„BABEŞ-BOLYAI" UNIVERSITY

CLUJ-NAPOCA

Faculty of Chemistry and Chemical Engineering

Computational studies in metal carbonyl chemistry

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CLUJ-NAPOCA – 2021

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Keywords: density functional theory, metal carbonyls, pentalene, cyclopentadienyl, ethylenedithiolate

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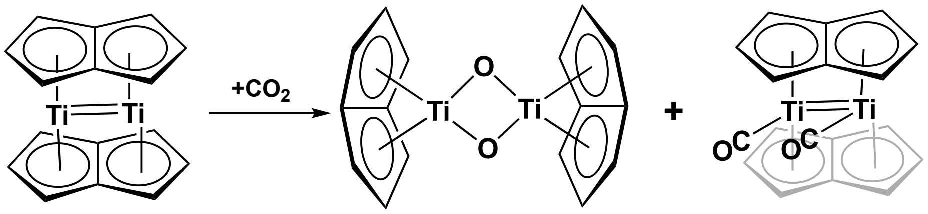
1. General considerations

Theoretical chemistry can be defined as the mathematical description of chemistry, and the term computational chemistry is generally used when a mathematical method is sufficiently well developed that it can be implemented in a computer. Aspects that can be investigated computationally include, among others, molecular geometry (bond lengths, angles, dihedrals), molecular energies (the most stable isomer at equilibrium), transition states, chemical reactivity (nucleophilic sites, electrophilic sites), IR/UV/NMR spectra, the interaction of a substrate with an enzyme (useful for example in the development of new drugs), physical properties of substances (useful in materials science). This thesis uses computational chemistry to solve problems in metal carbonyl chemistry.

2. Binuclear pentalene titanium carbonyls involved in the deoxygenation of carbon dioxide

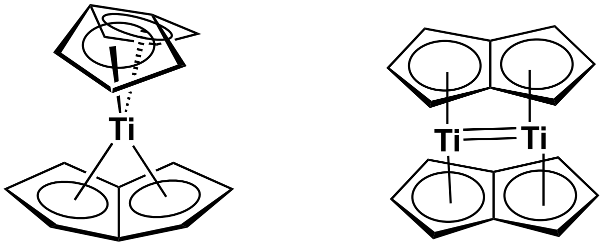
Pentalene titanium complexes have recently become of interest owing to their reactivity towards small molecules. Such small molecules include CO_2 of current concern relative to anthopogenic climate change. Thus $Pn^{\dagger}_2Ti_2$ ($Pn^{\dagger}$ = 1,4-$(iPr_3Si)_2C_8H_4$) readily deoxynates CO_2 to give the oxide $Pn_2Ti_2(\mu\text{-}O)_2$ fixing the CO by-product as the dicarbonyl $Pn^{\dagger}_2Ti_2(CO)_2$[2,3] (Figure 1). This reaction represents the first example of CO_2 as the carbon source for the carbonyl group in the synthesis of a metal carbonyl derivative. The pentalene titanium dialkyls Pn^*TiR_2 (Pn^* = C_8Me_6; R = Me, CH_2Ph) are also reactive towards CO_2, but in a different manner to give the corresponding carboxylates $Pn^*Ti(CO_2R)_2$ rather than to form titanium carbonyl derivatives[4].



$(\eta^5,\eta^5\text{-}C_8H_4R_2)Ti_2$ **$(\eta^8\text{-}C_8H_4R_2)_2Ti_2(\mu\text{-}O)_2$** **$(\eta^5,\eta^5\text{-}C_8H_4R_2)_2Ti_2(CO)_2$**

Figure 1. Reaction of bis(1,4-triisopropylsilylpentalene)dititanium, $Pn^{\dagger}{}_2Ti_2$, with carbon dioxide. The triisopropylsilyl substituents are omitted for clarity.

Both mononuclear and binuclear homoleptic pentalene-titanium derivatives are known (Figure 2). The mononuclear derivative $(\eta^8\text{-}C_8H_6)_2Ti$ has two unusual folded octahapto pentalene ligands with distorted tetrahedral orientation of the four ring centroid-titanium linkages and is formally a derivative of Ti(IV)[20]. The binuclear derivative Pn_2Ti_2 (Pn = complexed pentalene)[21] is formally a titanium(II) derivative but has a short Ti=Ti distance suggested to be a formal double bond[22]. Because of their low titanium oxidation states and titanium multiple bonds, Pn_2Ti_2 derivatives are reactive towards small molecules. Of particular interest is the reductive deoxygenation of CO_2 by $Pn^{\dagger}{}_2Ti_2$ to give the oxide $Pn^{\dagger}{}_2Ti_2(\mu\text{-}O)_2$ and the dicarbonyl $Pn^{\dagger}{}_2Ti_2(CO)_2$[2,3] (Figure 1). A monocarbonyl $Pn^{\dagger}{}_2Ti_2(CO)$ has also been obtained from the reaction of $Pn^{\dagger}{}_2Ti_2$ with CO en route to the dicarbonyl $Pn^{\dagger}{}_2Ti_2(CO)_2$. In addition a tricarbonyl $Pn^{\dagger}{}_2Ti_2(CO)_3$ is obtained by reaction of $Pn^{\dagger}{}_2Ti_2(CO)_2$ with excess CO at low temperatures and was obtained as orange crystals in a CO atmosphere. However, it was found to be too unstable for a determination by X-ray crystallography.



$(\eta^8\text{-}C_8H_6)_2Ti$ **$(\eta^5,\eta^5\text{-}C_8H_6)_2Ti_2$**

Figure 2. The homoleptic pentalene titanium complexes $\eta^8\text{-}Pn_2Ti$ and $\eta^5,\eta^5\text{-}Pn_2Ti_2$.

According to our DFT results, each C_5 ring in each pentalene ligand in the $Pn_2Ti_2(CO)_n$ (Pn = pentalene (C_8H_6); $n = 0, 1, 2, 3, 4$) functions as a pentahapto ligand to a titanium atom and thus can be considered as a five-electron donor so that each pentalene ligand contributes 10 electrons to the central Ti_2 unit. However, this bonding model has the two carbon atoms common to both titanium atoms functioning as a bridge. This leads to multiple center Ti_2C_2 bonding that creates difficulties in assigning a formal titanium-titanium bond order. Thus the short predicted Ti–Ti distance of 2.286 Å in the carbonyl-free lowest energy singlet Pn_2Ti_2 structure with an associated high Wiberg Bond Index (WBI) of 1.57 would suggest the formal quadruple bond leading to the favored 18-electron configuration for both titanium atoms. However, this contradicts the previously reported analysis[22] of this system using derivatives molecular orbital and fragment analysis to indicate a Ti=Ti double bond in these systems.

Density functional theory optimization of the carbonyl-free Pn_2Ti_2 system in singlet, triplet, and quintet spin states shows the singlet structure to lie 22.5 kcal/mol and 18.5 kcal/mol in energy below the isomeric triplet and quintet structures, respectively. However, for the experimentally known $Pn^{\dagger}_2Ti_2$ system ($Pn^{\dagger}$ = 1,3-$(iPr_3Si)_2C_8H_4$) the singlet, triplet and quintet spin state structures have essentially equal energies within 0.3 kcal/mol. This suggests the possibility of complicated magnetic behaviour. The Ti-Ti distance of 2.399 Å found in crystalline $Pn^{\dagger}_2Ti_2$ by X-ray crystallography is closest to the 2.415 Å Ti-Ti distance predicted for the triplet spin state structure.

Carbonylation of Pn_2Ti_2 results in successive lengthening of the Ti-Ti distance with a corresponding decrease in the Ti-Ti WBIs as CO groups are added. Three CO groups are the maximum number that can be introduced into a viable $Pn_2Ti_2(CO)_n$ derivative as indicated both by experimental and by the exothermic predicted CO dissociation energy of the tetracarbonyl $Pn_2Ti_2(CO)_4$. The lowest energy structure for the monocarbonyl $Pn_2Ti_2(CO)$ has a four-electron donor bridging η^2-μ-CO group in accord with the experimental $Pn^{\dagger}_2Ti_2(CO)$ structure. However, the lowest energy structure for the dicarbonyl $Pn_2Ti_2(CO)_2$ has exclusively terminal CO groups in a *cis* configuration in accord with the experimental $Pn^{\dagger}_2Ti_2(CO)_2$ structure obtained from reaction of $Pn^{\dagger}_2Ti_2$ with carbon dioxide. Two terminal CO groups are accompanied by a third highly unsymmetrical semibridging CO group in the lowest energy structures for the tricarbonyl

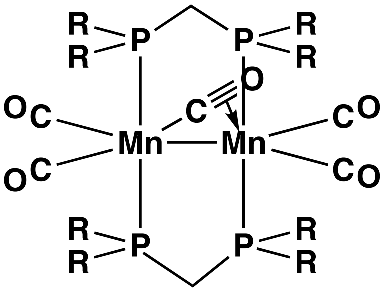
$Pn_2Ti_2(CO)_3$. However, the lowest energy structures for the tetracarbonyl $Pn_2Ti_2(CO)_4$ have exclusively terminal CO groups.

The data discussed in this chapter have been published in the Journal of Organometallic Chemistry[58].

3. Binuclear pentalene titanium carbonyls: comparison with related cyclopentadienyltitanium carbonyls

Titanium is the earliest transition metal known to form isolable metal carbonyl derivatives. However, since a neutral titanium atom has only four valence electrons, seven carbonyl groups are required to provide the 14 additional electrons for the titanium atom in a neutral binary carbonyl to have the favored 18-electron configuration of most stable metal carbonyl derivatives[59,60,61,62,63]. The resulting species, titanium heptacarbonyl, $Ti(CO)_7$, does not appear to be stable under ambient conditions but appears to be isolated in low temperature matrices[9]. However, stable seven-coordinate substitution products of $Ti(CO)_7$, including $(Me_2PCH_2CH_2PMe_2)Ti(CO)_5$ and $[MeC(CH_2PMe_2)_3]Ti(CO)_4$, have been synthesized[10] in which two to four CO groups are replaced by highly basic chelating phosphines. In addition, the experimentally known and structurally characterized seven-coordinate titanium carbonyl anions $[R_3SnTi(CO)_6]^-$ (R = Ph)[11] and $[R_3PAu \rightarrow Ti(CO)_6]^-$ (R = Et)[12] may also be considered as close relatives of $Ti(CO)_7$. The stable binary dianion $Ti(CO)_6^{2-}$, in which the central atom has the favored 18-electron configuration, is also known[7].

Another structural feature of unsaturated binuclear carbonyl derivatives of relatively oxophilic early transition metals, such as titanium, is a four-electron donor carbonyl group η^2-μ-CO bridging the central M_2 unit. Such a structural feature was first found in the stable binuclear manganese carbonyl complex $(Ph_2PCH_2PPh_2)_2Mn_2(CO)_4(\eta^2\text{-}\mu\text{-}CO)$, which has been structurally characterized by X-ray crystallography[70,71] (Figure 3). The η^2-μ-CO ligand is found to exhibit a short bonding Mn-O distance of 2.29 Å, indicating interaction of the oxygen atom as well as the carbon atom of the carbonyl group with the central M_2 unit. The bonding of a bridging carbonyl group to a central M_2 unit through its oxygen atom as well as through its carbon atom occurs mainly with the relatively oxophilic early transition metals. However, such four-electron donor bridging η^2-μ-CO groups are relatively rare, considering the large number of binuclear metal carbonyl derivatives. Nevertheless, theoretical studies on unsaturated binuclear early transition metal carbonyls such as $Cp_2V_2(CO)_n$ (n = 3, 2, 1)[72], $Cp_2Nb_2(CO)_n$ (n = 6, 4, 3, 2, 1)[73] and $Cp_2Ti_2(CO)_n$ (n = 7, 5, 4, 3, 2)[64] have provided additional examples of four-electron donor bridging η^2-μ-CO groups. The theoretical studies on $PnM_2(CO)_n$ (M = Mn[67], Fe[68], Co[69]) of the central to late transition metals predict the absence of low-energy structures having four-electron donor bridging η^2-μ-CO groups.



$(Ph_2PCH_2PPh_2)_2Mn_2(CO)_4(\eta^2$-$\mu$-CO)

Figure 3. Structure of $(Ph_2PCH_2PPh_2)_2Mn_2(CO)_4(\eta^2$-$\mu$-CO) showing the four-electron donor bridging η^2-μ-CO group.

According to our DFT results, the major differences between $PnTi_2(CO)_n$ and $Cp_2Ti_2(CO)_n$ structures with the same number of carbonyl groups relate to the constraints imposed by the pentahapto bonding of each pentalene ring to a titanium atom in the η^5,η^5-$PnTi_2$ structural unit. For the carbonyl-richest system $PnTi_2(CO)_n/Cp_2Ti_2(CO)_n$ (n = 8, 7), the relatively long Ti–Ti bonding distances found in the $Cp_2Ti_2(CO)_n$ derivatives are not found in the corresponding $PnTi_2(CO)_n$ derivatives because of this constraint. Thus the lowest energy $Cp_2Ti_2(CO)_8$ structures have all terminal CO groups with a very long Ti–Ti single bond of ~ 3.9 Å to give each titanium atom the favored 18-electron configuration[64]. Such long Ti–Ti bonds are not feasible in the corresponding $PnTi_2(CO)_8$ structures if pentahapto bonding of each pentalene ring to a titanium atom is maintained. The singlet $PnTi_2(CO)_8$ structure PnTi28-2S, lying only ~ 3 kcal/mol above the lowest energy $PnTi_2(CO)_8$ structure PnTi28-1T, also has exclusively terminal CO groups but a necessarily much shorter Ti-Ti bonding distance of ~ 3.0 Å. Other

$PnTi_2(CO)_8$ structures have a four-electron donor bridging η^2-μ-CO group despite the carbonyl-richness of this system. This, as well as the general prevalence of four-electron donor bridging η^2-μ-CO groups in most of the low-energy $PnTi_2(CO)_n$ structures (Table 4), suggests that the most favorable Ti–Ti distances in the η^5,η^5-$PnTi_2$ structural unit are also favorable Ti–Ti distances for bridging by a η^2-μ-CO group.

The low-energy structures for the heptacarbonyl $Cp_2Ti_2(CO)_7$ are of two types, namely a structure with a four-electron donor η^2-μ-CO group and a Ti–Ti single bond of lenght ~ 3.8 Å and a structure with exclusively terminal CO groups and a Ti=Ti double bond of lenght ~ 3.4 Å[64]. Even the shorter ~ 3.4 Å Ti=Ti distance in the latter structure appears to be too long to be incorporated into a η^5,η^5-$PnTi_2$ system while maintaining the favorable pentahapto bonding to both pentalene rings. The lowest energy $PnTi_2(CO)_7$ structure PnTi27-1T by a margin of ~ 5 kcal/mol is a triplet structure with a bridging η^2-μ-CO group but with a bonding Ti–Ti distance of only ~ 3.0 Å.

The two lowest energy structures for the hexacarbonyl $Cp_2Ti_2(CO)_6$ have all two-electron donor carbonyl groups and reasonable Ti≡Ti distancess of ~ 2.8 Å for the formal triple bonds required to give each titanium atom the favored 18-electron configuration. However, all of the low-energy $PnTi_2(CO)_6$ structures have a single four-electron donor η^2-μ-CO group albeit with similar Ti=Ti distances close to ~ 2.8 Å. However, the WBI's of these Ti=Ti interactions are consistent with formal bond orders no greater than two. Note that each titanium atom in a $PnTi_2(CO)_6$ structure with a four-electron donor η^2-μ-CO group and a formal Ti=Ti double bond has the favorable 18-electron configuration.

The low-energy structures of the carbonyl-poorer $Cp_2Ti_2(CO)_n$/$PnTi_2(CO)_n$ (n = 5, 4, 3, 2) systems all have at least one η^2-μ-CO group. The lowest energy $PnTi_2(CO)_n$ (n = 5, 4, 3, 2) structures by margins of at least ~ 10 kcal/mol are singlet structures with two η^2-μ-CO groups and Ti≡Ti triple bond distances of ~ 2.5 Å or even less as the number of CO groups is reduced (Table 4). Thus the lowest energy structure PnTi23-1S for the tricarbonyl $PnTi_2(CO)_3$ has two η^2-μ-CO groups and one terminal CO group. However, in the lowest energy $Cp_2Ti_2(CO)_3$ structure all three carbonyl groups are η^2-μ-CO groups. This suggests that the maximum number of four-electron η^2-μ-CO groups that can bridge the Ti–Ti bond in a η^5,η^5-$PnTi_2$ unit is two.

The data discussed in this chapter have been published in International Journal of Quantum Chemistry[78].

4. Reversible complexation of ammonia by breaking a manganese-manganese bond in a manganese carbonyl ethylenedithiolate complex: a theoretical study of an unusual type of Lewis acid

The chemistry of organosulfur derivatives of metal carbonyls dates back to the 1937 synthesis of derivatives of stoichiometry $RSFe(CO)_3$ (R = alkyl or aryl) by Hieber and Spacu using reactions of $Fe_3(CO)_{12}$ with thiols or disulfides[64]. Subsequent work by Hieber and Beck in 1960[79] showed these species to be the $(RS)_2Fe_2(CO)_6$ dimers and indicated all CO groups to be terminal groups from their ν(CO) frequencies. One of us (RBK) in 1962 used proton NMR to demonstrate the presence of two stereoisomers of the methyl derivative $(CH_3S)_2Fe_2(CO)_6$ (R = CH_3) (Figure 4) and then separated the two isomers by column chromatography[80]. Shortly thereafter Dahl and Wei[81] used X-ray crystallography to show the presence of an Fe–Fe bond of lenght 2.537 Å and two bridging ethylthiolate ligands in the axial-equatorial $(C_2H_5S)_2Fe_2(CO)_6$ isomer. Recently, both stereoisomers of $(CH_3S)_2Fe_2(CO)_6$ were both structurally characterized by X-ray crystallography[82]. Each iron atom in the $(RS)_2Fe_2(CO)_6$ complexes with an Fe–Fe single bond has the favored 18-electron configuration since the bridging RS ligands, considered as neutral species, donate two electrons to one iron atom and a single electron to the other iron atom.

The iron atoms in the binuclear ethylenedithiolate complex $H_2C_2S_2Fe_2(CO)_6$ have the favored 18-electron configuration with an Fe–Fe formal single bond and coordination of the ethylenedithiolate ligand through only the sulfur atoms. In order for the manganese atoms in the apparently corresponding manganese complex $H_2C_2S_2Mn_2(CO)_6$ to have likewise the favored 18-electron configuration, either the coordination of the ethylene double bond as well as the sulfur atoms of the ethylenedithiolate ligand or the formation of a formal Mn=Mn double bond must occur. The 1968 paper[91] suggested the coordination of the ethylene double bond as well as the sulfur atoms of the ethylenedithiolate ligand to provide both manganese atoms in $H_2C_2S_2Mn_2(CO)_6$ with the favored 18-electron configuration. This suggestion was subsequently confirmed by the structure of the diphenyl derivative $Ph_2C_2S_2Mn_2(CO)_6$ by X-ray crystallography[92]. The rapid reactions of $H_2C_2S_2Mn_2(CO)_6$ with bases such as ammonia might either involve the displacement of the coordinated double bond or rupture of the manganese-manganese bond by the base (Figure 5). We now use density functional theory to show this explanation of the reactivity of $H_2C_2S_2Mn_2(CO)_6$ with Lewis bases to involve the rupture of the manganese-manganese bond rather than the displacement of the coordinated C=C double-bond. Thus $H_2C_2S_2Mn_2(CO)_6$ represents a rare type of Lewis acid functioning by the displacement of a metal-metal bond.

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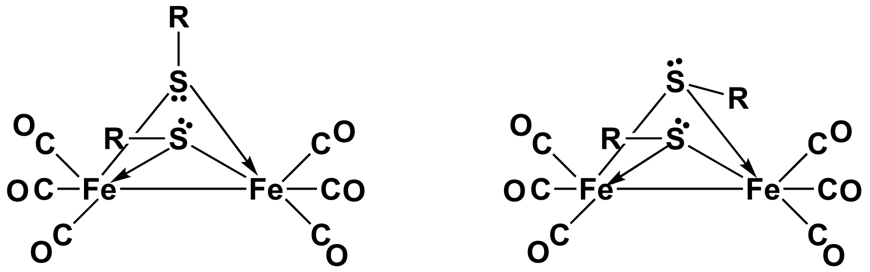
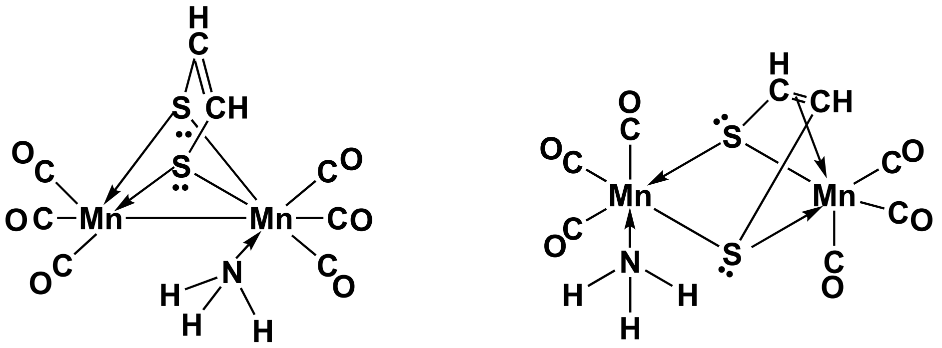


Axial-equatorial (ae) isomer **equatorial-equatorial (ee) isomer**

Figure 4. The two known stereoisomers of the $(RS)_2Fe_2(CO)_6$ derivatives.



$H_2C_2S_2Mn_2(CO)_6 \cdot NH_3$
structure originally proposed:
displacement of C=C double bond
by ammonia

$H_2C_2S_2Mn_2(CO)_6 \cdot NH_3$
structure suggested by theory:
breaking the Mn-Mn bond
by ammonia

Figure 5. Comparison of the originally proposed $H_2C_2S_2Mn_2(CO)_6 \cdot NH_3$ structure involving the displacement of the coordinated C=C double bond with the structure suggested by this theoretical study involving the breaking of the Mn–Mn bond.

According to our DFT studies, the structure of the binuclear ethylenedithiolate manganese carbonyl complex $H_2C_2S_2Mn_2(CO)_6$ with a complexed C=C double bond of the ethylenedithiolate ligand suggested when its original synthesis was reported in 1968[91] is now supported by our theoretical study. However, the reversible complexation of $H_2C_2S_2Mn_2(CO)_6$ with ammonia or trimethylphosphine to form adducts of the type $H_2C_2S_2Mn_2(CO)_6{\cdot}L$ does not involve displacing the complexed C=C double bond by the Lewis base as originally suggested. Instead the formation of such adducts involves a reversible rupture of the Mn-Mn bond in $H_2C_2S_2Mn_2(CO)_6$ upon complexation with Lewis bases. Thus $H_2C_2S_2Mn_2(CO)_6$ represents an unusual type of Lewis acid where complexation with Lewis bases involves the reversible rupture of a metal-metal bond.

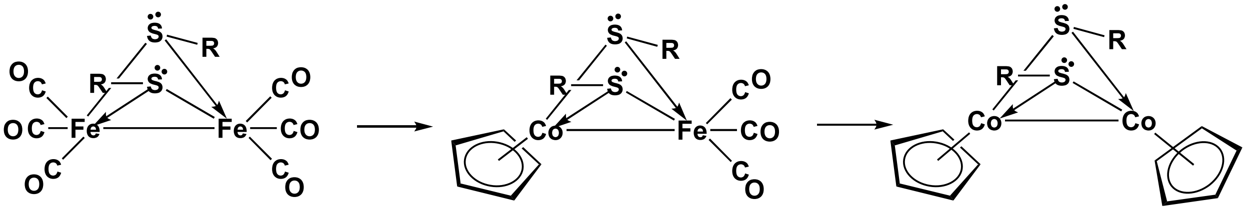
The thermodynamics of CO dissociation in the series $H_2C_2S_2Mn_2(CO)_n$ (n = 8 – 5) accounts for the formation of the hexacarbonyl $H_2C_2S_2Mn_2(CO)_6$ upon the reaction of $Mn(CO)_5Br$ with sodium ethylenedithiolate. Thus the octacarbonyl $H_2C_2S_2Mn_2(CO)_8$ is not a viable species since its CO dissociation is actually exothermic at ~ 7 kcal/mol. Even the resulting heptacarbonyl $H_2C_2S_2Mn_2(CO)_7$ is a marginal species since its CO dissociation is only slighly endothermic at ~7 kcal/mol. The resulting hexacarbonyl $H_2C_2S_2Mn_2(CO)_6$ however appears to be the thermodynamic sink in this system since its CO dissociation energy is considerable at ~ 32 kcal/mol.

The data discussed in this chapter have been published in Dalton Transactions[95].

5. The group 9 cyclopentadienylmetal *cis*-ethylenedithiolates as metallodithiolene ligands in metal carbonyl chemistry: analogies to benzene metal carbonyl complexes

The initial organosulfur metal carbonyl derivatives were iron derivatives of the type $(RS)_2Fe_2(CO)_6$ first prepared by Hieber and Spacu[64] from reactions of $Fe_3(CO)_{12}$ with thiols or disulfides and later demonstrated by Hieber and Beck[79] to be dimers (Figure 6). R. B. King[80] first separated two stereoisomers of $(CH_3S)_2Fe_2(CO)_6$ by column chromatography. Dahl and Wei[81] reported the first crystal structure determination of an $(RS)_2Fe_2(CO)_6$ derivative, namely $(C_2H_5S)_2Fe_2(CO)_6$. Recently both stereoisomers of $(CH_3S)_2Fe_2(CO)_6$ were structurally characterized by X-ray crystallography[82]. The experimental Fe–Fe distance of 2.537 Å in

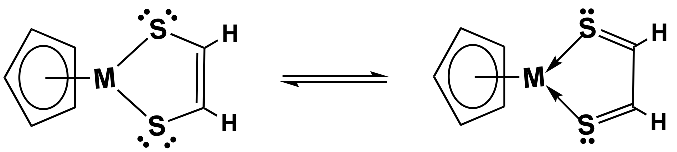
$(C_2H_5S)_2Fe_2(CO)_6$ suggested the iron-iron single bond required to give each iron atom the favored 18-electron configuration since each bridging RS ligand, considered as neutral species, donates two electrons to one iron atom and one electron to the other iron atom.



$R_2S_2Fe_2(CO)_6$ **$CpCo(SR)_2Fe(CO)_3$** **$Cp_2Co_2S_2R_2$**

Figure 6. Conversion of $(RS)_2Fe_2(CO)_6$ to $Cp_2Co_2(SR)_2$ by successive replacement of $Fe(CO)_3$ units with isoelectronic and isolobal CpCo units. Only one stereoisomer type is shown.

Heterometallic $CpCoS_2C_2H_2 \cdot M(CO)_n$ complexes can be dissected into a $CpCoS_2C_2H_2$ ligand and a metal carbonyl fragment. The $CpCoS_2C_2H_2$ ligand is a stable species which has been synthesized by reaction of $CpCo(CO)I_2$ with disodium ethylenedithiolate[91]. Nuclear Independent Chemical Shift (NICS) studies show the CoS_2C_2 ring in $CpCoS_2C_2H_2$ to be aromatic[97]. This aromaticity can be related to two possible canonical structures for a group 9 metal $CpMS_2C_2H_2$ (M = Co, Rh, Ir) derivative, namely the ethylenedithiolate structure with a 16-electron metal configuration with the neutral $H_2C_2S_2$ ligand as a two-electron donor and the dithioglyoxal structure with an 18-electron metal configuration (Figure 7). In addition, considering a ring sulfur atom to be analogous to a ring –CH=CH– unit (e.g., the thiophene-benzene analogy) and a CpCo moiety to be analogous to a BH unit makes $CpCoS_2C_2H_2$ an analogue of borepine (Figure 8). Thus a neutral pentahapto η^5-$(CpCoS_2C_2H_2)$ ligand is a six-electron donor to a transition metal ligand so that the heterometallic species $\{\eta^5$-$(CpCoS_2C_2H_2)\}Cr(CO)_3$ with a Co–Cr bond, analogous to benzene-chromium tricarbonyl, $(\eta^6$-$C_6H_6)Cr(CO)_3$ with the favored 18-electron chromium configuration, would be expected to be favorable species.

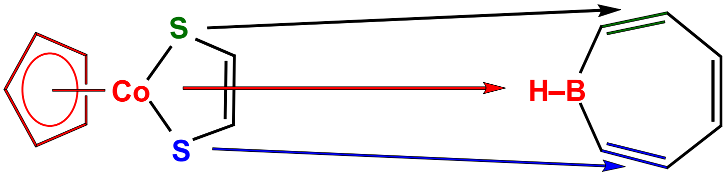


Ethylenedithiolate structure **Dithioglyoxal structure**

16-electron M configuration **18-electron M configuration**

M = Co, Rh, Ir

Figure 7. The ethylenedithiolate and dithioglyoxal canonical structures for the Group 9 metal complexes $CpMS_2C_2H_2$ (M = Co, Rh, Ir).



Cobalt ethylenedithiolate **Borepine**

Figure 8. Analogy between the cobalt ethylenedithiolate complex and borepine through the isoelectronic CpCo → BH and S → -CH=CH- relationships.

According to the results presented in the thesis, the $CpMS_2C_2H_2$ (M = Co, Rh, Ir) molecules are analogous to benzene in functioning as six-electron donor pentahapto metallodithiolene ligands in the lowest energy $CpMS_2C_2H_2Cr(CO)_n$ (n = 3, 2) and $CpMS_2C_2H_2Fe(CO)_2$ structures by substantial margins. Such pentahapto η^5-($CpMS_2C_2H_2$) bonding involves all five atoms of the MS_2C_2 ring including the C=C double bond and gives the central chromium or iron atom in the $CpMS_2C_2H_2{\cdot}Cr(CO)_3$ and $CpMS_2C_2H_2{\cdot}Fe(CO)_2$ the favored 18-electron configuration.

The C=C double bond of the $CpMS_2C_2H_2$ ligands (M = Co, Rh, Ir) is not involved in the trihapto bonding to the central chromium and iron atom in the lowest energy $CpMS_2C_2H_2{\cdot}Cr(CO)_4$ and $CpMS_2C_2H_2{\cdot}Fe(CO)_3$ structures in which the central chromium or iron atom requires only four electrons from the $CpMS_2C_2H_2$ ligand to attain the favored 18-electron configuration. Instead the $CpMS_2C_2H_2$ molecules are trihapto ligands bonding to the central chromium or iron atom through a heterometallic M–M′ (M′ = Cr, Fe) bond and two metal-sulfur bonds. Such structures are closely related to the originally synthesized iron carbonyl complexes $(RS)_2Fe(CO)_6$ (R = Me, Et, Ph, etc.) by replacing one of the $Fe(CO)_3$ units by an isoelectronic/isolobal CpM (M = Co, Rh, Ir) unit. Higher energy $CpMS_2C_2H_2\cdot Cr(CO)_4$ and $CpMS_2C_2H_2\cdot Fe(CO)_3$ structures involve the C=C double bond at least one of the sulfur atoms in the $CpMS_2C_2H_2$ ligands in the ligand-metal bonding but have metal-metal distances too long to suggest heterometallic metal-metal bonding.

The $CpMS_2C_2H_2\cdot Cr(CO)_5$ and $CpMS_2C_2H_2\cdot Fe(CO)_4$ structures require only two electrons from the $CpMS_2C_2H_2$ ligand for the central chromium and iron atoms to attain the favored 18-electron configuration. Since there are a number of subsets of the atoms in the MS_2C_2 ring that can provide two electrons, the potential eneregy surfaces of these systems are the most complicated of the systems studied in this work. In the lowest energy $CpMS_2C_2H_2\cdot Cr(CO)_5$ and $CpMS_2C_2H_2\cdot Fe(CO)_4$ structures the $CpMS_2C_2H_2$ ligand is a dihapto ligand that is bonded to the chromium or iron atom through a heterometallic M–M′ (M′ = Cr, Fe) bond and a metal-sulfur bond. Other types of dihapto ligand-metal bonding found in higher energy $CpMS_2C_2H_2\cdot Cr(CO)_5$ and $CpMS_2C_2H_2\cdot Fe(CO)_4$ structures include bonding only the C=C double bond of the ethylenedithiolate ligand to the chromium or iron atom as in a simple (olefin)$M(CO)_n$ complex or bonding of adjacent carbon and sulfur atoms in the $CpMS_2C_2H_2$ ligand to the chromium or iron atom. The latter mode of dihapto C,S bonding of the $CpMS_2C_2H_2$ ligand can be interpreted as a π-bond from a C=S double bond in the dithioglyoxal structure for $CpMS_2C_2H_2$ (Figure 7).

The data discussed in this chapter have been published in New Journal of Chemistry[103].

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