cation prior to Y≡Z coordination), or both, may depend upon the electronic and steric demands of the substrate. However, the tricarbonyl radical cation is able to coordinate



Scheme 24.

MeCN (Scheme 24), suggesting that it should also bind CO and RNC (ECCE process).

The main differences in the reduction mechanisms of the Cp and Cp* analogues of *cis*-$[Mo_2Cp'_2(\mu\text{-}SMe)_2(CO)_3(MeCN)]^{2+}$ for Cp′=Cp and Cp* thus result from the different lifetimes of the primary reduction product, *cis*-$[Mo_2Cp'_2(\mu\text{-}SMe)_2(CO)_3(MeCN)]^{\cdot +}$, and of the tricarbonyl intermediate(s) in the Cp* and Cp series. The ring-dependent selectivity of the *cis*-$[Mo_2Cp'_2(\mu\text{-}SMe)_2(CO)_3]^{\cdot +}$ site is evidenced by the chemical equilibrium in Scheme 24 which was not observable in the Cp system. Two different tricarbonyl intermediates were detected in the Cp* system [40], whereas their formation could only be inferred from trapping experiments in the Cp series (Schemes 16-17 [25]). This slowing down of the deactivation of the neutral tricarbonyl site(s) can be ascribed, at least in part, to the electronic effect of the rings, since, as emphasized in Section 2, Cp* derivatives are more resistant to decarbonylation than their Cp counterparts. Steric effects of the rings could also be significant here, since an isomerization of *cis*-$[Mo_2Cp'_2(\mu\text{-}SMe)_2(CO)_3]$ was suggested [40]. This is a step towards lowering the selectivity of a site, which was one of our primary objectives.

As indicated above, the substitution of Cp by Cp* causes a negative shift of the redox potentials, that is a shift of the redox orbitals to higher energies; although this has a small amplitude in *cis*-$[Mo_2Cp'_2(\mu\text{-}SMe)_2(CO)_3(Y{\equiv}Z)]^{2+}$ (Y≡Z=CO, $\Delta E^{red}_{1/2} = 110$ mV; Y≡Z=MeCN, ΔE^{red} ca. 90 mV), it indicates a (slight) increase in the electron density within the Cp* complex compared with the Cp derivative. This is consistent with the greater difficulty of substituting one CO of *cis*-$[Mo_2Cp^*_2(\mu\text{-}SMe)_2(CO)_4]^{2+}$ by an MeCN molecule (Section 2). The substitution of the rings, on the other hand, induces a substantial stabilization of the Mo^{II}–NCMe bond since the neutral (Mo^{II}–Mo^{II}) acetonitrile complex with Cp* rings is detected at low temperature, whereas under the same conditions, the MeCN-substituted radical cation with Cp ligands was too short-lived for detection. Similar stabilization of the Mo^{II}–NCO bond is shown by the fact that the two reductions of *cis*-$[Mo_2Cp^*_2(\mu\text{-}SMe)_2(CO)_3(NCO)]^{+}$ are reversible at room temperature (and even at 40°C), whereas the second reduction of the Cp′ analogue is reversible only at low temperature. This is assigned to stronger interactions between occupied metal orbitals and the π* orbitals of the ligands, due to the shift of the former to higher energies [40]. Therefore, in this case, Cp* complexes offer a better solution than their Cp analogues in terms of activation of substrates.

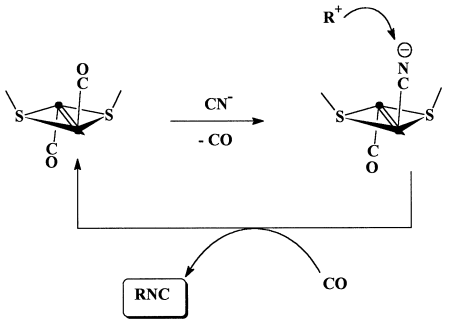
The characteristics of the ancillary ligands, which were shown above to affect the properties of substrate-binding sites, are also important in selectively activating a given site within a molecule containing several potentially reactive centres. This point is now considered in some detail.

3.3. *Modification of the bound substrate: control by the sulfur substituents*

The reactions of *trans*-$[Mo_2Cp_2(\mu\text{-}SR)_2(CO)_2]$ with isocyanide and cyanide, affording the *trans*-$[Mo_2Cp_2(\mu\text{-}SR)_2(CO)(Y{\equiv}Z)]^{z}$ derivatives (Y≡Z=CNR′, $z=$

0; $Y{\equiv}Z{=}CN^-$, $z=-1$), have been presented in Section 3.2.2. When $Y{\equiv}Z{=}CNR'$ the reaction is reversible, and treatment of the substituted complex (*trans-c* isomer) with CO regenerates the dicarbonyl parent. It was therefore conceivable that *trans*-$[Mo_2Cp_2(\mu\text{-}SR)_2(CO)_2]$ could be used as a platform for the assembly of various isocyanide ligands via successive reactions with cyanide and different alkylating agents; the assembled isocyanide ligand could then be released and the dicarbonyl parent regenerated by treating the substituted complex with carbon monoxide (Scheme 25) [38]. To achieve this, the indicated target, i.e. the cyanide ligand, must react with the alkylating agent. This is a general problem in the area of activation of small molecules at metal centres.

The product of the reaction of *trans*-$[Mo_2Cp_2(\mu\text{-}SMe)_2(CO)(CN)]^-$ with Me_3O^+ was the mixed thiolate/thioether-bridged complex, $[Mo_2Cp_2(\mu\text{-}SMe_2)(\mu\text{-}SMe)(CO)(CN)]$, so that it was necessary to find a way of redirecting the attack of the electrophile away from the sulfur lone pair towards the bound cyanide. The attack of the methylating agent on a sulfur lone pair suggested that the reaction was under orbital control. The substitution of the R groups in *trans*-$[Mo_2Cp_2(\mu\text{-}SR)_2(CO)(CN)]^-$ (R = Me, ^{i}Pr, Ph, CF_3), which allows the oxidation potential to be varied in a range extending over 0.53 V (*trans-c* and anti isomers), demonstrated that the electronic properties of the sulfur substituents determine the orientation of the approach of Me_3O^+ to the complex. Electron-withdrawing substituents such as CF_3 (and to a lesser extent Ph, see below), promoted N-methylation, whereas in complexes with electron-releasing R groups (Me, ^{i}Pr), an S-methylation was observed [38]. This is consistent with the reaction being switched from orbital to charge control on substitution of $R=CF_3$ for Me. The site of methylation was not affected by the geometry (*trans-c* or *trans-t*) of *trans,* syn-$[Mo_2Cp_2(\mu\text{-}SR)_2(CO)(CN)]^-$: when R = Me, both isomers undergo S-methylation, whereas methylation at the cyanide ligand was observed when $R=CF_3$. One of the resulting isocyanide complexes (*trans-c* isomer) was characterized by an X-ray crystal structure (Fig. 2). The syn/anti arrangement of the sulfur substituents affected the site of methylation of the cyanide complexes only when



- ● =Mo-Cp; the sulfur substituents were omitted

Scheme 25.

R = Ph. In this case, an isocyanide complex was obtained as the major product from the syn isomer, whereas the anti isomer was preferentially methylated at sulfur. Again, the difference is thought to be electronic in origin: the syn isomer is easier to oxidize than the anti analogue (by 80 mV) which favours N-alkylation. The observation that small shifts of redox potentials can induce profound differences in the nature the products is not unprecedented. A small shift (110 mV) of the oxidation potentials of $[Mo_2Cp_2(\mu\text{-}S_2CH_2)(\mu\text{-}S_2CRR')]$ was shown to be sufficient to switch the reaction with H^+ from a one-electron oxidation, suggesting initial protonation at a metal centre (R = R′ = Me), to an S–C bond cleavage (R = H, R′ = CO_2Me) [187]. This is also consistent with a change of the reaction from orbital (R = R′ = Me) to charge control (R = H, R′ = CO_2Me). Other examples showing the electronic influence of ligands on the site of protonation or alkylation include $[RSFe(CO)_3L]^-$ and $[RSFe(CO)_2L_2]^-$ complexes (L = CO or $P(OEt)_3$ R = alkyl or aryl) [194,195] and the protonation of $[FeH(CN)(R_2PCH_2CH_2PR_2)_2]$ (R = Et, Ph, *p*-tolyl) [196].

4. Conclusion

This review summarizes our synthetic and electrochemical studies of dinuclear thiolate-bridged complexes. Rational procedures have been established for the synthesis of the various $\{M_2(\mu\text{-}SR)_n\}$ compounds which were necessary for the chemical and electrochemical studies. The thorough exploration of their reactivity led us, for example, to the discovery of a range of compounds containing various nitrogenous ligands (organodiazenido, organohydrazido(2-), organodiazene, imido, amido, amino) bound to a conserved metal–sulfur site. The existence of these compounds, which can be regarded as functional models of intermediates involved in dinitrogen reduction, may lend support for a dinuclear (or indeed polynuclear) mechanism for certain steps of the N_2 fixation process. Further work in this area is already in progress.

We have also shown by selected examples how electrochemistry can contribute to the study of chemical problems. Electrochemical methods are well suited both to the generation of substrate-binding sites and to the study of the perturbations brought about by modifications of the environment of metal centres. One of the objectives of our work was to understand how the attachment of different ligands to a metal centre can be used to control the reactivity of complexes. We have shown how the electronic properties of ligands and their steric/geometric characteristics (sulfur substituents, nature of the sulfur bridges, Cp′ rings) can induce discrimination between substrates and control the reactivity and the selectivity of substrate-binding sites. Correct settings of these "adjusting screws" should eventually lead to the achievement of molecular recognition by rational design. However, the task of matching the electronic and steric characteristics of metal sites to the demands of a given substrate is complicated by the realization that the set of parameters which would favour the coordination of a substrate might be different from that which would facilitate its reduction when it is already bound to a metal centre. There is a

delicate balance to find here, but it should be possible to attain such a compromise. The electronic perturbations induced by ligand substitutions are strongly dependent on the particular complex, since they result from changes in the energy of orbitals; thus, the same modification of the environment of a metal centre in complexes with different geometries, co-ligands, etc. may affect their reactivities in different ways. This inevitably complicates the prediction of the quantitative effects of ligand substitutions on the reactivity of different complexes, even though these effects can be qualitatively anticipated. These conceptual difficulties and the clear need for further studies should not obscure the main point: that the design of synthetic binding sites capable of the same subtle reaction control as metalloenzymes is fast becoming a realistic goal for the inorganic chemist.

Acknowledgements

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