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Hydrosulfido complexes of transition metals

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Contents

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Abstract

Interest in hydrosulfido (SH) complexes stems from their relevance to metalloenzymes and metal sulfide catalysts for industrial hydrodesulfurization. This review provides an overview of the chemistry of hydrosulfido complexes of transition metals. Synthetic methods of hydrosulfido complexes will first be classified, followed by the description of their spectroscopic properties and structural features. Significant emphasis is also placed on the reactivities of hydrosulfido complexes including nucleophilic reactions, oxidative coupling, and sulfido cluster formation.

Keywords: Hydrosulfido; Sulfido; Synthesis; Reactivity; Polynuclear complexes; Clusters

Nomenclature

acac	acetylacetonato, $CH_3C(O)CHC(O)CH_3^-$
bipy	2,2′-bipyridine
^{t}BuCp	η^5-*tert*-butylcyclopentadienyl, $C_5H_4Bu^t$
cod	1,5-cyclooctadiene, C_8H_{12}
Cp	η^5-cyclopentadienyl, C_5H_5
Cp′	η^5-methylcyclopentadienyl, C_5H_4Me
Cp*	η^5-pentamethylcyclopentadienyl, C_5Me_5
Cp^{Et}	η^5-ethyltetramethylcyclopentadienyl, C_5Me_4Et
Cp^{tt}	η^5-1,3-di(*tert*-butyl)cyclopentadienyl, $C_5H_3Bu^t_2$-1,3
Cy	cyclohexyl, *c*-C_6H_{11}
DMAD	dimethyl acetylenedicarboxylate, MeOCOC≡CCOOMe
DMF	*N*,*N*-dimethylformamide, $HC(O)NMe_2$
dcpe	1,2-bis(dicyclohexylphosphino)ethane, $Cy_2PCH_2CH_2PCy_2$
dippe	1,2-bis(diisopropylphosphino)ethane, $Pr^i_2PCH_2CH_2PPr^i_2$
dmpe	1,2-bis(dimethylphosphino)ethane, $Me_2PCH_2CH_2PMe_2$
dppe	1,2-bis(diphenylphosphino)ethane, $Ph_2PCH_2CH_2PPh_2$
dppm	bis(diphenylphosphino)methane, $Ph_2PCH_2PPh_2$
dppp	1,3-bis(diphenylphosphino)propane, $Ph_2PCH_2CH_2CH_2PPh_2$
Fv	fulvalene, μ-η^5:η^5-$C_{10}H_8$
HDS	hydrodesulfurization
LS_3	1,3,5-tris[(4,6-dimethyl-3-mercaptophenyl)thio]-2,4,6-tris(*p*-tolylthio)-benzene(3−)
nbd	norbornadiene, C_7H_8
OAc	acetate, O_2CMe^-
OEP	octaethylporphyrinato(2−)
OTf	trifluoromethanesulfonate, $OSO_2CF_3^-$
phen	1,10-phenanthroline, $C_{12}H_8N_2$
phth	phthalimido
PPN	$(Ph_3P)_2N^+$

ppp	bis(2-diphenylphosphinoethyl)phenylphosphine, $PhP(CH_2CH_2PPh_2)_2$
p-Tol	*p*-tolyl, $C_6H_4CH_3$-*p*
py	pyridine, C_5H_5N
tfbb	tetrafluorobenzobarrelene
THF	tetrahydrofuran, C_4H_8O
triphos	1,1,1-tris(diphenylphosphinomethyl)ethane, $MeC(CH_2PPh_2)_3$

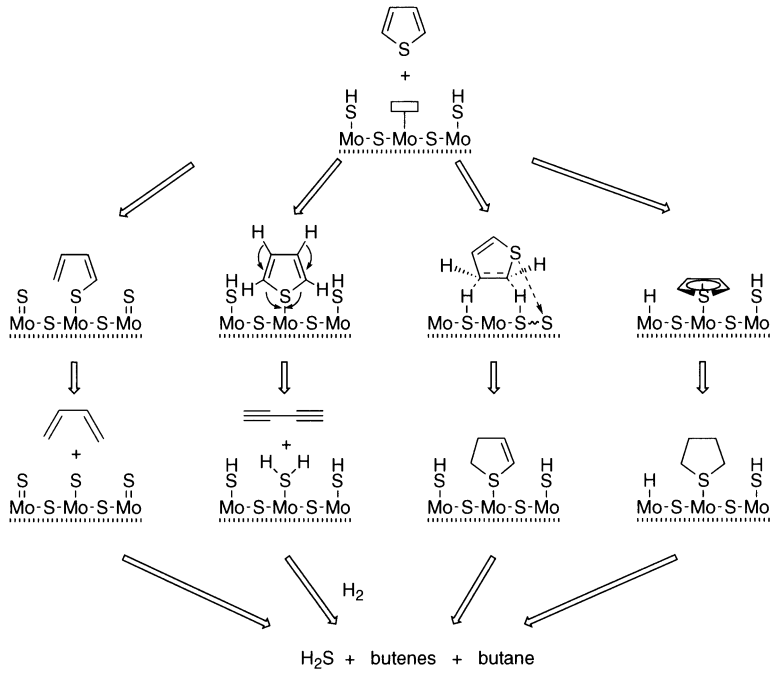
1. Introduction

Sulfur donor ligands have attracted much attention in recent years because of their flexible coordination ability, which leads to the formation of a variety of mono- and polynuclear metal–sulfur structures. Hydrosulfido (SH^-) ligand — also designated as hydrogensulfido, sulfhydryl, or mercapto ligand — is a fundamental member of the sulfur donor ligands. However, the chemistry of hydrosulfido complexes has been reviewed to a surprisingly less extent [1–4] compared to that of complexes with other sulfur donor ligands such as sulfido (S^{2-}) [5–17], polysulfido (S_n^{2-}) [10,17–20], thiolato (SR^-) [21–24], and thioether (dialkyl sulfide; SR_2) [25,26] ligands.

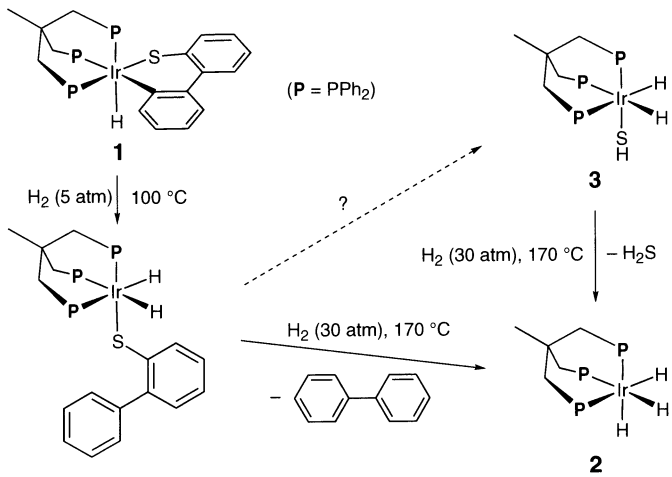
Apparently, hydrosulfido ligands are closely related to other sulfur donor ligands. One can easily understand that the coordination modes of hydrosulfido ligands resemble those of thiolato ligands: both of them act as a terminal, 1e donor and bridging, 3e or 5e donor ligands. The presence of a S–H bond, however, differentiates the property of the hydrosulfido complexes from that of the thiolato complexes. The S–H bond cleavage is associated with most of the reactions unique to hydrosulfido complexes which include the nucleophilic addition to α,β-unsaturated organic substrates and formation of sulfido clusters with higher nuclearity. From another point of view, a hydrosulfido ligand may be regarded as a protonated or hydrogenated form of a sulfido ligand. Indeed, hydrosulfido and sulfido complexes are often interconverted as described below.

Hydrosulfido moieties are proposed to play an important role in the hydrodesulfurization (HDS) process on metal sulfide surfaces. In the typical mechanisms shown in Scheme 1 [27], the SH groups supply hydrogen atoms for cleavage of the C–S bonds in sulfur-containing organic molecules. Indeed, the presence of the SH group has been demonstrated by FTIR studies on sulfided Mo/Al_2O_3 catalysts [28]. Extensive studies by using soluble model complexes have been performed to gain mechanistic knowledge of the HDS process [29]. Hydrosulfido complexes are postulated as intermediates or actually isolated in the hydrogenolysis of C–S bonds in transition metal thiolato complexes. For example, Bianchini and co-workers have

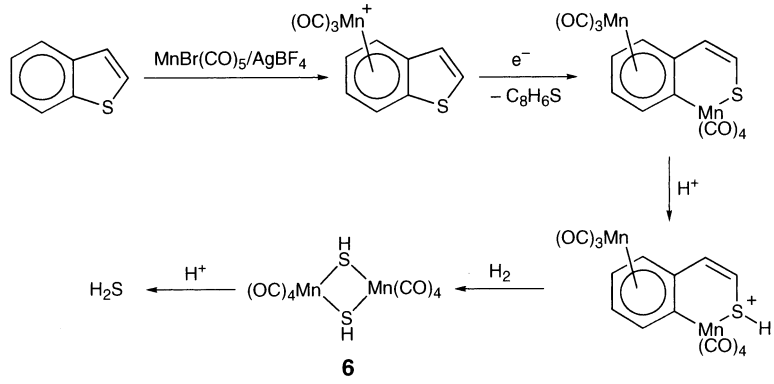
reported the hydrogenolysis of a thiairidacycle complex **1** derived from dibenzothiophene, which leads to the formation of biphenyl and the trihydrido complex [(triphos)IrH_3] (**2**) (Scheme 2) [30]. Although the hydrosulfido complex



Scheme 1.

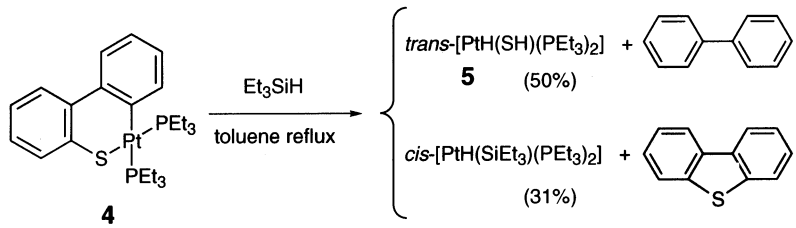


Scheme 2.



Scheme 3.

[(triphos)$IrH_2(SH)$] (**3**) is not detected in this transformation, intermediacy of **3** is proposed on the basis of the fact that the independently synthesized **3** is converted to the trihydrido complex **2** under the same conditions. On the other hand, the reaction of the thiaplatinacycle complex **4** with triethylsilane affords the hydrosulfidoplatinum complex [$PtH(SH)(PEt_3)_2$] (**5**) and a desulfurized hydrocarbon as shown in Eq. (1) [31].



(1)

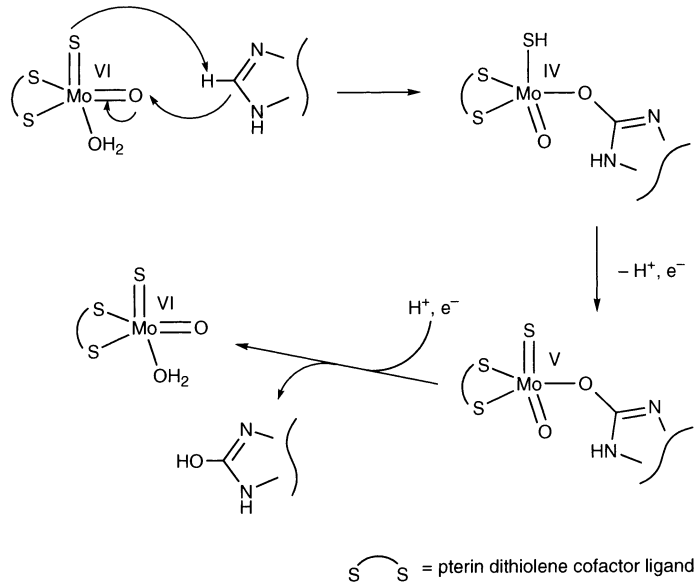
Scheme 3 depicts a more recent example of a manganese-mediated stoichiometric hydrodesulfurization of benzothiophene, which results in the formation of the hydrosulfido complex **6**, although the fate of the organic fragments is unclear [32].

In addition, metal sulfides such as MoS_2 and ZnS are known to catalyze hydrogenation of various substrates including elemental sulfur. An SH intermediate bound to the catalyst surface is involved in these hydrogenation reactions as well as the Claus process, which converts the toxic H_2S generated in the HDS reaction into elemental sulfur according to Eq. (2) [33].

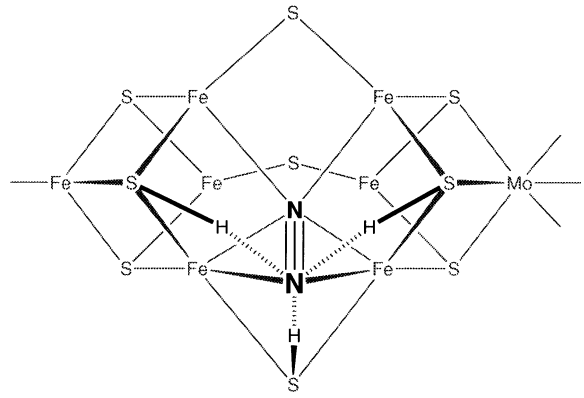
$$2H_2S + SO_2 \rightarrow 3/8S_8 + 2H_2O \quad (2)$$

Another interest in hydrosulfido complexes arises from their relevance to metalloenzymes containing M–SH functionalities in their active site. For example, in a proposed mechanism for xanthine oxidase, a mononuclear molybdenum enzyme which catalyzes the oxidative hydroxylation of aromatic heterocycles, a Mo–SH moiety is formed as a result of hydride or proton acceptance by a terminal sulfido ligand (Scheme 4) [10,34–38]. On the other hand, the presence of a W–SH moiety

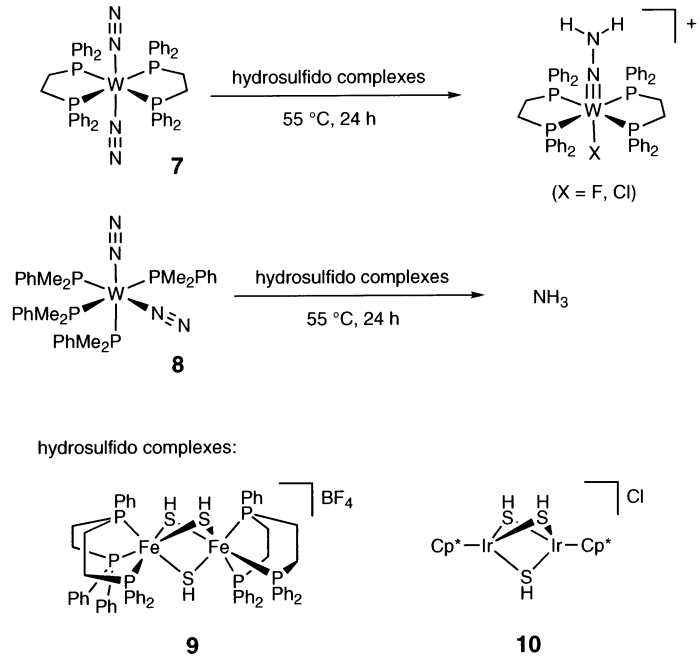
in the aldehyde ferredoxin oxidoreductase from hyperthermophilic organism *Pyrococcus furiosus* is postulated during its catalysis [34,39]. Involvement of SH groups in reduction of dinitrogen on FeMo-cofactor in MoFe-nitrogenase is also claimed by some theoretical investigations [40,41]. Scheme 5 depicts the mechanism proposed by Dance, in which the bridging sulfido ligands mediate the proton transfer to the dinitrogen molecule bound on the Fe_4 face in the FeMo-cofactor cluster via μ-SH intermediates [40]. In this context, it is noteworthy that the coordinated



Scheme 4.



Scheme 5.



Scheme 6.

dinitrogen on tungsten complexes **7** and **8** is transformed to a hydrazido(2–) ligand (NNH_2^{2-}) or even to ammonia by treatment with hydrosulfido-bridged dinuclear complexes **9** and **10** (Scheme 6) [42].

Finally, given that hydrosulfido complexes are inorganic mimics of thiols, it seems reasonable to expect that these complexes serve as building blocks for hydrosulfido- or sulfido-bridged polynuclear complexes by the reactions with heterometal complexes. These reactions provide a versatile method for rational synthesis of sulfido clusters with desired metal–sulfur compositions.

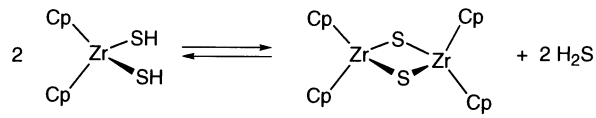
This review consists of three main sections dealing with synthesis, spectroscopic and structural properties, and reactivities of hydrosulfido complexes. At the end of the review, hydrosulfido complexes of transition metals are tabulated. The literature published up to the end of 1999 is covered. Although hydrosulfido complexes of metals other than Group 4–11 ones such as Be [43,44], Mg [45,46], Al [47], Ga [48,49], Zn [50,51], and Hg [52] are known, the chemistry of these species will not be discussed in detail.

2. Synthesis

Hydrosulfido complexes have been synthesized through a variety of methods. Hydrogen sulfide (H_2S) is the most versatile reagent for preparation of hydrosulfido

complexes. Various ligands such as halo, hydrido, alkyl, alkoxo, amido, and thiolato ligands are substituted by hydrosulfido ligands upon treatment with H_2S, whereas oxidative addition of H_2S to low-valent metal centers affords hydrido–hydrosulfido species. H_2S complexes may be regarded as primary products in these reactions. However, only a few of them have been isolated [53–55] and structurally characterized [56–58] because of their thermal instability. Another synthetic approach is the reaction of metal hydrido complexes with sulfur-supplying reagents, which results in insertion of a sulfur atom into the M–H bond and affords hydrosulfido complexes. Protonation and hydrogenation of sulfido ligands are of importance in relation to the catalysis of metalloenzymes and nonmolecular metal sulfides besides their synthetic utility. This section summarizes the preparative methods for hydrosulfido complexes.

A general problem associated with the preparation of hydrosulfido complexes is further aggregation of the mononuclear hydrosulfido complexes initially formed, which leads to the formation of polynuclear sulfido complexes or insoluble metal sulfides. As will be shown below, whether hydrosulfido complexes or sulfido complexes with higher nuclearity are formed often depends on the ancillary ligands [59]. The larger ancillary ligands tend to suppress the aggregation of hydrosulfido complexes and make their isolation successful. In some systems, mononuclear hydrosulfido complexes and sulfido complexes with higher nuclearity are in equilibrium. Thus, when the solution of the bis(hydrosulfido)zirconium complex $[Cp_2Zr(SH)_2]$ (**11**) is placed under a reduced pressure, the sulfido-bridged dimer $[Cp_2Zr(\mu_2\text{-}S)_2ZrCp_2]$ (**12**) is generated concurrent with a release of H_2S (Eq. (3)) [60].

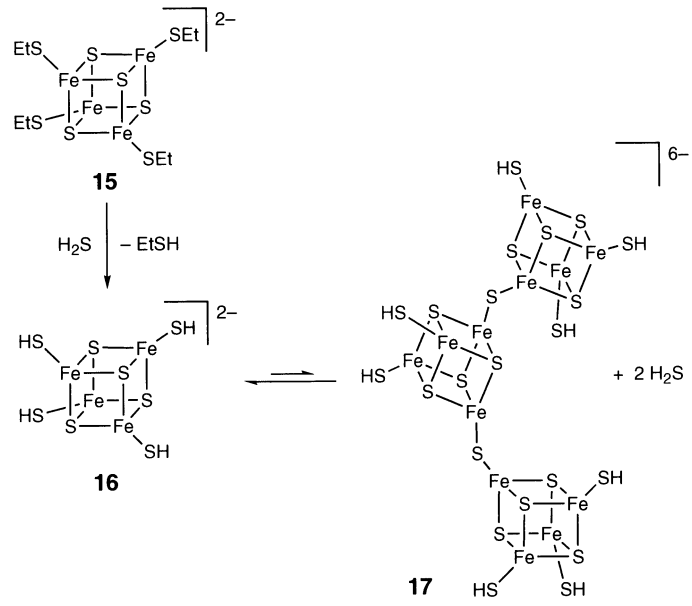


11 **12** (3)

The dimer **12** goes back to the mononuclear hydrosulfido complex **11** by addition of H_2S. It is to be noted that the corresponding complexes with bulkier cyclopentadienyl ligands $[(^tBuCp)_2Zr(SH)_2]$ (**13**) [61,62] and $[Cp^*_2Zr(SH)_2]$ (**14**) [63] do not dimerize under the same conditions. A more complicated equilibrium is observed in the sulfido-bridged 'polycubane' system, which involves three molecules of 'monocubanes' **16** and the 'tricubane' **17** derived from the condensation of hydrosulfido ligands in the monocubanes. (Scheme 7) [64]. In general, however, once sulfido bridge is formed, all SH ligands are consumed to give stable polynuclear sulfido complexes. As a consequence, sulfido clusters containing M–SH moieties are rare; the examples include $[Ni_3(\mu_3\text{-}S)_2(SH)(PEt_3)_5][BPh_4]$ (**18**) [65], $[Co_3(\mu_3\text{-}S)_2(\mu_2\text{-}SH)_2(\mu_2\text{-}PEt_2)(PHEt_2)_6][ClO_4]_2$ (**19**) [66] and $[(CpCr)_2\{Fe(SH)\}_2(\mu_3\text{-}S)_4]$ (**20**) [67].

2.1. Ligand substitution

Since the first hydrosulfido complex, $[Cp_2Ti(SH)_2]$ (**21**), was prepared in 1965 by the reaction of $[Cp_2TiCl_2]$ (**22**) with H_2S in the presence of triethylamine (Eq. (4))



Scheme 7.

[68], ligand substitution by using H_2S or hydrosulfide anion has been a convenient method for the synthesis of hydrosulfido complexes. The reactions with H_2S are often carried out in the presence of base, as exemplified by Eq. (4).

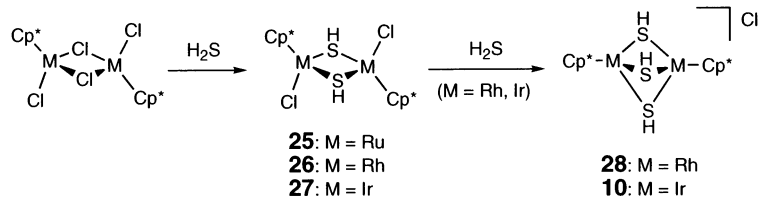
$$[Cp_2TiCl_2] + 2H_2S \xrightarrow[\text{r.t.}]{Et_3N} [Cp_2Ti(SH)_2] \quad (4)$$

(22) (21)

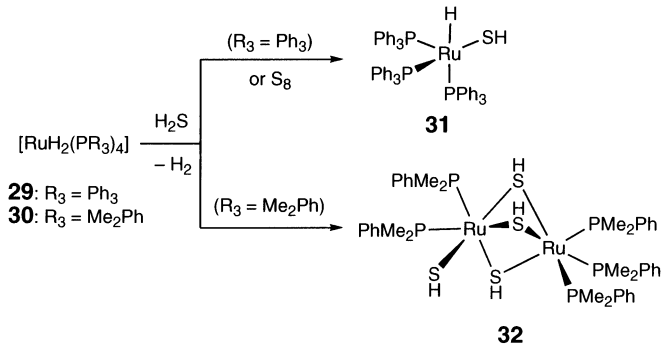
As for the hydrosulfide anion, R_4N^+ and PPN salts are sometimes employed instead of the more frequently used sodium salt to enhance the solubility of the anion.

In the ligand substitution, halo complexes are conventional starting materials. As an earlier example, $[Cp_2M(SH)_2]$ (M = Mo (**23**), W (**24**)) have been prepared by the reaction of $[Cp_2MCl_2]$ with NaSH [69]. The noble metal complexes $[Cp^*MCl(\mu_2\text{-}Cl)]_2$ (M = Ru [70], Rh, Ir [71,72]) react with an excess of H_2S to afford a series of hydrosulfido-bridged dinuclear complexes $[Cp^*MCl(\mu_2\text{-}SH)_2MClCp^*]$ (M = Ru (**25**), Rh (**26**), Ir (**27**)); prolonged reactions afford the triply-bridged cationic complexes $[Cp^*M(\mu_2\text{-}SH)_3MCp^*]Cl$ (M = Rh (**28**), Ir (**10**)) in the case of M = Rh or Ir (Scheme 8) [72].

Reactions of hydrido or alkyl complexes with H_2S also give hydrosulfido complexes with a loss of H_2 or hydrocarbons [73]. Yamamoto and co-workers have found that the hydrido complexes $[RuH_2(PR_3)_4]$ ($R_3 = Ph_3$ (**29**), Me_2Ph (**30**)) react with H_2S to afford the hydrosulfido complexes $[RuH(SH)(PPh_3)_3]$ (**31**) [74] and $[Ru(PMe_2Ph)_3(\mu_2\text{-}SH)_3Ru(SH)(PMe_2Ph)_2]$ (**32**) [75] (Scheme 9). The former complex can also be prepared by the reaction of the dihydrido complex **29** with S_8 [74]. In a similar manner, treatment of $[RuH_2(dppm)_2]$ with H_2S affords the hydrido–hy-



Scheme 8.

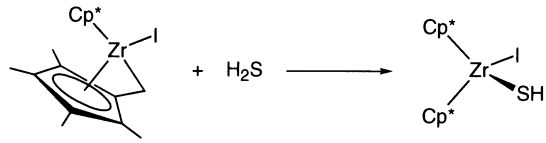


Scheme 9.

drosulfido complex [RuH(SH)(dppm)$_2$] (**33**) and the bis(hydrosulfido) complex [Ru(SH)$_2$(dppm)$_2$] (**34**) sequentially [76]. Alkanes are eliminated analogously in the reactions of alkyl complexes with H_2S, as exemplified by the reaction shown in Eq. (5) [63].

$$[Cp^*_2ZrMe_2] + 2H_2S \underset{60°C}{\rightarrow} [Cp^*_2\underset{\mathbf{14}}{Zr}(SH)_2] + 2MeH \quad (5)$$

As an elegant variation of this method, Bergman and co-workers have synthesized the partially hydrosulfided complex [Cp^*_2ZrI(SH)] (**35**) by the reaction of the cyclometalated zirconium complex **36** with H_2S (Eq. (6)) [77,78].



(6)

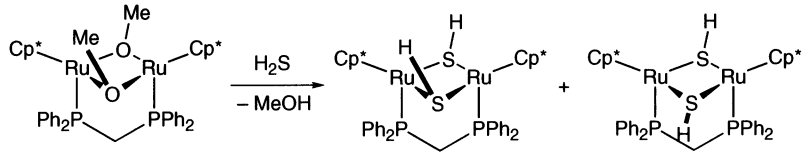
The hydrosulfido–iodo complex **35** is difficult to be obtained in a pure form by simple ligand substitution of [$Cp^*_2ZrI_2$]. Owing to the partially hydrosulfided nature, **35** can undergo α-elimination of hydrogen iodide, giving the reactive intermediate [$Cp^*_2Zr=S$] (**37**) (vide infra).

Hydroxo and alkoxo complexes also serve as a potential precursor for the synthesis of hydrosulfido complexes [79]. Their synthetic utility relies on the

stronger acidity of hydrogen sulfide than those of water and alcohols. Bercaw and co-workers have prepared the hydrosulfido complex [Cp*Ru(SH)(PMe_3)$_2$] (**38**) from the reaction of the hydroxo complex [Cp*Ru(OH)(PMe_3)$_2$] (**39**) with H_2S (Eq. (7)) during their study on the strength of metal–heteroatom bonds [80].

39 **38** (7)

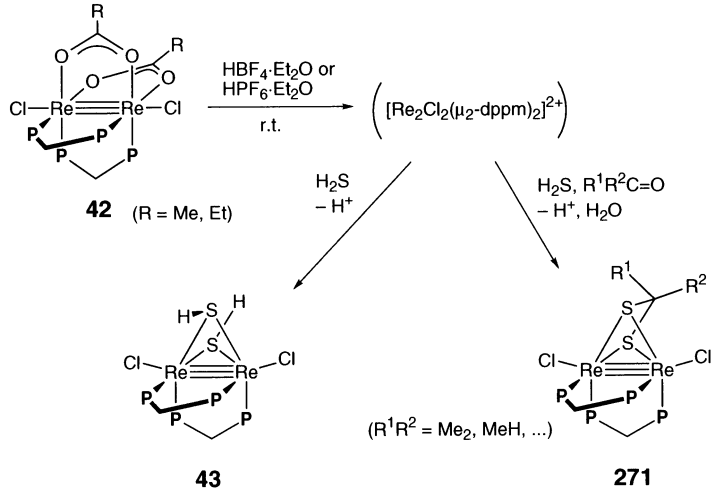
The bridging methoxo ligands in [Cp*Ru(μ_2-OMe)$_2$(μ_2-dppm)RuCp*] (**40**) are substituted by hydrosulfido ligands when treated with H_2S (Eq. (8)) [81].



40 *syn*-**41** *anti*-**41** (8)

Despite the stronger acidity of carboxylic acids, the carboxylato-bridged dirhenium(II) complex *cis*-[Re_2Cl_2(μ_2-O_2CR)$_2$(μ_2-dppm)$_2$] (**42**; R = Me, Et) reacts with H_2S to give the hydrosulfido-bridged dirhenium(II) complex *cis*-[Re_2Cl_2(μ_2-SH)$_2$(μ_2-dppm)$_2$] (**43**) with the aid of strong acids (Scheme 10) [82,83].

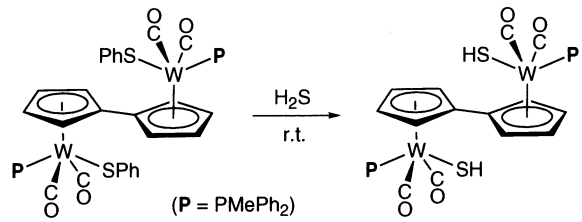
Holm and co-workers have synthesized the cubane-type iron–sulfur cluster $[Fe_4S_4(SH)_4]^{2-}$ (**16**), which had originally been prepared by Müller and co-workers in a somewhat serendipitous method [84], by the reaction of the corresponding thiolato cluster (**15**) and H_2S (Scheme 7) [64,85]. Similarly, the reaction of the fulvalene–thiolato complex [Fv{W(SPh)(CO)$_2$($PMePh_2$)}$_2$] (**44**) with H_2S affords



42 (R = Me, Et) **43** **271**

Scheme 10.

the corresponding hydrosulfido complex [Fv{W(SH)(CO)$_2$(PMePh$_2$)}$_2$] (**45**) as shown in Eq. (9) [86].



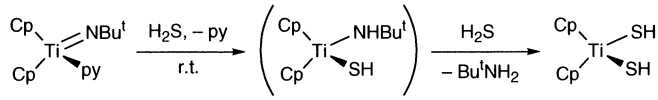
(9)

44 **45**

Formation of the bis(hydrosulfido)tungsten complex [W(SH)$_2$(CO)$_2$(phen)] (**46**) upon treatment of the bis(thiolato) complex [W(SBu^t)$_2$(CO)$_2$(phen)] with H_2S is also claimed [87]. The reaction of [Cp*IrCl(μ_2-H)(μ_2-SBu^n)IrClCp*] with H_2S results in replacement of not only the bridging hydrido ligand but the thiolato ligand to afford the hydrosulfido-bridged complex [Cp*IrCl(μ_2-SH)$_2$IrClCp*] (**27**) [88].

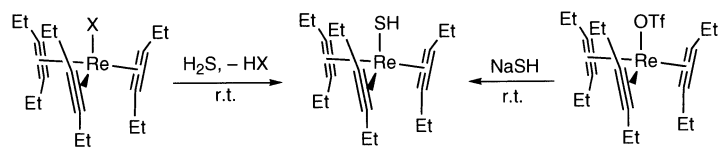
When the imido complex [Cp$_2$Ti(NBu^t)(py)] (**47**) is treated with H_2S, the bis(hydrosulfido) complex [Cp$_2$Ti(SH)$_2$] (**21**) along with t-butylamine and pyridine is formed [89]. As shown in Scheme 11, initial formation of the amido–hydrosulfido complex [Cp$_2$Ti(NHBu^t)(SH)] (**48**) is proposed in this transformation. Ligand substitution of the amido or hydroxo complex [ReX(EtC≡CEt)$_3$] (**49**; X = NH$_2$, OH) by H_2S affords the hydrosulfido complex [Re(SH)(EtC≡CEt)$_3$] (**50**) with a loss of ammonia or water (Scheme 12) [90]. Complex **50** is prepared more effectively, however, by the reaction of [Re(OTf)(EtC≡CEt)$_3$] (**51**) with NaSH.

In addition to the anionic ligands described above, neutral and weakly coordinated ligands can be replaced by a hydrosulfido ligand [91]. Sacconi and co-workers have prepared a series of the hydrosulfido complexes containing a multidentate phosphine ligand [M(SH)L]$^+$ (M = Fe (**52**), Co (**53**), Ni (**54**); L =



47 **48** **21**

Scheme 11.

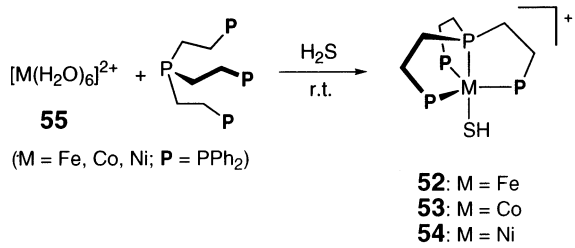


49 **50** **51**

(X = NH$_2$, OH)

Scheme 12.

$P(CH_2CH_2PPh_2)_3$) from the reactions of $[M(H_2O)_6]^{2+}$ (**55**) with H_2S in the presence of the tetradentate ligand (Eq. (10)) [92].



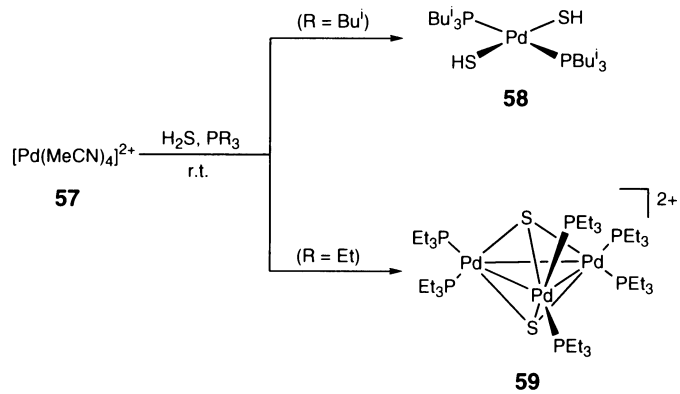
(10)

The corresponding reaction of $[Fe(H_2O)_6][ClO_4]_2$ with the tridentate phosphine ligand, ppp, affords the hydrosulfido-bridged diiron complex $[\{Fe(ppp)\}_2(\mu_2\text{-}SH)_3][ClO_4]$ (**9**) [93]. The related rhodium complex [LRh(SH)] (**56**; L = $P(CH_2CH_2PPh_2)_3$) is synthesized by the reaction of $[LRh(cod)]^+$ with hydrosulfide anion [94,95]. Dependence of the products upon the ancillary ligands is also observed in the reactions of $[Pd(CH_3CN)_4]^{2+}$ (**57**) with H_2S and phosphine ligands [96]. Thus, use of PBu^i_3 as the ligand leads to the isolation of the mononuclear hydrosulfido complex *trans*-$[Pd(SH)_2(PBu^i_3)_2]$ (**58**), whereas the tripalladium sulfido cluster $[Pd_3(\mu_3\text{-}S)_2(PEt_3)_6]^{2+}$ (**59**) is obtained if the sterically less demanding PEt_3 is employed (Scheme 13).

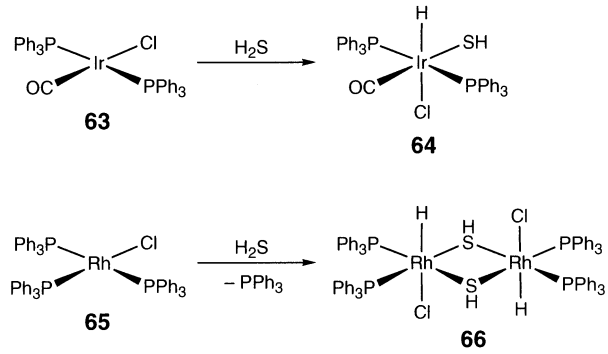
Even carbonyl ligands are replaced by hydrosulfide anion. For example, reactions of $[M(CO)_6]$ (M = Cr, Mo, W) with hydrosulfide anion give a series of anionic hydrosulfido complexes $[M(SH)(CO)_5]^-$ (M = Cr (**60**), Mo (**61**), W (**62**)) [97,98].

2.2. Oxidative addition of H_2S

As expected, oxidative addition of H_2S to low-valent metal centers leads to the formation of hydrosulfido complexes. For example, the reaction of Vaska's complex $[IrCl(CO)(PPh_3)_2]$ (**63**) with H_2S affords the mononuclear hydrido–hydro-



Scheme 13.

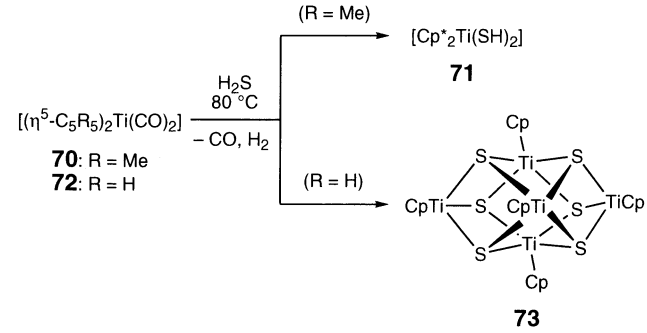


Scheme 14.

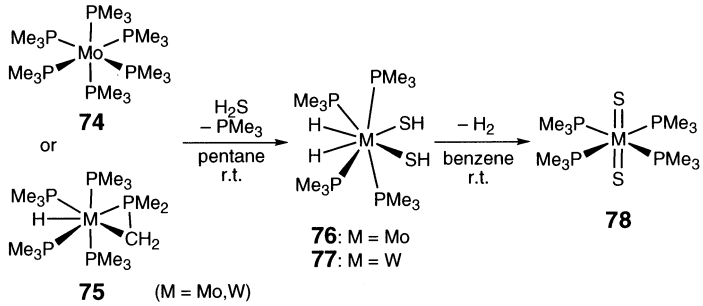
sulfido complex [IrHCl(SH)(CO)(PPh_3)$_2$] (**64**), whereas the corresponding reaction of Wilkinson's complex [RhCl(PPh_3)$_3$] (**65**) results in the formation of the hydrosulfido-bridged dirhodium complex [{RhHCl(PPh_3)$_2$}$_2$(μ_2-SH)$_2$] (**66**) [99] (Scheme 14). Oxidative addition of H_2S to the Ru(II) complexes [Cp*RuCl(PR_3)$_2$] (PR_3 = PEt_3 [100], 1/2 dippe [101]) in the presence of $NaBPh_4$ leads to the formation of the Ru(IV) hydrosulfido complex [Cp*RuH(SH)(PR_3)$_2$][BPh_4] ($PR_3 = PEt_3$ (**67**), 1/2 dippe (**68**)). The Ru(IV) complexes seem to be stabilized by the electron-donating Cp* ligand because the corresponding reaction of the Cp analogue affords the disulfido-bridged Ru(III) complex [{CpRu(PEt_3)$_2$}$_2$($\mu_2\eta^1$:η^1-S_2)]$^{2+}$ [100]. Reversible oxidative addition of H_2S to the W(0) complex [W(CO)$_3$(PR_3)$_2$] (R = Pr^i, Cy) is also claimed [102]. The 17e$^-$ species [Cp*Cr(CO)$_3$] reacts with H_2S to give the hydrosulfido complex [Cp*Cr(SH)(CO)$_3$] (**69**) and the hydrido complex [Cp*CrH(CO)$_3$] [103].

Because the primary products of the oxidative addition, the hydrido–hydrosulfido complexes, still have reactive SH and H functionalities, further substitution or aggregation reactions are expected to take place. Thus, the Ti(II) carbonyl complex [Cp$^*_2$Ti(CO)$_2$] (**70**) reacts with H_2S to give the bis(hydrosulfido) complex [Cp$^*_2$Ti(SH)$_2$] (**71**) with a loss of CO and H_2 [104], whereas the sterically less demanding Cp analogue [Cp_2Ti(CO)$_2$] (**72**) affords the pentanuclear sulfido cluster [(CpTi)$_5$(μ_3-S)$_6$] (**73**) (Scheme 15) [104,105]. Ligand substitution and oxidative addition provide complementary synthetic methods for [(η^5-C_5R_5)$_2$Ti(SH)$_2$], because the Cp*–hydrosulfido complex **71** could not be prepared by the former approach [60].

Parkin and co-workers have investigated the reactions of the molybdenum(0) complex [Mo(PMe_3)$_6$] (**74**) and the related cyclometalated complexes [MH(η^2-CH_2PMe_2)(PMe_3)$_4$] (**75**; M = Mo, W) with H_2S [106–108]. When the reactions are carried out in pentane, the hydrido–hydrosulfido complexes [MH_2(SH)$_2$(PMe_3)$_4$] (M = Mo (**76**), W (**77**)) are isolated owing to their low solubility (Scheme 16). Dissolving these complexes in benzene leads to the evolution of H_2, giving the bis(sulfido) complexes [MS_2(PMe_3)$_4$] (**78**). It is of interest that the reaction of the related tungsten(0) dinitrogen complex *cis*-[W(N_2)$_2$(PMe_2Ph)$_4$] (**8**) with H_2S, in situ

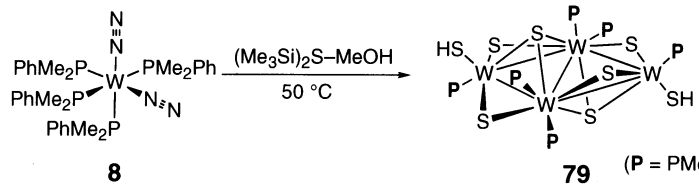


Scheme 15.



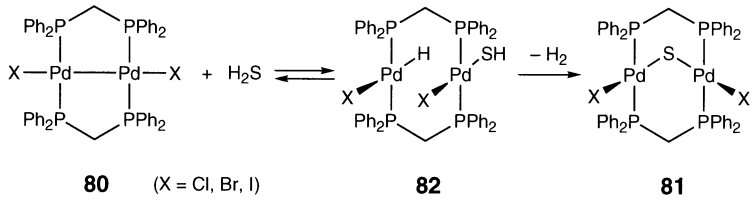
Scheme 16.

generated from $(Me_3Si)_2S$ and MeOH, results in the formation of the hydrosulfido–sulfido cluster $[W_4(\mu_3\text{-}S)_2(\mu_2\text{-}S)_4(SH)_2(PMe_2Ph)_6]$ (**79**) (Eq. (11)) [109,110].

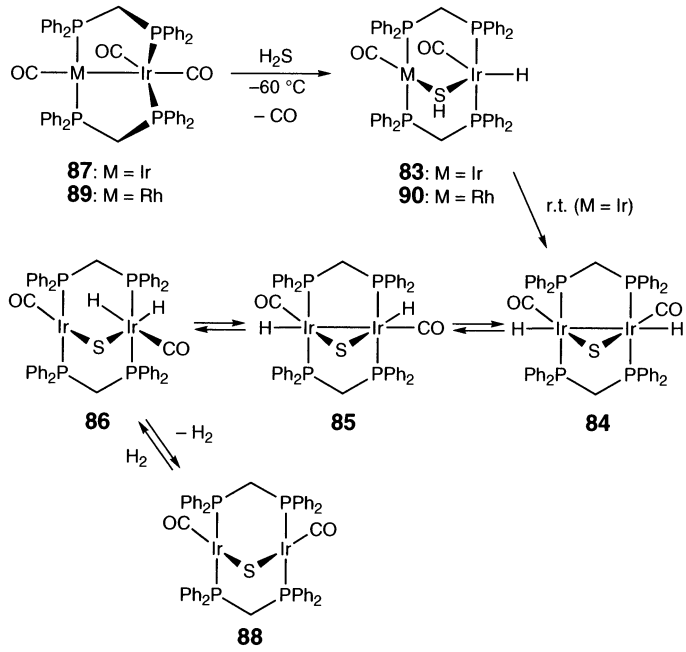


(11)

Dinuclear A-frame type and related complexes derived from oxidative addition of H_2S to dinuclear centers provide a certain class of hydrosulfido complexes. The reaction of the dinuclear complex $[Pd_2X_2(\mu_2\text{-dppm})_2]$ (**80**; X = Cl, Br, I) with H_2S affords the A-frame complex $[Pd_2X_2(\mu_2\text{-}S)(\mu_2\text{-dppm})_2]$ (**81**) via the hydrido–hydrosulfido complex **82** as shown in Scheme 17 [111–113]. On the other hand, the hydrido–hydrosulfido species $[Ir_2H(\mu_2\text{-}SH)(CO)_2(\mu_2\text{-dppm})_2]$ (**83**) as well as bis(hydrido)–sulfido intermediates **84**–**86** with the general formula $[Ir_2H_2(CO)_2(\mu_2\text{-}S)(\mu_2\text{-dppm})_2]$ are observed in the reaction of $[Ir_2(CO)_3(\mu_2\text{-dppm})_2]$ (**87**) with H_2S to eventually form the sulfido-bridged complex $[Ir_2(CO)_2(\mu_2\text{-}S)(\mu_2\text{-dppm})_2]$ (**88**) (Scheme 18) [114]. Interestingly, from the Rh/Ir heterobimetallic complex $[RhIr(CO)_3(\mu_2\text{-dppm})_2]$ (**89**), the H(SH) complex $[RhIrH(\mu_2\text{-}SH)(CO)_2(\mu_2\text{-dppm})_2]$ (**90**) is isolated; further hydrido rearrangements and reductive elimination of H_2 do

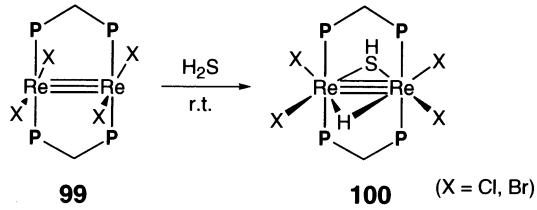


Scheme 17.

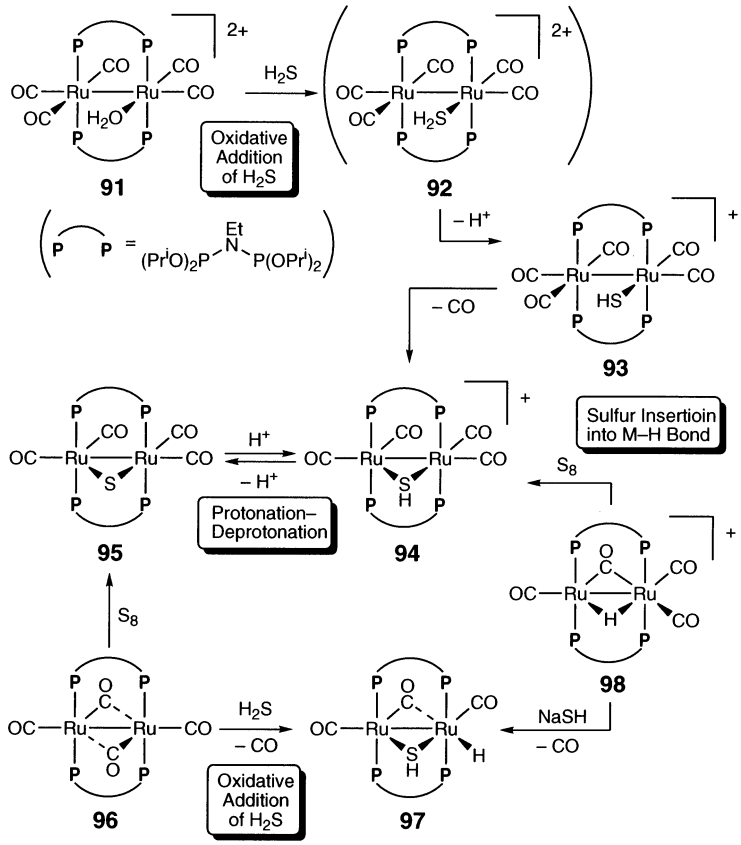


Scheme 18.

not take place. Scheme 19 outlines the transformations of the related diphosphazane-bridged dirutheium complexes, which includes not only oxidative addition of H_2S but ligand substitution by H_2S and insertion of a sulfur atom into a M–H bond on the dinuclear center, which will be described in the following sections [115–117]. Oxidative addition of H_2S across the Re≡Re triple bond in the dirhenium(II) complex $[Re_2X_4(\mu_2\text{-dppm})_2]$ (**99**; X = Cl, Br) gives rise to the formation of the hydrido- and hydrosulfido-bridged dirhenium(III) complex $[Re_2X_4(\mu_2\text{-H})(\mu_2\text{-SH})(\mu_2\text{-dppm})_2]$ (**100**) (Eq. (12)) [82,118].



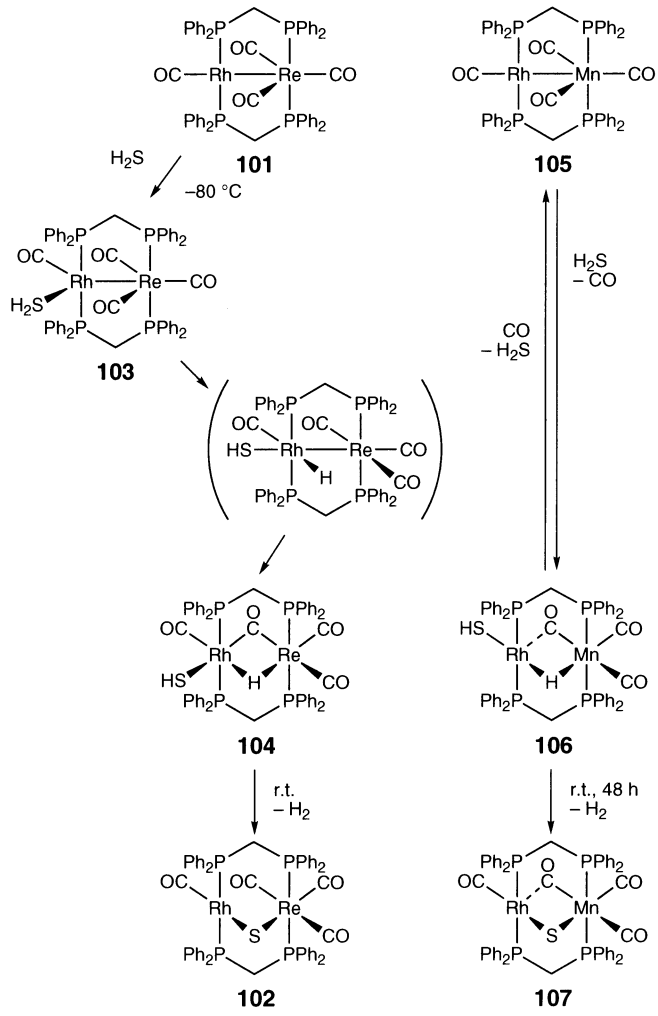
(12)



Scheme 19.

A related $Re_2(\mu_2\text{-H})(\mu_2\text{-SH})$ core is formed from the reaction of H_2S with $[Re_2(CO)_8(MeCN)_2]$, which contains a Re(0)–Re(0) single bond [119].

Oxidative addition of H_2S to heterobimetallic complexes provide a practical synthetic method for hydrosulfido-bridged heterobimetallic complexes as described above. Cowie and co-workers have studied the reactions of Rh/Re and Rh/Mn heterobimetallic complexes with H_2S. It is noteworthy that the reactions proceed differently between both systems (Scheme 20). The reaction of the Rh/Re heterobimetallic complex $[Rh(CO)(\mu_2\text{-dppm})_2Re(CO)_3]$ (**101**) with H_2S gives the sulfido-bridged tetracarbonyl complex $[Rh(CO)(\mu_2\text{-S})(\mu_2\text{-dppm})_2Re(CO)_3]$ (**102**) and H_2 [120]. The transient species $[Rh(CO)(H_2S)(\mu_2\text{-dppm})_2Re(CO)_3]$ (**103**) and $[Rh(SH)(CO)(\mu_2\text{-H})(\mu_2\text{-CO})(\mu_2\text{-dppm})_2Re(CO)_2]$ (**104**) are observed in the ^{1}H-NMR spectrum during this transformation. By contrast, the corresponding reaction of the Rh/Mn complex **105** affords the isolable hydrido–hydrosulfido complex $[Rh(SH)(\mu_2\text{-H})(\mu_2\text{-dppm})_2Mn(CO)_3]$ (**106**), and it releases H_2S to give the starting complex **105** upon treatment with CO; the intermediary H_2S complex is not observed [121]. The prolonged reaction (2 days) is necessary to convert the

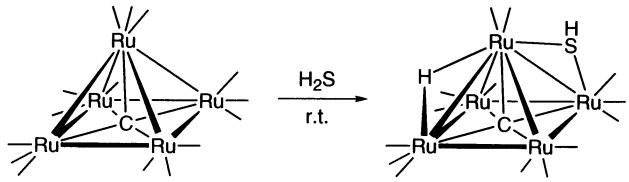


Scheme 20.

hydrido–hydrosulfido species **106** into the sulfido-bridged tetracarbonyl complex $[Rh(CO)(\mu_2\text{-}S)(\mu_2\text{-}dppm)_2Mn(CO)_3]$ (**107**). The additional carbonyl ligand required in the last conversion is believed to be supplied from the uncharacterized decomposition products. Facile α-elimination of H_2 from these dinuclear hydrido–hydrosulfido species is in marked contrast with the scarceness of the M=S bond formation from mononuclear late transition metal hydrido–hydrosulfido complexes [108], and is attractive in relation to conversion of H_2S into H_2 and S_8 (or sulfur-containing organic compounds) [113].

Intermediary hydrido–hydrosulfido species is also likely to be involved in the reaction of H_2S with coordinatively unsaturated tripalladium and triplatinum

centers of $[M_3(\mu_3\text{-CO})(\mu_2\text{-dppm})_3]^{2+}$ (**108**; M = Pd, Pt) (Scheme 21) [122]. As for the complexes with higher nuclearity, Lewis and co-workers have reported that oxidative addition of H_2S to the pentanuclear carbonyl cluster $[Ru_5C(CO)_{15}]$ (**111**) affords the hydrido–hydrosulfido cluster $[Ru_5(\mu_2\text{-H})C(\mu_2\text{-SH})(CO)_{14}]$ (**112**) (Eq. (13)) [123].

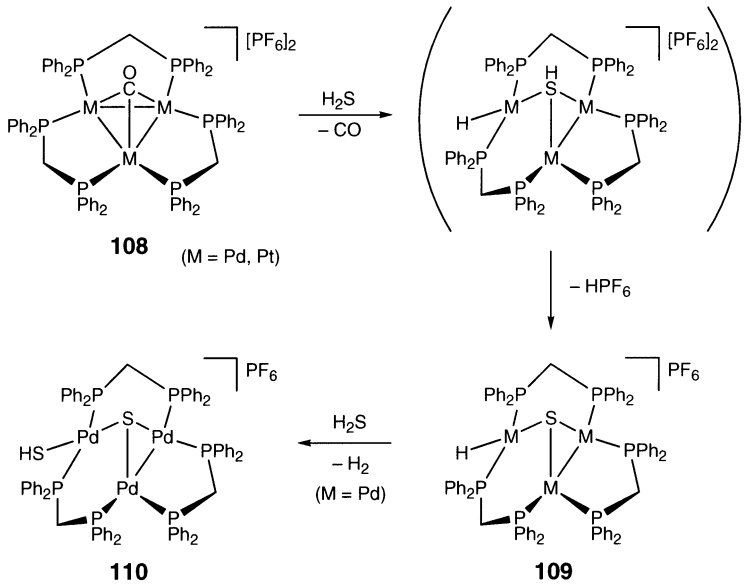


111 **112** (13)

These reactions of H_2S on multimetallic centers give some information about poisoning of heterogeneous noble-metal catalysts as well as adsorption of H_2S on metal sulfide surfaces employed for the HDS process.

2.3. Sulfur insertion into M–H bonds

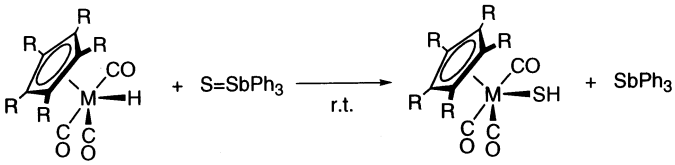
Reactions of hydrido complexes with sulfur-supplying reagents including elemental sulfur [74,124–126] and propylene sulfide [127] afford hydrosulfido complexes. The conversion of $[(\eta^5\text{-}C_5R_5)MH(CO)_3]$ (M = Cr, Mo, W; R = H, Me) into $[(\eta^5\text{-}C_5R_5)M(SH)(CO)_3]$ (**69**, **113**–**116**) by this method has been investigated extensively. Beck and co-workers have used propylene sulfide [127], whereas Herrmann's group



108 (M = Pd, Pt) **110** **109**

Scheme 21.

has employed S_8 as sulfur sources [128]. Quite recently, S=$SbPh_3$ has been shown to be an effective sulfur-supplying reagent to prevent the formation of the multi-insertion products $[(\eta^5\text{-}C_5R_5)M(S_nH)(CO)_3]$ with $n > 1$ (Eq. (14)) [129].

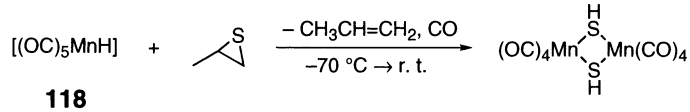


(M = Cr, Mo, W; R = H, Me)

69: M = Cr, R = Me
113: M = Mo, R = H
114: M = Mo, R = Me
115: M = W, R = H
116: M = W, R = Me

(14)

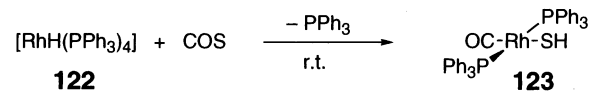
The reaction of the related fulvalene-bridged dinuclear complex $[Fv\{WH(CO)_3\}_2]$ with S_8 gives the bis(hydrosulfido) complex $[Fv\{W(SH)(CO)_3\}_2]$ (**117**) via the hydrido–hydrosulfido intermediate $[FvW_2H(SH)(CO)_6]$; however, **117** is unstable and decomposes to $[Fv\{W(CO)_3\}_2]$ containing a W–W bond [86]. The hydrosulfido-bridged dimanganese complex $[\{Mn(CO)_4\}_2(\mu_2\text{-}SH)_2]$ (**6**) is prepared by the reaction of $[MnH(CO)_5]$ (**118**) with propylene sulfide (Eq. (15)) [127].



118 **6**

(15)

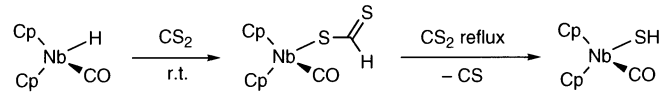
Carbon disulfide inserts into the Nb–H bond in the hydrido complex $[Cp_2NbH(CO)]$ (**119**) to give the dithioformato complex $[Cp_2Nb\{SC(S)H\}(CO)]$ (**120**), which is further transformed into the hydrosulfido complex $[Cp_2Nb(SH)(CO)]$ (**121**) in boiling CS_2 with a loss of CS (Scheme 22) [130]. Eq. (16) represents the preparation of the hydrosulfido complex **123** by using COS as a sulfur-supplying reagent [131].



122 **123**

(16)

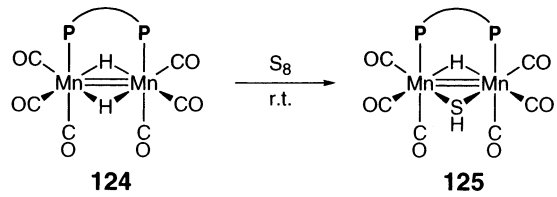
Similarly, the transformation of μ_2-hydrido ligands into μ_2-hydrosulfido ligands takes place, as exemplified by the reaction of diruthenium complex **98** described in



119 **120** **121**

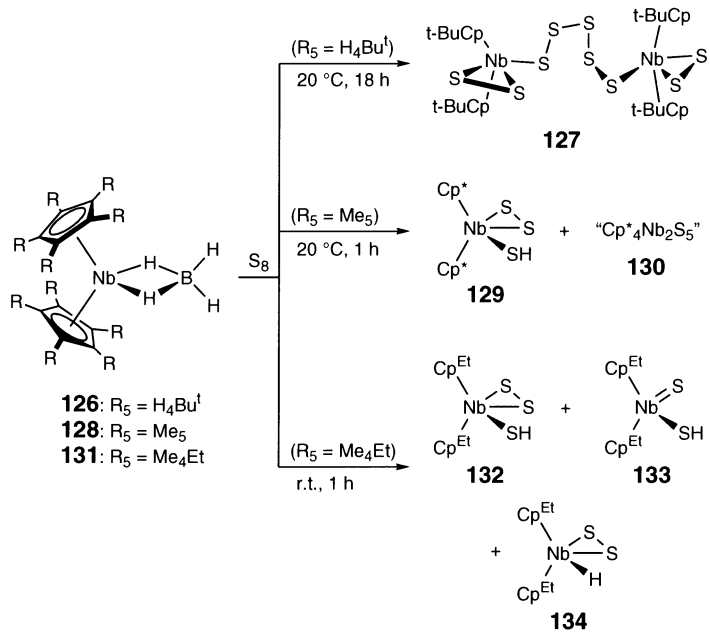
Scheme 22.

Scheme 19 [117] and the reaction of **124** shown in Eq. (17) [132]. Such sulfur-abstraction by M–H functionalities on multimetallic centers may have some relevance to the HDS process on nonmolecular metal sulfides.

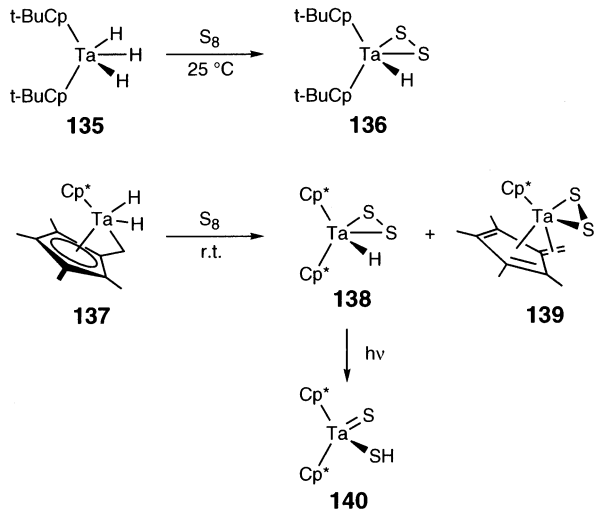


(17)

In their study on Group 5 metallocene–hydrosulfido complexes, Wachter and co-workers have often used more easily accessible BH_4 complexes as starting materials along with the corresponding hydrido complexes. Interestingly, the products strongly depend upon the metals and the substituents of the cyclopentadienyl rings: the reaction of $[(^tBuCp)_2Nb(BH_4)]$ (**126**) with S_8 affords the pentasulfido-bridged diniobium complex $[\{(^tBuCp)_2Nb(\eta^2\text{-}S_2)\}_2(\mu_2\text{-}S_5)]$ (**127**) [133,134], whereas the analogous reaction of the Cp* derivative **128** yields the disulfido–hydrosulfido complex $[Cp^*_2Nb(\eta^2\text{-}S_2)(SH)]$ (**129**) and a complex formulated tentatively as $[Cp^*_4Nb_2S_5]$ (**130**) (Scheme 23) [133,134]. From the Cp^{Et} analogue **131**, the corresponding disulfido–hydrosulfido complex **132** is obtained, together with the hydro



Scheme 23.



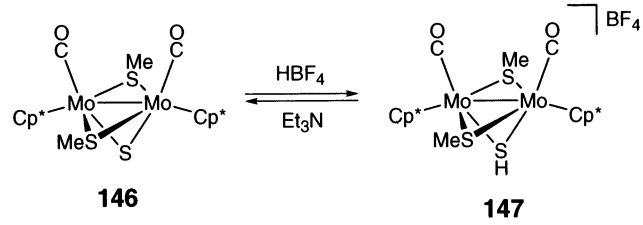
Scheme 24.

sulfido–sulfido complex **133** and the disulfido–hydrido complex **134** [135]. As for tantalum, only disulfido complexes are formed from the hydrido complexes $[(^tBuCp)_2TaH_3]$ (**135**) [134] and $[Cp^*(\eta^6\text{-}C_5Me_4CH_2)TaH_2]$ (**137**) [136] (Scheme 24). For some hydrido–disulfido complexes described above, intramolecular insertion of a sulfur atom of the disulfido ligands into a M–H bond takes place to give hydrosulfido complexes [135]. For example, irradiation of the (disulfido)(hydrido)tantalum complex $[Cp^*_2TaH(\eta^2\text{-}S_2)]$ (**138**) causes its isomerization to the hydrosulfido–sulfido complex $[Cp^*_2Ta(S)(SH)]$ (**140**) (Scheme 24) [136].

The hydrido–thiocarbamoyl complexes $[MoH\{\eta^2\text{-}C(S)NMe_2\}(diphos)_2]$ (**141**; diphos = dppe, depe) are converted into the aminocarbyne–hydrosulfido complexes $[Mo(SH)(\equiv CNMe_2)(diphos)_2]$ (**142**) upon heating (Scheme 25) [137]. The reaction is believed to proceed via initial formation of the Fischer carbene intermediate **143** followed by migration of the SH group from the carbene carbon to the Mo atom. A related mechanism has been proposed for the transformation of the metalladithioester complex $[RuI(CO)(PPh_3)_2\{C(S)SMe\}]$ with primary amines RNH_2 (R = Me, Pr^i, and so on) into the isocyanide–hydrosulfido complexes $[RuI(CO)(CNR)(PPh_3)(SH)]_2$ (**145**) [138].

2.4. Protonation and hydrogenation of sulfido complexes

Protonation of μ_2-sulfido complexes giving μ_2-hydrosulfido complexes is a well-established reaction [121,139–141]; the examples are shown in Scheme 19 [116] and Eq. (18) [142].



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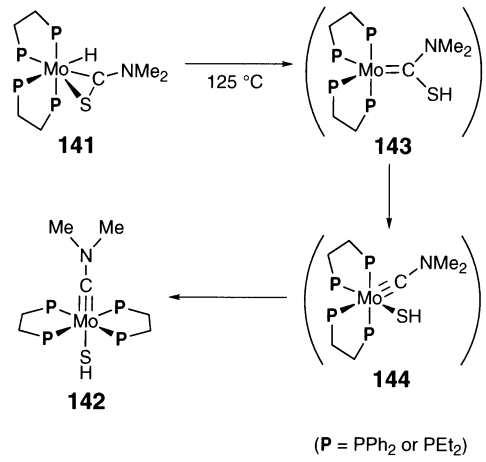
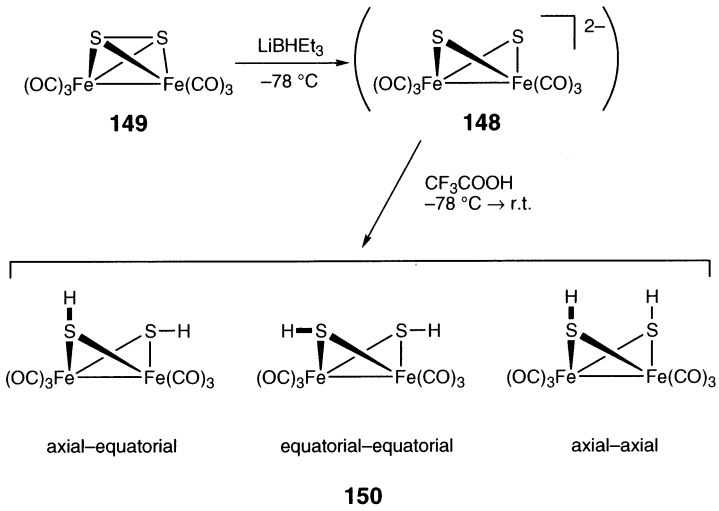


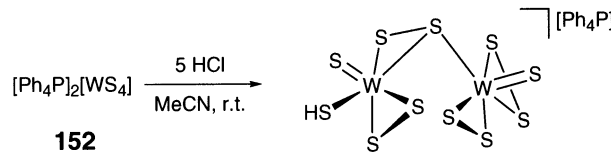
Scheme 25.



Scheme 26.

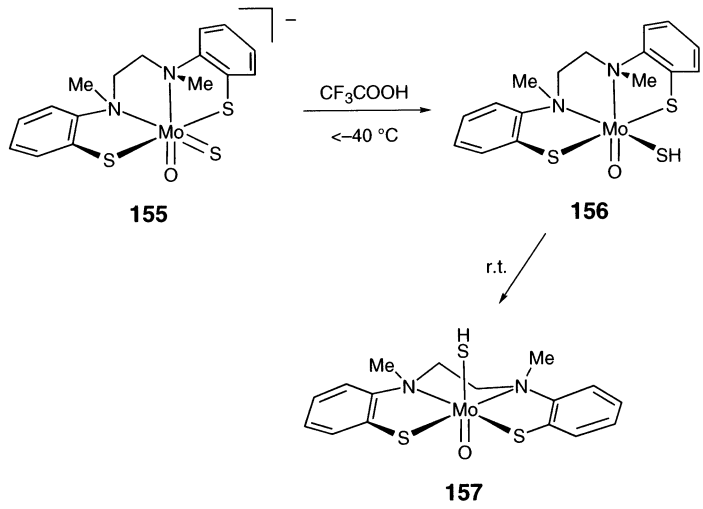
The resultant hydrosulfido complexes can usually be converted back to the parent sulfido complexes upon treatment with base. As expected, sulfido-bridged anionic species are easily protonated to afford hydrosulfido complexes. Seyferth and co-workers have demonstrated that the sulfido-bridged dianionic species $[\{Fe(CO)_3\}_2(\mu_2\text{-}S)_2]^{2-}$ (**148**), which is formed by the reaction of the disulfido complex $[\{Fe(CO)_3\}_2(\mu_2\text{-}\eta^2\text{:}\eta^2\text{-}S_2)]$ (**149**) with $LiBHEt_3$, undergoes protonation to give the hydrosulfido-bridged diiron complex $[\{Fe(CO)_3\}_2(\mu_2\text{-}SH)_2]$ (**150**) (Scheme 26) [143,144]. The related hydrosulfido–nitrosyl complex $[\{Fe(NO)_2\}_2(\mu_2\text{-}SH)_2]$ (**151**) is similarly synthesized by protonation of the sulfido-bridged dianionic complex $[[\{Fe(NO)_2\}_2(\mu_2\text{-}S)_2]^{2-}$ [145].

By contrast, protonation of terminal sulfido ligands is less common. In an earlier study, protonation of a dilute aqueous solution of WS_4^{2-} anion (**152**) has been shown to give the sulfido–hydrosulfido anion $[WS_3(SH)]^-$ (**153**) [146]. The crystal structure of this anion has recently been determined, although the hydrosulfido hydrogen atom is disordered and is not located [147]. However, when the protonation is carried out in MeCN, the dinuclear hydrosulfido complex $[W(S_2)(S)(SH)(\mu_2\text{-}\eta^2\text{:}\eta^1\text{-}S_2)W(S)(S_2)_2]^-$ (**154**) is obtained (Eq. (19)) [148].



152 **154** (19)

As a model for molybdenum hydroxylases and related enzymes, protonation of the molybdenum oxo–sulfido complex $[Ph_4P][Mo(O)(S)X]$ (**155**; $X = SC_6H_4N(Me)CH_2CH_2N(Me)C_6H_4S^{2-}$) has been investigated, which affords the hydrosulfido complex [Mo(O)(SH)X] (**156** and **157**) (Scheme 27) [149]. Unfortunately, both of the reactant and the products have not been characterized crystallographically. Protonation of the (sulfido)(thiolato)tantalum complex $[(^t BuCp)_2Ta(S)(SPr^i)]$ (**158**) gives the hydrosulfido complex $[(^t BuCp)_2Ta(SH)(SPr^i)][BF_4]$ (**159**) [150], although the reaction of the related hydrido complex $[(^t BuCp)_2TaH(S)]$ (**160**) with HCl results in a loss of H_2S to give the dichloro complex $[(^t BuCp)_2TaHCl_2]$ (**161**) [151] (Scheme 28). Reduction of the sulfido complex **160** with Na/Hg in the presence of H_2O affords the hydrido–hydrosulfido complex $[(^t BuCp)_2TaH_2(SH)]$ (**162**), probably via repetition of reduction and protonation [152]. In their extensive studies on the terminal chalcogenido complexes, Parkin and Howard have demonstrated that the sulfido complex $[Cp^*_2Zr(S)(py)]$ (**163**) reacts with acetophenone to afford the enolato–hydrosulfido complex $[Cp^*_2Zr\{OC(Ph)=CH_2\}(SH)]$ (**164**) as shown in Scheme 29 [153]. When **163** reacts with H_2S and Bu^tI, the bis(hydrosulfido) complex **14** and the hydrosulfido–iodo complex **35** are formed, respectively [154]. The reaction of the silanethiolato complex $[Ru(N)(SSiMe_3)Me_3]^-$ (**165**) with X^- (X = F, Cl) is believed to proceed via the terminal sulfido intermediate $[Ru(N)(S)Me_3]^{2-}$ (**166**), which is further transformed to the hydrosulfido complex $[Ru(N)(SH)Me_3]^-$ (**167**) by protonation with adventitious water (Scheme 30) [155].

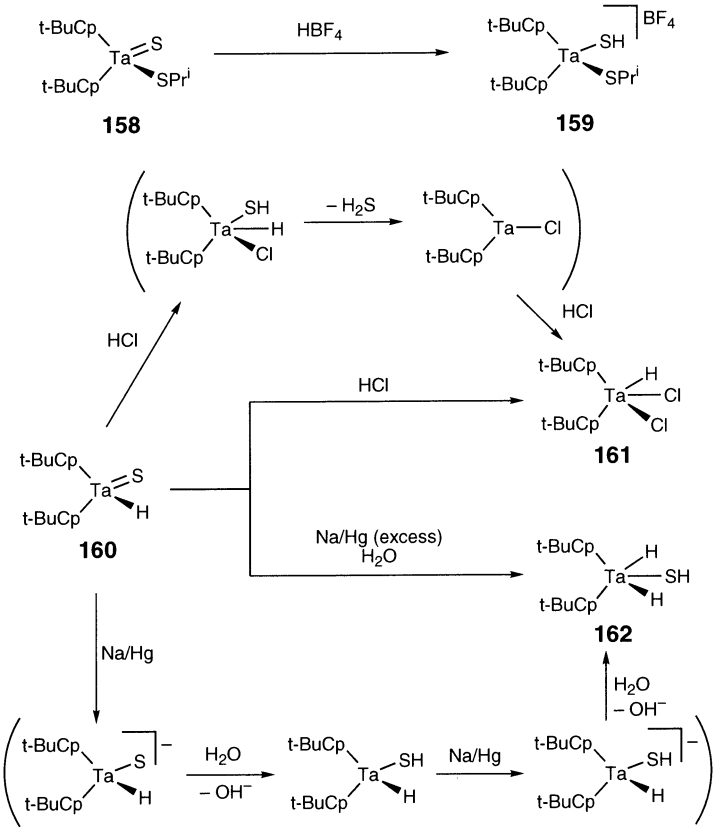


Scheme 27.

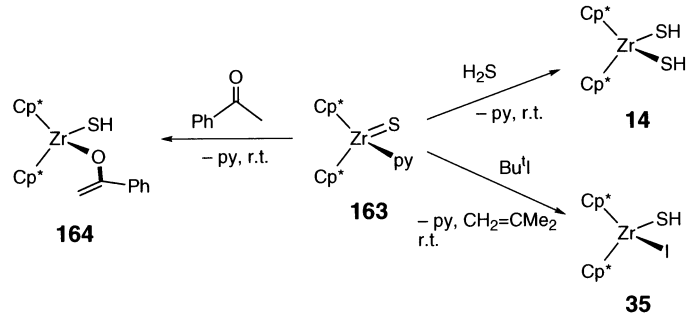
Protonation of μ_3-sulfido ligands to give μ_3-hydrosulfido complexes is virtually unknown. Treatment of the cubane-type sulfido cluster [{Mo(N(*p*-Tol))$_4$($S_2P(OEt)_2$)}$_4$(μ_3-S)$_4$] (**168**), which is in equilibrium with the sulfido-bridged dinuclear complex **169**, with trifluoroacetic acid gives the hydrosulfido- and sulfido-bridged dinuclear complex [{Mo(N(*p*-Tol))($S_2P(OEt)_2$)}$_2$(μ_2-S)(μ_2-SH)(μ_2-O_2CCF_3)] (**170**) (Scheme 31) [156]. Although the formation of $[Re_6(\mu_3\text{-}S)_7(\mu_3\text{-}SH)X_6]^{3-}$ was claimed upon protonation of the μ_3-sulfido ligands in the octahedral clusters $[Bu_4N]_4[Re_6(\mu_3\text{-}S)_8X_6]$ (X = Cl, Br, I) [157], the reaction products have very recently been reformulated as the oxidized clusters $[Re_6(\mu_3\text{-}S)_8X_6]^{3-}$ without the hydrosulfido ligands [158,159].

Complexes containing a sulfido bridge between a transition metal and a Group 14 element can be transformed into hydrosulfido complexes of the transition metal by protonolysis [160]. For example, the trimethylsilylthio complex $[Ph_4P][Ru(N)Me_3(SSiMe_3)]$ (**165**) is converted into the corresponding hydrosulfido complex $[Ph_4P][Ru(N)Me_3(SH)]$ (**167**) upon treatment with water (Scheme 30) [155]. In an earlier study, Collman and co-workers have demonstrated that the reaction of $[RhCl_2X]$ (**171**; X = a macrocyclic and monoanionic Schiff base ligand) with $NaSGeEt_3$ gives the bis(hydrosulfido)rhodium complex $[Rh(SH)_2X]$ (**172**), which is believed to be formed by hydrolysis of the bis(germylthio) complex **173** initially formed (Scheme 32) [161]. The S–Sn bonds in the μ_2- or μ_3-stannylthio ligands in [{$M(CO)_4$}$_2$(μ_2-$SSnMe_3$)$_2$] (**174**) and [{$M(CO)_3$}$_4$(μ_3-$SSnMe_3$)$_4$] (**175**; M = Mn, Re) are cleaved upon treatment with HCl to afford the di- and tetranuclear hydrosulfido complexes [{$M(CO)_4$}$_2$(μ_2-SH)$_2$] (M = Mn (**6**), Re (**176**)) and [{$M(CO)_3$}$_4$(μ_3-SH)$_4$] (M = Mn (**177**), Re (**178**)), respectively (Scheme 33) [162]. Protonolysis of a sulfide bridge connecting two different transition metal centers is also known. Thus,

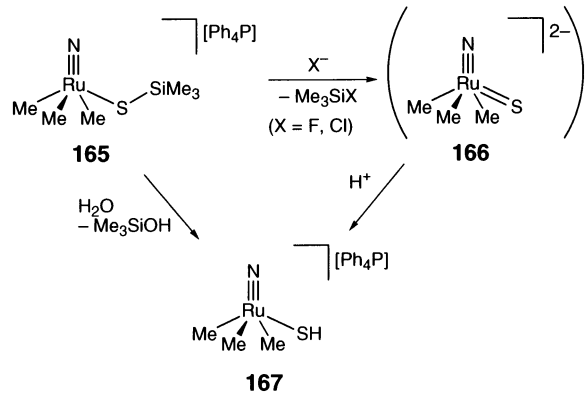
when the sulfido-bridged W/Zr heterobimetallic complex $[CpW(CO)_2(PMe_3)(\mu_2\text{-}S)ZrClCp_2]$ is treated with water, the hydrosulfidotungsten complex $[CpW(SH)(CO)_2(PMe_3)]$ (**179**) is obtained along with $[(Cp_2ZrCl)_2(\mu_2\text{-}O)]$ [163].



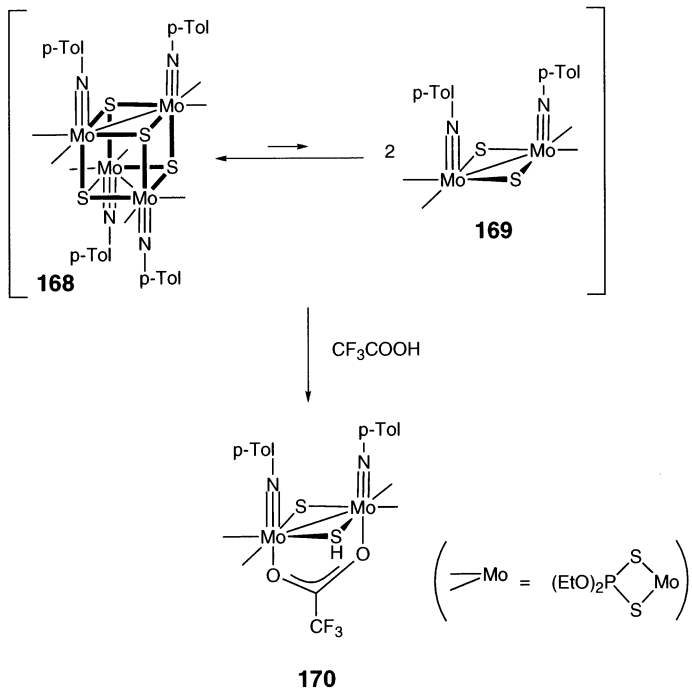
Scheme 28.



Scheme 29.



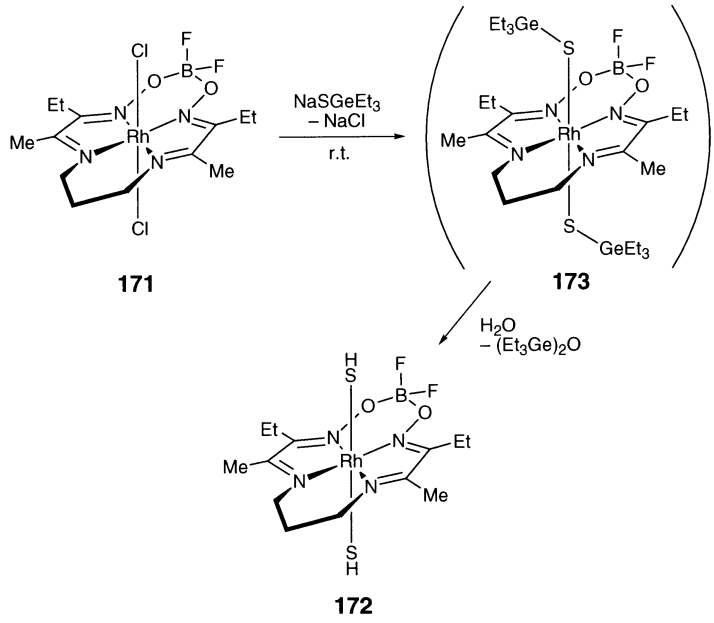
Scheme 30.



Scheme 31.

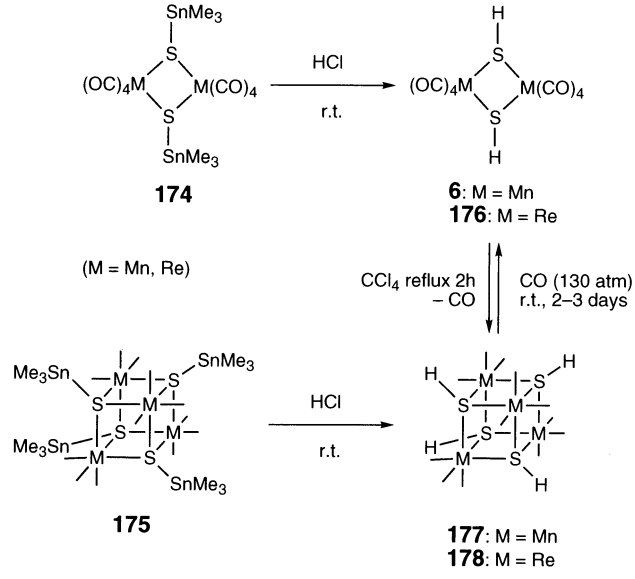
Hydrogenation of sulfido complexes is of particular interest because it has close relevance to the activation of H_2 molecule on nonmolecular metal sulfide surfaces and by hydrogenases. However, investigations in this field are still limited. Bergman, Andersen, and co-workers have recently reported that hydrogenation of the terminal sulfido ligand in the mononuclear titanium complex [Cp^*_2Ti(S)(py)]

(**180**) (Scheme 34) [164,165]. The starting sulfido complex **180** and the resultant hydrido–hydrosulfido complex [$Cp^*_2TiH(SH)$] (**181**) are in equilibrium, and studies using 2D exchange spectroscopy (EXSY) ^{1}H-NMR spectra suggest the presence of the η^2-dihydrogen intermediate [$Cp^*_2Ti(S)(\eta^2\text{-}H_2)$] (**182**). The phosphine-induced sulfur-abstraction of the disulfido complex [$Cp^*_2Ti(\eta^2\text{-}S_2)$] (**183**) under H_2 also gives



171 **173** **172**

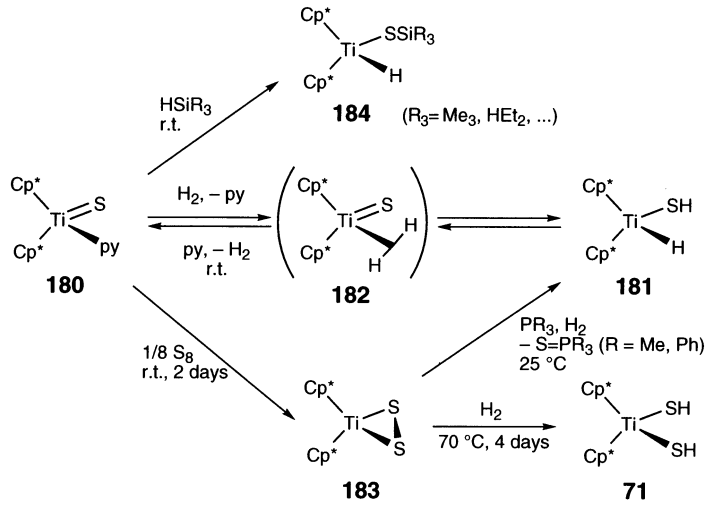
Scheme 32.



174 **6**: M = Mn, **176**: M = Re

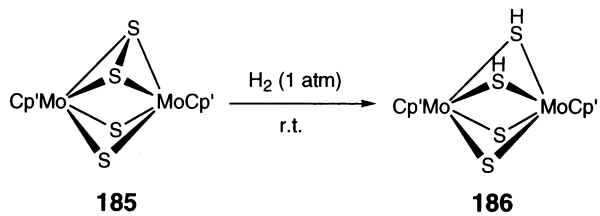
175 **177**: M = Mn, **178**: M = Re

Scheme 33.



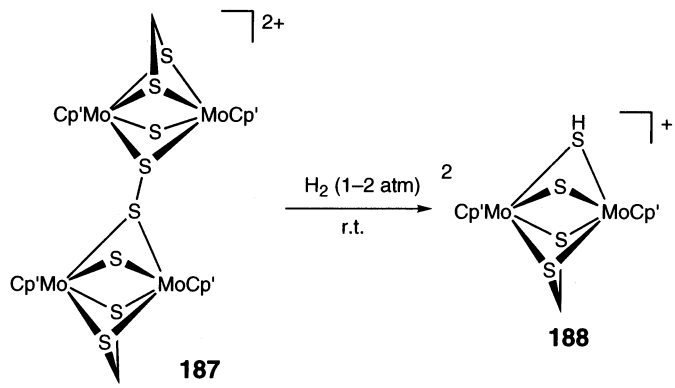
Scheme 34.

the hydrosulfido complex **181**; however, complex **181** failed to be isolated as a solid because of its instability under vacuum. On the other hand, **180** reacts with hydrosilanes to give the isolable hydrido–silanethiolato complexes **184**. The hydrogenation occurs not only across the metal–sulfur bond but across the S–S bond. Thus, the reaction of the disulfido complex **183** with H_2 gives the bis(hydrosulfido) complex $[Cp^*_2Ti(SH)_2]$ (**71**) [164,165]. In much earlier investigations, Rakowski DuBois and co-workers have revealed that similar homolytic cleavage of the H–H bond takes place on the μ_2-η^2:η^2-disulfido complex $[(Cp'Mo)_2(\mu_2\text{-}S_2)(\mu_2\text{-}S)_2]$ (**185**) to afford the hydrosulfido-bridged complex $[(Cp'Mo)_2(\mu_2\text{-}S)_2(\mu_2\text{-}SH)_2]$ (**186**) as shown in Eq. (20) [166].



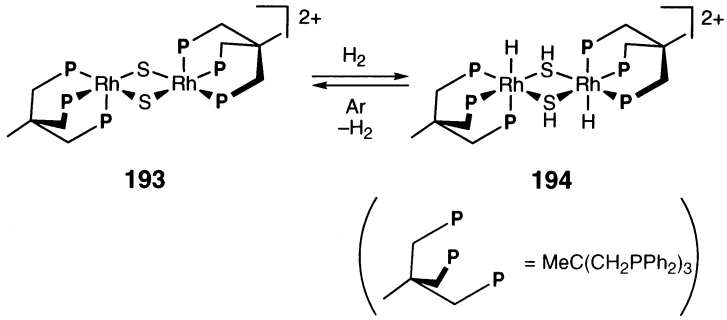
(20)

The disulfido ligand in the tetramolybdenum complex **187** also undergoes hydrogenation to give the hydrosulfido complex $[(Cp'Mo)_2(\mu_2\text{-}S_2CH_2)_2(\mu_2\text{-}S)(\mu_2\text{-}SH)]^+$ (**188**) (Eq. (21)) [141].

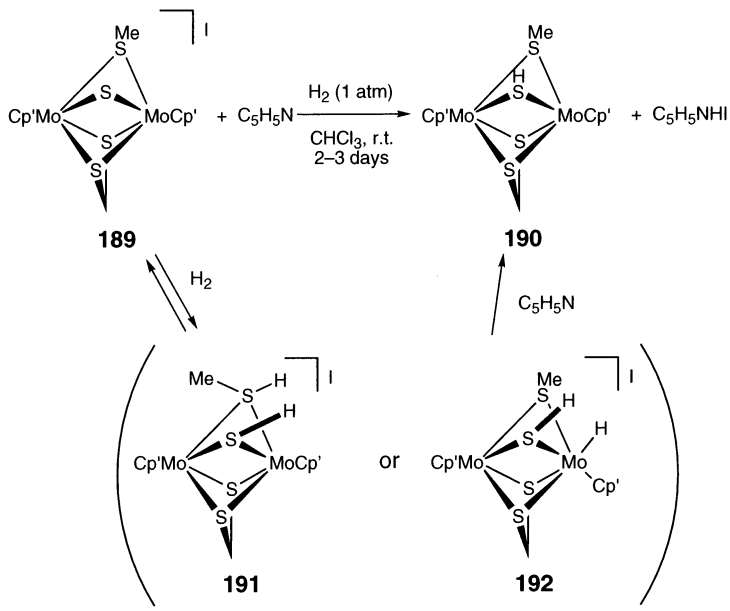


(21)

On the other hand, the reaction of the related cationic sulfido–thiolato complex $[(Cp'Mo)_2(\mu_2\text{-}S)(\mu_2\text{-}SMe)(\mu_2\text{-}S_2CH_2)]I$ (**189**) with H_2 in the presence of a base results in the formation of the uncharged hydrosulfido complex $[(Cp'Mo)_2(\mu_2\text{-}SH)(\mu_2\text{-}SMe)(\mu_2\text{-}S_2CH_2)]$ (**190**) and a proton (Scheme 35) [167]. The initial H_2 interaction either between sulfido- and thiolato-sulfur atoms (**191**) or across the Mo–S bond (**192**), is proposed for this heterolytic cleavage of the H–H bond [168]. These reactions may be involved in the transformations catalyzed by the sulfido-bridged dimolybdenum complexes, which include deuterium substitutions of thiophenes, hydrogenolysis of organic halides, and hydrogenation of the C=N bond in imines, isocyanates, and the N=N bond in azobenzene [169]. In connection with the latter mechanism, Bianchini and co-workers have reported the reversible reaction of the sulfido-bridged dirhodium complex $[\{(triphos)Rh\}_2(\mu_2\text{-}S)_2][BPh_4]_2$ (**193**) with H_2, giving the hydrosulfido-bridged hydrido complex $[\{(triphos)RhH\}_2(\mu_2\text{-}SH)_2][BPh_4]_2$ (**194**) (Eq. (22)) [170].



(22)

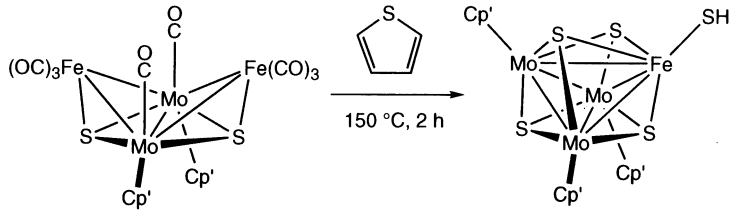


Scheme 35.

Related heterolytic cleavage of H_2 across the M–SR bond to afford the hydrido–thiol species, (H)M–S(H)R, is observed in the reaction of the coordinatively unsaturated thiolato–thioether complex $[Rh(PCy_3)(\text{'}^{bu}S_4\text{'})][BF_4]$ ($\text{'}^{bu}S_4\text{'}$ = 1,2-bis[(2-mercapto-3,5-di-*tert*-butylphenylthio]ethane(2–)) with H_2 [171,172].

2.5. C–S bond cleavage

In their extensive studies on the HDS-related reactivities of sulfido clusters, Curtis and co-workers have isolated the mixed-metal cubane-type cluster $[(Cp'Mo)_3(\mu_3\text{-}S)_4Fe(SH)]$ (**195**) from the reaction mixture of $[\{Cp'Mo(CO)\}_2(\mu_3\text{-}S)_2\{Fe(CO)_3\}_2]$ (**196**) with thiophene (Eq. (23)) [173].



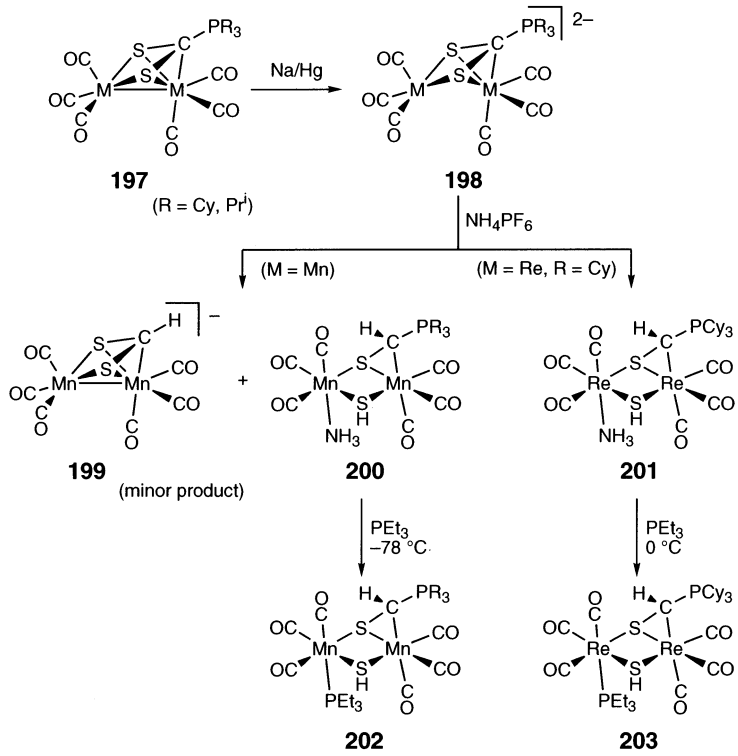
(23)

196 **195**

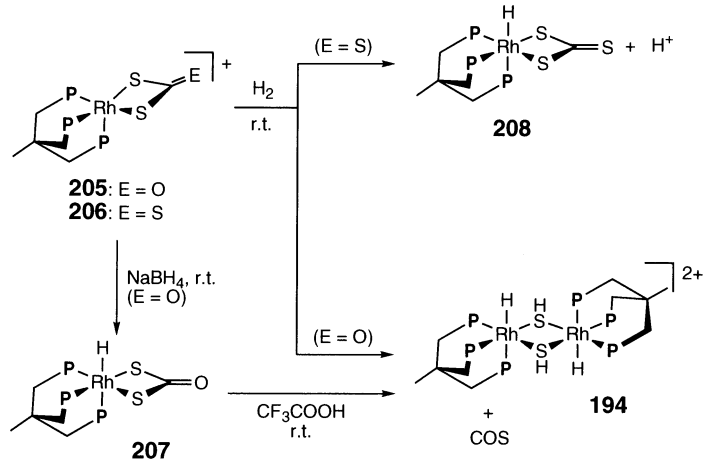
Although the detailed structure of this hydrosulfido cluster has been determined crystallographically, the yield of **195** is quite low. Formation of hydrosulfido complexes by hydrogenation and hydride reduction of thiolato complexes has some relevance to the industrial HDS process as we have already seen in, e.g. Eq. (1) [31] and Scheme 3 [32].

Reductive C–S bond cleavage in the chelating sulfur ligands leads to the formation of hydrosulfido complexes. The C–S bond in $\mu_2\text{-}S_2CPR_3$ ligands in Group 7 metal complexes **197** is cleaved by the reduction with Na/Hg and subsequent treatment with NH_4PF_6 to afford a series of hydrosulfido-bridged complexes $[M(CO)_3L(\mu_2\text{-}SH)(\mu_2\text{-}SCHPR_3)M(CO)_3]$ (**200**–**203**; M = Mn, Re; L = NH_3, PEt_3; R = Cy, Pr^i) as shown in Scheme 36 [174]. Reduction of the dithiocarbamato complex $[(triphos)Ni(S_2CNEt_2)][BPh_4]$ with $NaBH_4$ gives rise to the formation of the Ni(I) hydrosulfido complex [(triphos)Ni(SH)] (**204**) [175,176]. Bianchini and Meli have also reported the hydrogenation of the thiocarbonato complexes $[(triphos)Rh(S_2CE)][BPh_4]$ (E = O (**205**), S (**206**)) (Scheme 37) [177]. Treatment of the dithiocarbonato complex **205** with H_2 affords the hydrido–hydrosulfido complex $[\{(triphos)RhH\}_2(\mu_2\text{-}SH)_2]^{2+}$ (**194**) with concurrent formation of COS. This transformation is also achieved by hydride reduction of **205** followed by protonation of the resultant hydrido complex **207**. On the other hand, the hydrogenation of the CS_3 complex **206** results in the formation of the hydrido complex [(triphos)RhH(S_2CS)] (**208**) and a proton via heterolytic cleavage of H_2 instead of the C–S bond cleavage.

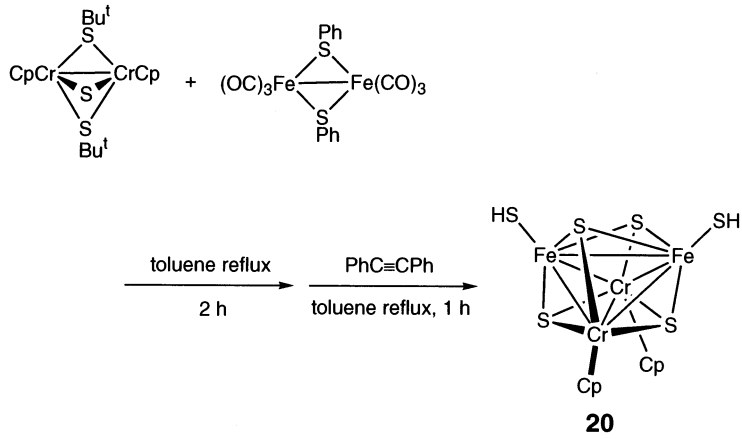
Furthermore, C–S bond cleavage is likely to occur in the formation of hydrosulfido clusters from thiolato-bridged complexes [178,179], exemplified by the reaction shown in Eq. (24) [67]. In these reactions, the source of hydrosulfido hydrogen atoms is not clear.



Scheme 36.



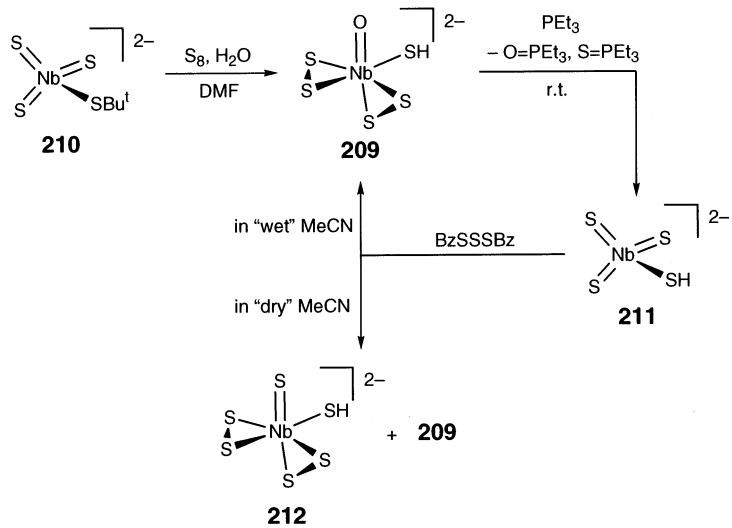
Scheme 37.



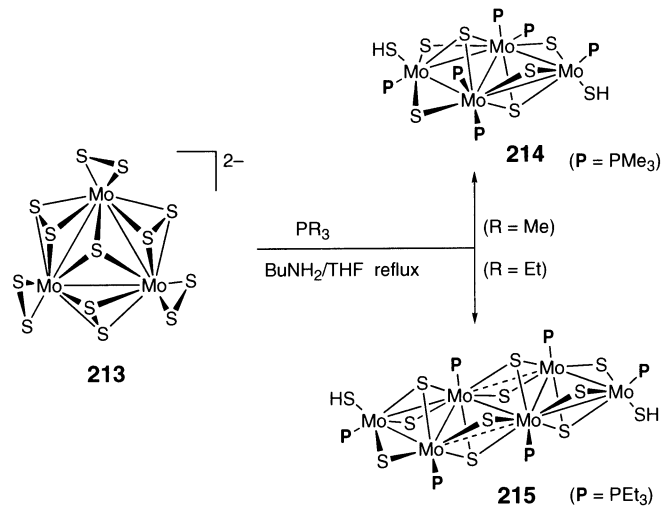
(24)

2.6. Miscellaneous

A few hydrosulfido complexes have been prepared by methods which can not be classified as any of the synthetic approaches described above. The stoichiometry of these reactions is often unclear. Coucouvanis and co-workers have prepared the niobium hydrosulfido complex $[Nb(O)(S_2)_2(SH)]^{2-}$ (**209**) by the reaction of $[Nb(S)_3(SBu^t)]^{2-}$ (**210**) with S_8 in H_2O–DMF (Scheme 38) [180]. The water serves as the source of the hydrosulfido hydrogen and the oxo ligand. Furthermore, the disulfido complex **209** is desulfurized upon treatment with PEt_3 to afford the



Scheme 38.



Scheme 39.

hydrosulfido–sulfido complex $[Nb(S)_3(SH)]^{2-}$ (**211**). Complex **211** is converted into the disulfido complexes **209** and **212** by the reaction with benzyl trisulfide.

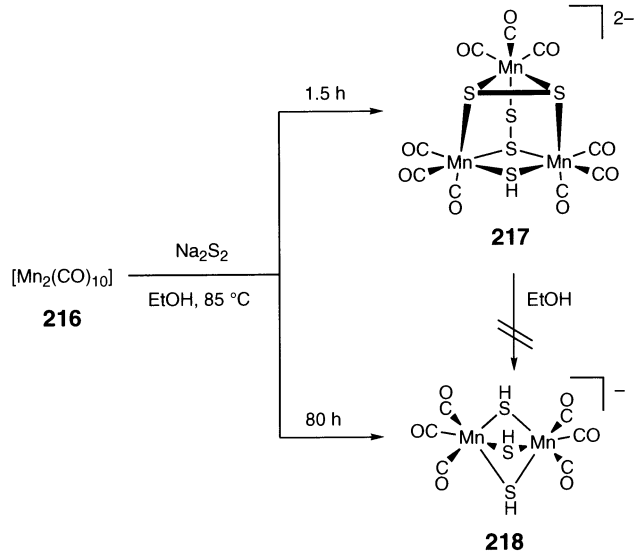
Saito and co-workers have demonstrated that the trimolybdenum sulfido–disulfido cluster $[NH_4]_2[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S_2)_3(S_2)_3]$ (**213**) reacts with tertiary phosphines in the presence of butylamine to afford the tetra- and hexanuclear hydrosulfido clusters $[Mo_4(\mu_3\text{-}S)_2(\mu_2\text{-}S)_4(SH)_2(PMe_3)_6]$ (**214**) and $[Mo_6(\mu_3\text{-}S)_4(\mu_2\text{-}S)_6(SH)_2(PEt_3)_6]$ (**215**) depending upon the nature of the phosphines employed (Scheme 39) [181,182].

The hydro(solvo)thermal reactions of $[Mn_2(CO)_{10}]$ (**216**) with Na_2S_2 results in the formation of the disulfido–hydrosulfido cluster $[\{Mn(CO)_3\}_3(S_2)_2(SH)]^{2-}$ (**217**) and triply bridged dimanganese complex $[\{Mn(CO)_3\}_2(\mu_2\text{-}SH)_3]^{-}$ (**218**) (Scheme 40) [183]. Although the product is dependent on the reaction time, the former compound is not converted into the latter upon treatment with EtOH.

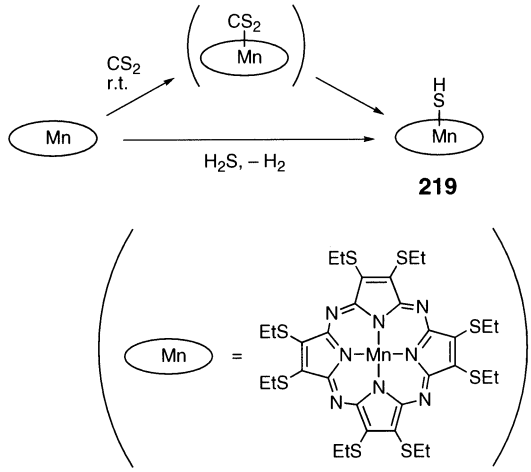
Carbon disulfide is used for the preparation of hydrosulfido complexes as shown in Scheme 41 [184]. The hydrosulfido hydrogen is believed to be derived from the solvent THF. Thiourea and their derivatives provide the hydrosulfido sulfur atom in a few reactions [185,186].

3. Spectroscopic and structural properties

IR and ^{1}H-NMR spectroscopy are useful for characterization of hydrosulfido complexes, because the band and signals ascribed to hydrosulfido moieties appear in a characteristic region in these spectra. In addition to these spectroscopic data, structures determined by X-ray crystallography are now available for a number of hydrosulfido complexes.



Scheme 40.



Scheme 41.

As we will see below, however, each method has its inherent problem, which prevents the confirmation of the presence of the hydrosulfido hydrogen atom; distinction between hydrosulfido and sulfido ligands is not necessarily easy. The combined application of more than two methods is therefore recommended for characterization of hydrosulfido complexes. Earlier investigations relying on only one of these methods should be interpreted carefully. The electron counting (the effective atomic number rule) as well as structural comparison with the related thiolato complexes will also help the characterization.

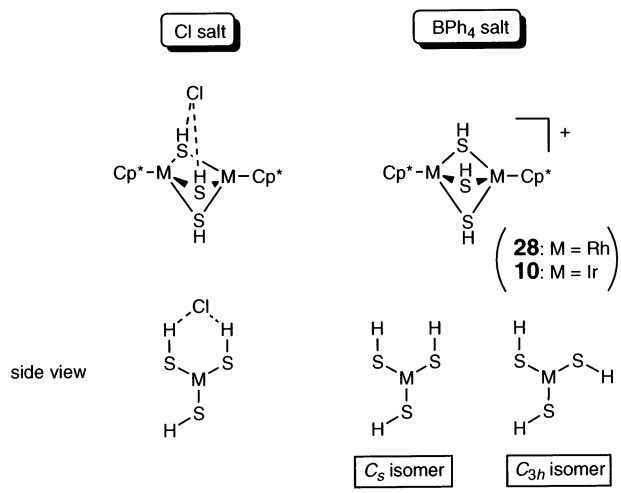
3.1. IR spectroscopy

Like organic thiols, most of hydrosulfido complexes exhibit characteristic bands around 2500 cm^{-1} assignable to the stretching of the S–H bond in their IR spectra. The ν_{SH} values are collected in Table 1. However, the absorption is generally weak and often missed [131,187]. As expected, this band shifts to a value around 1800 cm^{-1} upon deuteration of the hydrosulfido ligand. For some hydrosulfido complexes, the ν_{SD} values are reported, which are also included in Table 1.

In the cationic hydrosulfido-bridged complexes [Cp*M(μ_2-SH)$_3$MCp*]Cl (M = Rh (**28**), Ir (**10**)), lower ν_{SH} values (2231 and 2199 cm^{-1} for **28** and **10**, respectively) are observed in the IR spectra recorded in the solid state, which might be ascribed to the hydrogen bonds between the hydrosulfido hydrogen atoms and the chloride anion [72]. Indeed, X-ray analysis of the rhodium complex **28** has demonstrated that the hydrosulfido hydrogen atoms in two of the three bridging hydrosulfido ligands lie towards the chloride anion, as shown in Scheme 42. By contrast, the corresponding BPh_4 salts of **28** and **10** exhibit the ν_{SH} bands in a usual region (2492 and 2478 cm^{-1}) in the IR spectra. Furthermore, preservation of these hydrogen bonds in solution is supported by the ^{1}H-NMR spectroscopy (vide infra). It is to be mentioned, however, that such a lower shift of the wavenumbers is not observed for other hydrosulfido complexes in which the presence of hydrogen bonds is suggested on the basis of crystallography (see Section 3.3).

3.2. ^{1}H-NMR spectroscopy

As shown in Table 1, resonances ascribed to hydrosulfido protons are usually observed in a characteristic range of -4 to $+2$ ppm in the ^{1}H-NMR spectrum

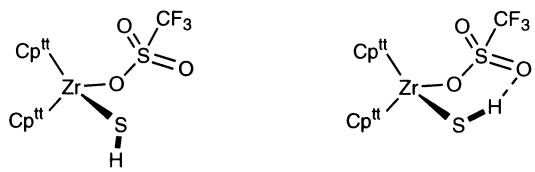


Scheme 42.

[188], which is a slightly higher field than the region for organic thiol protons (1–4 ppm) [189]. The SH resonances are, however, often masked by other resonances such as those of aliphatic protons because of the small intensities of hydrosulfido signals, especially when they are split by other nuclei such as ^{1}H, ^{31}P, ^{103}Rh, and ^{195}Pt. The assignment of hydrosulfido resonances is further hampered when fluxional and exchange process of hydrosulfido hydrogen atoms causes broadening and collapse of the SH resonances.

Still, the ^{1}H-NMR spectroscopy is a good technique to characterize hydrosulfido complexes, and to investigate their solution behavior. The ^{1}H-NMR studies have demonstrated that a number of hydrosulfido-bridged dinuclear complexes exist in more than two isomeric forms in solution (see Table 1). Such isomerism is mainly caused by the inversion of the sulfur atoms in the hydrosulfido ligands, as exemplified by the diiron complex shown in Scheme 26 [143,144]. In some systems, these isomers are interconverted on an NMR time scale as observed in the related thiolato-bridged complexes [190]. For example, the hydrosulfido-bridged Ti/Mo(W) heterobimetallic complexes exist as a mixture of *syn* and *anti* isomers, and exhibit a fluxional behavior (see Scheme 62) [191]; the activation energy for the titanium–tungsten complex $[Cp_2Ti(\mu_2\text{-}SH)_2W(CO)_4]$ (**220**) has been estimated to be 76 kJ mol^{-1} at the coalescence temperature of 85°C.

The hydrogen bonds in $[Cp^*M(\mu_2\text{-}SH)_3MCp^*]Cl$ (M = Rh (**28**), Ir (**10**)) described in Section 3.1 are maintained in solution. For example, the ^{1}H-NMR spectrum of **28** exhibits three hydrosulfido resonances, two of which are in relatively lower field (2.99 and 3.19 ppm) than the other (-1.60 ppm) [72]. The former resonances are ascribed to the hydrogen-bonded SH protons, and the latter is to the 'free' SH proton. This assignment is verified by the comparison of the spectrum with that of the corresponding BPh_4 salt, in which all of the SH resonances are observed in a normal range (-1.64 to -1.24 ppm). In addition, the spectrum of the BPh_4 salt indicates the presence of two isomers, one is the C_{3h} isomer showing only one SH resonance, and the other is the C_s isomer, which gives rise to three inequivalent resonances (Scheme 42). An intramolecular hydrogen bond with the triflate oxygen atom in a minor isomer of $[Cp^{tt}_2Zr(OTf)(SH)]$ (**221**) accounts for the unusually low-field shifted hydrosulfido resonance (6.27 ppm) for this isomer [192].



221

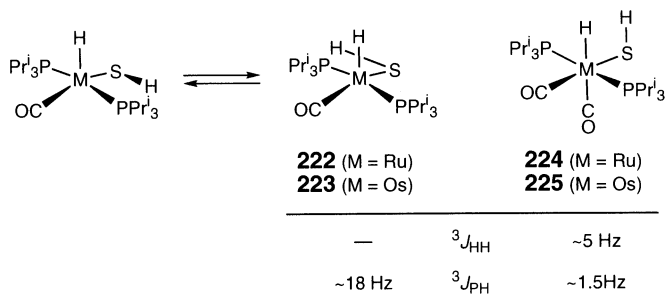
Hydrosulfido protons couple with the ^{1}H and ^{31}P nuclei bound to the metals as well as the metal nuclei with spin $I = 1/2$ such as ^{103}Rh and ^{195}Pt; the values of the coupling constants are collected in Table 1. The splitting pattern provides structural information of hydrosulfido complexes including the stereochemistry around the

metal center. Esteruelas and co-workers have applied the Karplus relationship, which correlates the values of the vicinal $^3J_{HH}$ coupling constants in saturated hydrocarbons with the H–C–C–H dihedral angles [193], to the hydrido–hydrosulfido complexes $[MH(SH)(CO)(PPr^i_3)_2L]$ (M = Ru, Os; L = none (**222** and **223**), CO (**224** and **225**)) [194]. Thus, because the five-coordinate complexes **222** and **223** exhibit no coupling between the hydrido and hydrosulfido protons, these complexes are believed to have the conformation with the H–M–S–H dihedral angle of 90° according to the Karplus curve (Scheme 43). The equivalence of the two phosphine ligands in the $^{31}P\{^1H\}$-NMR spectra is explained by rapid change in the orientation of the SH group as shown in the scheme. In contrast, the vicinal coupling in the six-coordinate complexes **224** and **225** is clearly observed ($^3J_{HH} = \sim 5$ Hz), and the $^3J_{PH}$ values (~ 1.5 Hz) are significantly smaller than those of the five-coordinate complexes **222** and **223** (~ 18 Hz). On the basis of these observations, a conformation in which the S–H group lies perpendicular to the P–M–P vector is proposed for the complexes **224** and **225**.

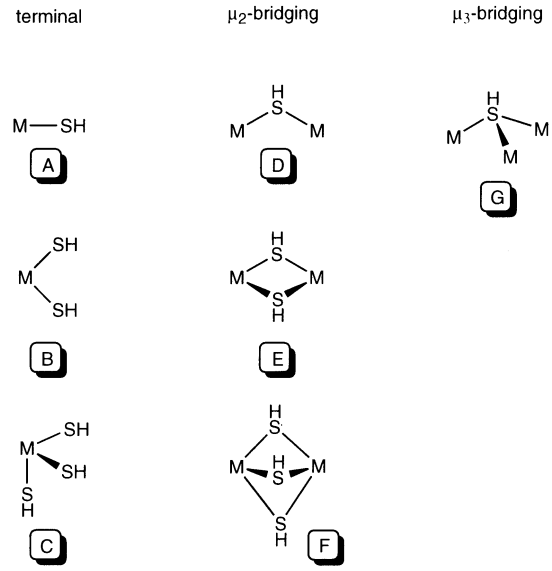
3.3. Structural features

In crystallographic studies on some hydrosulfido complexes, SH hydrogen atoms are found at reasonable positions in the difference Fourier map. These hydrogen atoms usually lie with the S–H distances of 1.0–1.4 Å (Table 1) [76,155]. However, because of the low electron density of the hydrogen atom, location of the hydrosulfido hydrogen atoms by X-ray analyses is accompanied by some ambiguity, and therefore spectroscopic supports for the presence of the hydrosulfido hydrogen atoms are desirable for characterization of hydrosulfido complexes. When the hydrosulfido ligands are terminal, the M–S distances may be diagnostic; the distances of M–SH bonds should generally be longer than those of M=S bonds.

Hydrogen-bonded structures involving hydrosulfido hydrogen atoms have been revealed by X-ray crystallography for some hydrosulfido complexes [195,196]; the examples include the dirhodium complex **28** depicted in Scheme 42 [72]. In addition, the presence of an attractive interaction between the μ_2-SH ligand and π-electrons of the phenyl group is suggested in the hydrosulfido-bridged diruthenium complex $[Ru(PMe_2Ph)_3(\mu_2\text{-}SH)_3Ru(SH)(PMe_2Ph)_2]$ (**32**) [75].



Scheme 43.



Scheme 44.

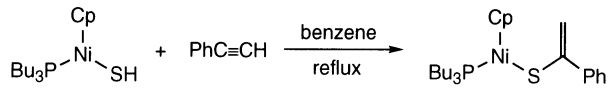
Finally, the coordination modes of hydrosulfido ligands are outlined briefly. Like the related thiolato complexes, hydrosulfido complexes take a variety of coordination modes as shown in Scheme 44 [1,2]. Some of the structural types are worth commenting on. The first homoleptic hydrosulfido complex $[Au(SH)_2]^-$ (**226**) falls in category the type B [197]. The complex containing three terminal SH ligands at one metal center (type C) is limited to the molybdenum complex *mer*-$[Mo(O)(SH)_3\{SC(Bu^t)CHC(Bu^t)O\}]^-$ (**227**) [198]. It seems curious that μ_3-SH complexes (type G) are rather scarce and none of them are structurally characterized. One of the limited examples is the cubane-type platinum complex $[(PtMe_3)_4(\mu_3\text{-}SH)_4]$ (**228**) [199]. Although the structures of the closely related thiolato and hydroxo complexes $[(PtMe_3)_4(\mu_3\text{-}X)_4]$ (X = SMe [200], OH [201]) are available, the X-ray structure of the cubane-type hydrosulfido complex **228** has not been revealed.

4. Reactions

Obviously, it lies in their reactivity that the chemistry of hydrosulfido complexes is conspicuous compared with that of the related thiolato complexes. Hydrosulfido complexes are often referred as 'metallathiols', and some of their reactivities are parallel to those of organic thiols.

4.1. Addition reactions

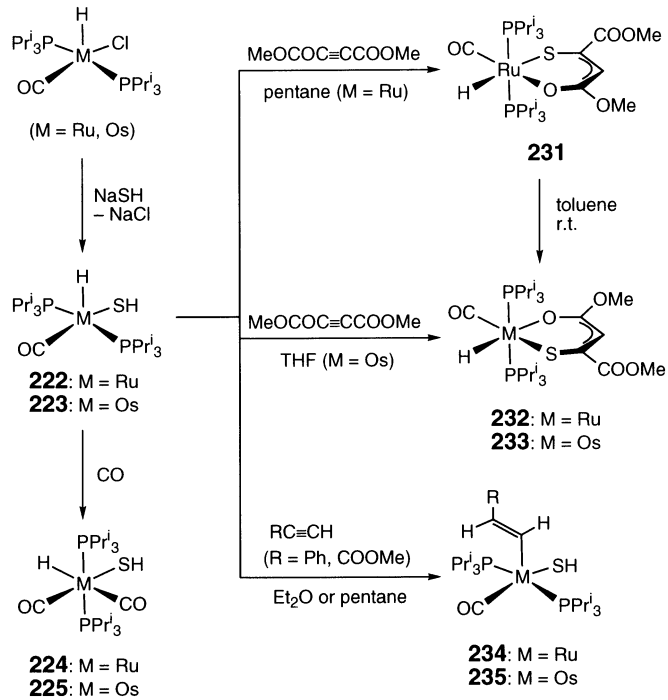
Addition reactions of hydrosulfido complexes toward unsaturated organic substrates are common. These reactions lead to the formal insertion of the organic fragments into the S–H bonds in the hydrosulfido complexes. In an earlier investigation, addition of the nickel hydrosulfido complex [CpNi(SH)(PBu^n_3)] (**229**) to phenylacetylene has been shown to give the vinylthiolato complex [CpNi{SC(Ph)=CH_2}(PBu^n_3)] (**230**) (Eq. (25)) [202].



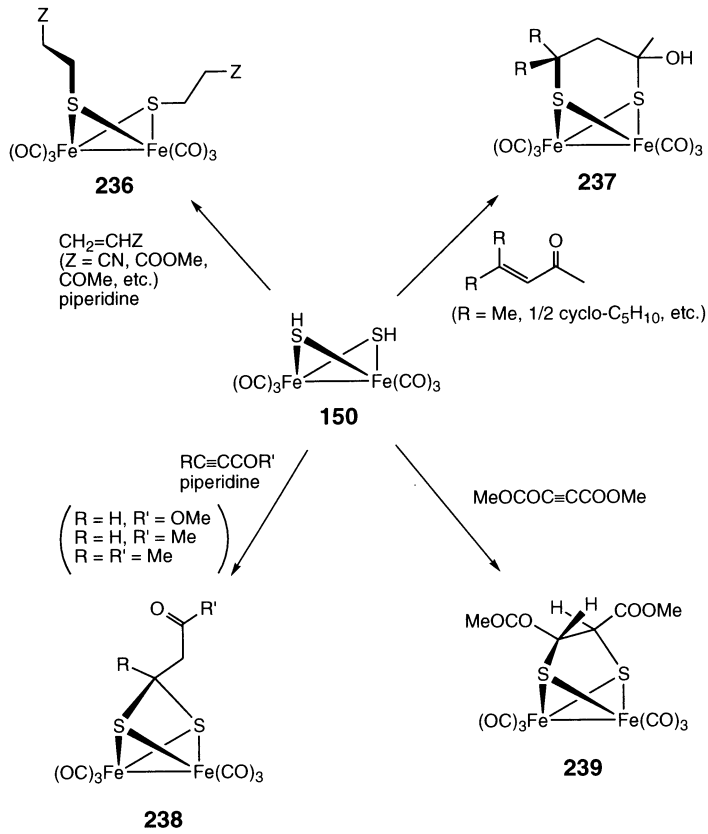
(25)

229 **230**

A recent example of the Michael-type addition involves the five-coordinate hydrosulfido complexes [MH(SH)(CO)(PPr^i_3)$_2$] (M = Ru (**222**), Os (**223**)) (Scheme 45) [194]. The reaction of the Ru complex **222** with DMAD initially afford the six-coordinate monothio-β-diketonato complex **231** with the hydrido ligand *trans* to the sulfur atom. When dissolved in toluene, **231** isomerizes to the final product **232** with the hydrido ligand *cis* to the sulfur atom. The similar reaction of the osmium hydrosulfido complex **223** directly affords the monothio-β-diketonato complex **233** corresponding to **232**. On the other hand, phenylacetylene and methyl propiolate



Scheme 45.



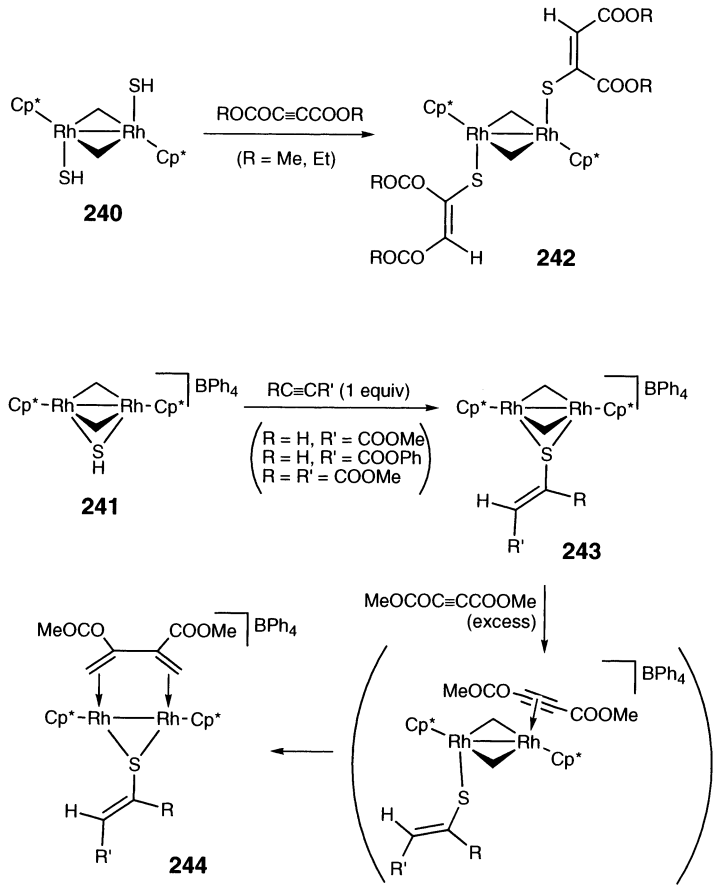
Scheme 46.

insert into the M–H bond rather than the S–H bond to give the vinyl complexes **234** and **235**. Reactivities of the related six-coordinate complexes **224** and **225** toward alkynes have not been investigated.

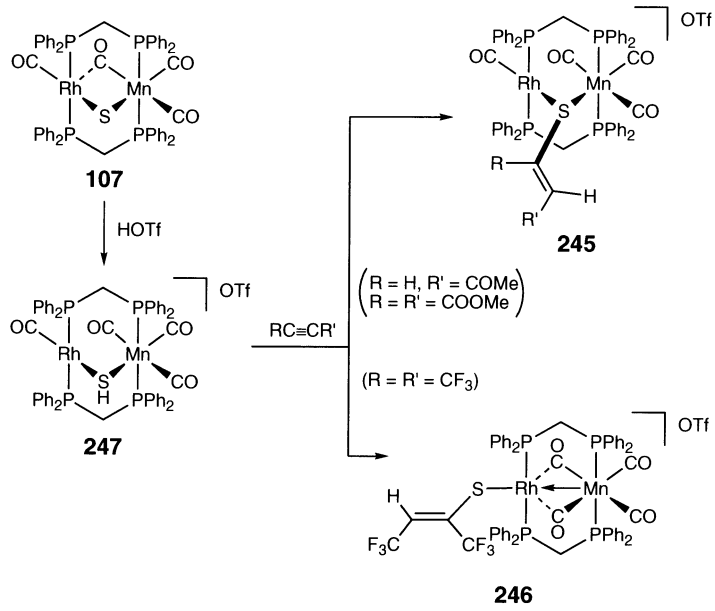
Seyferth and co-workers have revealed that the hydrosulfido-bridged diiron complex $[\{Fe(CO)_3\}_2(\mu_2\text{-}SH)_2]$ (**150**) reacts with a variety of α,β-unsaturated carbonyl compounds to afford the corresponding thiolato-bridged diiron complexes **236**–**239** (Scheme 46) [144,203]. Sterically less demanding alkenes with C=O and C≡N groups such as methyl vinyl ketone afford the 2:1 products, i.e. the bis(thiolato) complexes **236**. By contrast, in the case of α,β-unsaturated ketones with two β-substituents, one of the SH groups adds to the C=C bond, and the remaining SH group adds to the C=O group in the alkanethiolato functionality initially formed. As a consequence, the hydroxydithiolato complexes **237** are obtained. In a similar manner, two consecutive Michael additions toward one molecule of alkynes with electron-withdrawing groups take place to afford either a 1,1-addition product **238** or a 1,2-addition product **239** depending upon the substituents of the alkynes.

Related Michael additions have been reported for the methylene-bridged dirhodium hydrosulfido complexes (Scheme 47) [204]. Both terminal (**240**) and bridging (**241**) hydrosulfido complexes react with activated alkynes to afford the vinylthiolato complexes **242** and **243**, respectively. Upon treatment with an excess of DMAD, the latter complex is further converted into the μ_2-butadiene complex **244** arising from the coupling of the two bridging methylene ligands in **243** and the incoming DMAD molecule.

Heterobimetallic complexes with bridging hydrosulfido ligands show similar reactivities. Thus, the vinylthiolato complexes **245** and **246** are obtained from the reactions of the hydrosulfido-bridged Rh/Mn complex **247**, which is prepared by protonation of the corresponding sulfido-bridged complex **107**, with activated alkynes (Scheme 48) [121]. Depending upon the nature of the alkynes used, the resultant vinylthiolato ligand bridges the two metal centers (in **245**) or is terminally bound to the Rh atom (in **246**). The hydrosulfido-bridged Ti/Mo complex



Scheme 47.



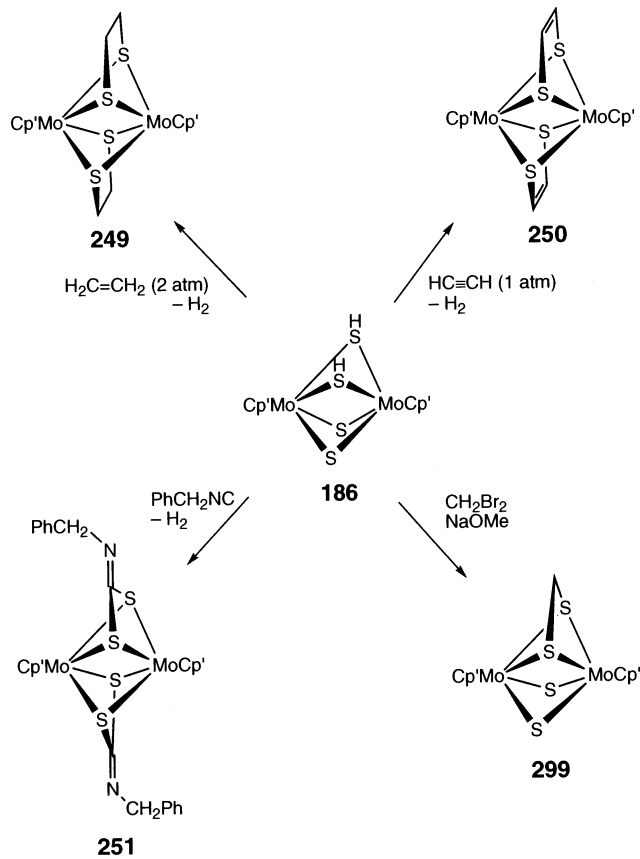
Scheme 48.

$[Cp_2Ti(\mu_2\text{-}SH)_2Mo(CO)_4]$ (**248**) reacts with methyl acrylate in the presence of triethylamine to afford the alkanethiolato-bridged complex $[Cp_2Ti(\mu_2\text{-}SCH_2CH_2COOMe)_2Mo(CO)_4]$ [191].

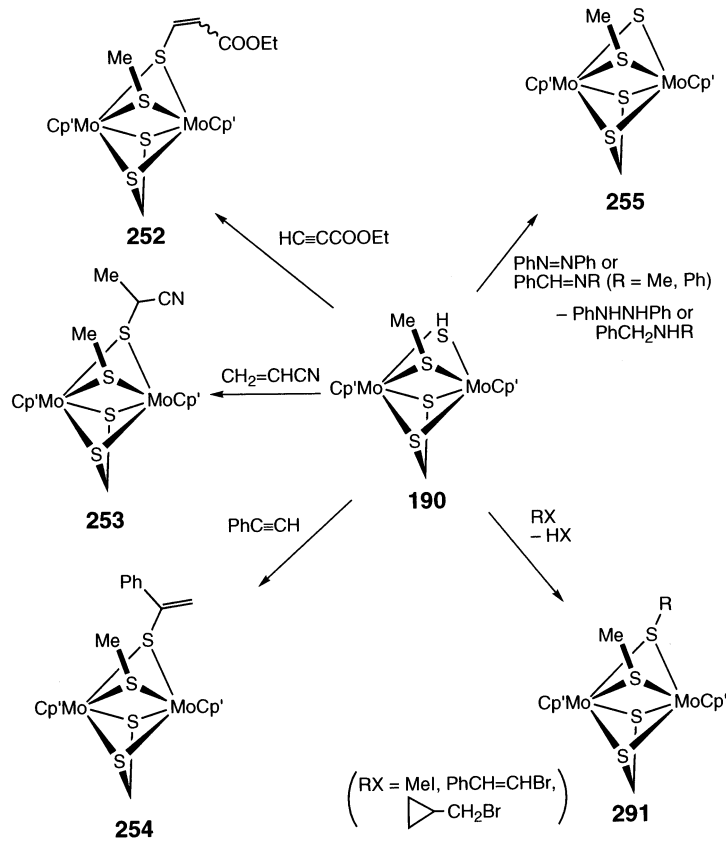
Extensive investigations carried out by Rakowski DuBois and co-workers [168,169,205] have revealed that the hydrosulfido-bridged dimolybdenum complexes exhibit unique reactivities toward various unsaturated substrates including unactivated alkenes and alkynes. For example, the hydrosulfido–sulfido complex $[(Cp'Mo)_2(\mu_2\text{-}S)_2(\mu_2\text{-}SH)_2]$ (**186**) reacts with unsubstituted ethylene and acetylene to afford the bis(dithiolato) complexes **249** and **250** as shown in Scheme 49 [166]. Benzyl isocyanide also reacts with the hydrosulfido–sulfido functionalities in **186** to give the dithiocarbonimidato-bridged complex **251** [166]. Interestingly, **186** catalyzes the hydrogenation of a variety of nitrogen-containing substrates such as azobenzene [206] as well as S_8 [166]. Scheme 50 outlines the reactivities of the hydrosulfido- and thiolato-bridged dimolybdenum complex $[(Cp'Mo)_2(\mu_2\text{-}S_2CH_2)(\mu_2\text{-}SH)(\mu_2\text{-}SMe)]$ (**190**) [207]. Complex **190** reacts with not only activated alkynes and alkenes but unactivated alkynes such as phenylacetylene to afford the insertion products **252**–**254**. It is of interest that the regioselectivity of the reaction with acrylonitrile is different with that of Michael-type addition observed for the diiron complex **150** (Scheme 46). Furthermore, reduction of the N=N and C=N bonds in azobenzene and imines by **190** takes place to yield the corresponding hydrazine and amines with concurrent formation of the Mo(III)/Mo(IV) mixed-valence complex **255**.

The reactivities of the cationic molybdenum complex $[(CpMo)_2(\mu_2\text{-}S_2CH_2)(\mu_2\text{-}S)(\mu_2\text{-}SH)][OTf]$ (**256**) is noteworthy because the C≡N triple bonds in nitriles and

isocyanides are cleaved on the sulfur-bridged dimolybdenum center under mild conditions [208,209]. For example, the reaction of **256** with nitriles under H_2 gives the dithiocarboxylato complex **257** along with ammonia (Scheme 51). The proposed mechanism is depicted in Scheme 52 [209]. The iminothiolato species **258** is proposed to form initially. Although this intermediate has not been detected, it is trapped as the spectroscopically characterized dicationic *N*-protonated species **259** upon treatment with an excess of acid. The iminothiolato intermediate **258** then reacts with H_2, in a similar manner to the related cationic sulfido–thiolato complexes, to give the neutral hydrosulfido species **260** and a proton (see Scheme 35). Subsequent intramolecular addition of the SH group to the C=N bond results in the formation of the aminodithiolato species **261**, which is further converted into the final product, the dithiocarboxylato complex **257**, upon protonolysis of the C–N bond releasing ammonia. For isocyanides, the C≡N bond cleavage by **256** in the presence of H_2 takes place similarly and affords the dithioformato complex $[(CpMo)_2(\mu_2\text{-}S_2CH_2)(\mu_2\text{-}S_2CH)][OTf]$ (**262**) and the corresponding primary amines



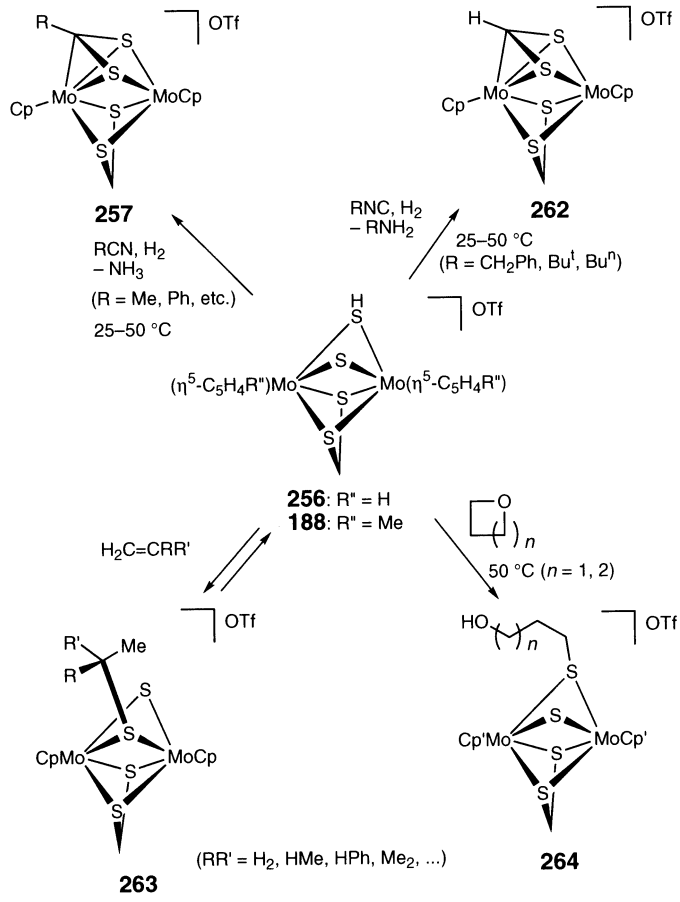
Scheme 49.



Scheme 50.

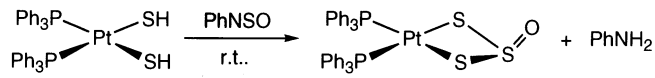
(Scheme 51). In contrast to nitriles, butyl isocyanide reacts with **256** even in the absence of H_2 at 50°C, giving the butyldithiocarbamato complex $[(CpMo)_2(\mu_2\text{-}S_2CH_2)(\mu_2\text{-}S_2CNHBu^n)][OTf]$. As a related reaction, Rauchfuss and Ruffing have reported the palladium-assisted conversion of methyl isocyanide into methyldithiocarbamato ligands on the tungsten hydrosulfido complex $[Cp_2W(SH)_2]$ (**24**) [210]. Interestingly, **256** reacts with alkenes reversibly to give the thiolato complexes **263** (Scheme 51) [211]. Complex **256** also catalyzes oligomerization of 1,1-disubstituted alkenes [212]. When **188**, the Cp′ analogue of **256**, is treated with cyclic ethers such as THF, the hydroxyalkanethiolato complexes **264** are obtained [213].

Angelici and Gingerich have described the nucleophilic addition of the anionic hydrosulfido complex $[W(SH)(CO)_5]^-$ (**62**) toward a variety of organic electrophiles including carbonyl compounds and heterocumulenes as shown in Scheme 53 [97,214]. In a similar manner, the nickel complex $[CpNi(SH)(PBu^n_3)]$ (**229**) reacts with RNCO and RNCS, giving the addition products $[CpNi\{SC(E)NHR\}(PBu^n_3)]$ (E = O, S) [215]. Addition of [PPN][Au(SH)$_2$] (**226**) to RNCS has also been reported recently [216]. On the other hand, the reaction of the bis(hydrosulfido)platinum complex *cis*-$[Pt(SH)_2(PPh_3)_2]$ (**265**) with PhNSO affords $[Pt(S_3O)(PPh_3)_2]$ (**266**) and aniline (Eq. (26)), whereas the corresponding reaction of



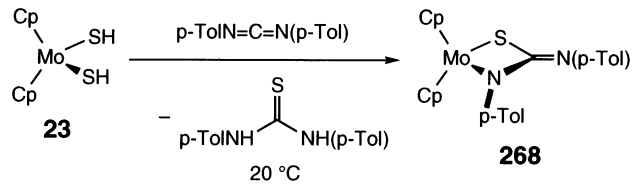
Scheme 51.

the ruthenium complex $[CpRu(SH)(PPh_3)_2]$ (**267**) gives the addition product $[CpRu\{SS(O)NHPh\}(PPh_3)_2]$, which decomposes within a few hours [160].

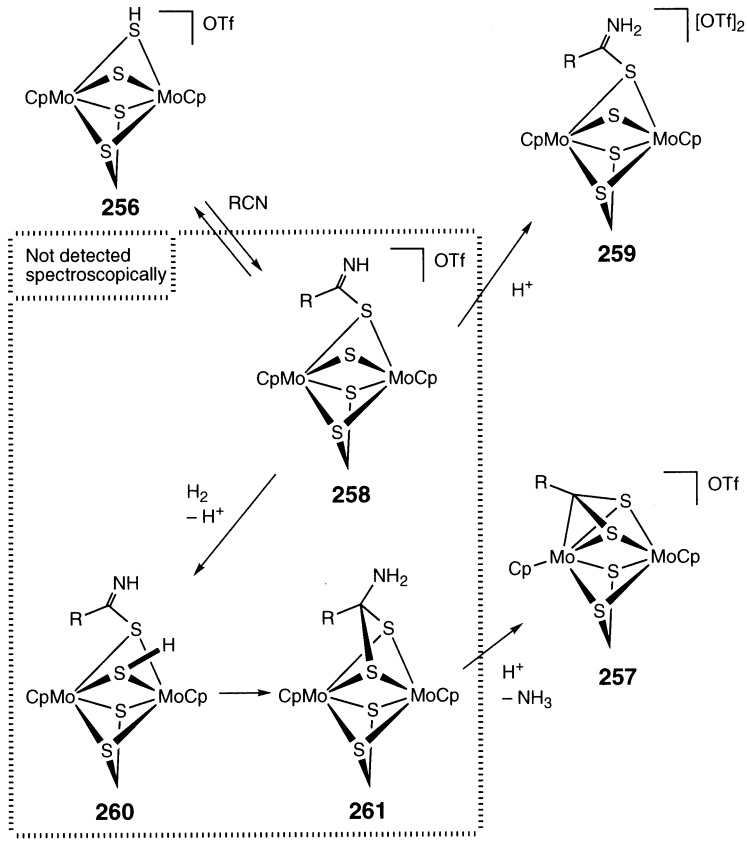


265 **266** (26)

An attempt to generate the unsaturated '$Cp_2Mo{=}S$' species by elimination of H_2S from **23** with the aid of the carbodiimide *p*-TolN=C=N(*p*-Tol) gives rise to the formation of the cycloaddition product $[Cp_2Mo\{SC(=N(p\text{-Tol}))N(p\text{-Tol})\}]$ (**268**) (Eq. (27)) [217].

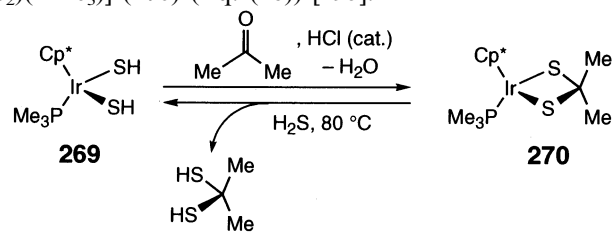


(27)



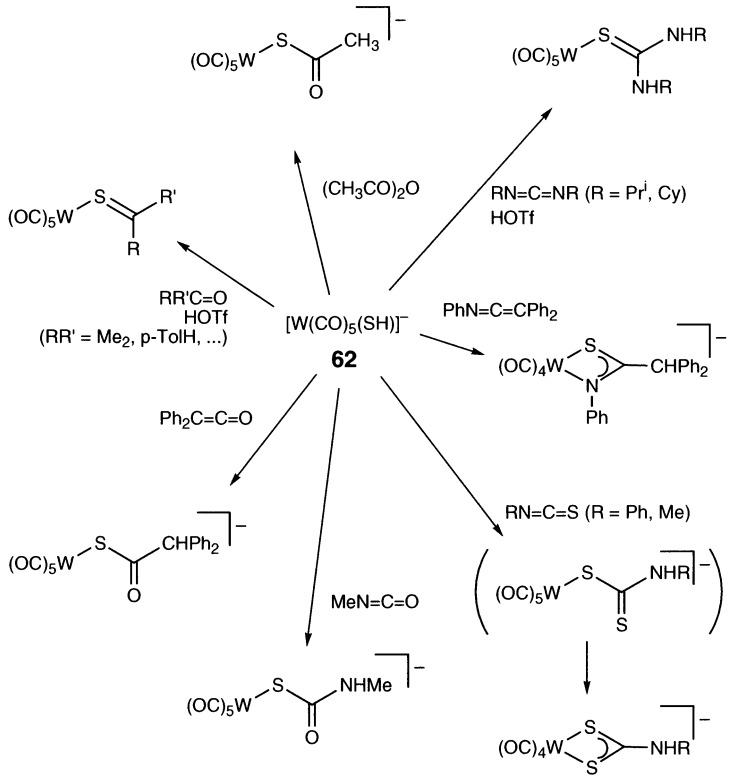
Scheme 52.

Addition of bis(hydrosulfido) complexes to carbonyl compounds has been investigated. Thus, the reaction of the iridium complex [Cp*Ir(SH)$_2$(PMe$_3$)] (**269**) with acetone results in the formation of the dithiametallacyclobutane complex [Cp*Ir(S$_2$CMe$_2$)(PMe$_3$)] (**270**) (Eq. (28)) [195].



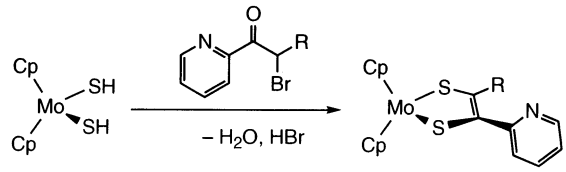
(28)

When the resultant *gem*-dithiolato complex **270** is treated with H_2S at 80°C, the *gem*-dithiol $Me_2C(SH)_2$ is obtained along with the hydrosulfido complex **269**. In this connection, when ketones or aldehydes $R^1R^2C{=}O$ is present in the preparation of the Walton's bis(hydrosulfido) complex [Re$_2$Cl$_2$(μ_2-SH)$_2$(μ_2-dppm)$_2$] (**43**), the (*gem*-dithiolato)-bridged dirhenium complex [Re$_2$Cl$_2$(μ_2-S$_2$CH$_2$R^{1}R^2)(μ_2-dppm)$_2$] (**271**) is obtained (Scheme 10) [82,83].



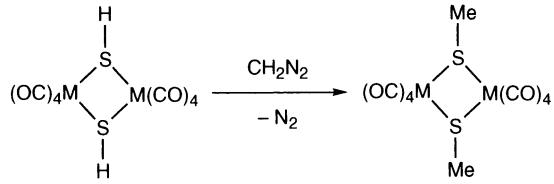
Scheme 53.

Pilato and co-workers have recently shown that α-bromoketones react with bis(hydrosulfido) complexes $[Cp_2Mo(SH)_2]$ (**23**) [218] and $[(dppe)M(SH)_2]$ (M = Ni (**272**), Pd (**273**), Pt (**274**)) [219] to afford the dithiolene complexes (Eq. (29)).



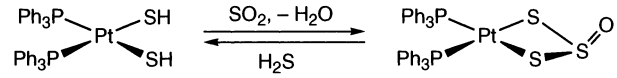
23 **275** (29)

Diazomethane has been used to convert some Group 7 hydrosulfido complexes into the corresponding methanethiolato complexes [220], as exemplified by Eq. (30) [221].



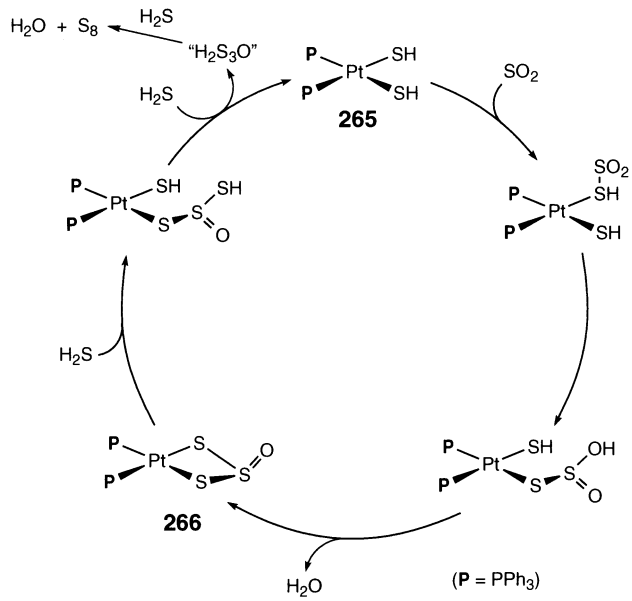
6: M = Mn
176: M = Re
276: M = Mn
277: M = Re (30)

Hydrosulfido complexes react with a variety of inorganic electrophiles. Shaver et al. have reported that the bis(hydrosulfido)platinum complex *cis*-$[Pt(SH)_2(PPh_3)_2]$ (**265**) reacts with SO_2 to give $[Pt(S_3O)(PPh_3)_2]$ (**266**) with a loss of H_2O (Eq. (31)) [222].



265 **266** (31)

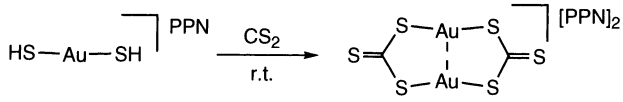
The hydrosulfido complex **265** is regenerated upon treatment of **266** with H_2S. Futhermore, the complexes **265** and **266** catalyze the Claus reaction (Eq. (2)). The proposed catalytic cycle is shown in Scheme 54. One of the cleavage product, designated as 'H_2S_3O,' is believed to be a key intermediate in the Claus process and is expected to react readily with H_2S to afford H_2O and S_8. In much earlier investigations, Kubas and co-workers have demonstrated that the Rakowski DuBois's complexes $[\{(\eta^5\text{-}C_5Me_nH_{5-n})Mo\}_2(\mu_2\text{-}S)_2(\mu_2\text{-}SH)_2]$ ($n = 0$ (**278**), 1 (**186**), 5 (**279**)) catalyze the hydrogenation of SO_2 [223,224]. The proposed mechanism is somewhat complicated. The hydrosulfido complex **279** first reacts with SO_2 to afford the disulfido complex **280** along with an insoluble material tentatively formulated as $[Cp^*MoS_3]_x$ (**281**) (Scheme 55). Besides **280** (see Eq. (20)), **281** reacts with H_2 to regenerate the hydrosulfido complex **279**; the excess of sulfur atoms in **281** is released as H_2S. In the second catalytic cycle, the reaction of the disulfido complex **280** with SO_2 yields the SO_2 adduct **282**, which further reacts with SO_2 to



Scheme 54.

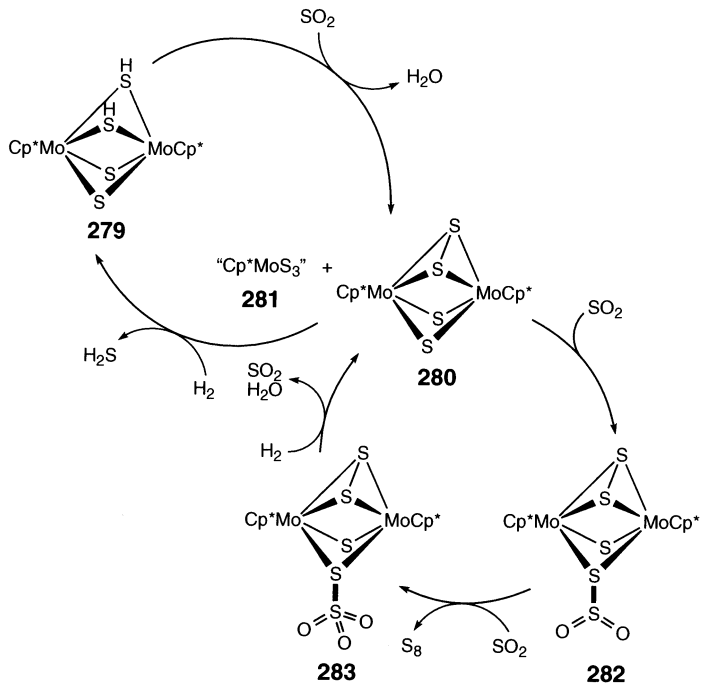
give the S_2O_3 complex **283** accompanied by production of S_8. Hydrogenation of **283** results in the regeneration of the disulfido complex **280** with concurrent formation of SO_2 and H_2O. Both reaction cycles are proposed to be involved in the catalytic reduction of SO_2. The H_2S produced in the former cycle is converted into S_8 by the Claus reaction (Eq. (2)) under the same conditions.

Nucleophilic attack of the hydrosulfido complex $[CpRu(SH)(PPh_3)_2]$ (**267**) toward CS_2 affords an insertion product formulated as $[\{CpRu(PPh_3)\}(\mu_2\text{-}S_2CS)Ru(PPh_3)_2Cp]$ (**284**) (Scheme 56) [225]. Involvement of the intermediary S_2CSH species **285** is supported by the isolation of the analogous S_2CSR complexes from the reaction of the thiolato complexes $[CpRu(SR)(PPh_3)_2]$ and CS_2. On the other hand, the reaction of the bis(hydrosulfido)gold complex $[PPN][Au(SH)_2]$ (**226**) with CS_2 resulted in the formation of μ_2-η^1:η^1-trithiocarbonato complex $[PPN]_2[Au_2(\mu_2\text{-}\eta^1\text{:}\eta^1\text{-}CS_3)_2]$ (**286**) (Eq. (32)) [216,226,227].

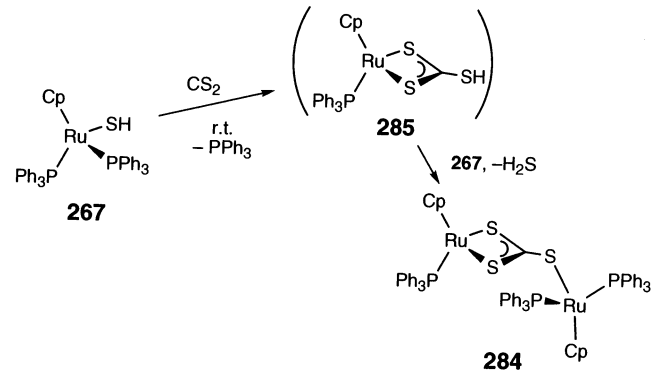


226 **286** (32)

Related transformation of [(triphos)Ni(SH)] (**204**) into the trithiocarbonato complex [(triphos)Ni(CS_3)] and the CS_2 complex [(triphos)Ni(CS_2)] has been reported,



Scheme 55.



Scheme 56.

although it involves disproportionation of Ni(I) to Ni(II) and Ni(0) [228]. In contrast, CS_2 insertion into the M–H bond rather than the M–SH bond takes place in the hydrido–hydrosulfido complex [Cp*IrH(SH)(PMe_3)] (**287**) [195].

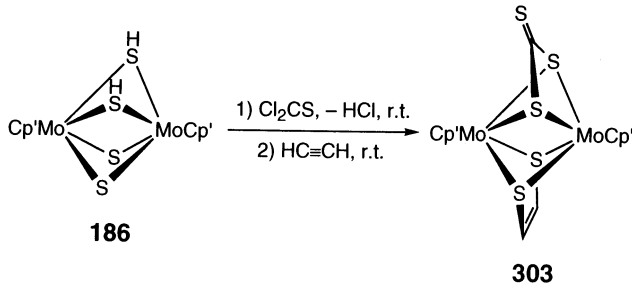
Comparison of the reactivities between terminal and bridging SH ligands is of interest. Vahrenkamp have noted that the reactivity of bridging SH groups is reduced by coordination of the lone pair electrons on the S atom to the second metal center [229]. In fact, the hydrosulfido-bridged complex [{$W(CO)_5$}$_2$(μ_2-SH)]$^-$ (**288**) is known to react with electrophiles such as $Ph_2C{=}C{=}O$ only in the presence of a strong base, which contrasts with vital reactivities of the corresponding terminal hydrosulfido complex [$W(SH)(CO)_5$]$^-$ (**62**) (Scheme 53) [97,214]. Kaneko, Isobe, and co-workers have recently carried out the competition reaction of terminal and bridging hydrosulfido complexes **240** and **241** with DMAD. In contrast to the tungsten complexes described above, the hydrosulfido-bridged dirhodium complex **241** reacts much faster than the terminal one (**240**) in spite of the cationic nature of the bridging complex **241** (Scheme 47) [204].

4.2. Nucleophilic substitution

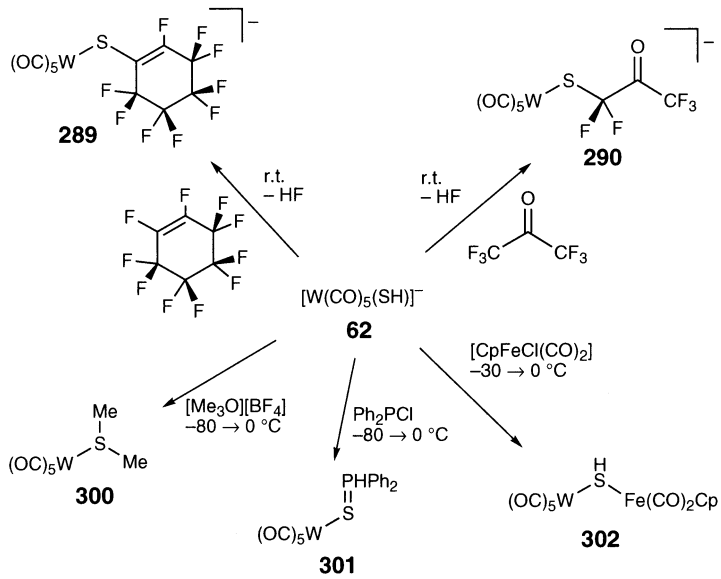
Nucleophilic substitution of hydrosulfido complexes toward alkyl halides is a well-established reaction. The mononuclear complex [$W(SH)(CO)_5$]$^-$ (**62**) reacts with a perfluorinated alkene and ketone to afford the corresponding thiolato complexes **289** and **290** (Scheme 57) [214]. Similarly, Rakowski DuBois's complex [(Cp′Mo)$_2$(μ_2-S_2CH_2)(μ_2-SH)(μ_2-SMe)] (**190**) is converted to the thiolato complexes **291** upon treatment with alkyl bromides and iodides (Scheme 50) [207]. Pignolet and co-workers have described the related nucleophilic substitution of the hydrosulfido-bridged diiridium complexes **292** and **293**, which leads to the formation of the thiolato complexes **294**–**297** (Scheme 58) [188]; consecutive substitution of the bis(hydrosulfido) complex **292** toward dihaloalkanes takes place to give **295**. In a similar manner, the bis(hydrosulfido)dimolybdenum complex **186** is converted into the dithiolato complex **299** (Scheme 49) [230]. Scheme 59 shows thallium-assisted

nucleophilic substitution reactions of the dimanganese complex [{$Mn(CO)_3$}$_2$(μ_2-H)(μ_2-SH)(μ_2-dppm)] (**125**) [132]. The Ti/Mo heterobimetallic complex [$Cp_2Ti(\mu_2$-$SH)_2Mo(CO)_4$] (**248**) undergoes methylation upon treatment with methyl iodide and triethylamine to afford the corresponding methanethiolato complex [$Cp_2Ti(\mu_2$-$SMe)_2Mo(CO)_4$] [191]. As for mononuclear complexes, the dithiaplatinacycle complex [$Pt(S_2CH_2)(PR_3)_2$] ($R_3 = Ph_3$, $MePh_2$, Me_2Ph) is formed by treatment of *cis*-[$PtCl_2(PR_3)_2$] with NaSH in the presence of CH_2Cl_2 [231].

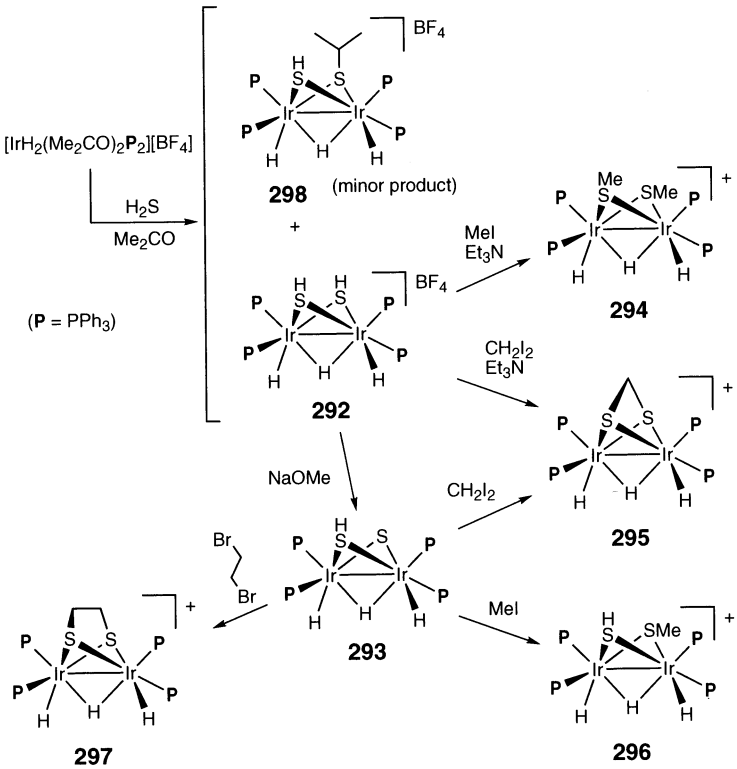
The anionic hydrosulfido complex $[W(SH)(CO)_5]^-$ (**62**) reacts with a trimethyloxonium salt, a chlorophosphine, and the chloroiron complex [$CpFeCl(CO)_2$] to afford the dimethyl thioether complex **300**, the phosphinesulfido complex **301**, and the hydrosulfido-bridged iron–tungsten complex **302**, respectively (Scheme 57) [232]. When the bis(hydrosulfido)molybdenum complex **186** is treated with thiophosgene and then with acetylene, the trithiocarbonato- and dithiolene-bridged complex [$(Cp'Mo)_2(\mu_2$-$S_2CS)(\mu_2$-$S_2C_2H_2)$] (**303**) is obtained as shown in Eq. (33) [230].



(33)



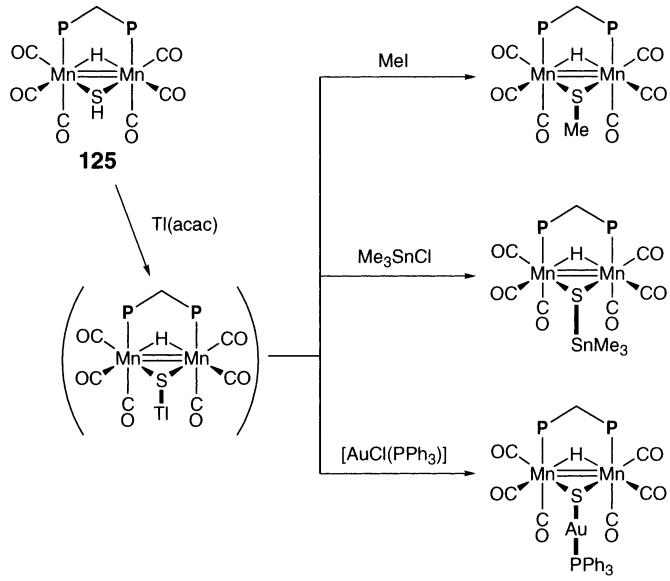
Scheme 57.



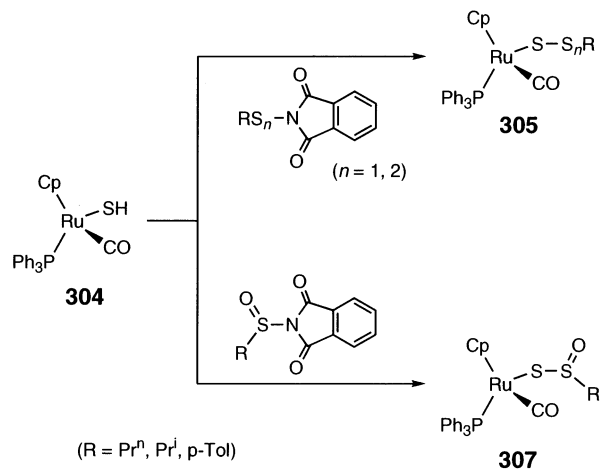
Scheme 58.

Shaver et al. have demonstrated that RS_n–imide type reagents ($n = 1, 2$) are effective for synthesizing polysulfanido complexes ($M–S_{n+1}R$) from the corresponding hydrosulfido complexes. For example, the hydrosulfido complex $[CpRu(SH)(CO)(PPh_3)]$ (**304**) reacts with RS_nphth (phth = phthalimido; $n = 1, 2$) to afford the polysulfanido complexes $[CpRu(S_{n+1}R)(CO)(PPh_3)]$ (**305**) (Scheme 60) [233,234]. The polysulfanido complexes $[Cp_2Ti(SSR)_2]$, $[Cp_2Ti(SR)(SSSR)]$ [235], and $[CpW(CO)_3(S_nR)]$ ($n = 2, 3$) [236,237] have been prepared by using this class of sulfur-transfer reagents. 1,1′-Thiobisbenzimidazole (imide–S–imide) also reacts with $[Cp_2Ti(SH)_2]$ (**21**) to afford the polysulfido complexes $[(Cp_2Ti)_2(\mu_2\text{-}\eta^1\text{:}\eta^1\text{-}S_3)_2]$ and $[Cp_2Ti(\eta^2\text{-}S_5)]$ (**306**) [60]. Similarly, the reaction of RS(O)phth with hydrosulfido complexes leads to the formation of thiosulfinato complexes such as $[CpRu\{SS(O)R\}(CO)(PPh_3)]$ (**307**) (Scheme 60) [233,234,238] and $[CpW\{SS(O)R\}(CO)_3]$ [236,237]. Reactions of this type are known only for terminal hydrosulfido complexes.

Formation of the polysulfido complex **306** from the reaction of $[Cp_2Ti(SH)_2]$ (**21**) with S_8 [239] or with S_nCl_2 ($n = 1–3$) in the presence of pyridine [240] has been reported in the 1960s (Eq. (34)). Later, the polysulfido complexes $[(^tBuCp)_2M(\eta^2\text{-}$

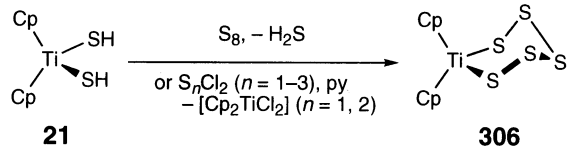


Scheme 59.



Scheme 60.

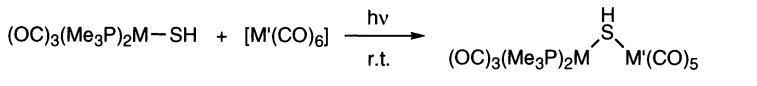
S_5)] (M = Zr, Hf) [62] and [$Cp_2Mo(\eta^2$-$S_4)$] [241] have been prepared by the reactions of the corresponding hydrosulfido complexes with S_8.



(34)

4.3. Adduct formation

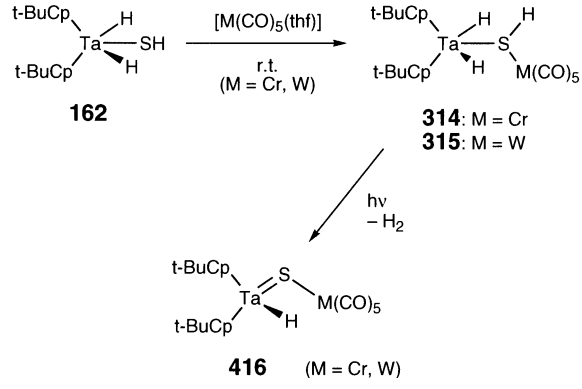
As described above, the sulfur atom in hydrosulfido ligands behaves as a nucleophile by using the lone pairs on the sulfur atom. This is also the case in the reactions with Lewis acidic metal centers, which afford hydrosulfido-bridged polynuclear complexes. From the synthetic point of view, such a reaction provides a practical method for the synthesis of hydrosulfido-bridged heterometallic complexes, a complement to the oxidative addition of H_2S across heterodinuclear centers (Section 2.2). Compared with the related thiolato-bridged complexes [242], however, examples of hydrosulfido-bridged complexes prepared by this method are rather limited, probably because of the various reactivities of the S–H bond in hydrosulfido complexes. Vahrenkamp and Küllmer have prepared a series of hydrosulfido-bridged heterometallic complexes $[(OC)_5M'(\mu_2\text{-}SH)M(CO)_3(PMe_3)_2]$ (**308**–**313**; M = Mn, Re; M′ = Cr, Mo, W) by using this synthetic approach (Eq. (35)) [243].



(35)

308: M = Mn, M' = Cr **311**: M = Re, M' = Cr
309: M = Mn, M' = Mo **312**: M = Re, M' = Mo
310: M = Mn, M' = W **313**: M = Re, M' = W

Both *fac* and *mer*,*trans* isomers are isolated for each complex except for the Mn–Mo one **309**, for which only *mer*,*trans* isomer is known. As a related reaction, formation of the hydrosulfido-bridged complexes $[(^t\text{BuCp})_2TaH_2(\mu_2\text{-}SH)M(CO)_5]$ (M = Cr (**314**), W (**315**)) from $[(^t\text{BuCp})_2TaH_2(SH)]$ (**162**) and $[M(CO)_5(thf)]$ has recently been reported (Scheme 61) [152]. The bis(hydrosulfido) complexes $[(\eta^5\text{-}C_5H_4R)_2Ti(SH)_2]$ (R = H (**21**), Me (**316**)) are versatile synthetic precursors for hydrosulfido-bridged heterobimetallic complexes. They react with $[M(CO)_4(nbd)]$



162

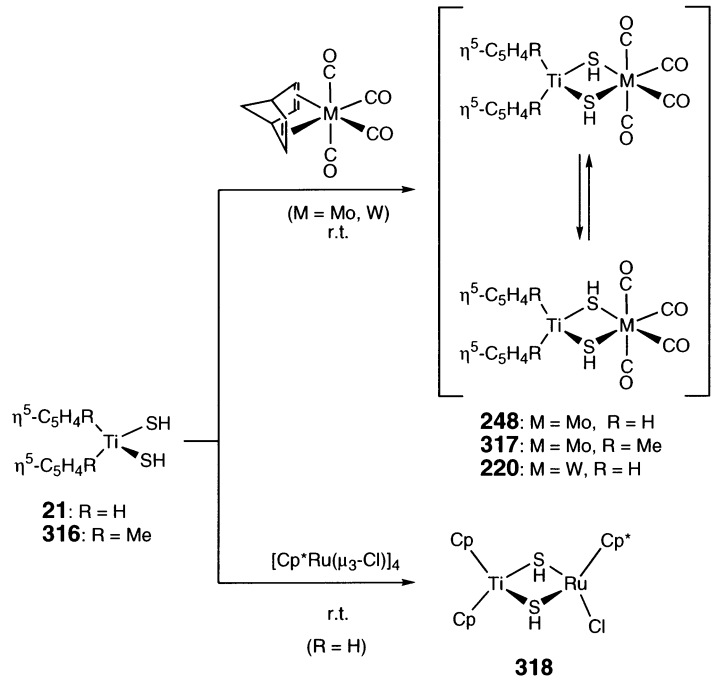
314: M = Cr
315: M = W

416 (M = Cr, W)

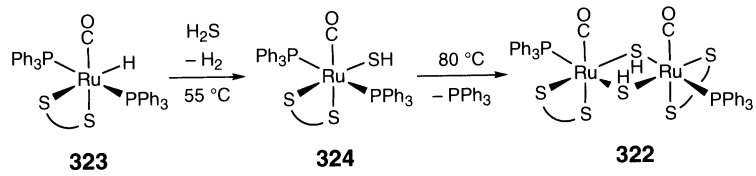
Scheme 61.

(M = Mo, W) and [Cp*Ru(μ_3-Cl)]$_4$ to afford the heterobimetallic complexes [(η^5-$C_5H_4R)_2Ti(\mu_2$-SH)$_2$M(CO)$_4$] (**220**, **248**, and **317**) [191] and [$Cp_2Ti(\mu_2$-SH)$_2$RuClCp*] (**318**) [244,245], respectively (Scheme 62). It is to be noted that most hydrosulfido complexes used in these reactions are early transition metal complexes. Rauchfuss and Amarasekera have attempted the reaction of the ruthenium hydrosulfido complex [CpRu(SH)(PPh_3)$_2$] (**267**) and [CpRu(OTf)(PPh_3)$_2$] (**319**) [124]. Although they observed the formation of the hydrosulfido-bridged species [{CpRu(PPh_3)$_2$}$_2$(μ_2-SH)]$^+$ (**320**), this species decomposed rapidly at room temperature. However, there is no doubt that much more hydrosulfido complexes, especially late transition metal ones, will be used in this synthetic reaction.

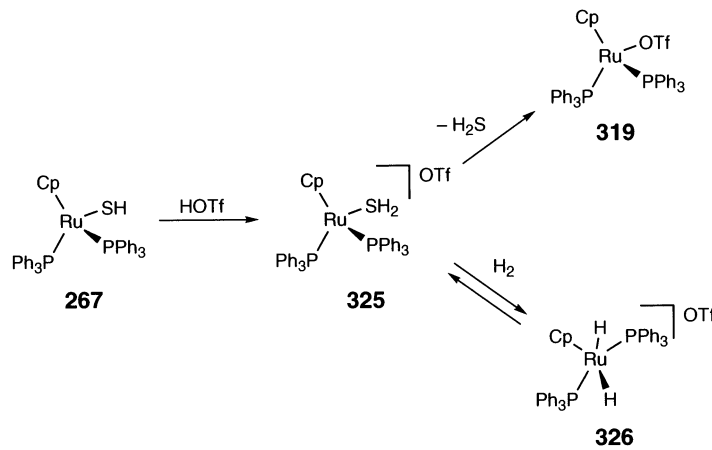
Adduct formation reactions of hydrosulfido complexes are not restricted to heterometallic system. For example, the homometallic and symmetrical hydrosulfido-bridged complexes [{M(CO)$_5$}$_2$(μ_2-SH)]$^-$ (M = Cr (**321**), W (**288**)) are obtained by the reactions of the hydrosulfido complexes [M(SH)(CO)$_5$]$^-$ (M = Cr (**60**), W(**62**)) and [M(CO)$_5$(thf)] [246]. Another variation of the reactions described above is the dimerization of hydrosulfido complexes induced by a loss of donor ligands. Thus, the hydrosulfido-bridged diruthenium complex [{Ru(S_2CNMe_2)(CO)(PPh_3)}$_2$(μ_2-SH)$_2$] (**322**) is derived from the corresponding mononuclear complexes **324** (Scheme 63) [247]. Scheme 33 represents another example of such dimerization; the hydrosulfido-bridged dinuclear complexes [{M(CO)$_4$}$_2$(μ_2-SH)$_2$] (M = Mn (**6**), Re (**176**)) are converted into the tetranuclear complexes [{M(CO)$_3$}$_4$(μ_2-SH)$_4$] (M = Mn (**177**), Re (**178**)) with a loss of the CO ligands [162].



Scheme 62.



Scheme 63.

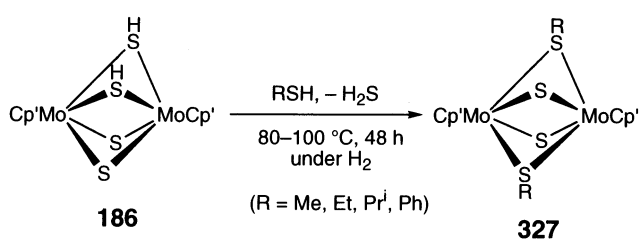


Scheme 64.

4.4. Substitution of SH group

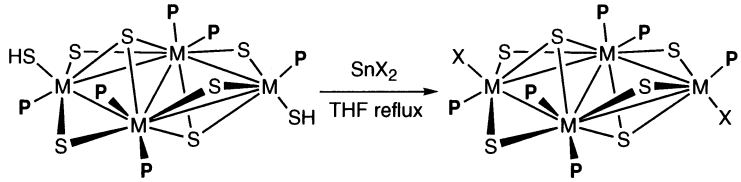
Hydrosulfido ligands are easily replaced when treated with Brønsted acid substrates. Although intermediary H_2S complexes have been detected upon protonation of hydrosulfido complexes in some systems, the resultant H_2S ligands are extremely labile and easily substituted by the conjugate base of the acid added. Rauchfuss and Amarasekera have revealed that treatment of $[CpRu(SH)(PPh_3)_2]$ (**267**) with HOTf affords the H_2S species $[CpRu(SH_2)(PPh_3)_2][OTf]$ (**325**), which turns into $[CpRu(OTf)(PPh_3)_2]$ (**319**) with a loss of H_2S (Scheme 64) [124]. Under dihydrogen, the H_2S species **325** establishes an equilibrium involving the dihydrido complex $[CpRuH_2(PPh_3)_2]^+$ (**326**).

Eq. (36) shows the hydrosulfido–thiolato exchange reaction of $[(Cp'Mo)_2(\mu_2\text{-}S)_2(\mu_2\text{-}SH)_2]$ (**186**) [166]. This reaction, like the similar thiolato exchange reaction of a tungsten complex [87], may involve initial protonation of the hydrosulfido ligands by the thiols.



(36)

Treatment of molybdenum and tungsten hydrosulfido–sulfido clusters $[M_4(\mu_3\text{-}S)_2(\mu_2\text{-}S)_4(SH)_2(PR_3)_6]$ (**214**: M = Mo, $R_3 = Me_3$ [182]; **79**: M = W, $R_3 = Me_2Ph$ [109,110]) with SnX_2 (X = Cl, Br, I) results in replacement of SH ligands by halide anions (Eq. (37)).



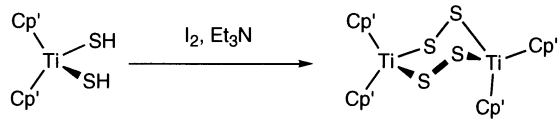
214: M = Mo, P = PMe_3
79: M = W, P = PMe_2Ph

328: M = Mo, P = PMe_3, X = Cl, Br, I
329: M = W, P = PMe_2Ph, X = Cl

(37)

4.5. Oxidative coupling

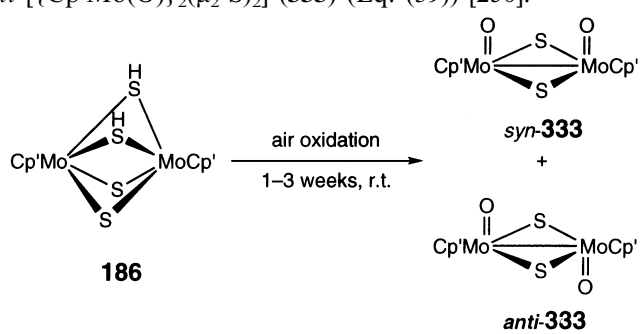
Like organic thiols, hydrosulfido complexes undergo oxidation to form a S–S bond. In an earlier investigation, formation of the disulfido complex $[(H_2O)_5Cr(\mu_2\text{-}S_2)Cr(OH_2)_5]^{4+}$ upon oxidation of $[Cr(SH)(OH_2)_5]^{2+}$ with I_2 was claimed by Sykes and co-workers, although the product had not been fully characterized [248]. Later, Rauchfuss and co-workers have shown that the bis(hydrosulfido) complex $[Cp'_2Ti(SH)_2]$ (**316**) is oxidized with I_2 in the presence of NEt_3 to give the disulfido-bridged complex $[(Cp'_2Ti)_2(\mu_2\text{-}\eta^1\text{:}\eta^1\text{-}S_2)_2]$ (**330**) (Eq. (38)) [249].



316 **330**

(38)

Oxidation of the ruthenium hydrosulfido complex $[CpRu(SH)(PPh_3)_2]$ (**267**) takes place similarly to afford the disulfido complex **331** (Scheme 65) [124]. When $[Cp_2Fe][PF_6]$ is used as an oxidant, an intermediary $\mu_2\text{-}S_2H_2$ complex **332** has been observed in the ^{1}H-NMR spectrum of the reaction mixture. Air oxidation of related (hydrosulfido)ruthenium complexes has also been reported by Puerta and co-workers [100,101]. Formation of the disulfido complex **280** from the reaction of the bis(hydrosulfido) complex **279** with SO_2 (Scheme 55) [223,224] or azobenzene [206] may be regarded as an intramolecular oxidative coupling of two hydrosulfido ligands in **279**. On the other hand, air oxidation of **186** affords the oxo–sulfido complexes *syn*- and *anti*-$[\{Cp'Mo(O)\}_2(\mu_2\text{-}S)_2]$ (**333**) (Eq. (39)) [250].

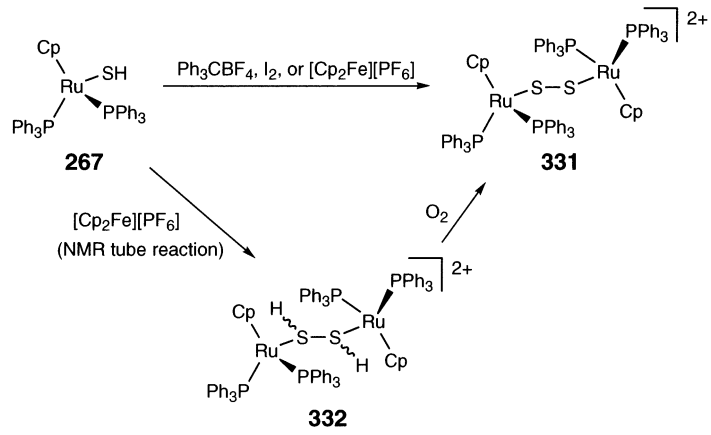


186

syn-**333**

anti-**333**

(39)



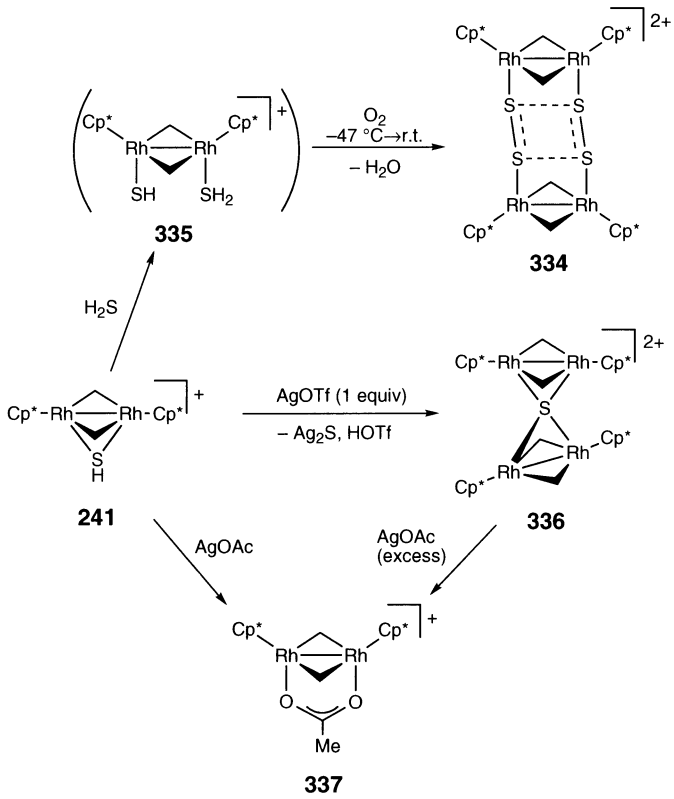
Scheme 65.

Isobe et al. have revealed that the hydrosulfido-bridged complex $[(Cp^*Rh)_2(\mu_2\text{-}CH_2)_2(\mu_2\text{-}SH)]^+$ (**241**) is oxidized with oxygen in the presence of H_2S to afford the tetrarhodium complex $[\{(Cp^*Rh)_2(\mu_2\text{-}CH_2)_2\}_2(\mu_4\text{-}S_4)][OTf]_2$ (**334**) with a bridging rectangular cyclotetrasulfur ligand (Scheme 66) [251]. Because the bridging hydrosulfido complex **241** does not react with O_2 in the absence of H_2S, initial formation of the hydrosulfido–H_2S species **335** is proposed. On the other hand, treatment of the hydrosulfido-bridged complex **241** with an equimolar amount of AgOTf results in the formation of the μ_4-sulfido complex $[\{(Cp^*Rh)_2(\mu_2\text{-}CH_2)_2\}_2(\mu_4\text{-}S)][OTf]_2$ (**336**) [252]. Here, no oxidation occurs, and the silver cation seems to behave as a scavenger of hydrosulfide anion. Both **241** and **336** lose their sulfur ligands by treatment with an excess of silver salts which contain anions with strong coordination ability such as acetate anion.

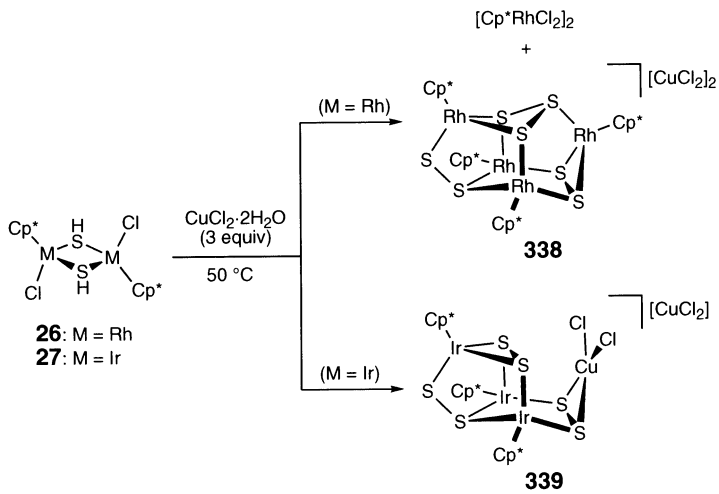
When the hydrosulfido-bridged complexes **26** and **27** are treated with a Cu(II) salt, oxidative S–S bond formation takes place to afford the di- and trisulfido clusters **338** and **339**, although the yield of the former cluster is quite low (Scheme 67) [253]. Oxidants other than the Cu(II) salt such as I_2 and $[Cp_2Fe][PF_6]$ are not effective for these transformations.

4.6. Deprotonation

Rakowski DuBois and co-workers have determined the pK_a values of the hydrosulfido-bridged cationic complexes $[\{(\eta^5\text{-}C_5R_5)Mo\}_2(\mu_2\text{-}S_2CH_2)(\mu_2\text{-}S)(\mu_2\text{-}SH)][OTf]$ ($R_5 = H_5$ (**256**), H_4Me (**188**), Me_5 (**340**)) by measuring the equilibrium constant of the acid–base reactions [141]. The pK_a values of the Cp and Cp′ derivatives are similar (8.3 ± 1 and 8.4 ± 1, respectively), whereas that of the Cp* analogue **340** is significantly larger (10.3 ± 1) probably because of the more electron donating nature of the Cp* ligand. In addition, the pK_a values of some hydrosulfido



Scheme 66.



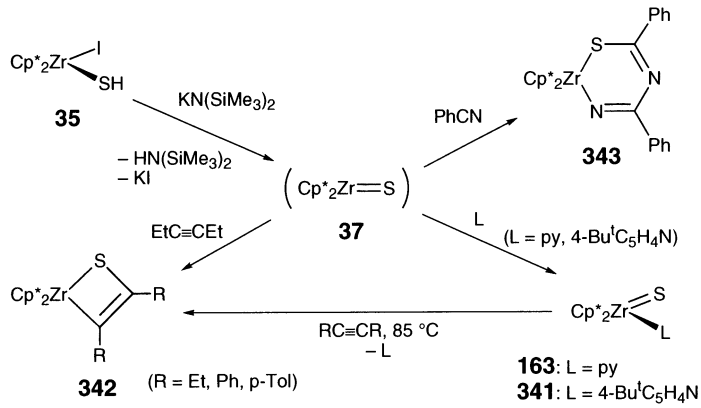
Scheme 67.

complexes have been estimated by the reactions with bases whose pK_a values are known [42,129]. For example, the pK_a value of the hydrosulfido–sulfido complex $[(CpMo)_2(\mu_2\text{-}S)_2(\mu_2\text{-}SH)_2]$ (**278**) is estimated to be in the range of 10–18 on the basis of the deprotonation reactions with triethylamine and methoxide anion [141]. These observations suggest that the cationic nature of the dimolybdenum complexes **188**, **256**, and **340** enhances the acidity dramatically.

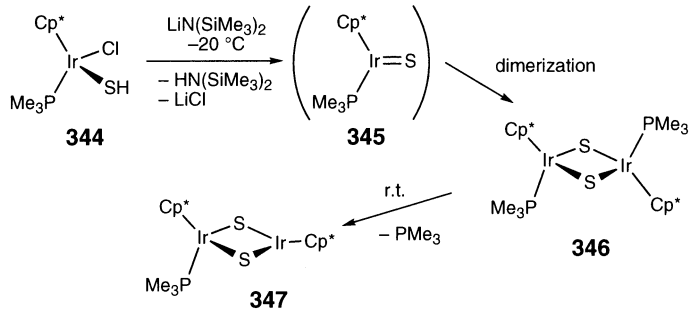
As is expected from these pK_a values, hydrosulfido complexes undergo deprotonation. Deprotonation of μ_2-hydrosulfido complexes affords the corresponding μ_2-sulfido complexes, especially when the μ_2-SH complex is obtained by the protonation of the isolable μ_2-S complex. The examples are shown in Scheme 19 [116] and Eq. (18) [142]. In the nucleophilic reactions of hydrosulfido complexes, addition of base often enhances the nucleophilicity of the hydrosulfido ligand. Deprotonation of the hydrosulfido ligand with base may be responsible for the acceleration of the reaction.

Proton transfer reactions mediated by sulfur atoms are involved in a number of biological systems [254]. In connection with biological nitrogen fixation, protonation of coordinated dinitrogen in **7** and **8** by hydrosulfido-bridged complexes **9** and **10** (Scheme 6) is noteworthy [42]. It is of interest that the corresponding reactions using H_2S and thiols result in the oxidation of the tungsten center rather than protonation of the coordinated dinitrogen.

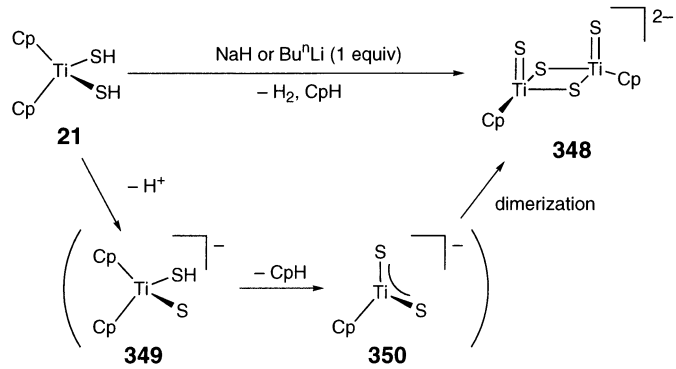
α-Dehydrohalogenation of hydrosulfido–halo complexes induced by base provides a valuable route to generate metal–sulfido complexes. Sulfido species formed by this pathway are usually as quite reactive as other metal–heteroatom multiple bonded species prepared by such strategy [77,78,255,256]. Bergman and co-workers have demonstrated that the hydrosulfido–iodo complex $[Cp^*_2ZrI(SH)]$ (**35**) reacts with a strong base to afford the unsaturated sulfido species $[Cp^*_2Zr=S]$ (**37**), which forms adducts with pyridines and undergoes cycloaddition reactions with 3-hexyne and benzonitrile (Scheme 68) [77,78]. On the other hand, dehydrochlorination of the iridium complex $[Cp^*IrCl(SH)(PMe_3)]$ (**344**) leads to the dimerization of the



Scheme 68.



Scheme 69.



Scheme 70.

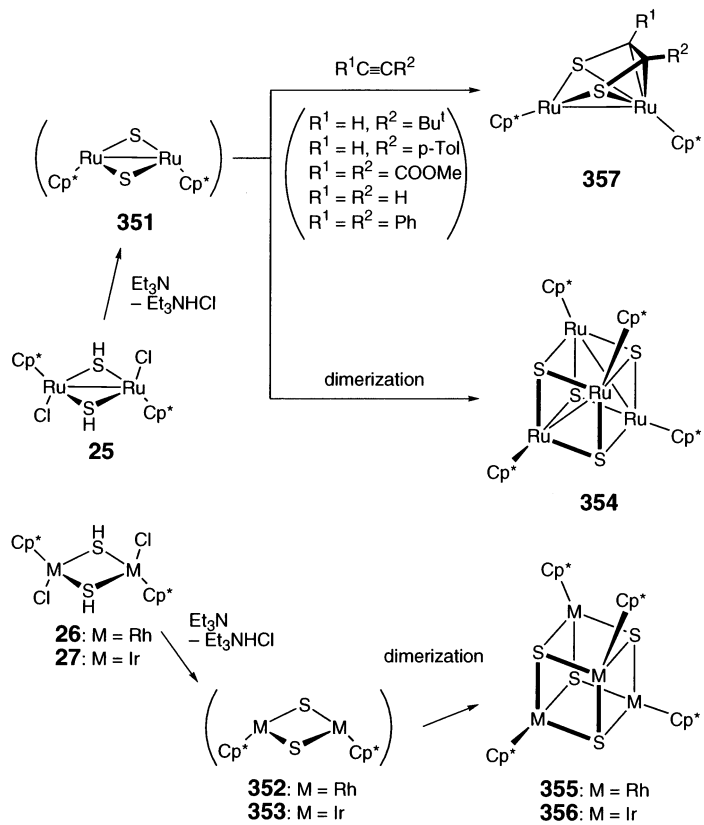
Ir=S species **345** to give the sulfido-bridged diiridium complex [Cp*Ir(PMe_3)(μ_2-S)$_2$IrCp*] (**347**) as the final product (Scheme 69) [257,258]. Elimination of cyclopentadiene induced by a strong base has been reported by Kubas and co-workers [259]. Thus, when the bis(hydrosulfido)titanium complex [$Cp_2Ti(SH)_2$] (**21**) is treated with an equimolar amount of NaH in THF, the dinuclear thiotitanate anion [{CpTi(S)}$_2$(μ_2-S)$_2$]$^{2-}$ (**348**) is obtained with concurrent formation of H_2 and cyclopentadiene (Scheme 70). The reaction is believed to proceed via initial deprotonation of **21**, followed by α-elimination of cyclopentadiene and subsequent dimerization of the resultant anionic $CpTiS_2$ fragment **350**. *n*-Butyllithium also deprotonates the hydrosulfido complex **21** to give the same anion, **348** [260]. The X-ray analysis of the sodium salt has revealed that Na(thf)$_n$ ($n = 1$, 3) fragments interact with the sulfido ligands in **348** [259]. The thiotitante anion **348** reacts with metal halide complexes to afford a series of mixed-metal sulfido clusters containing titanium (vide infra) [16,260,261].

Dinuclear hydrosulfido–halo complexes also undergo α-dehydrohalogenation reaction to form dinuclear sulfido-bridged species. Thus, our group has recently demonstrated that the reactions of the hydrosulfido-bridged complexes [(Cp*MCl)$_2$(μ_2-SH)$_2$] (M = Ru (**25**), Rh (**26**), Ir (**27**)) with triethylamine lead to the

formation of the sulfido-bridged species $[(Cp^*M)_2(\mu_2\text{-}S)_2]$ (M = Ru (**351**), Rh (**352**), Ir (**353**)) (Scheme 71) [71,72,262]. As for iridium, the formation of the sulfido-bridged diiridium intermediate **353** has been observed by the ^{1}H-NMR spectrum at the early stage of the reaction [71,72]. In the absence of trapping reagents, the tetranuclear cubane-type clusters $[(Cp^*M)_4(\mu_3\text{-}S)_4]$ (M = Ru (**354**), Rh (**355**), Ir (**356**)) are formed through dimerization of the sulfido-bridged species **351**–**353**. On the other hand, when the dehydrohalogenation of the ruthenium complex **25** is carried out in the presence of alkynes, the sulfido-bridged species **351** is trapped as the dithiolene-bridged complexes **357** [262]. Utility of α-elimination for sulfido cluster synthesis will further be described in Section 4.7.

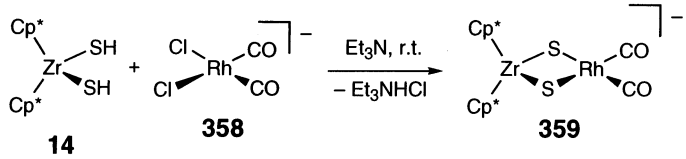
4.7. Formation of polynuclear sulfido complexes

In addition to deprotonation and subsequent self-condensation reactions, hydrosulfido complexes behave as metalloligands toward various metal complexes with concomitant S–H bond cleavage, leading to the formation of sulfido complexes with



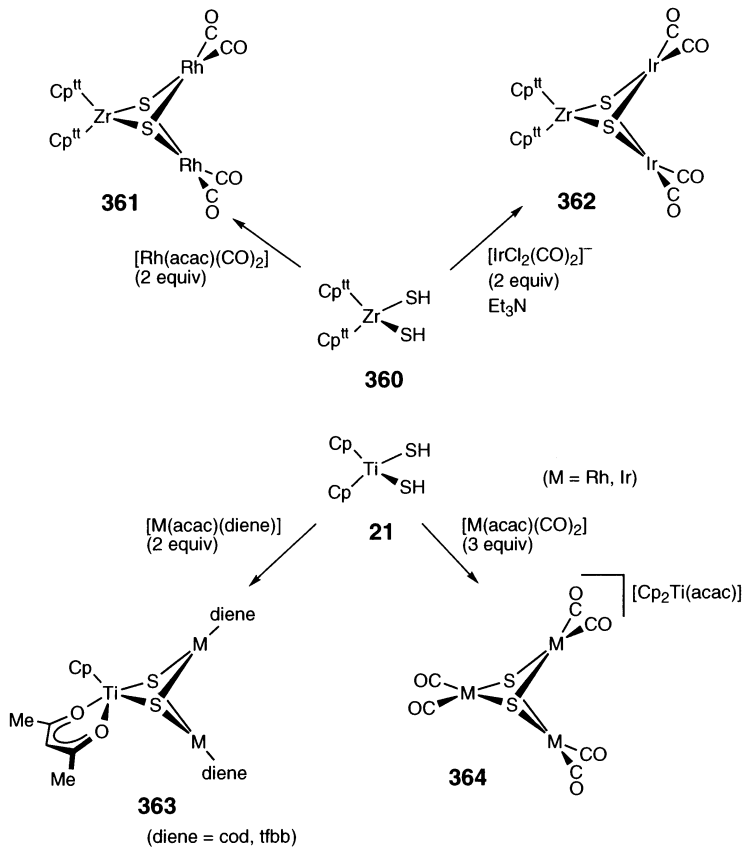
Scheme 71.

higher nuclearity. Indeed, metathetical reactions of hydrosulfido complexes with halo, hydrido, alkyl, alkoxo, and imido complexes are effective for the synthesis of polynuclear sulfido complexes. Kalck et al. have revealed that the bis(hydrosulfido)zirconium complex $[Cp^*_2Zr(SH)_2]$ (**14**) reacts with $[Ph_4As][RhCl_2(CO)_2]$ (**358**) in the presence of triethylamine to afford the sulfido-bridged early–late heterobimetallic complex $[Ph_4As][Cp^*_2Zr(\mu_2\text{-}S)_2Rh(CO)_2]$ (**359**) (Eq. (40)) [263].



(40)

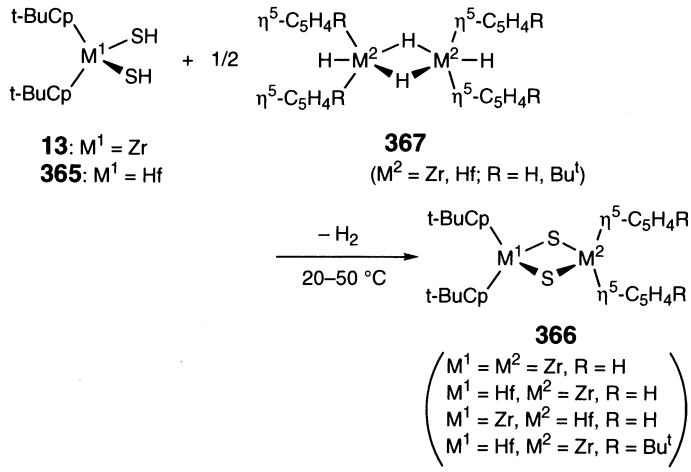
Quite recently, related reactions have been reported by Oro, Ciriano, and their co-workers. The bis(hydrosulfido)zirconium complex $[Cp^{tt}_2Zr(SH)_2]$ (**360**) reacts reasonably with two equivalents of $[Rh(acac)(CO)_2]$ [192] and $[IrCl_2(CO)_2]^-$ [264] to afford the $ZrRh_2$ and $ZrIr_2$ trinuclear sulfido clusters $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{M(CO)_2\}_2]$



Scheme 72.

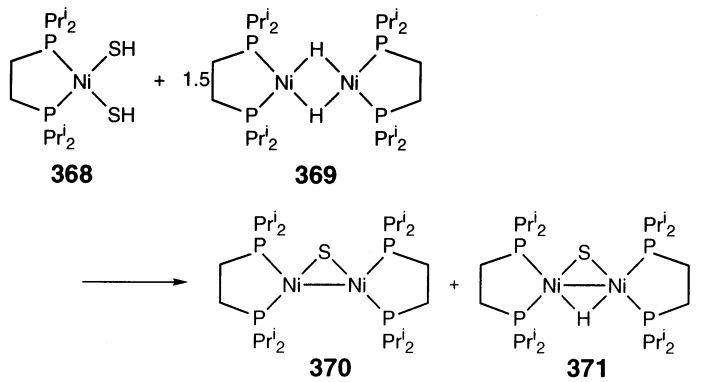
(M = Rh (**361**), Ir (**362**)), respectively (Scheme 72). By contrast, the analogous reactions of the titanium hydrosulfido complex [$Cp_2Ti(SH)_2$] (**21**) with rhodium and iridium acetylacetonato complexes are accompanied by elimination of cyclopentadiene or sulfido transfer reactions. Thus, the reactions of **21** with the diene complexes [M(acac)(diene)] (M = Rh, Ir; diene = cod, tfbb) afford the heterotrinuclear complexes [CpTi(acac)(μ_3-S)$_2${M(diene)}$_2$] (**363**) in which one of the Cp ligands in **21** is replaced by an acac ligand, whereas the corresponding reactions with the carbonyl complexes [M(acac)$(CO)_2$] results in the formation of the anionic homotriangular clusters [$M_3(\mu_3\text{-S})_2(CO)_6]^-$ (**364**) [265]. The sulfido transfer in the latter reaction may be ascribed to the higher Lewis acidity of the late transition metal centers.

Eq. (41) shows the reactions between hydrosulfido and hydrido complexes of Group 4 metals reported by Tainturier et al. [266].



(41)

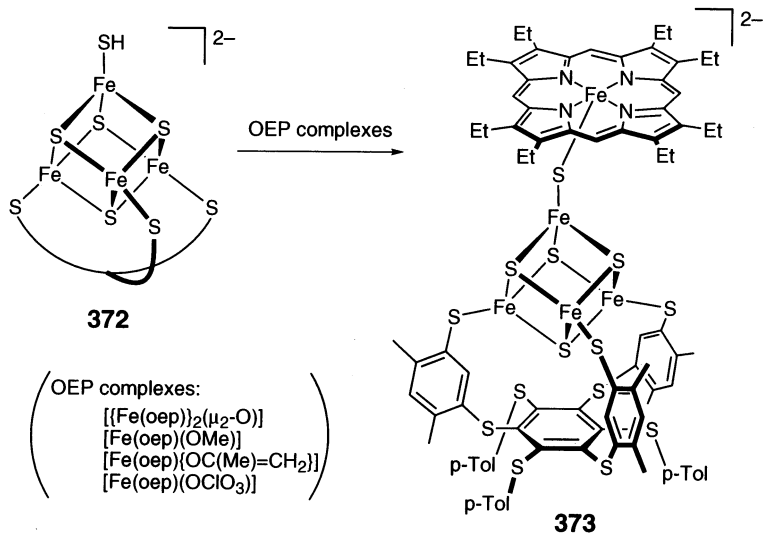
Sulfido-bridged heterometallic complexes **366** are formed with concomitant liberation of H_2. For the preparation of [(^{t}BuCp)$_2$Zr(μ_2-S)$_2$ZrCp_2], the dimethyl complex [Cp_2ZrMe_2] can be used instead of the corresponding hydrido complex **367**. In this connection, Herrmann and Fischer have attempted the reaction of the hydrosulfidotungsten complex [Cp*W(SH)$(CO)_3$] (**116**) with the methylchromium complex [CpCrMe$(CO)_3$], which yielded, however, a complex mixture containing the homometallic product [{CpCr$(CO)_2$}$_2$(μ_2-S)] [267]. Jones and Vicic have recently investigated the reaction of the hydrosulfido complex [(dippe)Ni$(SH)_2$] (**368**) with



(42)

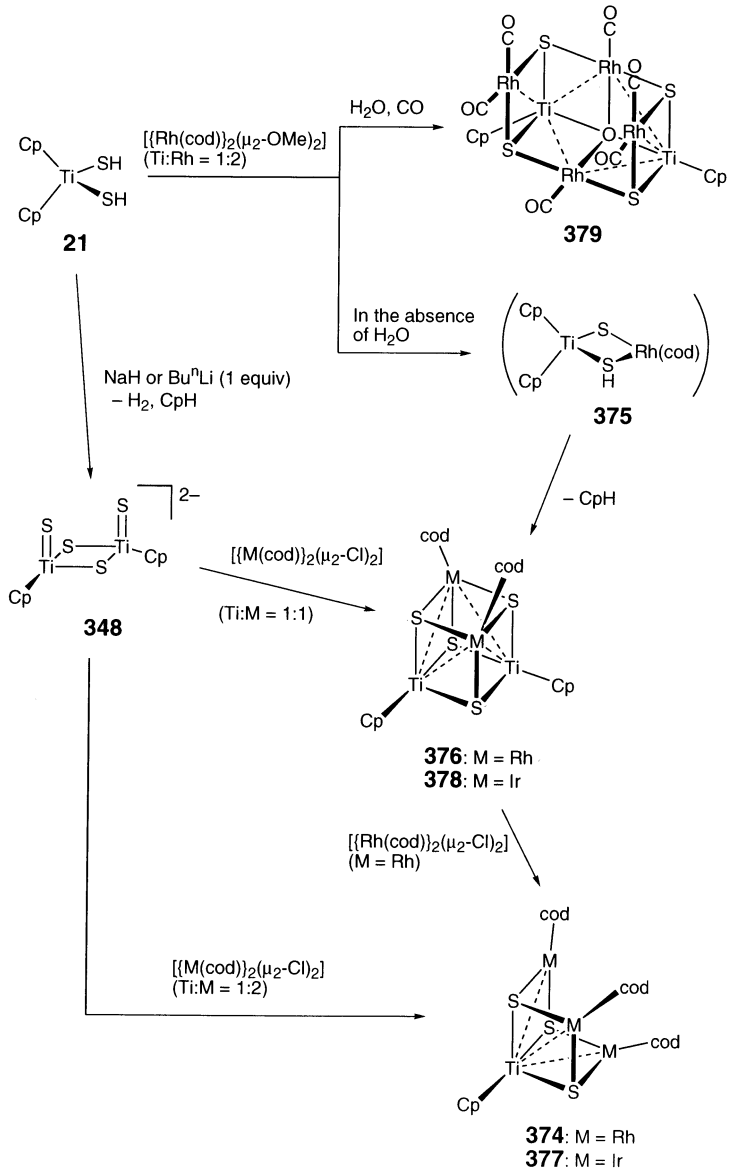
the hydrido complex [{Ni(dippe)}$_2$(μ_2-H)$_2$] (**369**), which gives the Ni(I) complex [{Ni(dippe)}$_2$(μ_2-S)] (**370**) and the Ni(I)/Ni(II) mixed-valence complex [{Ni(dippe)}$_2$(μ_2-H)(μ_2-S)] (**371**) (Eq. (42)) [268].

Alkoxo and hydroxo ligands are also good leaving groups in the reaction with hydrosulfido complexes. Holm and co-workers have used this approach to link two distinct biological building blocks: a Fe_4S_4 cubane-type cluster and heme [85]. Thus, the site-differentiated iron–sulfur cubane-type cluster $[Fe_4S_4(LS_3)(SH)]^{2-}$ (**372**) reacts with the Fe(III) porphyrin complexes with methoxo, enolato, and bridging oxo as well as perchlorato ligands to afford the $[Fe_4S_4]$–S–heme assemble (**373**), which may have some relevance to the active site of sulfite reductase (Eq. (43)).



(43)

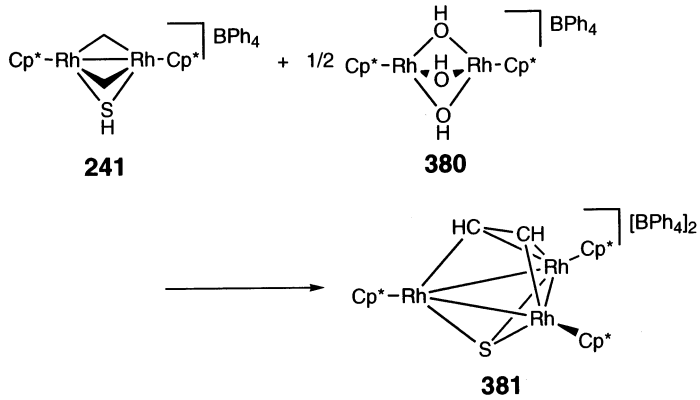
Oro, Ciriano, and co-workers have extensively studied on the reactions of the titanium hydrosulfido complex [$Cp_2Ti(SH)_2$] (**21**) with methoxo complexes of Group 9 metals. The reaction of **21** with [{Rh(cod)}$_2$(μ_2-OMe)$_2$] leads to the formation of the corner-sulfido voided incomplete cubane-type sulfido clusters [(CpTi){Rh(cod)}$_3$(μ_3-S)$_3$] (**374**) (Scheme 73) [269,270]. The reaction is believed to proceed via the hydrosulfido- and sulfido-bridged intermediate [Cp_2Ti(μ_2-S)(μ_2-SH)Rh(cod)] (**375**) and the Ti_2Rh_2 cubane-type sulfido cluster **376** formed by elimination of cyclopentadiene from **375** [260]. The TiM_3S_3 clusters (**374** and **377**) can be obtained by the reactions of Kubas's thiotitanate anion **348** with the chloro complexes [{M(diene)}$_2$(μ_2-Cl)$_2$] in a Ti:M ratio of 1:2 [260]. On the other hand, we have independently demonstrated that the $Ti_2M_2S_4$ cubane-type sulfido clusters [(CpTi)$_2${M(cod)}$_2$(μ_3-S)$_4$] (M = Rh (**376**), Ir (**378**)) are formed when the same reactions are carried out in a Ti:M ratio of 1:1 [261]. The cubane-type cluster **376** is further converted into the $TiRh_3S_3$ incomplete cubane-type cluster **374** upon treatment with [{Rh(cod)}$_2$(μ_2-Cl)$_2$] [16,271]. Interestingly, the reaction of **21** with [{Rh(cod)}$_2$(μ_2-OMe)$_2$] in the presence of water and subsequent carbonylation afford the fused incomplete cubane-type oxo–sulfido cluster [(CpTi)$_2$(μ_4-O)(μ_3-S)$_4$$Rh_4(CO)_6$] (**379**) [270].



Scheme 73.

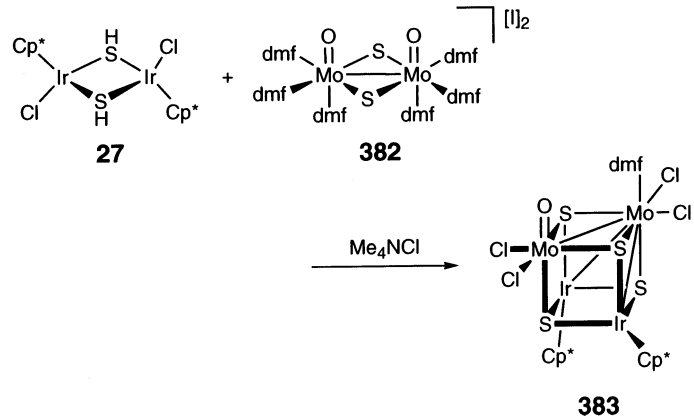
The reaction of the hydrosulfido-bridged dirhodium complex $[(Cp^*Rh)_2(\mu_2\text{-}CH_2)_2(\mu_2\text{-}SH)][BPh_4]$ (**241**) with the hydroxo-bridged complex $[(Cp^*Rh)_2(\mu_2\text{-}OH)_3][BPh_4]$ (**380**) leads to the formation of the trinuclear sulfido cluster $[(Cp^*Rh)_3(\mu_3\text{-}S)(\mu_3\text{-}\eta^2\text{:}\eta^1\text{:}\eta^1\text{-}C_2H_2)][BPh_4]_2$ (**381**) (Eq. (44)) [272].

It is to be noted that the two bridging methylene ligands in **241** are coupled to form



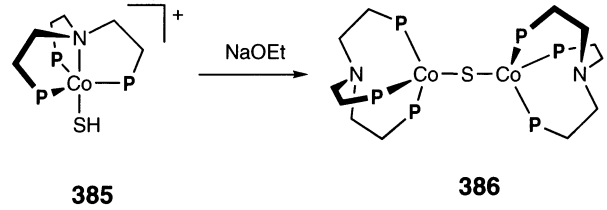
(44)

the acetylene ligand in the product **381**, although the overall reaction stoichiometry is not clear. Elimination of H_2O is also likely to be involved in the reaction of the hydrosulfido complex $[(Cp^*IrCl)_2(\mu_2\text{-}SH)_2]$ (**27**) with the oxodimolybdenum complex $[\{Mo(O)(dmf)_3\}_2(\mu_2\text{-}S)_2]I_2$ (**382**) in the presence of Me_4NCl, which results in the formation of the $Mo_2Ir_2S_4$ mixed-metal cubane-type sulfido cluster $[(Cp^*Ir)_2\{MoCl_2(O)\}\{MoCl_2(dmf)\}(\mu_3\text{-}S)_4]$ (**383**) (Eq. (45)) [273].



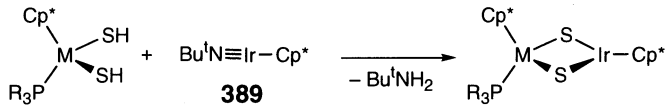
(45)

As we have already seen in Section 2, elimination of H_2S from two hydrosulfido complexes leads to the formation of sulfido-bridged complexes. Herrmann and Fischer have reported the transformation of the hydrosulfido complex [CpCr(SH)-$(CO)_3$] (**384**) into the sulfido-bridged complex $[\{CpCr(CO)_2\}_2(\mu_2\text{-}S)]$ with concurrent liberation of H_2S as well as CO [267]. The hydrosulfidocobalt(II) complex $[(L)Co(SH)]^+$ (**385**; $L = N(CH_2CH_2PPh_2)_3$) is converted into the sulfido-bridged Co(I) complex $[\{(L)Co\}_2(\mu_2\text{-}S)]$ (**386**) by treatment with NaOEt (Eq. (46)) [274].



(46)

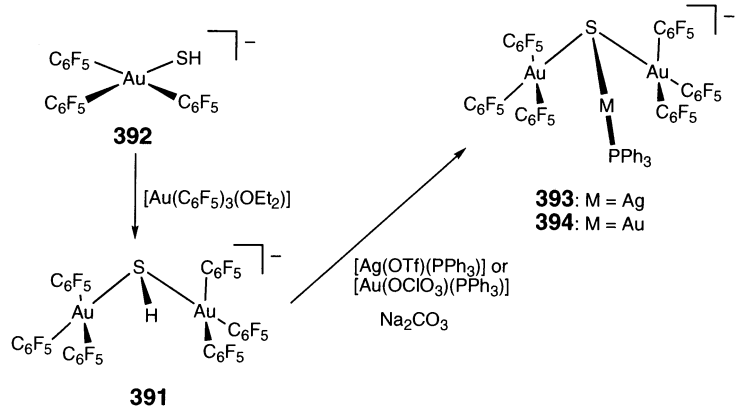
Butylamine is eliminated from the reactions of the hydrosulfido complexes $[Cp^*M(SH)_2(PR_3)]$ (**387**: M = Rh, R = Me; **388**: M = Ir, R = *p*-Tol) with the imido complex $[Cp^*Ir(NBu^t)]$ (**389**), and the sulfido-bridged complexes $[Cp^*M(PR_3)(\mu_2\text{-}S)_2IrCp^*]$ (**390**) are formed as shown in Eq. (47) [257,258].



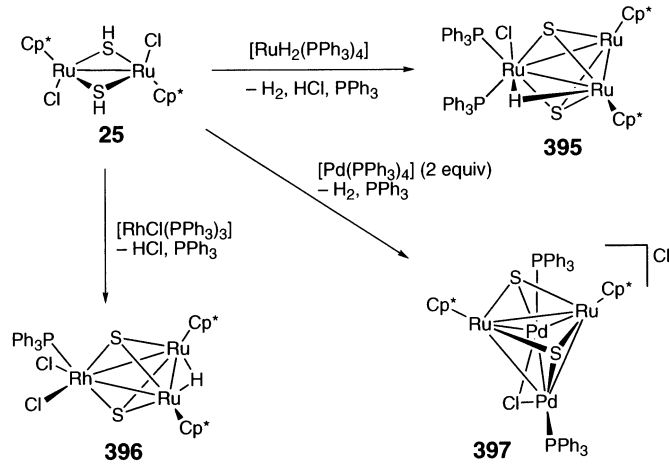
387: M =Rh, R = Me
388: M =Ir, R = p-Tol

(M = Rh, Ir) (47)

The weakly coordinated anion in $[MX(PPh_3)]$ (M = Ag, X = OTf; M = Au, X = ClO_4) is replaced by the hydrosulfido-bridged gold complex $[Bu^n_4N][\{Au(C_6F_5)_3\}_2(\mu_2\text{-}SH)]$ (**391**), prepared from the mononuclear hydrosulfido complex $[Bu^n_4N][Au(C_6F_5)_3(SH)]$ (**392**), to afford the Au_2Ag and Au_3 sulfido complexes **393** and **394** (Scheme 74) [187].

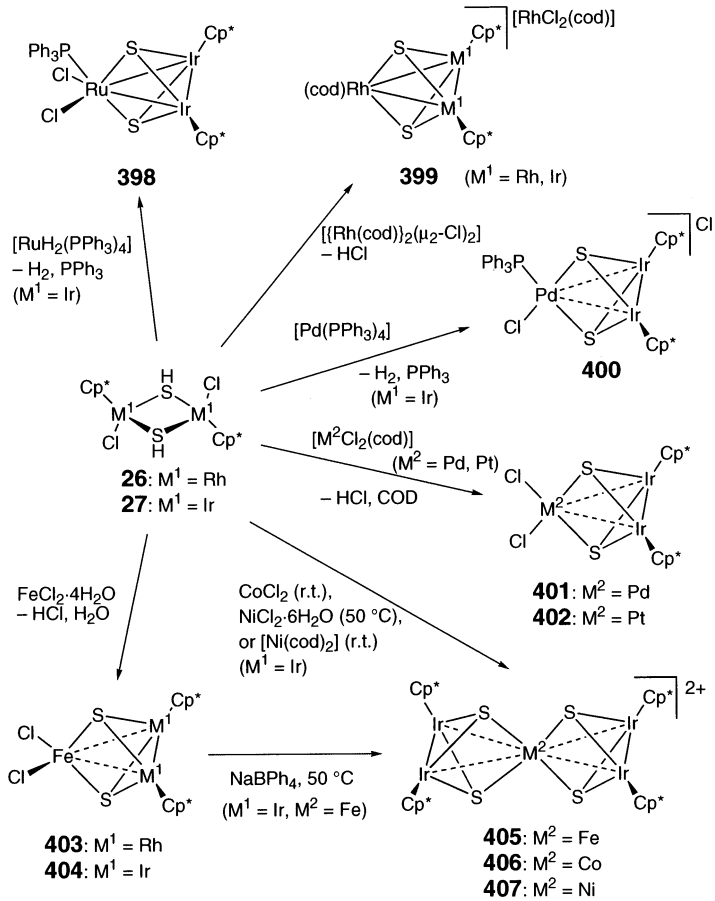


Scheme 74.

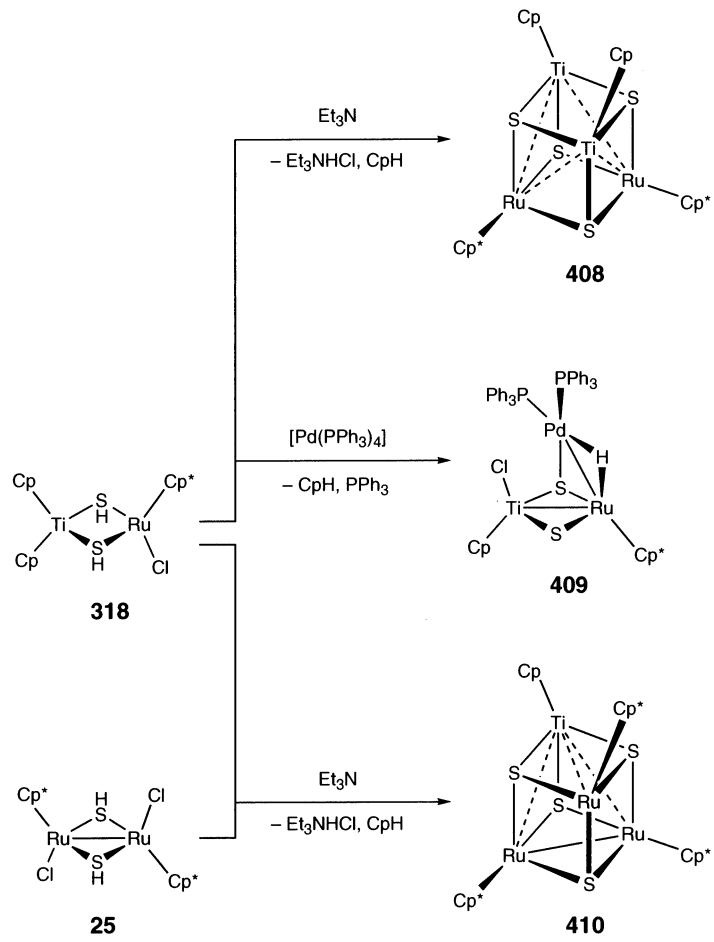


Scheme 75.

Our group has recently established the synthetic utility of the hydrosulfido-bridged dinuclear complexes $[(Cp^*MCl)_2(\mu_2\text{-}SH)_2]$ (M = Ru (**25**), Rh (**26**), Ir (**27**)) for the synthesis of a series of tri-, tetra-, and pentanuclear mixed-metal sulfido clusters as shown in Schemes 75 and 76. Like the formation of the cubane-type clusters **354**–**356** (Scheme 71) [71,72,262], these reactions may involve α-dehydrochlorination of the hydrosulfido complexes because the resultant clusters contain the $M(\mu\text{-}S)_2M$ fragment in their framework. The ruthenium complex **25** reacts with $[RuH_2(PPh_3)_4]$ and $[RhCl(PPh_3)_3]$ to afford the 48e$^-$ triangular clusters $[(Cp^*Ru)_2(\mu_3\text{-}S)_2(\mu_2\text{-}H)RuCl(PPh_3)_2]$ (**395**) [262] and $[(\mu_2\text{-}H)(Cp^*Ru)_2(\mu_3\text{-}S)_2RhCl_2(PPh_3)]$ (**396**) [70], respectively (Scheme 75). The corresponding reaction with $[Pd(PPh_3)_4]$, however, results in the formation of the tetranuclear cluster $[(Cp^*Ru)_2(\mu_3\text{-}S)_2\{Pd(PPh_3)\}_2(\mu_2\text{-}Cl)]Cl$ (**397**) [275], whose $Pd_2Ru_2S_2$ core is similar to that in the related cluster $[(Cp^*Ru)_2(\mu_3\text{-}S)_2Pd_2(\mu_2\text{-}SPr^i)(SPr^i)(PPh_3)]$ prepared by the reaction of the disulfido-bridged diruthenium complex $[(Cp^*Ru)_2(\mu_2\text{-}S_2)(\mu_2\text{-}SPr^i)_2]$ with $[Pd(PPh_3)_4]$ [276]. Similarly, the Group 9 metal analogues, especially the iridium complex **27**, can also be used for the synthesis of mixed-metal sulfido clusters **398**–**402** (Scheme 76, see



Scheme 76.

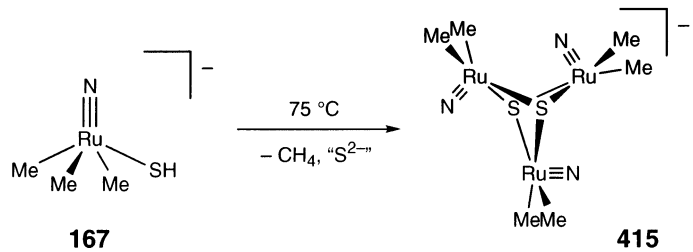


Scheme 77.

also Scheme 67 [253] and Eq. (45) [273]) [71,277,278]. Complex **27** reacts even with the first transition series metals to give the mixed-metal pentanuclear clusters **405**–**407** with a bow-tie framework [279]. It is to be noted the metal–metal distances and the dihedral angle between the two M^1Ir_2 planes are affected by the number of total electrons in these bow-tie clusters.

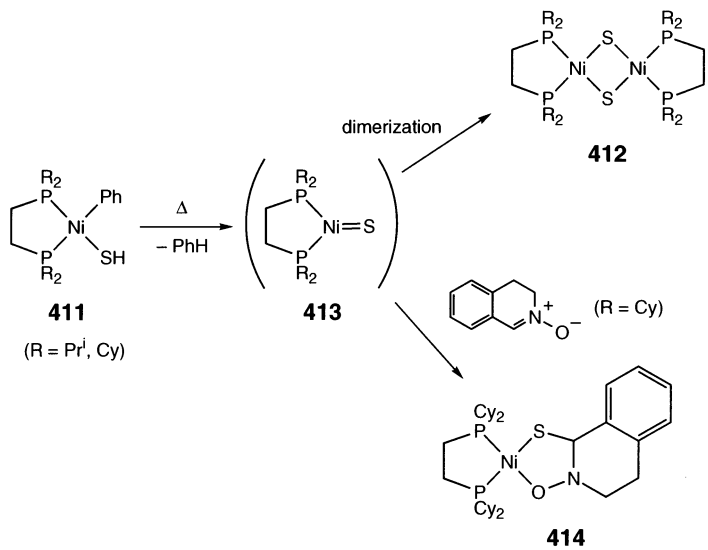
The hydrosulfido-bridged heterobimetallic complex $[Cp_2Ti(\mu_2\text{-}SH)_2RuClCp^*]$ (**318**) serves as a versatile precursor for the synthesis of mixed-metal sulfido clusters containing titanium. Thus, α-elimination of not only HCl but cyclopentadiene from **318** takes place to afford the cubane-type sulfido cluster $[(CpTi)_2(Cp^*Ru)_2(\mu_3\text{-}S)_4]$ (**408**) [244,245], whereas the reaction of **318** with $[Pd(PPh_3)_4]$ results in the formation of the TiRuPd heterotrimetallic sulfido cluster $[(CpTiCl)(Cp^*Ru)\{Pd(PPh_3)_2\}(\mu_3\text{-}S)(\mu_2\text{-}S)(\mu_2\text{-}H)]$ (**409**) with a unique $M_3(\mu_3\text{-}S)(\mu_2\text{-}S)$ core (Scheme 77) [280]. Interestingly, when a 1:1 mixture of the hydrosulfido-bridged TiRu and Ru_2 complexes is treated with triethylamine, the crossed condensation product $[(CpTi)(Cp^*Ru)_3(\mu_3\text{-}S)_4]$ (**410**) is predominantly obtained [281].

Jones and Vicic have found that the phenyl–hydrosulfido complexes [NiPh(SH)(diphos)] (**411**; diphos = dippe and dcpe) readily lose benzene and are converted into the sulfido-bridged dinickel complexes [{Ni(diphos)}$_2$(μ_2-S)$_2$] (**412**) upon heating (Scheme 78) [268,282]. The intermediary mononuclear sulfido species [Ni(S)(diphos)] (**413**) is trapped by a nitrone as the metallacycle product **414** when diphos is dcpe. α-Elimination of alkane is likely to be involved in the thermolysis of the hydrosulfido–methyl complex [Ph_4P][Ru(N)Me_3(SH)] (**167**), which gives the sulfido-bridged triruthenium complex [Ph_4P][{Ru(N)Me_2}$_3$(μ_3-S)$_2$] (**415**) presumably with liberation of methane and sulfido anion (Eq. (48)) [155].



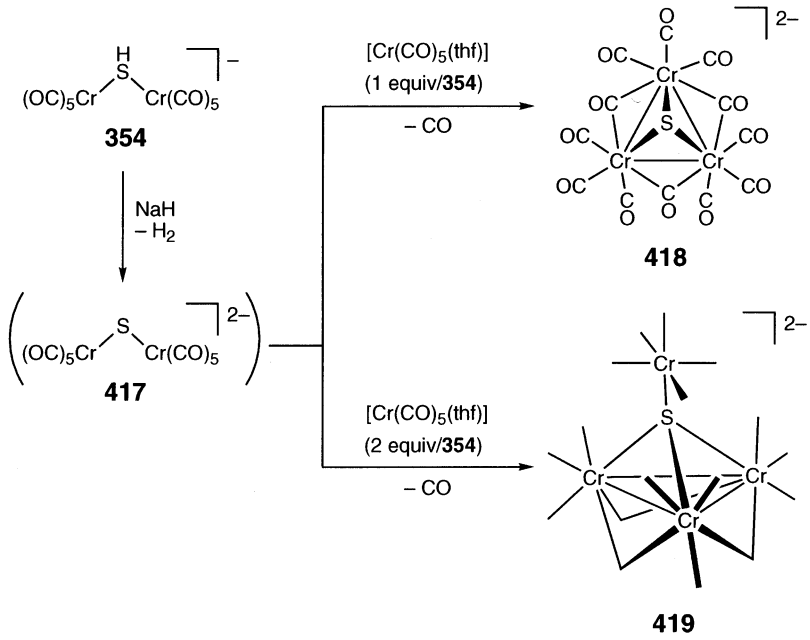
167 **415** (48)

By contrast, light-induced loss of H_2 from the heterobimetallic hydrido–hydrosulfido complexes [(^{t}BuCp)$_2$TaH_2(μ_2-SH)M(CO)$_5$] (M = Cr (**314**), W (**315**)) leads to the formation of the sulfido-bridged heterobimetallic complexes [(^{t}BuCp)$_2$TaH(μ_2-S)M(CO)$_5$] (**416**), which do not dimerize (Scheme 61) [152]. As for main group metals, the cubane-type Ga_4S_4 cluster [(Bu^{t}Ga)$_4$(μ_3-S)$_4$] is obtained by thermal



411 **413** **412** **414**

Scheme 78.

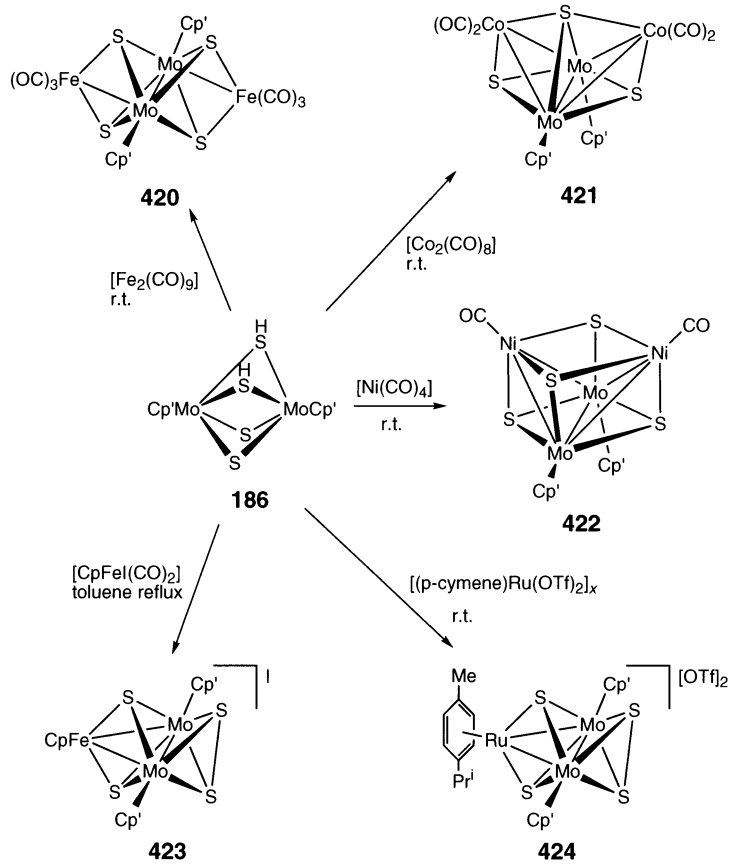


Scheme 79.

α-elimination of isobutane from the hydrosulfido-bridged gallium complex $[(Bu^t_2Ga)_2(\mu_2\text{-}SH)_2]$ [48].

Deprotonation of hydrosulfido complexes enhances the nucleophilicity of the complexes. Reactive sulfido species thus formed can be used to synthesize sulfido clusters. For example, treatment of the hydrosulfido-bridged complex $[PPN][(OC)_5Cr(\mu_2\text{-}SH)Cr(CO)_5]$ (**321**) with NaH leads to the formation of the sulfido species $[(\mu_2\text{-}S)\{Cr(CO)_5\}_2]^{2-}$ (**417**), which further reacts with $[Cr(CO)_5(thf)]$ to afford the trichromium sulfido cluster $[PPN]_2[Cr_3(\mu_3\text{-}S)(\mu_2\text{-}CO)_3(CO)_9]$ (**418**) [283] and the tetrachromium sulfido cluster $[PPN]_2[Cr_4(\mu_4\text{-}S)(\mu_2\text{-}CO)_3(CO)_{14}]$ (**419**) [284] depending upon the amount of $[Cr(CO)_5(thf)]$ added (Scheme 79). This strategy has been applied to the synthesis of the related Mo_3, W_3, Cr_2W, and Mo_2W sulfido clusters and even a CrMoW heterotrimetallic sulfido cluster [283].

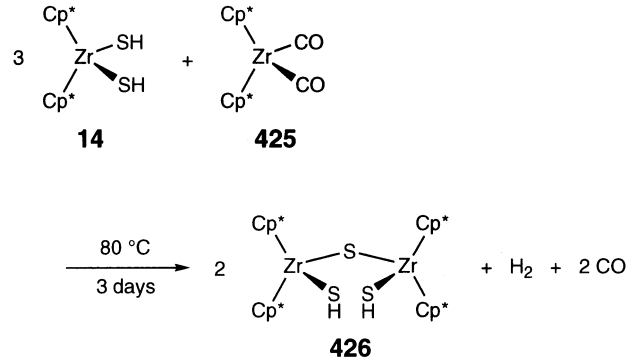
Rakowski, DuBois and Curtis have independently demonstrated that the bis(hydrosulfido)-bridged dimolybdenum complex $[(Cp'Mo)_2(\mu_2\text{-}S)_2(\mu_2\text{-}SH)_2]$ (**186**) reacts with zerovalent metal carbonyl complexes to afford a series of mixed-metal sulfido clusters such as the Mo_2Fe_2 raft-type **420** [285–288], the Mo_2Co_2 butterfly-type **421**, and the Mo_2Ni_2 cubane-type cluster **422** [288] (Scheme 80). Formation of the cubane-type sulfido clusters $[(CpMo)_2\{M(NO)\}_2(\mu_3\text{-}S)_4]$ (M = Fe, Co) from the Cp



Scheme 80.

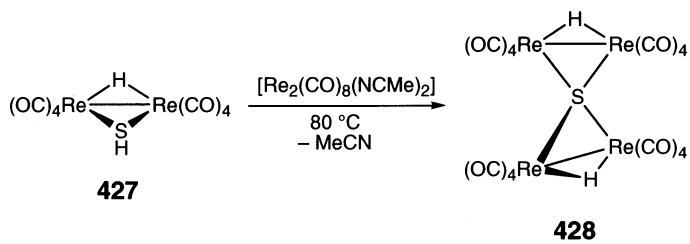
analogue $[(CpMo)_2(\mu_2\text{-}S)_2(\mu_2\text{-}SH)_2]$ (**278**) and the nitrosyl complexes $[M(NO)_n(CO)_{4-n}]$ (M = Fe, $n = 2$; M = Co, $n = 1$) has been reported more recently [289]. In contrast to the most reactions described above, these reactions obviously involve the oxidative addition of the S–H bonds in the hydrosulfido complexes toward the incoming heterometal centers because the formal oxidation state of metals in the resultant clusters is increased during the cluster formation [351]. The hydrosulfido-bridged dimolybdenum complex **186** also reacts with Fe(II) and Ru(II) complexes to afford the triangular clusters **423** [286] and **424** [290] as shown in Scheme 80, although the formal oxidation state of the metals does not change in these reactions.

The metalladithiol $[Cp^*_2Zr(SH)_2]$ (**14**) reacts with the carbonyl complex $[Cp^*_2Zr(CO)_2]$ (**425**) to give the sulfido–hydrosulfido complex $[\{Cp^*_2Zr(SH)\}_2(\mu_2\text{-}S)]$ (**426**) (Eq. (49)) [63].



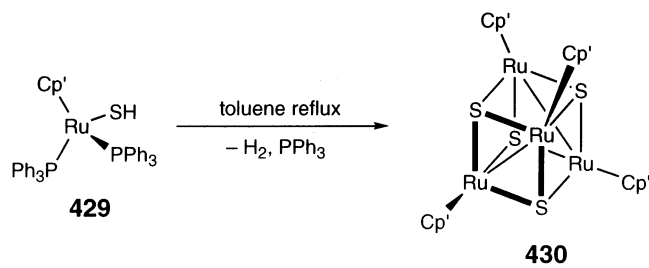
(49)

Complex **426** can also be prepared by the reaction of $[Cp^*_2ZrPh_2]$ with H_2S [78]. Another example of nuclearity expansion by apparent oxidative addition of hydrosulfido ligands is given by the reaction of the hydrosulfido-bridged complex $[\{Re(CO)_4\}_2(\mu_2\text{-}H)(\mu_2\text{-}SH)]$ (**427**) with $[Re_2(CO)_8(NCMe)_2]$, which results in the formation of the spirocyclic complex $[\{Re(CO)_4\}_4(\mu_4\text{-}S)(\mu_2\text{-}H)_2]$ (**428**) (Eq. (50)) [119].



(50)

Rauchfuss and co-workers have revealed that thermolysis of the Ru(II) hydrosulfido complex $[Cp'Ru(SH)(PPh_3)_2]$ (**429**) leads to the formation of the Ru(III) cubane-type sulfido cluster $[(Cp'Ru)_4(\mu_4\text{-}S)_4]$ (**430**) along with H_2 and PPh_3 (Eq. (51)) [291,292]. This transformation may also be associated with oxidative addition of the hydrosulfido ligands.



(51)

5. Conclusions

It is now apparent that hydrosulfido moieties bound to metal(s) are important intermediates in some industrial and biological reactions catalyzed by metal sulfides and metalloproteins. From the inorganic synthetic point of view, hydrosulfido complexes have been shown to be useful building blocks for rational synthesis of polynuclear metal sulfide complexes. Extensive studies have led to development of various preparative methods for hydrosulfido complexes, although they are considerably sensitive to the nature of the ancillary ligands. Unique reactivities of hydrosulfido complexes have also been demonstrated which include addition reactions and nucleophilic substitution. However, much more investigations are necessary to reveal the role of the SH functionality in sulfido-mediated proton transfer reactions relating to biological processes as well as in activation of H_2 on metal sulfide surfaces. Further study will give insights into the mechanisms of intriguing industrial and biological processes including HDS, heterolytic cleavage of H_2, and nitrogen fixation. There is no doubt that preparation of hydrosulfido complexes containing any kind of metals and ancillary ligands as well as their use as building blocks for sulfido cluster synthesis will continue to be a major subject in the chemistry of hydrosulfido complexes.

Appendix A

Table 1 contains selected data for hydrosulfido complexes of transition metals. The complexes are arranged according to the metals, i.e. from early transition metals to late transition metals. Mixed-metal complexes are placed at the end of the section of the earlier transition metals involved. In each metal section, complexes are listed from mononuclear to polynuclear ones, and in order of haptic-ity of the ancillary ligands and the numbers of hydrosulfido ligands.

Table 1
Hydrosulfido complexes of transition metals

Compound	IR[a]	^{1}H-NMR[b]	Remarks[c]	Ref.
Group 4 metals				
$[Cp^*_2TiH(SH)]$ (**181**)	–	2.62	Isolated as a mixture with $Ph_3P{=}S$	[164,165]
$[Cp_2Ti(SH)_2]$ (**21**)	2530	3.38	The Cp′ analogue **316** is reported [191,294]. X-ray for the Cp* analogue **71** [104]: S–H: 1.21(8), 1.40(7); Ti–S–H: 106(3), 116(3)	[60,68,293]
$[Cp_2Ti(SH)(\mu_2\text{-}O)TiCp(\mu_2\text{-}S)_2TiCp_2]$	–	–	X-ray; the SH hydrogen atom is located.	[295]
$[Cp_2Ti(\mu_2\text{-}SH)_2Mo(CO)_4]$ (**248**)	2556, 2522	2.1	The Cp′ analogue **317** is reported.	[191]
$[Cp_2Ti(\mu_2\text{-}SH)_2W(CO)_4]$ (**220**)	2550, 2517	2.05		[191]
$[Cp_2Ti(\mu_2\text{-}SH)_2RuClCp^*]$ (**318**)	2492	2.10	X-ray; S–H: 1.13, 1.20; Ti–S–H: 96.0, 100.4; Ru–S–H: 94.1, 98.6	[244,245]
$[Cp^*_2Zr(OH)(SH)]$	–	0.83		[154]
$[Cp^*_2ZrI(SH)]$ (**35**)	–	2.69		[77,78]
$[Cp^*_2Zr\{OC(Ph){=}CH_2\}(SH)]$ (**164**)	2596	1.50	X-ray	[153]
$[Cp^{tt}_2Zr(OTf)(SH)]$ (**221**)	–	4.04 (major), 6.27 (minor)	X-ray; the SH hydrogen atom is located; two isomers exist in solution.	[192]
$[Cp_2Zr(SH)_2]$ (**11**)	2550	1.94	The ^{t}BuCp (**13**) [61,62] and Cp^{tt} (**360**) [192] analogues are reported. X-ray for the Cp* analogue **14** [63]	[60]
$[\{Cp^*_2Zr(SH)\}_2(\mu_2\text{-}S)]$ (**426**)	–	1.34		[78]
$[(Bu^tC_5H_4)_2Hf(SH)_2]$ (**365**)	–	1.75		[61,62]
Group 5 metals				
$[Ph_4P]_2[Nb(S)_3(SH)]$ (**211**)	–	0.65	X-ray	[180]
$[Et_4N]_2[Nb(O)(S_2)_2(SH)]$ (**209**)	2544 (1848)	−0.09	X-ray; the sulfido analogue **212** is briefly mentioned.	[180]
$[Cp_2Nb(SH)(CO)]$ (**121**)	–	–	X-ray	[130]
$[Cp^{Et}_2Nb(S)(SH)]$ (**133**)	–	−0.41	X-ray	[135]
$[Cp^*_2Nb(S_2)(SH)]$ (**129**)	–	−1.64	X-ray; the Cp^{Et} analogue **132** is reported [135].	[133,134]
$[\{CpNb(CO)_2\}_2(\mu_2\text{-}SH)_2]$	–	–	Originally reported as a sulfido-bridged complex [296]; see also reference 16 in ref [298]	[296,297]

Table 1 (*Continued*)

Compound	IR[a]	^{1}H-NMR[b]	Remarks[c]	Ref.
$[\{CpNb(CO)_2\}_2(\mu_2\text{-}SH)_2(\mu_2\text{-}S)]$	–	–	Originally reported as a complex with three sulfido ligands [296]; see also reference 16 in ref [298]	[296,297]
$[(^t BuCp)_2TaH_2(SH)]$ (**162**)	2555, 2542	−1.46 ($^3J_{HH} = 8$)		[152]
$[Cp^*_2TaS(SH)]$ (**140**)	2538	−0.28		[136]
$[(^t BuCp)_2Ta(SH)(SPr^i)][BF_4]$ (**159**)	2564	–		[150]
$[Cp'_2Ta(SH)(CO)]$	–	−2.1	Decomposes above −30°C	[125]
$[Cp'_2Ta(SH)(\eta^2\text{-}COS)]$	–	−0.10	Decomposes above −25°C	[125]
$[(^t BuCp)_2TaH_2(\mu_2\text{-}SH)Cr(CO)_5]$ (**314**)	2715	−2.25 ($^3J_{HH} = 7$)		[152]
$[(^t BuCp)_2TaH_2(\mu_2\text{-}SH)W(CO)_5]$ (**315**)	2870	−1.37 ($^3J_{HH} = 7$)	X-ray	[152]
Group 6 metals				
$[Cr(SH)(OH_2)_5][SO_4]$	2560	–		[299]
$[Cr(SH)(CO)_5]$	–	–		[300]
[PPN][Cr(SH)(CO)$_5$] (**60**)	–	−4.67	Na(18-crown-6) salt is also reported [301]. X-ray for Na(cryptand) salt [98]: S–H: 1.17(8); Cr–S–H: 134(4)	[97,246]
trans-$[Cr(SH)_2(dmpe)_2]$	2563	–	X-ray	[302]
$[Cp^*Cr(SH)(CO)_3]$ (**69**)	–	−3.44	The Cp analogue **384** is reported [128].	[128,129]
[PPN][$\{Cr(CO)_5\}_2(\mu_2$-SH)] (**321**)	–	−3.58	X-ray; Et_4N [300] and Na(18-crown-6) [301] salts are also reported.	[246,303]
fac-$[(OC)_5Cr(\mu_2\text{-}SH)Mn(CO)_3(PMe_3)_2]$ (**308**)	–	−3.39 ($^3J_{PH} = 9.6$)	The *mer*, *trans* isomer is also isolated (δ_{SH}: −3.85; $^3J_{PH} = 9.8$).	[243]
fac-$[(OC)_5Cr(\mu_2\text{-}SH)Re(CO)_3(PMe_3)_2]$ (**311**)	–	−2.71 ($^3J_{PH} = 8.4$)	The *mer*, *trans* isomer is also isolated (δ_{SH}: −2.31; $^3J_{PH} = 6.2$).	[243]
[PPN][Mo(SH)(CO)$_5$] (**61**)	–	−3.38	Na(cryptand) [98] and Na(18-crown-6) [301] salts are also reported.	[97,246]
$[MoH_2(SH)_2(PMe_3)_4]$ (**76**)	–	–		[106]
$[Ni(phen)_3][Mo(SH)(bipy)(CO)_3]$	–	–		[304]
$[Mo(SH)(S_2CNEt_2)_3]$	2480	–	X-ray; S–H: 0.72; Mo–S–H: 108.0	[305]
$[Mo(SH)(\equiv CNMe_2)(dppe)_2]$ (**142**)	2568	−3.98 ($^3J_{PH} = 6.7$)	X-ray; S–H: 1.63; Mo–S–H: 95.5; depe analogue is reported.	[137]
mer-$[C_3S_2HBu^t_2]$-$[\overline{Mo(O)(SH)_3\{SC(Bu^t)CHC(Bu^t)O\}}]$ (**227**)	2600	–	X-ray	[198]

Table 1 (*Continued*)

Compound	IR[a]	^{1}H-NMR[b]	Remarks[c]	Ref.
$[MoO(SH)(16ansS_4)][OTf]$	–	–	X-ray; $16ansS_4$ = 1,5,9,13-tetrathiacyclohexadecane	[306,307]
$[Mo(SH)(16ansS_4)]_2[OTf]_2$	–	–	X-ray; $16ansS_4$ = 1,5,9,13-tetrathiacyclohexadecane	[306]
trans-[Mo(O)(SH)X] (**157**)	–	–	The *cis* isomer **156** isomerizes to **157** at r.t.; $X = SC_6H_4N(Me)CH_2CH_2N(Me)C_6H_4S^{2-}$	[149]
$[CpMo(SH)(CO)_3]$ (**113**)	–	–	The Cp* analogue **114** is reported [129].	[127–129]
$[Cp_2Mo(SH)_2]$ (**23**)	2498	−2.36		[69]
$[PPN]_2[\{Mo(CO)_4\}_2(\mu_2\text{-}SH)_2]$	–	−2.24		[246]
$[\{Mo(N(p\text{-}Tol))(S_2P(OEt)_2)\}_2\text{-}(\mu_2\text{-}O_2CCF_3)(\mu_2\text{-}S)(\mu_2\text{-}SH)]$ (**170**)	2456	–	X-ray; S–H: 1.2(2); Mo–S–H: 99(8), 111(8)	[156]
$[\{Cp^*Mo(CO)\}_2(\mu_2\text{-}SMe)_2(\mu_2\text{-}SH)]\text{-}[BF_4]$ (**147**)	2470	−2.13	X-ray	[142]
$[(Cp'Mo)_2(\mu_2\text{-}SH)(\mu_2\text{-}SMe)(\mu_2\text{-}S_2CH_2)]$ (**190**)	2380	−1.35	2-Thiophenethiolato and SCH_2COOMe analogues are reported [308].	[167,207]
$[(CpMo)_2(\mu_2\text{-}S)(\mu_2\text{-}SH)(\mu_2\text{-}S_2CH_2)]\text{-}[OTf]$ (**256**)	2420	–	Br salt [208,309] as well as the Cp′ (**188**) and Cp* (**340**) analogues [141] is reported.	[141]
$[(Cp^*Mo)_2(\mu_2\text{-}S)_2(\mu_2\text{-}SH)_2]$ (**279**)	2410	−1.44; −1.50	Two isomers exist in solution. The Cp (**278**) [166], Cp′ (**186**) [166], C_5H_4COOMe [311], and $C_5H_4CH_2CH_2NMe_2$ [312] analogues are reported. For preparation of the Cp′ analogue **186**, see also: ref [287] and reference 20 in ref [288]	[166,224,310]
$[Mo_4(\mu_3\text{-}S)_2(\mu_2\text{-}S)_4(SH)_2(PMe_3)_6]$ (**214**)	2516	–	X-ray	[181,182]
$[Mo_6(\mu_3\text{-}S)_4(\mu_2\text{-}S)_6(SH)_2(PEt_3)_6]$ (**215**)	2497	–	X-ray	[181]
mer, *trans*-$[(OC)_5Mo(\mu_2\text{-}SH)Mn(CO)_3(PMe_3)_2]$ (**309**)	–	−3.37 ($^3J_{PH}$ = 9.0)		[243]
fac-$[(OC)_5Mo(\mu_2\text{-}SH)Re(CO)_3(PMe_3)_2]$ (**312**)	–	−2.21 ($^3J_{PH}$ = 8.4)	The *mer*, *trans* isomer is also isolated (δ_{SH}: −2.33; $^3J_{PH}$ = 9.6).	[243]
$[Et_4N][W(SH)(CO)_5]$ (**62**)	2350	1.38	PPN [97], Na(cryptand) [98], Li [232], and Ph_4As [246] salts are reported. X-ray for Na(18-crown-6) salt [301]	[54,246]
$K_4[W(CN)_7(SH)]$	–	–	X-ray; CN and SH ligands are disordered.	[313]
$[Ph_4P][WS_3(SH)]$ (**153**)	–	–	X-ray: the SH and three S ligands are disordered.	[146,147]
$[WH_2(SH)_2(PMe_3)_4]$ (**77**)	2546 (1850)	–		[107,108]

Table 1 (*Continued*)

Compound	IR[a]	^{1}H-NMR[b]	Remarks[c]	Ref.
$[W(SH)_2(CO)_2(phen)]$ (**46**)	–	–		[87]
$[CpW(SH)(CO)_3]$ (**115**)	2530	−2.75	The Cp* analogue **116** [128,129] as well as $[CpW(SH)(CO)_2(PMe_3)]$ (**179**) [163] is reported.	[127–129,237,314]
$[Fv\{W(SH)(CO)_3\}_2]$ (**117**)	–	−2.28 ($^2J_{WH} = 4.6$)	The $(CO)_2(PMePh_2)$ analogue **45** is reported.	[86]
$[Cp_2W(SH)_2]$ (**24**)	2488	−1.46		[69,293]
$[Et_4N][\{W(CO)_5\}_2(\mu_2\text{-}SH)]$ (**288**)	–	−1.70	Ph_4As salt is also reported [246]. X-ray for Na(18-crown-6) salt [301]	[97,246]
$[\{W(CO)_4\}_2(\mu_2\text{-}SH)_2]$	2570, 2540	0.12		[54]
$[Ph_4P][W(SH)_2(S_2)(\mu_2\text{-}S)(\mu_2\text{-}\eta^1\text{:}\eta^2\text{-}S_2)\text{-}W(O)(S)]$	–	–	X-ray	[315]
$[Ph_4P][(HS)(S)(S_2)W(\mu_2\text{-}\eta^2\text{:}\eta^1\text{-}S_2)\text{-}WS(S_2)_2]$ (**154**)	–	–	X-ray	[148]
$[\{CpW(CO)_3\}_2(\mu_2\text{-}SH)][SbF_6]$	2552	–		[316]
$[W_4(\mu_3\text{-}S)_2(\mu_2\text{-}S)_4(SH)_2(PMe_2Ph)_6]$ (**79**)	2512	–	X-ray; S–H: 1.28; W–S–H: 116.4	[109,110]
fac-$[(OC)_5W(\mu_2\text{-}SH)Mn(CO)_3(PMe_3)_2]$ (**310**)	–	−2.54 ($^3J_{PH} = 9.6$)	The *mer*, *trans* isomer is also isolated (δ_{SH}: −2.95; $^3J_{PH} = 9.4$).	[243]
fac-$[(OC)_5W(\mu_2\text{-}SH)Re(CO)_3(PMe_3)_2]$ (**313**)	–	−1.76 ($^3J_{PH} = 8.3$)	The *mer*, *trans* isomer is also isolated (δ_{SH}: −1.76; $^3J_{PH} = 8.4$).	[243]
$[(OC)_5W(\mu_2\text{-}SH)Re(CO)_2(PMe_3)_3]$	–	−2.16		[317]
$[(OC)_5W(\mu_2\text{-}SH)Fe(CO)_2Cp]$ (**302**)	–	−2.17		[232]
Group 7 metals				
$[Mn(SH)(CO)_5]$	–	–	Readily lose CO to give $[\{Mn(CO)_4\}_2(\mu_2\text{-}SH)_2]$ (**6**)	[162]
mer,*trans*-$[Mn(SH)(CO)_3(PMe_3)_2]$	2559	−3.86 ($^3J_{PH} = 4.2$)	Contaminated with the *fac* isomer: δ_{SH} −3.33 ($^3J_{PH} = 10.5$)	[220]
$[Mn(SH)(CO)_2(PMe_3)_3]$	2570	−3.80 ($^3J_{PH} = 16.7, 4.6$)		[317]
mer,*trans*-$[Mn(SH)(CO)_3\{P(OMe)_3\}_2]$	2580, 2384	−3.70 ($^3J_{PH} = 11.6$)		[317]
[Mn(oespz)(SH)] (**219**)	–	10.3	X-ray; oespz = 2,3,7,8,12,13,17,18-octakis(ethylsulfanyl)--5,10,15,20-tetraazaporphyrinato(2–)	[184]

Table 1 (*Continued*)

Compound	IR[a]	^{1}H-NMR[b]	Remarks[c]	Ref.
$[\{Mn(CO)_3\}_2(\mu_2\text{-dppm})(\mu_2\text{-H})(\mu_2\text{-SH})]$ (**125**)	–	−0.8 ($^3J_{PH} = 20$); −2.3 ($^3J_{PH} = 15$)	Two isomers exist in solution; μ_2-$(EtO)_2PN(Et)P(OEt)_2$ analogue is reported.	[132]
$[Mn(CO)_3(PEt_3)(\mu_2\text{-SH})(\mu_2\text{-SCHPCy}_3)\text{-}Mn(CO)_3]$ (**202**)	–	−3.29 ($^3J_{PH} = 16$)	μ_2-$SCHPPr^i_3$ analogue is reported.	[174]
$[\{Mn(CO)_4\}_2(\mu_2\text{-SH})_2]$ (**6**)	2568, 2529, 2480	−0.54	The *syn* and *anti* isomers exist. ν_{SD}: 1867, 1841; 1806 cm^{-1} [318].	[127,162,318]
$[\{Mn(CO)_3(PMe_3)\}_2(\mu_2\text{-SH})_2]$	2480	−2.97 ($^3J_{PH} = 15$)		[220]
$[\{Mn(CO)_2(PMe_3)\}_2(\mu_2\text{-SH})_2(\mu_2\text{-CO})]$	2530	−2.38 ($^3J_{PH} = 2.5$)		[220]
$[Ph_4P][\{Mn(CO)_3\}_2(\mu_2\text{-SH})_3]$ (**218**)	2524, 2495, 2487	–	X-ray; S–H: 1.15(5), 1.38(5); Mn–S–H: 99(2), 111(2), 117(2)	[183]
$[Ph_4P]_2[\{Mn(CO)_3\}_3(\mu_3\text{-}\eta^1\text{:}\eta^1\text{:}\eta^1\text{-}S_2)\text{-}(\mu_3\text{-}\eta^1\text{:}\eta^1\text{:}\eta^2\text{-}S_2)(\mu_2\text{-SH})_2]$ (**217**)	–	–	X-ray	[183]
$[\{Mn(CO)_3\}_4(\mu_3\text{-SH})_4]$ (**177**)	2561	−3.16		[162]
$[(OC)_3Mn(\mu_2\text{-SH})(\mu_2\text{-dppm})_2Rh(CO)]\text{-}[BF_4]$ (**247**)	–	−2.67 ($^3J_{PH} = 13, 11$)	OTf salt is also reported.	[121]
mer, *trans*-$[Re(SH)(CO)_3(PMe_3)_2]$	2560	−2.77 ($^3J_{PH} = 4.8$)	The *fac* isomer is also isolated (δ_{SH}: −2.37; $^3J_{PH} = 9.5$).	[220]
$[Re(SH)(CO)_2(PMe_3)_3]$	2558	−2.72 ($^3J_{PH} = 13.2, 5.8$)		[317]
$[Re(SH)(EtC{\equiv}CEt)_3]$ (**50**)	2555	1.15		[90]
$[Re(CO)_3(NH_3)(\mu_2\text{-SH})(\mu_2\text{-SCHPCy}_3)\text{-}Re(CO)_3]$ (**201**)	–	−1.13	X-ray; the PEt_3 analogue **203** is reported.	[174]
$[\{Re(CO)_4\}_2(\mu_2\text{-SH})_2]$ (**176**)	2572, 2541, 2490	−0.89	The *syn* and *anti* isomers exist.	[162]
syn-$[\{Re(CO)_3(PMe_3)\}_2(\mu_2\text{-SH})_2]$	2553, 2524, 2475	−1.13 ($^3J_{PH} = 11.5$)	The *anti* isomer is also reported (ν_{SH}: 2570, 2400, 2380; δ_{SH}: −1.25 ($^3J_{PH} = 12.0$)).	[220]
$[(ReCl)_2(\mu_2\text{-SH})_2(\mu_2\text{-dppm})_2]$ (**43**)	2451	–	X-ray; S–H: 1.2(1), 1.5(2); Re–S–H: 98(6)–112(9)	[82,83]
$[(ReBr_2)_2(\mu_2\text{-H})(\mu_2\text{-SH})(\mu_2\text{-dppm})_2]$ (**100**)	2532	16.2	X-ray; Cl analogue is reported.	[82,118]
$[\{Re(CO)_4\}_2(\mu_2\text{-H})(\mu_2\text{-SH})]$ (**427**)	–	−0.47		[119]
$[\{Re(CO)_3\}_4(\mu_3\text{-SH})_4]$ (**178**)	2548	−1.18		[162]
$[Re_5(CO)_{17}(\mu_2\text{-SH})(\mu_4\text{-S})_2\{C(NMe_2)_2\}_2]$	–	1.85	X-ray	[186]

Table 1 (*Continued*)

Compound	IR[a]	^{1}H-NMR[b]	Remarks[c]	Ref.
Group 8 metals				
$[Et_4N][Fe(SH)(CO)_4]$	–	−4.08		[319]
$[Fe(SH)_2(dmpe)_2]$	2550	−7.02 ($^3J_{PH}$ = 7.5)	X-ray	[302]
$[Fe(SH)\{P(CH_2CH_2PPh_2)_3\}][BPh_4]$ (**52**)	–	–	X-ray	[92]
[Fe(tap)(SH)]	–	6.75	X-ray; tap = 5,10,15,20-tetrakis(*p*-methoxyphenyl)-porphyrinato(2–); oep analogue is briefly described [85].	[320]
$[\{Fe(CO)_3\}_2(\mu_2\text{-NHMe})(\mu_2\text{-SH})]$	2358; 2326	−1.27; −3.59	Isolated as a mixture of two isomers	[321]
$[\{Fe(CO)_3\}_2(\mu_2\text{-SH})_2]$ (**150**)	–	0.02, −2.21; −0.40; −2.43	Three isomers exist in solution.	[143,144]
$[\{Fe(NO)_2\}_2(\mu_2\text{-SH})_2]$ (**151**)	2546	–		[145]
$[(ppp)Fe(\mu_2\text{-SH})_3Fe(ppp)][ClO_4]$ (**9**)	–	–	X-ray; BF_4 salt is also reported.	[93]
$[Fe_3(CO)_9(\mu_2\text{-SH})(\mu_3\text{-SBu}^t)]$	–	–	X-ray	[179]
$[Bu_4N]_2[Fe_4(\mu_3\text{-S})_4(SH)(LS_3)]$ (**372**)	–	46.5	LS_3 = a tridentate thiolate ligand	[85]
$[Ph_4P]_2[\{Fe(SH)\}_4(\mu_3\text{-S})_4]$ (**16**)	–	47.6	X-ray; Bu^n_4N [85] and Pr^n_4N [64] salts are also reported.	[84,85]
$[(HS)Fe(Cp'Mo)_3(\mu_3\text{-S})_4]$ (**195**)	–	–	X-ray	[173]
$[\{Fe(SH)\}_2(CpCr)_2(\mu_3\text{-S})_4]$ (**20**)	2310	–	X-ray; S–H: 1.6	[67]
$[RuH(SH)(PPh_3)_3]$ (**31**)	2525	1.6 ($^3J_{PH}$ = 16, $^3J_{HH}$ = 1)		[74]
$[RuH(SH)(CO)(PPr^i_3)_2]$ (**222**)	–	1.76 ($^3J_{PH}$ = 17.4)		[194]
$[Ru(CH{=}CHPh)(SH)(CO)(PPr^i_3)_2]$ (**234**)	–	1.49 ($^3J_{PH}$ = 16.2)	CH=CHCOOMe analogue is reported.	[194]
$[RuH(SH)(CO)_2(PPh_3)_2]$	–	−3.00 ($^3J_{PH}$ = 4.9, $^3J_{HH}$ = 2.6)	The PPr^i_3 analogue **224** is reported [194].	[322]
$[Ru(SH)_2(CO)_2(PPh_3)_2]$	–	−1.93 ($^3J_{PH}$ = 6.8)	X-ray; S–H: 1.0(2), 1.2(1); Ru–S–H: 84(12), 99(14)	[76,322]
$[RuH(SH)(dppm)_2]$ (**33**)	–	−3.55		[76]
$[Ru(SH)_2(dppm)_2]$ (**34**)	–	−1.92 (*cis*). −3.73 (*trans*; $^3J_{PH}$ = 5.7)	Isolated as a *cis*-*trans* mixture	[76]
$[Ph_4P][Ru(N)Me_3(SH)]$ (**167**)	2521 (1830)	−0.64	X-ray; S–H: 1.1(2); Ru–S–H: 100(10)	[155]
$[Ru(SH)(S_2CNMe_2)(CO)(PPh_3)_2]$ (**324**)	–	–	X-ray; the SH hydrogen atom is located.	[247]
[Ru(NO)(SH)(ttp)]	–	−6.20	ttp = tetra-*p*-tolylporphyrinato(2–)	[79]
$[CpRu(SH)(PPh_3)_2]$ (**267**)	–	−3.15 ($^3J_{PH}$ = 7)	The Cp′ (**429**) [291], ThiCp [124] (ThiCp = η^5-$C_5H_4CH_2C_4H_3S$), and dppe [160] analogues are reported.	[124,160, 225,291]

Table 1 (*Continued*)

Compound	IR[a]	^{1}H-NMR[b]	Remarks[c]	Ref.
[CpRu(SH)(CO)(PPh_3)] (**304**)	–	−3.58 ($^3J_{PH}$ = 7)	X-ray	[124,225,234,291]
[Cp*Ru(SH)(PMe_3)$_2$] (**38**)	2508	−4.54 ($^3J_{PH}$ = 8.42)	dippe analogue is reported [101].	[80]
[Cp*RuH(SH)(PEt_3)$_2$][BPh_4] (**67**)	2670	−2.79 ($^3J_{PH}$ = 8.4)	X-ray; S–H: 1.56; Ru–S–H: 123.97; the dippe analogue **68** is reported [101].	[100]
[{Ru(PMe_2Ph)$_3$}$_2$(μ_2-SH)$_3$][PF_6]	2540	–		[73]
[($PhMe_2P$)$_3$Ru(μ_2-SH)$_3$Ru(SH)-(PMe_2Ph)$_2$] (**32**)	2525 (1810)	−1.9 to −3.2	X-ray; S–H: 1.19(7)–1.37	[75]
[RuI(SH)(CNMe)(CO)(PPh_3)]$_2$ (**145**)	–	–	Pr, Bu, and CH_2Ph analogues are reported.	[138]
[{Ru(S_2CNMe_2)(PPh_3)}$_2$(μ_2-SH)$_2$] (**322**)	–	–	X-ray; the SH hydrogen atoms are located.	[247]
[Ru_2(CO)$_3$H(μ_2-P–P)$_2$(μ_2-SH)] (**97**)	–	−1.67 ($^3J_{PH}$ = 13.8)	P–P = (Pr^iO)$_2$PN(Et)P(OPr^i)$_2$	[115,117]
[{Ru(CO)$_2$}$_2$(μ_2-P–P)$_2$(μ_2-SH)][SbF_6] (**94**)	–	0.63 ($^3J_{PH}$ = 13.9)	P–P = (Pr^iO)$_2$PN(Et)P(OPr^i)$_2$	[116,117]
[{RuCl(bisallyl)}$_2$(μ_2-Cl)(μ_2-SH)]	2463	−0.34; −0.64	Bisallyl = η^3:η^3-$C_{10}H_{16}$; not isolated in analytically pure form; two isomers exist in solution.	[323]
[{CpRu(PPh_3)$_2$}$_2$(μ_2-SH)][OTf] (**320**)	–	−2.17 ($^3J_{PH}$ = 7)	Decomposes within a few minutes	[124]
[(Cp*RuCl)$_2$(μ_2-SH)$_2$] (**25**)	2462 (1792)	5.13; 5.11	Two isomers exist in solution. X-ray; S–H: 1.18; Ru–S–H: 109.5	[70]
[(Cp*Ru)$_2$(μ_2-SH)$_2$(μ_2-dppm)] (**41**)	–	−2.77 ($^3J_{PH}$ = 11.7)		[81]
[Ru_5(μ_5-C)(μ_2-H)(μ_2-SH)(CO)$_{14}$] (**112**)	–	−3.02		[123]
[Ru_6(μ_4-S)(μ_2-SH)(μ_3-pyS)(μ_2-CO)$_2$-(CO)$_{15}$]	2481	–	X-ray; pyS = 2-SC_5H_4N	[178]
[OsH(SH)(CO)(PPr^i_3)$_2$] (**223**)	–	4.14 ($^3J_{PH}$ = 18.7)		[194]
[Os(CH=CHPh)(SH)(CO)(PPr^i_3)$_2$] (**235**)	–	3.42 ($^3J_{PH}$ = 17.7)		[194]
[OsH(SH)(CO)$_2$(PPr^i_3)$_2$] (**225**)	–	−2.46 ($^3J_{HH}$ = 6.0, $^3J_{PH}$ = 1.2)	(CO){P($OMe)_3$}(PPr^i_3)$_2$ analogue is reported.	[194]
[Os_3(CO)$_{10}$(μ_2-SH)(μ_2-dmpymt)]	–	2.25	X-ray; dmpymt = 4,6-dimethylpyrimidine-2-thione	[324]
[Os_5(μ_5-C)(μ_2-H)(μ_2-SH)(CO)$_{14}$]	–	–	Not isolated; a related pentadecacarbonyl cluster is also reported.	[123]

Table 1 (*Continued*)

Compound	IR[a]	^{1}H-NMR[b]	Remarks[c]	Ref.
Group 9 metals				
$[Co(SH)\{P(CH_2CH_2PPh_2)_3\}][BPh_4]$ (**53**)	–	–	The $N(CH_2CH_2PPh_2)_3$ analogue **385** is reported.	[92]
$\{[Co(\mu_2\text{-}SH)(14aneN_4)][ClO_4]\}_n$	2554	–	X-ray; Co–S–H: 87(5)–92(6); 14aneN$_4$ = 1,4,8,11-tetraazacyclotetradecane	[196]
$[\{Co(\mu_2\text{-}SH)(14aneN_4)\}_2][SH]_2$	2577, 2531	–	X-ray; 14aneN$_4$ = 1,4,8,11-tetraazacyclotetradecane	[196]
$[(CpCo)_2(\mu_2\text{-}PMe_2)_2(\mu_2\text{-}SH)][PF_6]$	–	–		[140]
$[Co_3(\mu_3\text{-}S)_2(\mu_2\text{-}SH)_2(\mu_2\text{-}PEt_2)(PHEt_2)_6][ClO_4]_2$ (**19**)	–	−2.25	X-ray	[66]
$[Rh(SH)(CO)(PPh_3)_2]$ (**123**)	–	−1.21 ($^2J_{RhH}$ = 1.6, $^3J_{PH}$ = 18.1)	X-ray; S–H: 1.3	[131]
$[Rh(SH)\{P(CH_2CH_2PPh_2)_3\}]$ (**56**)	2540	−3.11	X-ray	[94,95]
$[RhH(SH)\{P(CH_2CH_2PPh_2)_3\}][OTf]$	2560	−2.52		[94,95]
[RhH(SH)X]	–	–	X = a macrocyclic ligand, $CH_2\{CH_2N{=}CMeC(Et){=}NO\}_2BF_2^-$	[161]
$[Rh(SH)_2X]$ (**172**)	2580	−1.55	X = a macrocyclic ligand, $CH_2\{CH_2N{=}CMeC(Et){=}NO\}_2BF_2^-$	[161]
$[Cp^*RhPh(SH)(PMe_3)]$	–	−2.994 (d, J = 3.6)		[325]
$[Cp^*Rh(SH)_2(PMe_3)]$ (**387**)	–	–		[258]
$[\{RhHCl(PPh_3)_2\}_2(\mu_2\text{-}SH)_2]$ (**66**)	–	–	X-ray; S–H: 1.04; Rh–S–H: 99(2), 104(2)	[99]
$[\{Rh(CO)\}_2(\mu_2\text{-dppm})_2(\mu_2\text{-}SH)][PF_6]$	–	2.82		[139]
$[\{(triphos)RhH\}_2(\mu_2\text{-}SH)_2][BPh_4]_2$ (**194**)	2540	2.12	X-ray; Rh–S–H (av.): 92(6)	[170]
$[(Cp^*Rh)_2(\mu_2\text{-}CH_2)_2(\mu_2\text{-}SH)][BPh_4]$ (**241**)	2496	−2.730	X-ray; BF_4 salt is also reported.	[326]
$[\{Cp^*Rh(SH)\}_2(\mu_2\text{-}CH_2)_2]$ (**240**)	2550	−3.317 ($^2J_{RhH}$ < 1)	X-ray; the SH hydrogen atoms are located.	[326]
$[(Cp^*RhCl)_2(\mu_2\text{-}SH)_2]$ (**26**)	2511	−0.14; −0.23	X-ray; S–H: 1.23, 1.24; Rh–S–H: 83.8–110.5; two isomers exist in solution.	[71,72]
$[(Cp^*Rh)_2(\mu_2\text{-}SH)_3]Cl$ (**28**)	2231	3.19, 2.99, −1.60	X-ray; S–H: 1.12–1.29; Rh–S–H: 100.1–108.8; BPh_4 salt (two isomers in solution) is also reported.	[72]
$[(HS)Rh(\mu_2\text{-}H)(\mu_2\text{-dppm})_2Mn(CO)_3]$ (**106**)	–	−0.31 ($^2J_{RhH}$ = 2, $^3J_{PH}$ = 16)		[121]
$[(OC)Rh(\mu_2\text{-}SH)(\mu_2\text{-dppm})_2IrH(CO)]$ (**90**)	–	−2.91 ($^3J_{PH}$ = 6.4)		[114]
$[IrClH(SH)(CO)(PPh_3)_2]$ (**64**)	–	–	X-ray; the SH and CO groups are disordered.	[99,327]

Table 1 (*Continued*)

Compound	IR[a]	^{1}H-NMR[b]	Remarks[c]	Ref.
$[IrCl_2(SH)(PMe_2Ph)_3]$	–	−1.08	X-ray; S–H: 1.00(1)	[91]
$[IrH(SH)(PMe_3)_4][PF_6]$	–	−2.05 ($^3J_{PH}$ = 16, $^3J_{HH}$ = 2)	X-ray; S–H: 1.321(66); Ir–S–H: 111(3)	[328]
$[Ir(NO)(SH)(PPh_3)_2][ClO_4]$	2525	–	Not isolated in analytically pure form	[329]
$[Ir(NO)(SH)_2(PPh_3)_2]$	2544	−1.05 ($^3J_{PH}$ = 12.7)		[329,330]
[(triphos)IrH_2(SH)] (**3**)	–	−2.58		[30]
[Cp*IrCl(SH)(PMe_3)] (**344**)	2512	−1.13 ($^3J_{PH}$ = 3.7)		[257,258]
[Cp*IrH(SH)(PMe_3)] (**287**)	2524	−2.18 ($^3J_{PH}$ = 4.6, $^3J_{HH}$ = 1.8)	The CS_2 insertion product, [Cp*Ir{SC(S)H}(SH)(PMe_3)], is also reported.	[195]
[Cp*Ir$(SH)_2(PMe_3)$] (**269**)	2521, 2496	−1.93 ($^3J_{PH}$ = 4.5)	X-ray; S–H: 1.02(14), 1.25(18); the P(*p*-Tol)$_3$ analogue **388** is reported [258].	[195]
$[Ir_2H(\mu_2\text{-SH})(CO)_3(\mu_2\text{-dppm})_2]$ (**83**)	–	−1.07	Stable only at −60°C or below	[114]
$[\{IrH(PPh_3)_2\}_2(\mu_2\text{-H})(\mu_2\text{-S})(\mu_2\text{-SH})]$ (**293**)	2672	0.39; −0.91	X-ray; two isomers exist in solution.	[188]
$[\{IrH(PPh_3)_2\}_2(\mu_2\text{-H})(\mu_2\text{-SH})(\mu_2\text{-SPr}^i)]$-$[BF_4]$ (**298**)	2673	−2.4; −0.1; 0.4	X-ray; three isomers exist in solution. The SMe analogue **296** is reported.	[188]
$[\{IrH(PPh_3)_2\}_2(\mu_2\text{-H})(\mu_2\text{-SH})_2][BF_4]$ (**292**)	2677, 2523	0.50, −2.51; −3.36; −0.24	X-ray; three isomers exist in solution.	[188]
$[(Cp^*IrCl)_2(\mu_2\text{-SH})_2]$ (**27**)	2492	1.01; 0.91	X-ray; S–H: 1.30; Ir–S–H: 95.1, 112.5; two isomers exist in solution.	[71,72]
$[(Cp^*Ir)_2(\mu_2\text{-SH})_3][BPh_4]$ (**10**)	2478	−0.71, −0.83, −1.08; −0.34	X-ray; two isomers exist in solution. Cl salt is also reported.	[72]
Group 10 metals				
$[NiH(SH)(PCy_3)_2]$	–	–		[331]
$[NiPh(SH)(PEt_3)_2]$	2560	−2.0 ($^3J_{PH}$ = 18)	*p*-Tol and *p*-$MeOC_6H_4$ analogues are reported.	[332]
[NiPh(SH)(dippe)] (**411**)	–	−1.23 ($^3J_{PH}$ = 25.3, 3.5)	dcpe analogue is reported.	[282]
$[Ni(SH)_2$(dppe)] (**272**)	2535	−0.77	The dippe (**368**) [268] and $(p\text{-Tol})_2PCH_2CH_2PPh_2$ [335] analogues are reported.	[219,333,334]
[Na(15-crown-5)][Ni(SH)(S_2L)]	2517	−2.4	X-ray; S–H: 1.120; Ni–S–H: 100.0; S_2L = 1,3-imidazolidinyl-*N*,*N*′-bis(-2-benzenethiolato)	[336]

Table 1 (*Continued*)

Compound	IR[a]	^{1}H-NMR[b]	Remarks[c]	Ref.
[Ni(SH)(triphos)] (**204**)	–	–	X-ray	[175,176]
[Ni(SH){N($CH_2CH_2PPh_2$)$_3$}]	2545	–		[274]
[Ni(SH){($PPh_2CH_2CH_2$)$_2$-$NCH_2CH_2NHEt_2$}][BF_4]$_2$	–	–	X-ray	[337]
[Ni(SH)L][BPh_4]	–	–	L = ppp, ($Ph_2PCH_2CH_2$)$_2$NPr^n	[337]
[Ni(SH){P($CH_2CH_2PPh_2$)$_3$}][BPh_4] (**54**)	–	–	X-ray; N($CH_2CH_2PPh_2$)$_3$ analogue is reported.	[92]
[CpNi(SH)(PBu^n_3)] (**229**)	2500–2700	5.25 ($^3J_{PH}$ = 1)		[338]
[{Ni(μ_2-SH)(14aneN$_4$)}$_2$][SH]$_2$	2529, 2579	–	X-ray; 14aneN$_4$ = 1,4,8,11-tetraazacyclotetradecane; [{Ni(μ_2-SH)(14aneN$_4$)}$_2$][Ni(SH)$_2$(14aneN$_4$)][ClO_4]$_2$ is also reported.	[196]
[Ni_3(μ_3-S)$_2$(SH)(PEt_3)$_5$][BPh_4] (**18**)	–	−1.85 ($^3J_{PH}$ = 15.4)	X-ray; S–H: 1.20(15); Ni–S–H: 116(6)	[65]
trans-[Pd(SH)$_2$(PBu^i_3)$_2$] (**58**)	–	−1.33 ($^3J_{PH}$ = 10)	X-ray; *cis*-PPh_3 analogue is reported [339].	[96]
[PdMe(SH)(dcpe)]	–	0.248 ($^3J_{PH}$ = 16, 5)		[126]
[Pd(SH)$_2$(dppe)] (**273**)	2542	−0.55	(p-Tol)$_2$$PCH_2CH_2PPh_2$ analogue is reported [335]	[219,334,340]
[Na(15-crown-5)][Pd(SH)(S_2L)]	2535	−2.4	X-ray; S–H: 1.259; Pd–S–H: 96.0; S_2L = 1,3-imidazolidinyl-*N*,*N*′-bis(2-benzenethiolato)	[336]
[(HS)Pd(μ_2-S)(μ_2-dppm)$_2$Pd(SH)]	–	−1.60 ($^3J_{PH}$ = 5.47)		[111]
[{(allyl)Pd}$_2$(μ_2-SH)$_2$]	2535, 2510	–	Decomposes above −60°C	[341]
[Pd_3(SH)(μ_3-S)(μ_2-dppm)$_3$][PF_6] (**110**)	–	−2.16 ($^3J_{PH}$ = 8)		[122]
trans-[PtH(SH)(PEt_3)$_2$] (**5**)	2561	−1.1 ($^3J_{PH}$ = 11, $^3J_{HH}$ = 3)	PPh_3 [344] and P(CH_2Ph)$_3$ [345] analogues are reported.	[342,343]
trans-[PtI(SH)(PEt_3)$_2$]	–	−0.8 ($^3J_{PH}$ = 11)		[342]
trans-[Pt(SH)$_2$(PEt_3)$_2$]	–	−1.5 ($^3J_{PH}$ = 10)		[342]
cis-[Pt(SH)$_2$(PPh_3)$_2$] (**265**)	2560	0.18 ($^3J_{PH}$ = 8.5)	X-ray; the *trans* isomer is briefly mentioned in ref [222].	[231,334,339,340,346]
[PtH(SH)(dppp)]	–	−0.3 ($^3J_{PH}$ = 21.0, 5.3; $^3J_{HH}$ = 4.2)		[347]
[PtMe(SH)(dppe)]	2550, 2540	−0.14 ($^2J_{PtH}$ = 59.0)		[348]

Table 1 (*Continued*)

Compound	IR[a]	^{1}H-NMR[b]	Remarks[c]	Ref.
[PtPh(SH)(dcpe)]	–	0.168 ($^3J_{PH} = 16$, 6,$^2J_{PtH} = 65$)	X-ray; CH_2Bu^t and Me analogues are reported	[126]
[Pt(SH)$_2$(dcpe)]	–	0.282 ($^3J_{PH} = 9$, 6,$^2J_{PtH} = 59$)	The dppe analogue **274** [219] and *p*-Tol$_2$PCH$_2$CH$_2$PPh$_2$ analogue [335] are reported.	[126]
[PtH(SH)(triphos)]	–	−0.50 ($^3J_{PH} = 20.0$, 4.5; $^3J_{HH} = 4.0$)		[347]
[Na(15-crown-5)][Pt(SH)(S$_2$L)]	2520	−1.7	S$_2$L = 1,3-imidazolidinyl-*N*,*N*′-bis-(2-benzenethiolato)	[336]
trans-[{PtH(PEt$_3$)$_2$}$_2$(μ_2-SH)][BF$_4$]	–	−0.4		[349]
[(allyl)Pt(SH)]$_x$	–	–	Thermally unstable	[341]
[(PtMe$_3$)$_4$(μ_3-SH)$_4$] (**228**)	2537	−3.29 ($^2J_{PtH} = 15.2$)		[199]
Group 11 metals				
[Ag(SH){S = C(NEt$_2$)NHCOPh}$_3$]	–	–	X-ray	[185]
[PPN][Au(SH)$_2$] (**226**)	–	−1.22	X-ray	[197]
[PPN][Au(C$_6$F$_5$)(SH)]	–	−1.16	C$_6$H$_{5-n}$(NO$_2$)$_n$ ($n = 1$, 3) analogues are reported.	[350]
[Bu$_4$N][Au(C$_6$F$_5$)$_3$(SH)] (**392**)	–	−0.45		[187]
[Bu$_4$N][{Au(C$_6$F$_5$)$_3$}$_2$(μ_2-SH)] (**391**)	–	–	X-ray; the SH hydrogen atom is located.	[187]

[a] ν_{SH} in cm^{-1}. Corresponding ν_{SD} values are in parentheses.
[b] δ in ppm. *J* values are in Hz.
[c] Bond distances in (Å); angles in (°).

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