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Review

Advances in the chemistry of organometallic complexes with 1,2-dichalcogenolato-*o*-carborane ligands

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Contents

Abstract

This review describes recent advances in the synthesis and structural characterization of organometallic complexes with 1,2-dichalcogenolato-1,2-dicarba-*closo*-dodecaborane (**12**) ($E_2C_2B_{10}H_{10}$, where E = S, Se, Te) ligands, with emphasis on the complexes that show interesting reactivity patterns.

Keywords: Dichalcogenolato ligands; *o*-Carborane; Organometallic complexes; Lanthanide; Synthesis

1. Introduction

Mononuclear Cp*M half-sandwich complexes are useful model complexes in which one hemisphere of the coordination shell is blocked by a six-electron donor substituted cyclopentadienyl ring. Chalcogenolato ligands can be accommodated in the remainder of the coordination sphere to form a variety of complexes [1,2].

In this connection, 1,2-dicarba-*closo*-dodecaborane-1,2-dichalcogenolates (*ortho*-carborane dichalcogenolates) are of particular interest as sterically demanding, chemically robust chelating dichalcogenolato ligands. The dilithium dichalcogenolate carboranes $Li_2E_2C_2B_{10}H_{10}$ (E = S, Se, Te) can easily be prepared by the insertion of elemental chalcogen into the Li–C bonds of dilithium carborane which can be obtained by the reaction of carborane with *n*-butyl lithium [3,4]. Owing to their rigid backbone, carborane dichalcogenolato ligands have allowed the synthesis of complexes exhibiting novel structures [5].

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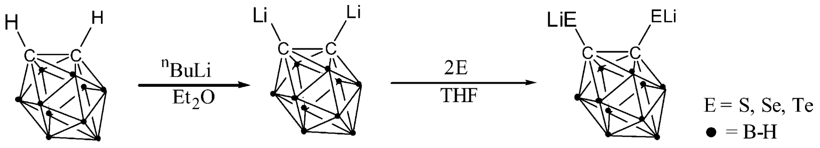

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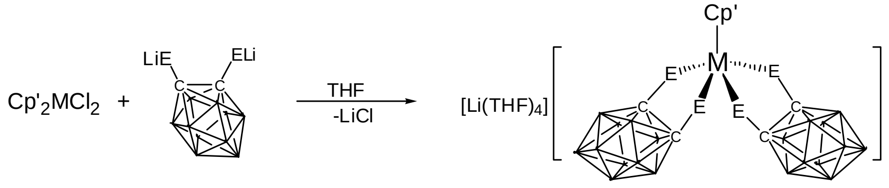
The molecular structure of the lithium reagent $Li_2S_2C_2B_{10}H_{10}$ is a dimer in the solid state. One lithium atom of the dilithium dithiolate carborane is linked to three sulfur atoms to form a binuclear structure and the other lithium atom is bound to the three oxygen atoms of the THF ligands and one sulfur atom of the carborane dithiolate (Fig. 1).

2. Synthesis of the complexes

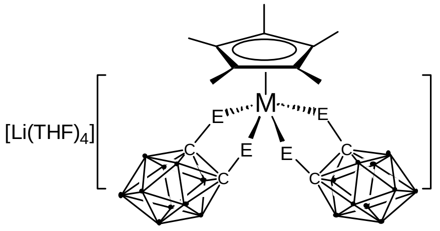
2.1. Titanium, zirconium and hafnium complexes

Metallocene complexes Cp'_2MCl_2 ($Cp' = \eta^5-C_5H_5$, $\eta^5-{}^tBuC_5H_4$, $\eta^5-1,3-{}^tBu_2C_5H_3C_5H_3$; M = Ti, Zr, Hf) react with dilithium carborane dichalcogenolates $Li_2E_2C_2B_{10}H_{10}$ (E = S, Se) to form mononuclear ionic half-sandwich complexes $[Li(THF)_4][Cp'M(E_2C_2B_{10}H_{10})_2]$ (**2**) [6] in which one of the cyclopentadienyl ring is lost. Attempts to synthesize neutral metallocene complexes $Cp'_2M(E_2C_2B_{10}H_{10})$ from the substitution reactions of Cp'_2MCl_2 (M = Ti, Zr, Hf) with an equimolar amount of $Li_2E_2C_2B_{10}H_{10}$ (E = S, Se), led only to the complexes **2**, isolated as sole products.



2 $Cp' = \eta^5-C_5H_5$, $\eta^5-{}^tBuC_5H_4$, $\eta^5-{}^tBu_2C_5H_3$;
M = Ti, Zr Hf; E = S, Se

Analogous complexes $[Li(THF)_4][Cp^*M(E_2C_2B_{10}H_{10})_2]$ ($Cp^* = \eta^5-C_5Me_5$; M = Ti, Zr, Hf; E = S, Se) (**3**) can be directly obtained from the reaction of Cp^*MCl_3 (M = Ti, Zr, Hf) with $Li_2E_2C_2B_{10}H_{10}$ (E = S, Se). The molecular structures of **2** ($Cp' = \eta^5-C_5H_5$, $\eta^5-{}^tBuC_5H_4$, $\eta^5-1,3-{}^tBu_2C_5H_3$; M = Ti; E = S) and **3** (M = Zr; E = S, Se) have been determined by X-ray crystallographic studies [6].



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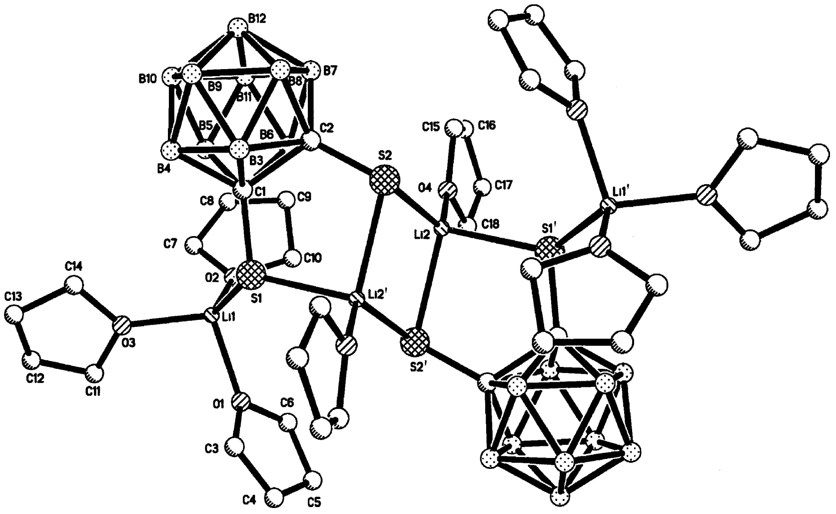
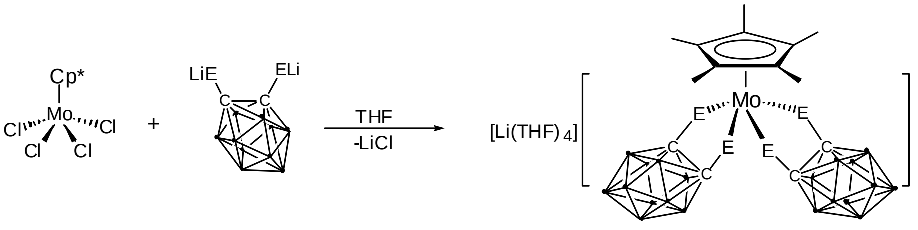


Fig. 1. Molecular structure of $[(THF)_4Li_2S_2C_2B_{10}H_{10}]_2$ (**1**).

2.2. Molybdenum and tungsten complexes

The reaction between Cp^*MoCl_4 and $Li_2E_2C_2B_{10}H_{10}$ in THF solution leads to the salts of $[Li(THF)_4][Cp^*Mo(E_2C_2B_{10}H_{10})_2]$ (E = S, Se) (**4**), in which the molybdenum atom is reduced from Mo(V) to Mo(IV) by the chalcogenolato ligands [7,8].



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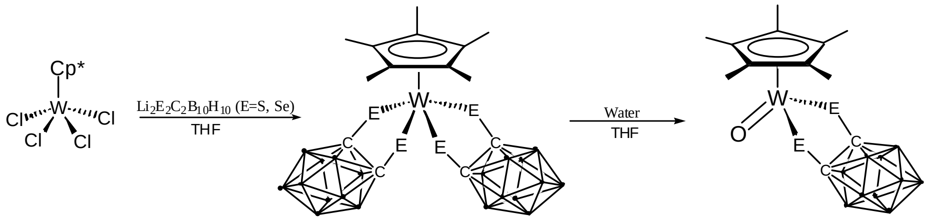
The ^1H-NMR spectra of both complexes **4** exhibit the intense signals (δ = 1.85 ppm (E = S) and 1.88 ppm (E = Se)) arising from the methyl substituents of the Cp* ring thereby indicating complexes to be diamagnetic.



5 **6**

The analogous tungsten derivative Cp^*WCl_4 reacts with $Li_2E_2C_2B_{10}H_{10}$ (E = S, Se) under the same reaction conditions to give a neutral symmetrical bis (carborane dichalcogenolate) tungsten complexes $Cp^*W(E_2C_2B_{10}H_{10})_2$ (E = S, Se) (**5**) in good yields. The complexes **5** can easily be converted to the corresponding terminal oxo complexes $Cp^*W(O)(E_2C_2B_{10}H_{10})$ (**6**) in THF solution in the presence of limited amounts of water [8]. Both complexes **5** and **6** are shown to be paramagnetic by their NMR spectra.

The X-ray crystal structures of the 15-electron neutral complexes $Cp^*W(E_2C_2B_{10}H_{10})_2$ (E = S, Se) (**5**) (Fig. 2) show that the tungsten atom is located in the center of a tetragonal pyramid. The WSe_2C_2 rings are planar. The X-ray crystal structure of $Cp^*W(O)(Se_2C_2B_{10}H_{10})$ (**6**) (Fig. 3) indicates a distorted tetrahedral coordination sphere with a W=O distance of 1.754 Å and a planar WSe_2C_2 ring.

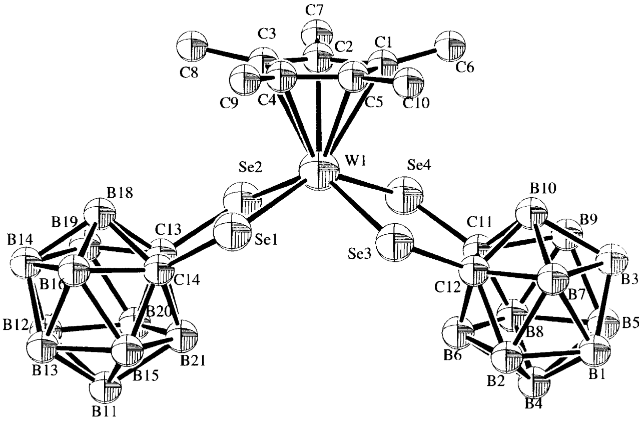


Fig. 2. Molecular structure of $Cp^*W(Se_2C_2B_{10}H_{10})_2$ (**5**).

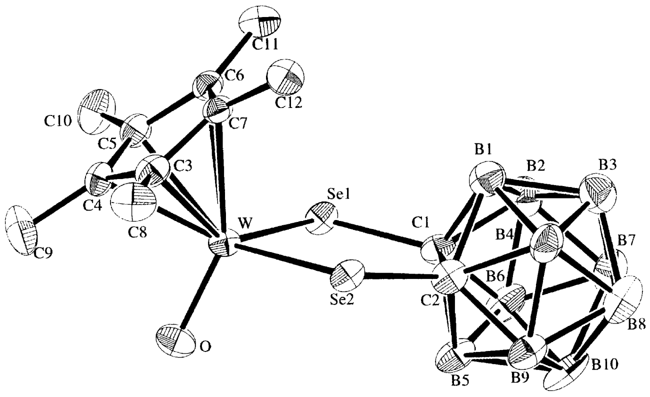
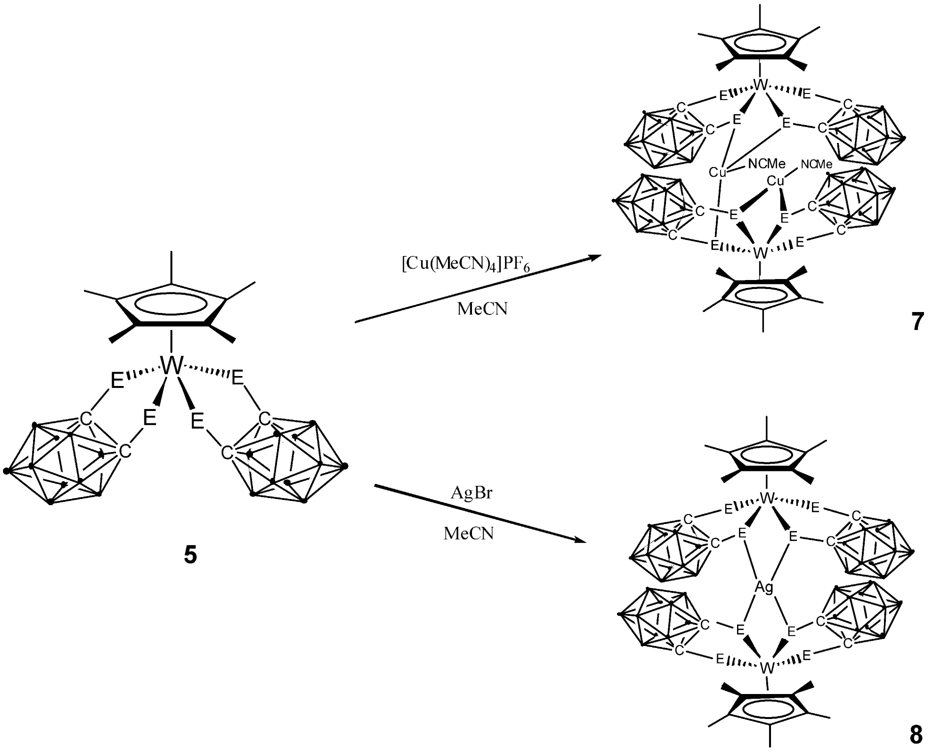


Fig. 3. Molecular structure of $Cp^*W(O)(Se_2C_2B_{10}H_{10})$ (**6**).

Complexes **5** (E = S, Se) with two chelate carborane dichalcogenolato ligands react with $[Cu(MeCN)_4]PF_6$ or AgBr in CH_3CN solution to form heterometallic tetranuclear complexes $[Cp^*W(E_2C_2B_{10}H_{10})_2Cu(CNMe)_2]_2$ (E = S, Se) (**7**) and heterometallic trinuclear complexes $[Cp^*W(E_2C_2B_{10}H_{10})_2]_2Ag$ (E = S, Se) (**8**), respectively [8].



This complex has a chiral molecular structure. The molecular structure of $[Cp^*W(S_2C_2B_{10}H_{10})_2Cu(CNMe)_2]_2$ (**7**) is shown in Fig. 4. One Cu atom as a bridge is connected with three sulfur atoms of the carborane dithiolato ligands and an acetonitrile in a distorted tetrahedral geometry. The other Cu atom is coordinated with two sulfur atoms and an acetonitrile in a trigonal geometry. The molecular structure of $[Cp^*W(S_2C_2B_{10}H_{10})_2]_2Ag$ (**8**) (Fig. 5) indicates that the $Cp^*W(E_2C_2B_{10}H_{10})_2$ units are linked through a Ag atom connected via four chalcogen atoms of the carborane dichalcogenolato ligands.

Reaction of the binuclear complex $[CpMo(NO)I_2]_2$ with $H_2S_2C_2B_{10}H_{10}$ in the presence of Et_3N leads to the 18-electron mononuclear ionic complex $[NEt_3H][CpMo(NO)(S_2C_2B_{10}H_{10})I]$ [9]. The molecular structure of the anion exhibited approximate square pyramidal geometry.

In contrast to the cyclopentadienyl complexes, the coordinatively unsaturated mononuclear complex $Tp^*Mo(O)Cl_2$ (Tp^* = hydrotris(3,5-dimethyl pyrazolyl) borate) reacts with $Li_2E_2C_2B_{10}H_{10}$ (E = S, Se and Te) in THF solution to produce the mononuclear penta-coordinate, formally 14-electron complexes $Tp^*Mo(O)(E_2C_2B_{10}H_{10})$ (**9**) (E = S, Se, Te). The molecular structure of $Tp^*Mo(O)(Se_2C_2B_{10}H_{10})$ (Fig. 6) reveals that the bond length between molybdenum and oxygen (1.657(4) Å) is shorter than the normal Mo=O double bond and there is no ligand *trans* to the Mo=O bond.

2.3. Rhenium complexes

The reaction of 1,2-dilithium carborane dichalcogenolate $Li_2E_2C_2B_{10}H_{10}$ (E = S, Se) with the half-sandwich

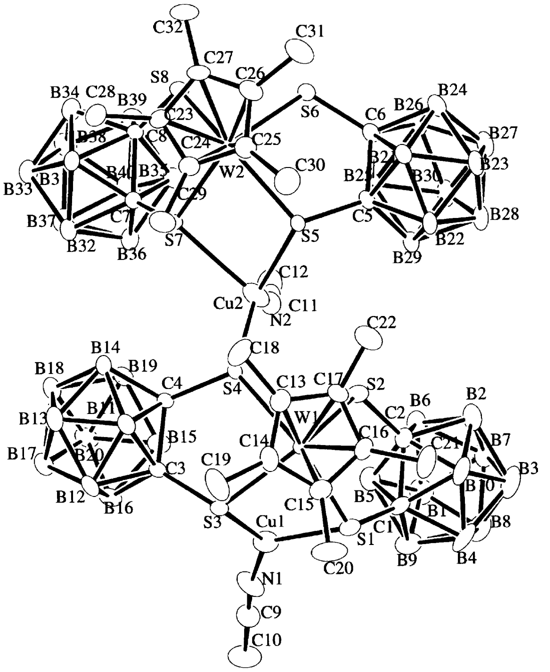


Fig. 4. Molecular structure of $[Cp^*W(S_2C_2B_{10}H_{10})_2Cu(CNMe)_2]_2$ (**7**).

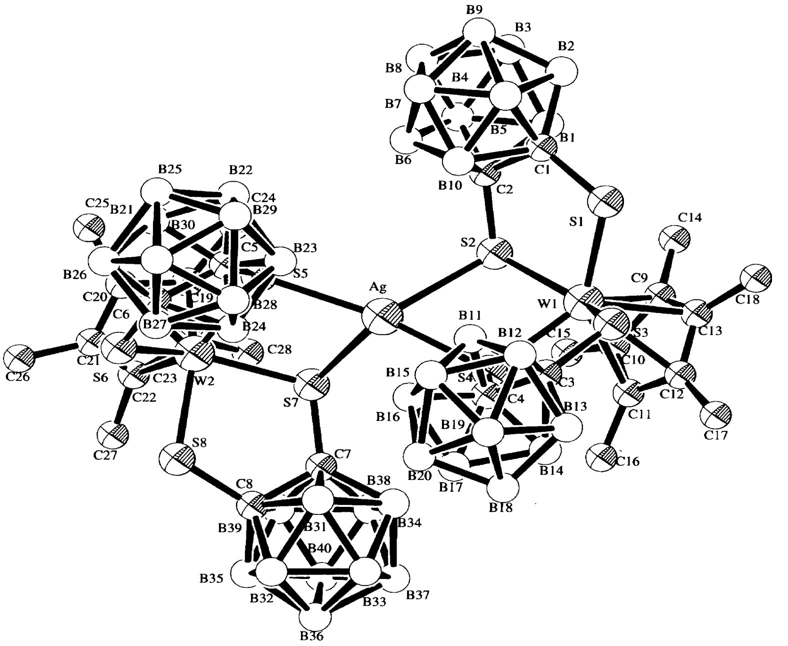


Fig. 5. Molecular structure of $[Cp^*W(S_2C_2B_{10}H_{10})_2]_2Ag$ (**8**).

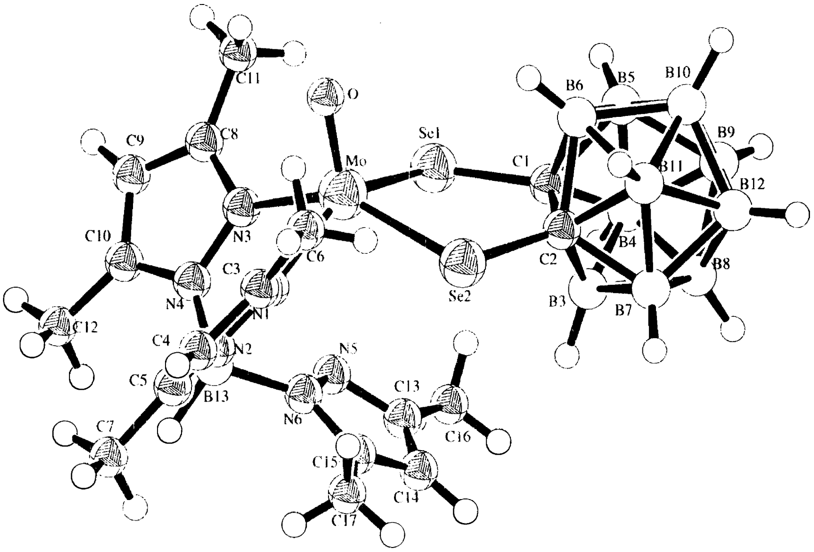
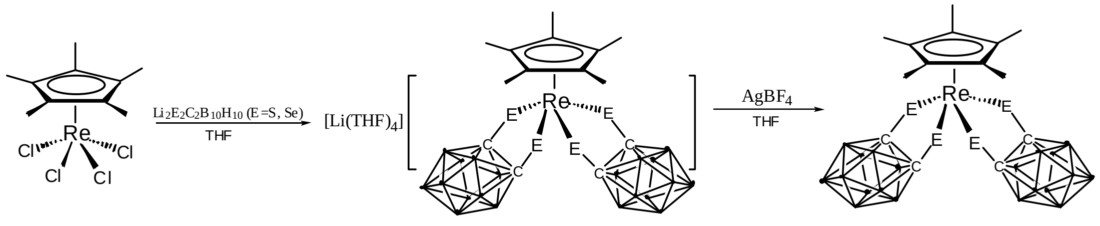


Fig. 6. Molecular Structure of $Tp^*Mo(O)(Se_2C_2B_{10}H_{10})$ (**9**).

pentamethylcyclopentadienyl rhenium complex Cp^*ReCl_4 in THF solution leads to the mononuclear salts $[Li(THF)_4]$ $[Cp^*Re(E_2C_2B_{10}H_{10})_2]$ (E = S, Se) (**10**) [8] in which the rhenium atom is reduced from Re(V) to Re(IV). Those violet salts are shown to be paramagnetic by their ^1H- and ^{13}C-NMR spectra. The $[Li(THF)_4][Cp^*Re(E_2C_2B_{10}H_{10})_2]$ salts can easily be oxidized by $AgBF_4$ to form green neutral products $Cp^*Re(E_2C_2B_{10}H_{10})_2$ (E = S, Se) (**11**) in very high yields. The ^1H- and ^{13}C-NMR spectra of these complexes exhibit strong methyl signals for the Cp* ring.



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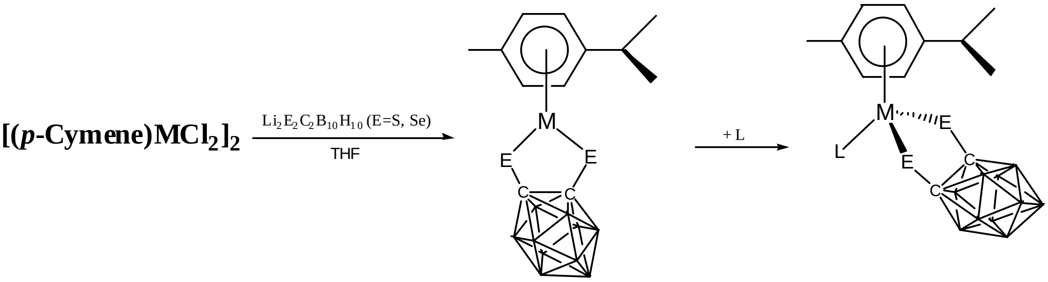
The molecular structures of complexes **10** and **11** exhibit of square pyramidal geometry similar to that of the $[NBu_4][Re(O)(S_2C_2B_{10}H_{10})_2]$ complex [9].

2.4. Iron, ruthenium and osmium complexes

The half-sandwich ruthenium(II) nitrosyl carborane dichalcogenolate complexes $Cp^*Ru(NO)(E_2C_2B_{10}H_{10})$ (E = S, Se, Te) can be prepared by the reactions of $Cp^*Ru(NO)Cl_2$ with $Li_2E_2C_2B_{10}H_{10}$ (E = S, Se, Te) [10]. The 16-electron half-sandwich η^6-(4-isopropyl toluene) Ru(II) and Os(II) complexes (*p*-cymene)$M(S_2C_2B_{10}H_{10})$ (**12**) (M = Ru, Os) have also been synthesized. These coordinatively unsaturated mononuclear complexes can be converted into the coordinatively saturated 18-electron derivatives by reactions with electron donor ligands, such as triphenyl phosphine (Ph_3P), *t*-butyl isocyanide (^{t}BuNC) and carbon monoxide (CO) [11].



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Attempts to combine the $[E_2C_2B_{10}H_{10}]$ (E = S, Se) building block with two 17-electron fragments such as $[CpFe(CO)_2]$ and $[CpRu(PPh_3)]$ were unsuccessful, although gold(I) complexes of the $[S_2C_2B_{10}H_{10}][Au(PR_3)]_2$ type have been obtained [12] and mercury(II)-bridged oligocarboranes are known [13]. Instead, $CpFe(CO)_2Cl$ reacts with $Li_2Se_2C_2B_{10}H_{10}$ in a molar ratio of 2:1 to give black prismatic crystals of $Cp_2Fe_2(CO)_3(\mu\text{-}Se_2C_2B_{10}H_{10})$ (**14**) in high yield [5]. The carborane-1,2-diselenolate bridge combines a [CpFe(CO)] and a $[CpFe(CO)_2]$ fragment (Fig. 7); one iron atom carries only one carbonyl group in addition to a formal three-electron chelate ligand $[(B_{10}H_{10})C_2Se(Se\text{–}R)]$ (R = $CpFe(CO)_2$). The long Fe(1) ··· Fe(2) separation distance (4.067 Å) excludes any direct metal–metal interaction.

The analogous reaction of $CpRu(PPh_3)_2Cl$ with the dilithium carborane dithiolate reagent $Li_2S_2C_2B_{10}H_{10}$ did not give a product analogous to the corresponding iron complex $Cp_2Fe_2(CO)_3(\mu\text{-}Se_2C_2B_{10}H_{10})$ but instead the symmetrical binuclear complex $Cp_2Ru_2(\mu\text{-}S_2C_2B_{10}H_{10})_2$ (**15**) with two *o*-carborane dithiolate bridges (Figs. 7 and 8). Each CpRu fragment is attached to one terminal and two bridging sulfur ligands. The Ru–Ru distance of 2.7781 Å corresponds to a single bond [5].

Reaction of the chloro-bridged dimer $[Cp^*RuCl(\mu\text{-}Cl)]_2$ with dilithium diselenolate carborane $Li_2S_2C_2B_{10}H_{10}$ in THF solution led to a black crystalline complex

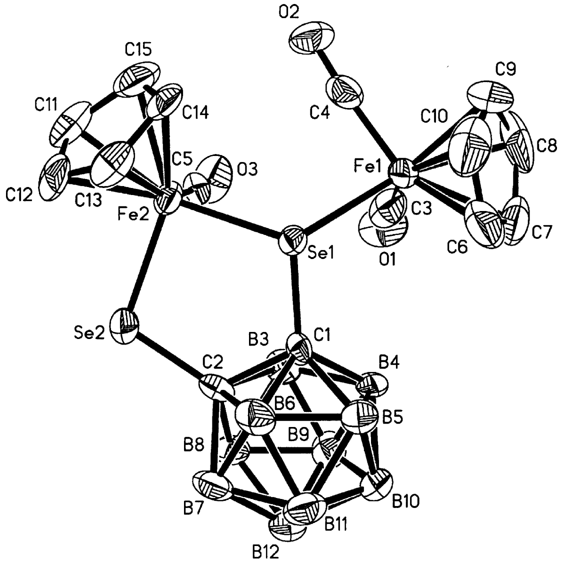


Fig. 7. Molecular structure of $Cp_2Fe_2(CO)_3(\mu\text{-}Se_2C_2B_{10}H_{10})$ (**14**).

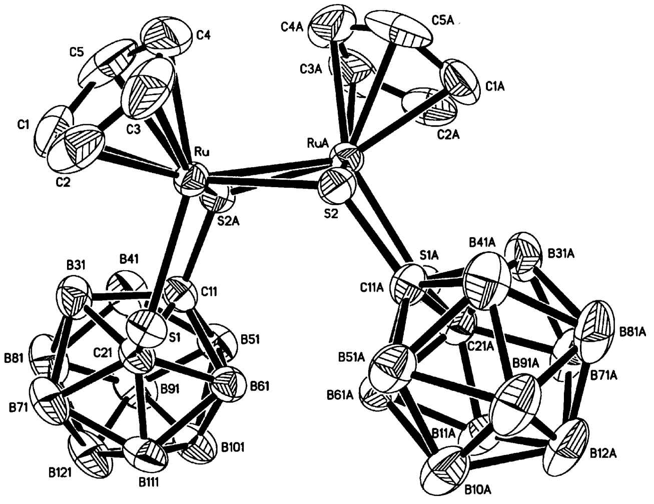


Fig. 8. Molecular structure of $Cp_2Ru_2(\mu\text{-}S_2C_2B_{10}H_{10})_2$ (**15**).

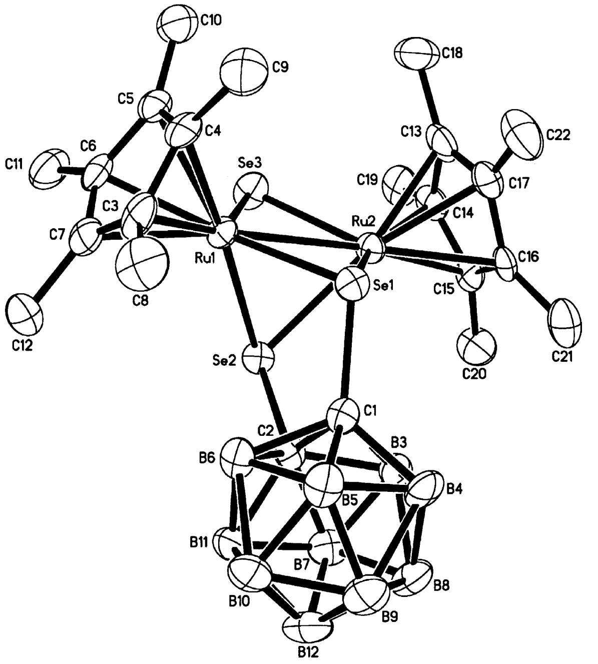


Fig. 9. Molecular structure of $Cp^*_2Ru_2(\mu\text{-}Se)(\mu\text{-}Se_2C_2B_{10}H_{10})$ (**16**).

$Cp^*_2Ru_2(\mu\text{-}Se)(\mu\text{-}Se_2C_2B_{10}H_{10})$ (**16**). In this complex, each Ru center is connected to three selenium atoms which are all bridging (Fig. 9). The Ru–Ru single bond distance (2.7877 Å) may therefore be compared to the corresponding distance in the binuclear complexes such as $[Cp^*_2Ru_2(\mu\text{-}SeC_6H_4\text{–}Me(4))_3]Cl$ (2.685(3) Å) [14]. The remarkable formation of a monoselenide bridge can be ascribed to steric hindrance caused by the voluminous Cp* rings.

2.5. Cobalt, rhodium and iridium complexes

The dilithium carborane dichalcogenolates $Li_2E_2C_2B_{10}H_{10}$ (E = S, Se) react with the half-sandwich iridium chloro-bridged dimer $[Cp^*IrCl(\mu\text{-}Cl)]_2$ to give the green 16-electron CpIr complexes $Cp^*Ir(E_2C_2B_{10}H_{10})$ (E = S, Se) (**17**) [15,16]. These complexes can take up 2-electron ligands L, such as L = CO, CN^tBu, pyridine, phosphines, to produce the coordinatively saturated 18-electron complexes $Cp^*Ir(L)(E_2C_2B_{10}H_{10})$ (E = S, Se; L = CO, CN^tBu, pyridine, PMe_3, PPh_3) (**18**) [15].

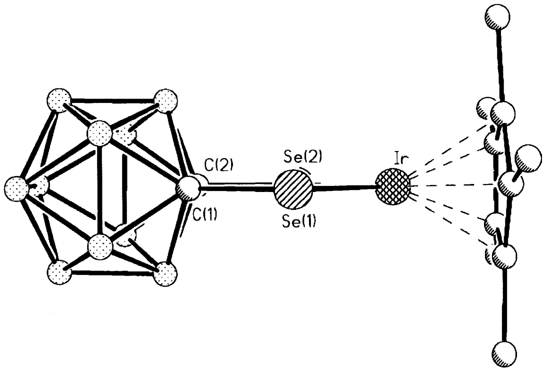


Fig. 10. Molecular structure of $Cp^*Ir(Se_2C_2B_{10}H_{10})$ (**17**).

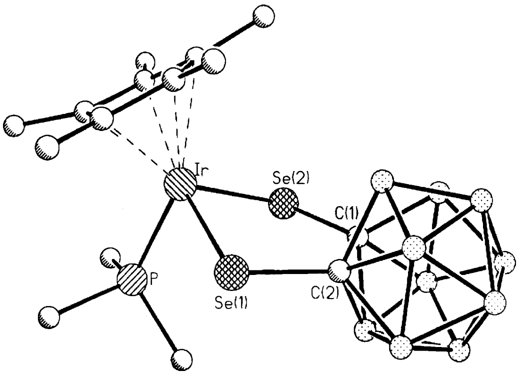
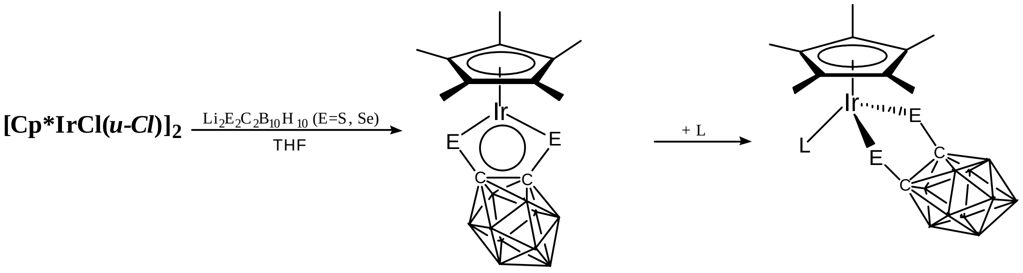


Fig. 11. Molecular structure of $Cp^*Ir(PMe_3)(Se_2C_2B_{10}H_{10})$ (**18**).

The molecular structures of $Cp^*Ir(Se_2C_2B_{10}H_{10})$ (**17**) and $Cp^*Ir(PMe_3)(Se_2C_2B_{10}H_{10})$ (**18**) (Figs. 10 and 11) were determined by X-ray crystal structure analysis. The molecular structure of $Cp^*Ir(Se_2C_2B_{10}H_{10})$ (**17**) exhibits point group symmetry C_{2v} with two perpendicular mirror planes. The short distances of Ir–Se and C–Se bonds in the coordinatively unsaturated mononuclear complex attributed to π-type interactions [17]. Addition of PMe_3 to form the 18-electron complex $Cp^*Ir(PMe_3)(Se_2C_2B_{10}H_{10})$ (**18**) leads to C_s symmetry with only one mirror plane left. The iridadiselenolene heterocycle in $Cp^*Ir(Se_2C_2B_{10}H_{10})$ is bent in $Cp^*Ir(PMe_3)(Se_2C_2B_{10}H_{10})$ with a dihedral angle at the Se···Se vector of 156.1°. Apparently, the ligand L = PMe_3 destroys the pseudoaromatic $IrSe_2C_2$ system [15].



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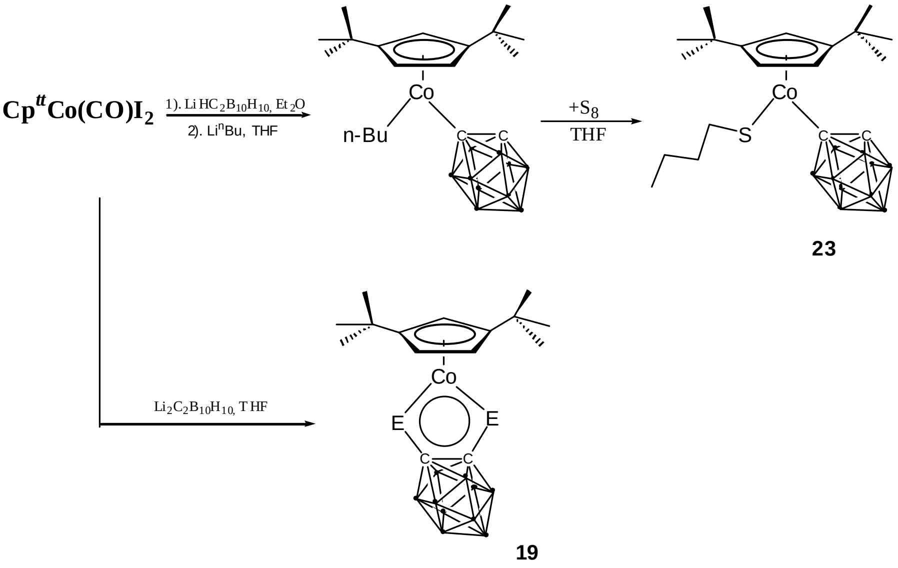
Analogous 16-electron half-sandwich cobalt and rhodium complexes $Cp'Co(S_2C_2B_{10}H_{10})$ (**19**) ($Cp' = \eta^5$-Cp and η^5-${}^tBu_2C_5H_3$) [18,19] and $Cp^*Rh(E_2C_2B_{10}H_{10})$ (E = S, Se) (**20**) [20] have also been synthesized by the reactions of $Cp'Co(CO)I_2$ with $Li_2S_2C_2B_{10}H_{10}$ and $[Cp^*RhCl(\mu\text{-}Cl)]_2$ with $Li_2E_2C_2B_{10}H_{10}$ (E = S, Se), respectively. The corresponding 18-electron complexes $Cp'Co(L)(S_2C_2B_{10}H_{10})$ (**21**) and $Cp^*Rh(L)(E_2C_2B_{10}H_{10})$ (E = S, Se) (**22**) have been prepared by addition of two-electron ligands L (L = CO, CN^tBu, PMe_3) [19,20].

The reaction of $Cp^{tt}Co(CO)I_2$ with the mono-lithium *o*-carborane ($LiHC_2B_{10}H_{10}$), which was prepared from the reaction of carborane ($H_2C_2B_{10}H_{10}$) with an equivalent of Li^nBu in Et_2O solution, leads to a one-carbon substituted product, which further reacts with excess of Li^nBu to give $Cp^{tt}Co(HC_2B_{10}H_{10})(^nBu)$. Sulfur can be inserted into the cobalt–carbon bond of the butyl group in THF solution to form the thiolate product $Cp^{tt}Co(HC_2B_{10}H_{10})(S^nBu)$ (**23**) as dark red diamagnetic crystals. The non-equivalent carbon atoms of carborane group in **23** are clearly detectable in the ^{13}C-NMR spectra at $\delta = 68.1$ and 59.8 ppm. The electron-impact mass spectra exhibit a clear molecular peak with high intensity. The complex $Cp^{tt}Co(CO)I_2$ reacts with $Li_2E_2C_2B_{10}H_{10}$ (E = S, Se) to give the 16-electron complexes $Cp^{tt}Co(E_2C_2B_{10}H_{10})$ (**19**) (E = S, Se).



The molecular structure of complex **23** shows coordinative unsaturation in the steric sense around the cobalt center in the two-legged piano-stool geometry (Fig. 12). The complexes $Cp^{tt}Co(S_2C_2B_{10}H_{10})$ (**19**) contain a chelating dithiolate carborane ligand and a planar CoS_2C_2 ring similar to the molecular structure of the Ir complex (**17**) (Fig. 13).

The dirhodium complexes with *o*-carborane dichalcogenolate bridging ligands $Rh_2(CO)_4(\mu\text{-}E_2C_2B_{10}H_{10})$ (E = S, Se) (**24**) [8,21] have recently been prepared from the rhodium carbonyl complex $Rh_2(CO)_4(\mu\text{-}C)_2$ and $Li_2E_2C_2B_{10}H_{10}$ (E = S, Se) in THF solution. The complexes were isolated in good yields as red crystals. The carborane dithiolate ligand was found to bridge two rhodium atoms (Fig. 14). The Rh–Rh distance of 2.890 Å corresponds to a strong interaction between the two Rh atoms.

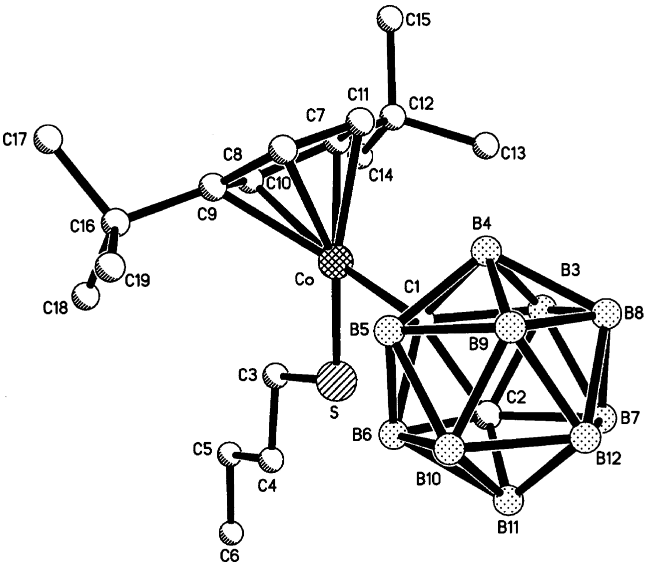


Fig. 12. Molecular structure of $Cp^{tt}Co(HC_2B_{10}H_{10})(S^nBu)$ (**23**).

2.6. Nickel and palladium complexes

Reaction of $Ni(COD)_2$ (COD = 1,5-cyclooctadiene) with two equivalents of $Li_2E_2C_2B_{10}H_{10}$ (E = S, Se) in THF solution in air at room temperature gives the mononuclear complexes $[Li(THF)_4]_2[Ni(E_2C_2B_{10}H_{10})_2]$ (E = S, Se) (**25**) [22]. However, $Ni(COD)_2$ reacts with one and a half equivalents of $Li_2E_2C_2B_{10}H_{10}$ (E = S, Se) in THF solution in air at room temperature (rt) to give the binuclear complexes $[Li(THF)_4]_2[Ni_2(E_2C_2B_{10}H_{10})_3]$ (E = S,

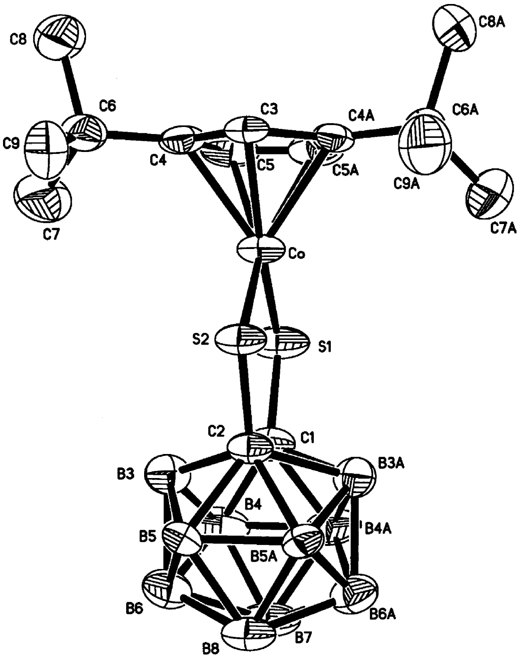


Fig. 13. Molecular structure of $Cp^{tt}Co(S_2C_2B_{10}H_{10})$ (**19**).

Se) (**26**). The bis triphenyl phosphine nickel complex $[(PPh_3)_2Ni(S_2C_2B_{10}H_{10})]$ (**27**) can be obtained in high yield by the reaction of $(PPh_3)_2NiCl_2$ and $Li_2S_2C_2B_{10}H_{10}$ in THF solution. The complexes **25**–**27** can be also directly synthesized by the reactions between $NiCl_2$ and $Li_2E_2C_2B_{10}H_{10}$ (E = S, Se) in different molar ratios [23,24]. Adding excess of $Li_2E_2C_2B_{10}H_{10}$ (E = S, Se) to **26** leads to the formation of complexes **25** which can be also produced from the reaction of **27** with excess of $Li_2E_2C_2B_{10}H_{10}$. However, attempts to obtain **26** from **27** were not successful (Scheme 1).

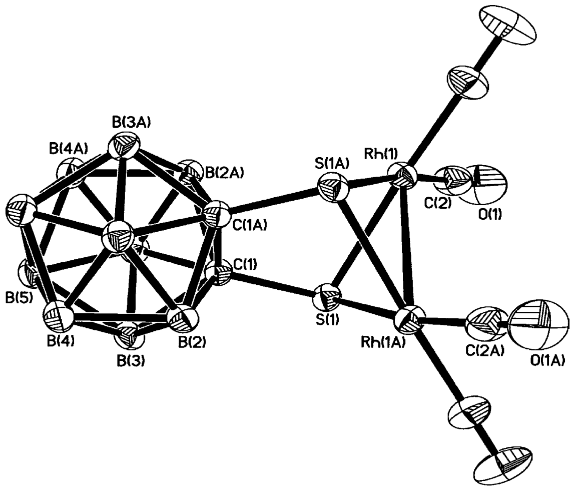
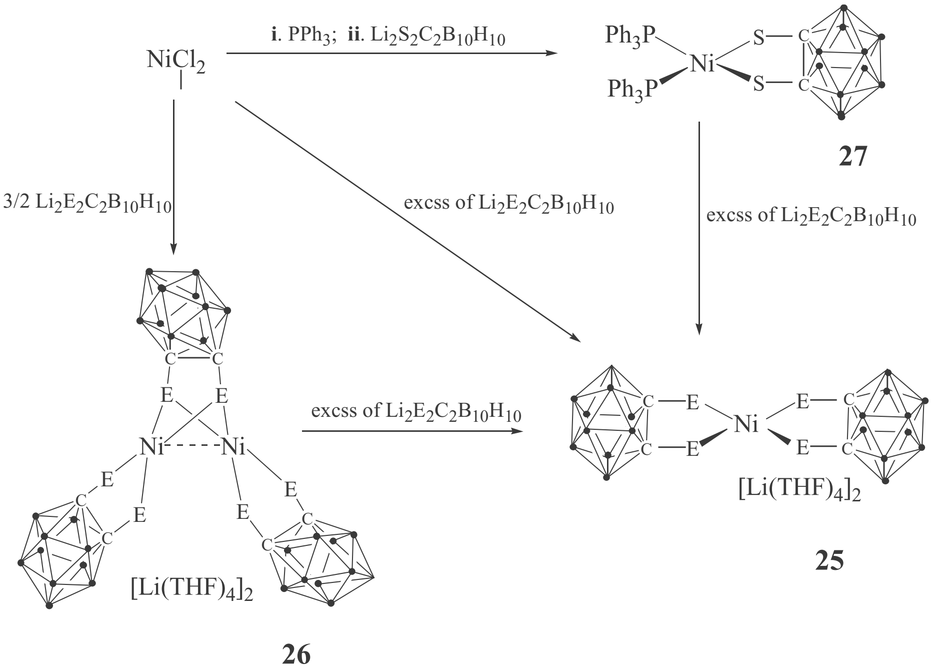


Fig. 14. Molecular structure of $Rh_2(CO)_4(\mu\text{-}S_2C_2B_{10}H_{10})$ (**24**).

The molecular structures of the complexes **25**–**27** were determined by X-ray diffraction. **25** is a salt and the complex with a molecular structure consisting of two well-separated alternating layers of the discrete tetrahedral cation $[Li(THF)_4]^+$ and the complex anion $[Ni(E_2C_2B_{10}H_{10})_2]^{2-}$. In the anion, the Ni atom is coordinated to four sulfur atoms of two dithio-carboranes in a distorted square planar arrangement. In **26**, the two nickel atoms are bridged by two sulfur atoms of one dithio-carborane to give a dinuclear structure with a metal–metal interaction (Fig. 15). In



Scheme 1. Synthesis of Ni dichalcogenolate carborane complexes.

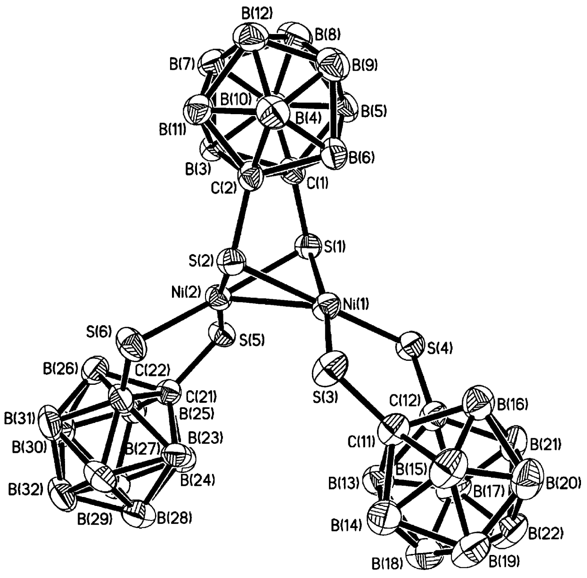


Fig. 15. Molecular structure of $[Li(THF)_4]_2[Ni_2(S_2C_2B_{10}H_{10})_3]$ (**26**).

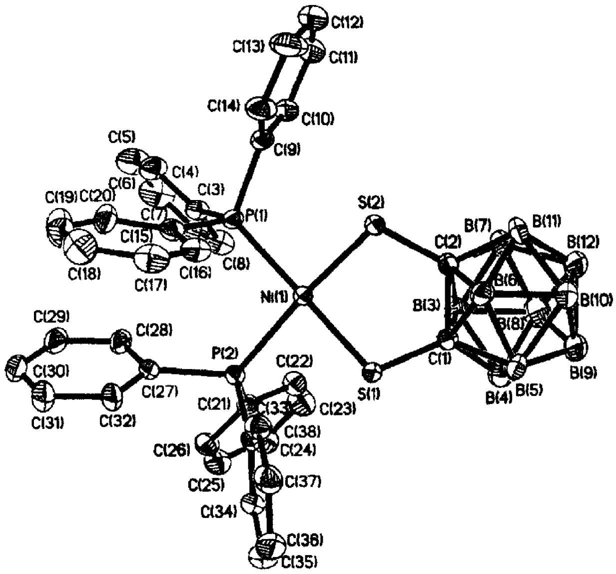


Fig. 16. Molecular structure of $[(PPh_3)_2Ni(S_2C_2B_{10}H_{10})]$ (**27**).

the molecular structure of **27** (Fig. 16), the nickel is coordinated to two P atoms of the PPh_3 ligand and two sulfur atoms of the dithio-carborane in a distorted square planar arrangement.

2.7. Lanthanide complexes

Although some cyclopentadienyl transition metal complexes of the d-block elements with *o*-carborane dichalcogenolate ligands have been synthesized during the last 4 years, the chemistry of the related organolanthanide dichalcogenolate carborane complexes is still underdeveloped. However, reactions of $[CpLn(\mu\text{-}Cl)]_2$ (Ln = Nd, Yb, Dy, Gd, Er) with an equivalent of $Li_2E_2C_2B_{10}H_{10}$ (E = S, Se) in THF solution were found to give the ionic binuclear *o*-carborane dichalcogenolate bridged complexes $[Li(THF)_4][CpLn(E_2C_2B_{10}H_{10})]_2$ (**28**) (E = S, Se; Ln = Nd, Yb, Dy, Gd, Er) [25].

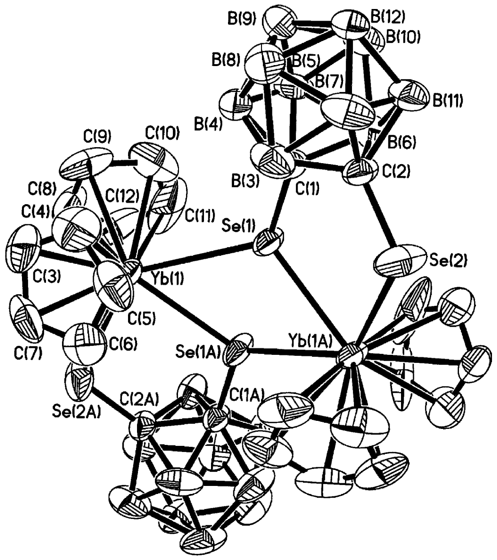
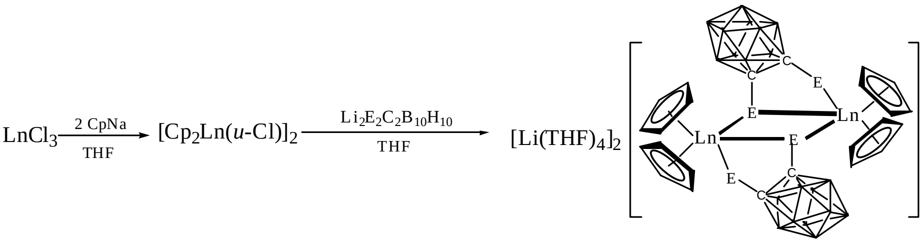


Fig. 17. Molecular structure of $[Li(THF)_4][CpYb(Se_2C_2B_{10}H_{10})]_2$ (**28**).



28

E = S, Se; Ln = Nd, Yb, Dy, Gd, Er

The molecular structures of the complexes $[Li(THF)_4][CpLn(E_2C_2B_{10}H_{10})]_2$ (E = S, Ln = Nd, Yb; E = Se, Ln = Yb) (**28**) have been determined by X-ray diffraction (Fig. 17). Each Cp_2Ln fragment is connected to one terminal and two bridging chalcogen atoms of the *o*-carborane dichalcogenolate ligands. The central $Ln_2(\mu\text{-}E_2)$ of the four-membered rings are not planar. There is no direct metal–metal bonding interaction in these complexes.

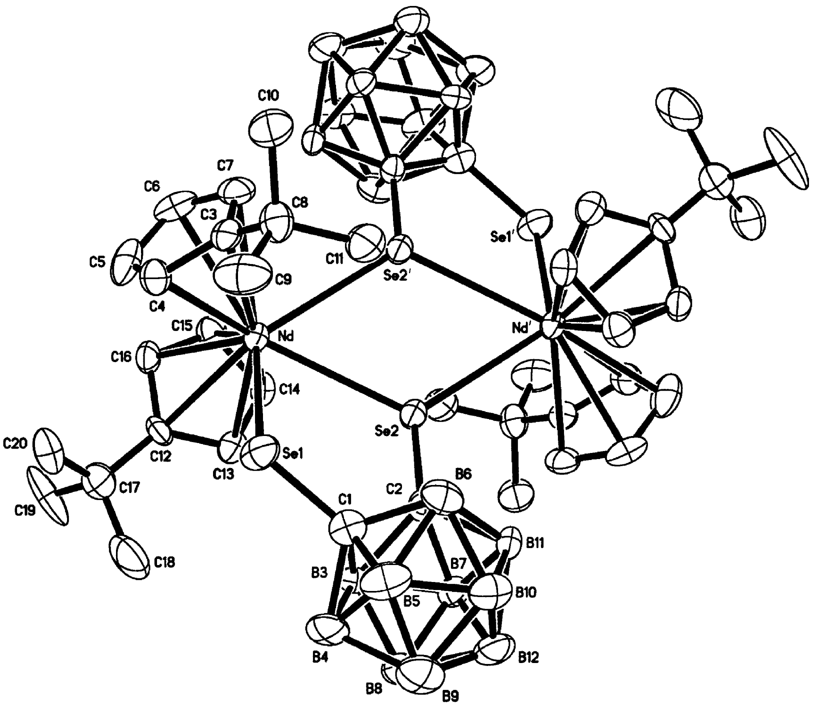


Fig. 18. Molecular structure of $[Li(THF)_4][Cp^{tt}Nd(Se_2C_2B_{10}H_{10})]_2$ (**29**).

For the purpose of comparison, similar *tert*-butyl substituted cyclopentadienyl complexes $[Li(THF)_4][Cp^{\#}Ln(E_2C_2B_{10}H_{10})]_2$ (**29**) ($Cp^{\#} = \eta^5$-$^tBuC_5H_4$, η^5-$^tBu_2C_5H_3$; E = S, Se; Ln = Nd, Yb, Dy, Gd, Er) were also investigated and structurally characterized [3] (Fig. 18).

3. Reactivity studies

Although numerous organothiolate complexes of transition metal have been reported, and in some cases, their chemistry has been studied [26], the chemistry of complexes containing chelating 1,2-dicarba-*closo*-dodecaborane-1,2-dichalcogenolate ligands has received only scant attention.

3.1. Coordination reactions

In view of the nucleophilic behavior of chalcogen ligands and easy formation of μ-chalcogen bridges in heterobimetallic complexes, it is not surprising that the neutral half-sandwich rhenium dichalcogenolate carborane complexes of the type $[Cp^*Re(E_2C_2B_{10}H_{10})_2]$ (E = S, Se) (**11**)

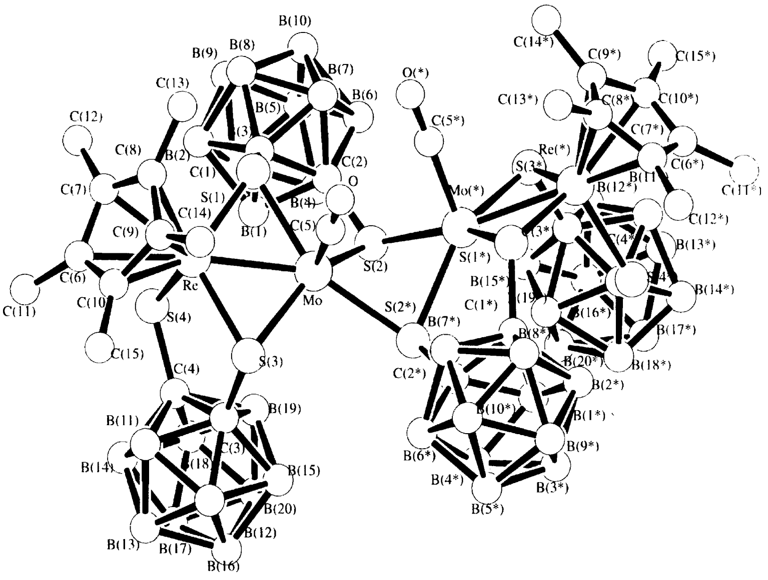
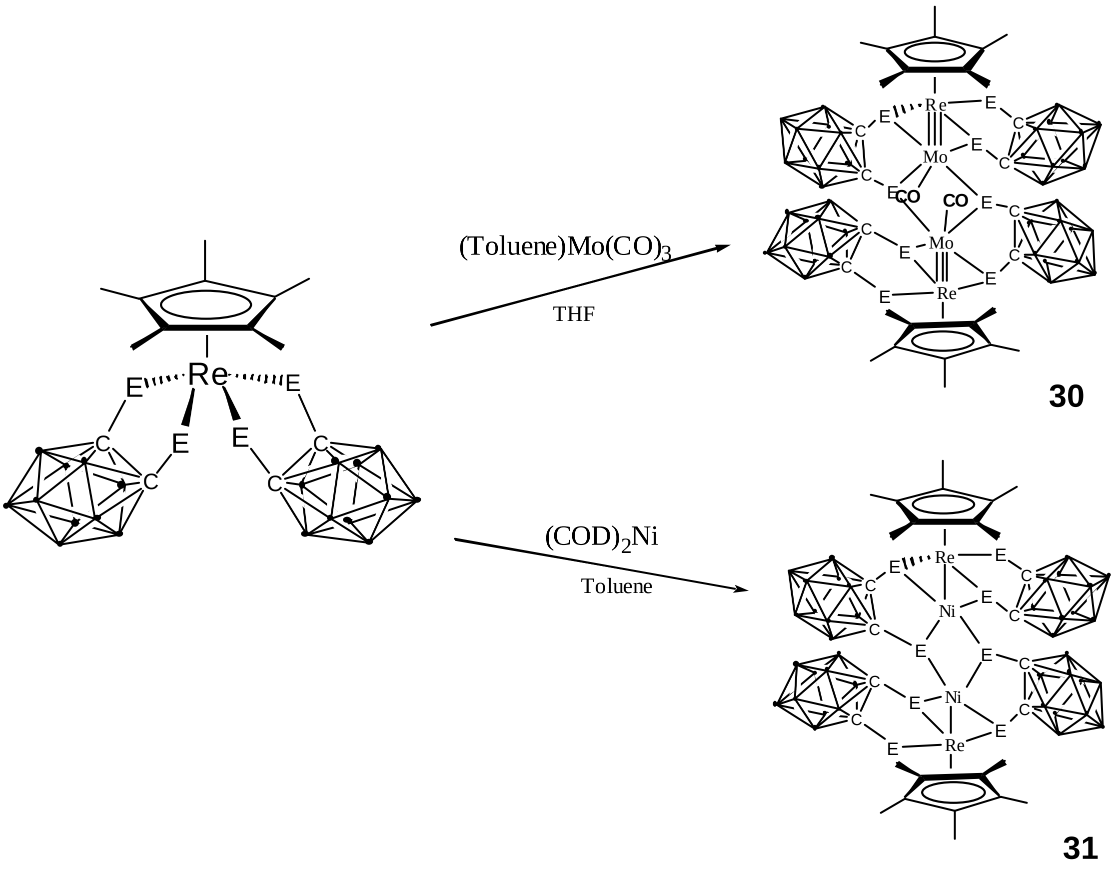


Fig. 19. Molecular structure of $[Cp^*Re(S_2C_2B_{10}H_{10})_2Mo(CO)]_2$ (**30**).

act as organometallic bidentate ligands through their chalcogen atoms. Thus, the complexes [Cp*Re($E_2C_2B_{10}H_{10}$)$_2$] react with the toluene-stabilized tricarbonyl molybdenum fragment (C_7H_8)Mo(CO)$_3$ to give the hetero-tetranuclear complexes [Cp*Re($E_2C_2B_{10}H_{10}$)$_2$Mo(CO)]$_2$ (E = S, Se) (**30**) in which the chalcogen atoms of the *o*-carborane dichalcogenolate ligands assume a bridging function. However, [Cp*Re($E_2C_2B_{10}H_{10}$)$_2$] complexes react with (COD)$_2$Ni to give [Cp*Re($S_2C_2B_{10}H_{10}$)$_2$Ni]$_2$ (**31**) [7,8]. Both of the complexes **30** and 3**1** are diamagnetic. In the ^{1}H- and ^{13}C-NMR spectra of **30** and **31**, the methyl groups of the Cp* ligands are easily recognized by the intense signals of their methyl substituents.

The analogous *o*-carborane carborane diselenolate complex [Cp*Re($Se_2C_2B_{10}H_{10}$)$_2$Mo(CO)]$_2$ was also synthesized and characterized by X-ray structure analysis. A strong metal–metal bond between Re and Mo atoms (2.6205(7) Å) was observed.

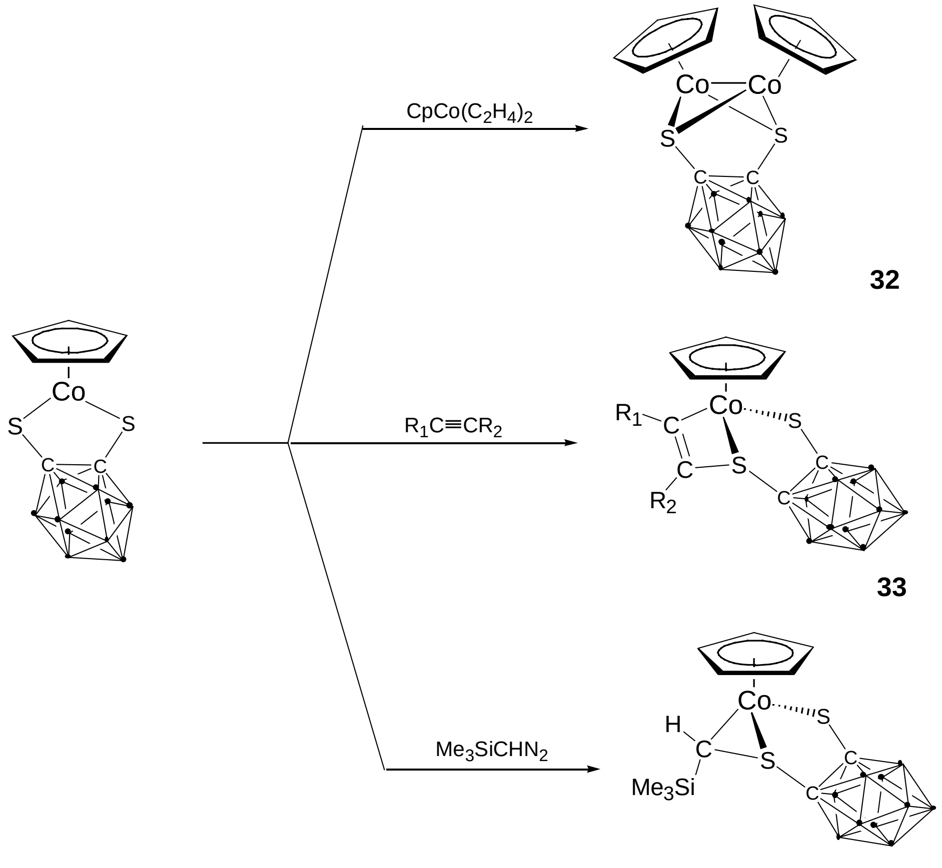
The molecular structure of the hetero-tetranuclear complex [Cp*Re($S_2C_2B_{10}H_{10}$)$_2$Ni]$_2$ (**31**) was also determined by X-ray diffraction (Fig. 20). The molecule of [Cp*Re($S_2C_2B_{10}H_{10}$)$_2$Ni]$_2$ (**31**) possesses three perpendicular mirror planes. The plane of the $Ni_2(\mu\text{-}S)_2$ ring is in the middle and bridged via two S atoms of the carborane dithiolate ligands. The Re–Ni distances (2.4744(8) Å) and the capping angles (Re–S–Ni: 66.52°) in the other two planes indicate the strong direct interaction between Re and Ni atoms.



The molecular structure of [Cp*Re($S_2C_2B_{10}H_{10}$)$_2$Mo(CO)]$_2$ (**30**), complex was found to contain four *o*-carborane dithiolate chelating ligands. Two of these ligands are arranged so that one S atom of each chelate ligands bridges Re and Mo atoms and another S atoms bridges two Mo atoms (Fig. 19). Each of Mo atoms bears a single carbonyl ligand. The four-membered rings connecting the Re and Mo atoms through two S atoms of the carborane dithiolate ligands are almost planar. The shorter bond distances between Re and Mo (2.5868(2) Å) lie in the range for triple bonds, so that each of Mo and Re centers in the complex is formally an 18-electron system.

3.2. Addition reactions

The mononuclear 16-electron dithio-*o*-carboranylcobalt complex CpCo($S_2C_2B_{10}H_{10}$) reacts with 1 eq. of CpCo-(C_2H_4)$_2$ in toluene to give the binuclear complex (CpCo)$_2$ ($S_2C_2B_{10}H_{10}$) (**32**) in which each CpCo unit is attached to both sulfur atoms of a 1,2-dithio-*o*-carborane ligand [16].



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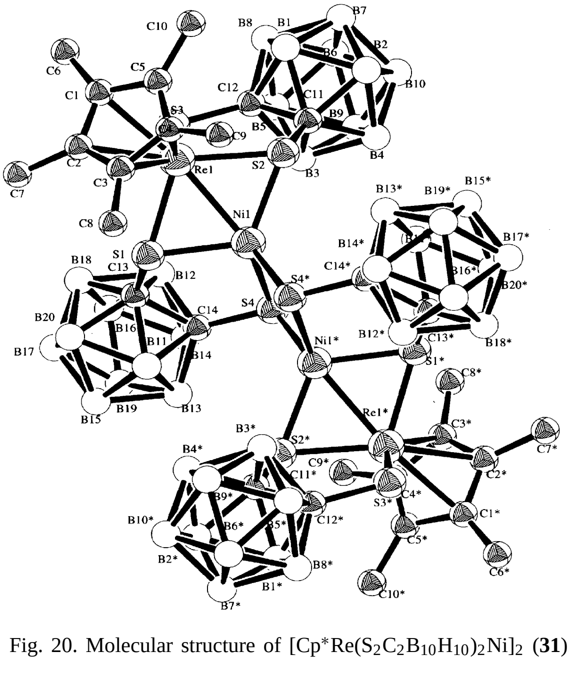


Fig. 20. Molecular structure of $[Cp^{*}Re(S_2C_2B_{10}H_{10})_2Ni]_2$ (**31**).

The addition reaction of $CpCo(S_2C_2B_{10}H_{10})$ with an alkyne forms the alkyne adducts $CpCo(R_1C{=}CR_2)(S_2C_2B_{10}H_{10})$ (**33**) but the reaction of the cobaltadithio-*o*-carborane complex with trimethylsilyldiazomethane in dichloromethane solution gives the trimethylsilyl methylene adduct (**34**) [18].

The violet mononuclear 16-electron *o*-carborane dichalcogenolate rhodium complexes $Cp^{tt}Rh(E_2C_2B_{10}H_{10})$ (E =

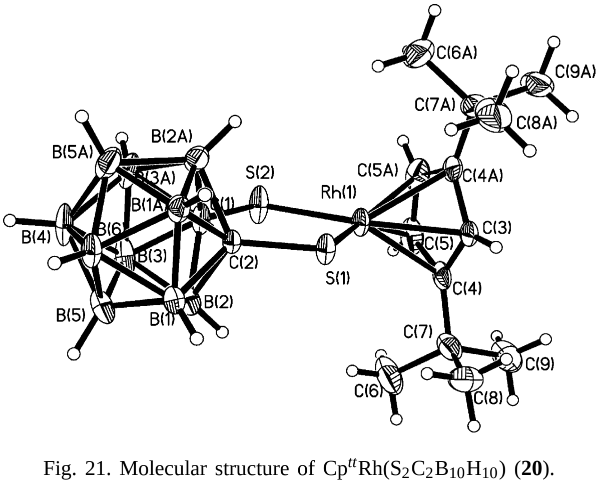
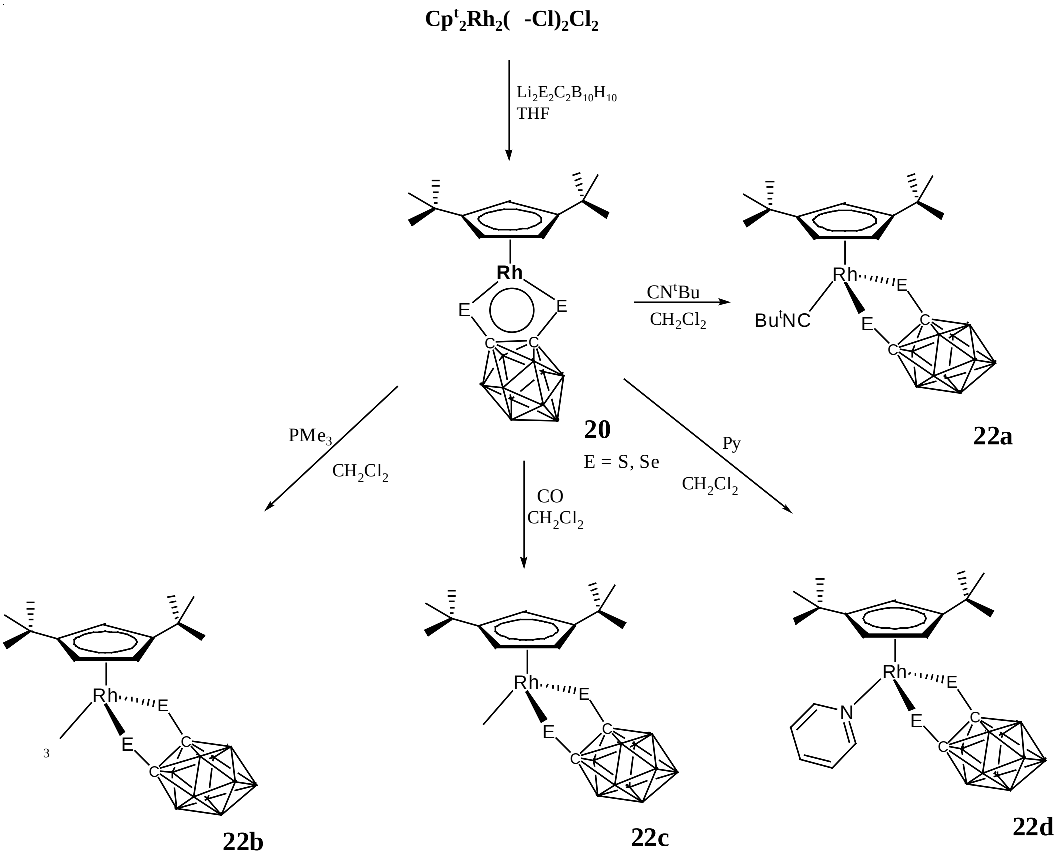


Fig. 21. Molecular structure of $Cp^{tt}Rh(S_2C_2B_{10}H_{10})$ (**20**).

S, Se) (**20**) react with two electron donor ligands L, such as *t*-BuNC, PMe_3, CO and pyridine, to give the orange 18-electron dichalcogenolate carborane complexes (**22a**–**22d**) [19].

The molecular structure of **20** (Fig. 21) is similar to that of the analogous Cp*Ir complex $Cp^*Ir(Se_2C_2B_{10}H_{10})$ (**17**) and to $Cp^{tt}Co(S_2C_2B_{10}H_{10})$ (**19**). The rhodadithiolene heterocyclic ring in **20** is planar. The ring of the rhodadithiolene



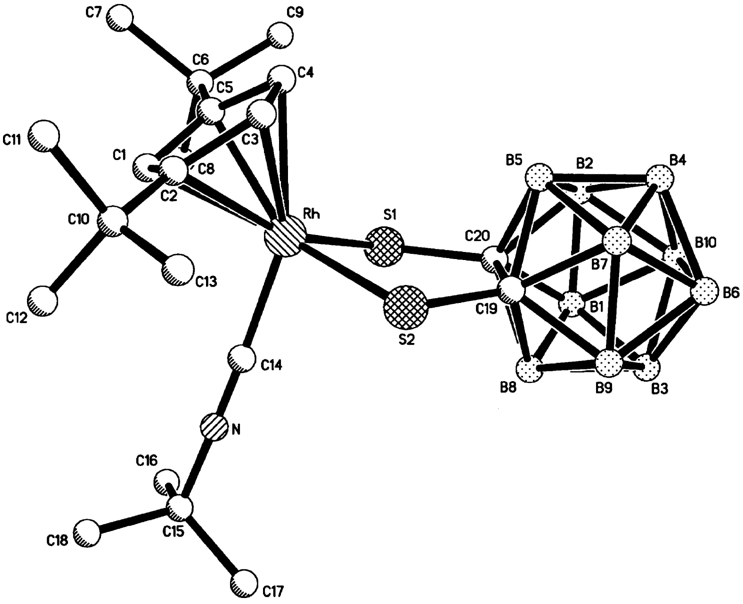
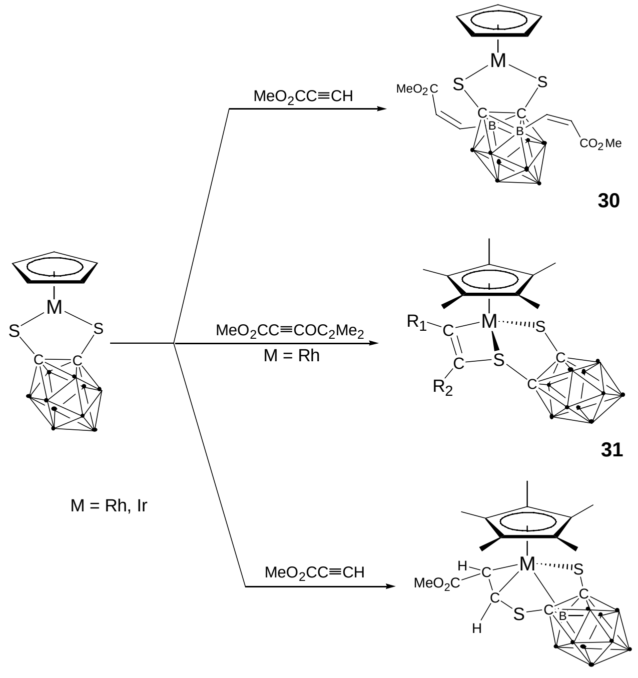


Fig. 22. Molecular structure of $Cp^{tt}Rh(CN^tBu)(S_2C_2B_{10}H_{10})$ (**22a**).

is bent when the *tert*-butyl isonitrile ligands is coordinated with a Rh atom (Fig. 22).

3.3. Carborane substitution

In the 16-electron half-sandwich complexes Cp*M($S_2C_2B_{10}H_{10}$) (M = Rh, Ir) (**20** and **17**) and (*p*-cymene)M($S_2C_2B_{10}H_{10}$) (M = Ru, Os) (**12**), the metal centers, the metal sulfur bonds, and the B(3,6)–H bonds of the *o*-carborane cages are reactive sites for reactions with unsaturated substrates [27]. Thus, reactions of Cp*Rh($S_2C_2B_{10}H_{10}$) with methyl acetylenemonocarboxylate or dimethyl acetylenedicarboxylate form B(3,6)-substitution products of the carborane cluster or acetylene addition/insertion products [28–32].



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