

1. Introduction

1.1 Metal complexes

Coordination compounds have been known since the 18th century.^[1] However, their physicochemical properties were not well understood due to the absence of a proper theory. For example, the nature of ammonia ligand was not clear in complex $\text{CoCl}_3 \cdot 6\text{NH}_3$. In 1893, Alfred Werner proposed the structure of $\text{CoCl}_3 \cdot 6\text{NH}_3$ as an octahedral $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ complex (A, Figure 1.1).^[2] This hypothesis was the inception of Werner's theory, which allowed a new way of interpreting the presence of coordinating ligands around transition metals,^[3] and resulted in an exponential increase in the study of transition metals in various ligand environments.^[4] Later on, other theories, for example, the crystal field theory, the molecular orbital theory, and the ligand field theory were proposed to elucidate certain characteristics of some metal complexes which could not be explained by Werner's theory.^[5] Although organometallic (hybrid of organic and inorganic chemistry) complexes were known since 1827,^[6] the boost in organometallic chemistry started around 1950 after the discovery of landmark complexes such as ferrocene^[7] and Fischer-carbenes^[8].

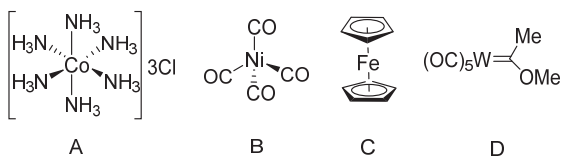


Figure 1.1: Selected examples of some milestone metal complexes; A: Werner's structure of $\text{CoCl}_3 \cdot 6\text{NH}_3$; B: first binary metal-carbonyl complex; C: ferrocene; D: first Fischer-carbene complex.

1.2 Multinuclear metal complexes

Complexes containing more than one metal are referred to as di- or multinuclear complexes. A very broad library of multinuclear complexes has been accessed and consists of both homo- and heterometallic systems. Multinuclear complexes are interesting in several regards as they may, for example, promote cooperativity between different metals in one system, provide structural motifs known as metalloligands for the design of specific materials, and alter the physical

properties of the system.^[9] Depending on the ways to arrange two or more metals in a complex, multinuclear complexes can be divided into two categories: i) complexes with a direct metal-metal bond, ii) two or more metals connected by bridging ligands.

1.2.1 Multinuclear complexes with direct metal-metal bond(s)

In 1938, the solid-state structure of $[\text{Fe}_2(\text{CO})_9]$ was determined by X-ray diffraction studies and, for the first time, the concept of metal-metal bond was proposed in a molecular complex.^[10] The diamagnetic character of $[\text{Fe}_2(\text{CO})_9]$ can be explained by the pairing of two electrons on the Fe atoms, however, some theoretical arguments favour spin coupling *via* the carbonyl bridges without a direct Fe-Fe bond.^[11] The concrete evidence of direct metal-metal bond came in 1957 *via* the solid-state structure determination of $[\text{Mn}_2(\text{CO})_{10}]$, the latter featuring an unsupported Mn-Mn single bond (Figure 1.2).^[12]

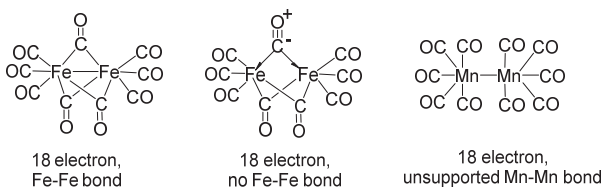


Figure 1.2: Structural representation of $\text{Fe}_2(\text{CO})_9$ and $\text{Mn}_2(\text{CO})_{10}$.^[11-12]

The breakthrough result in the field of metal-metal bonds was published in the early 1960s by Cotton, where the first quadruple bond was structurally characterized in the $[\text{Re}_2\text{Cl}_8]^{2-}$ ion.^[13] The four unpaired electrons in the 5d orbitals of Re^{3+} are paired together to form a quadruple bond. After this work, a spiked interest in this field eventually resulted in metal-metal bonds with bond orders ranging from single to quintuple.^[10] The bonding situation in such complexes was investigated to get an in depth knowledge of metal-metal bonds. An overview of the bonding situation in quadruple bonds (*vide infra*) has been discussed by Cotton and others (Figure 1.3).^[10] Complexes with metal-metal bonds of lower bond order can also be described in a similar manner. To form a quadruple bond, each metal must have at least four unpaired electrons in the

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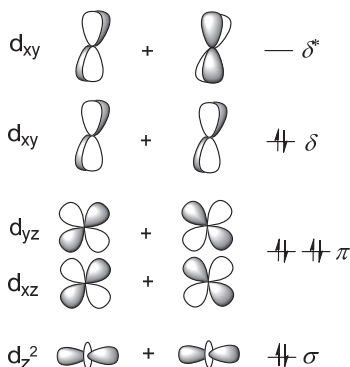


Figure 1.3: Overlap of d-orbitals involved in quadruple bond formation in $[\text{Re}_2\text{Cl}_8]^{2-}$ ion and the resulting energy levels.^[10]

outermost d-orbital. For example, in the $[\text{Re}_2\text{Cl}_8]^{2-}$ ion, each Re atom is in the +3 oxidation state and possesses four unpaired electrons that can lead to bond formation with the other Re atom. The positive axial overlap between two d_{z^2} orbitals results in the formation of a sigma bond (σ) and the corresponding negative overlap leads to an antibonding orbital (σ^*). The lateral overlap between two d_{xz} orbitals on the one hand and two d_{yz} orbitals on the other hand, resulting in $d_{xz} + d_{xz}$ and $d_{yz} + d_{yz}$ combinations, gives rise to degenerate orthogonal π -orbitals. The corresponding negative overlap results in the corresponding antibonding π^* -orbitals. Finally, the lateral overlap between d_{xy} orbitals results in the formation of δ and δ^* orbitals. The relative

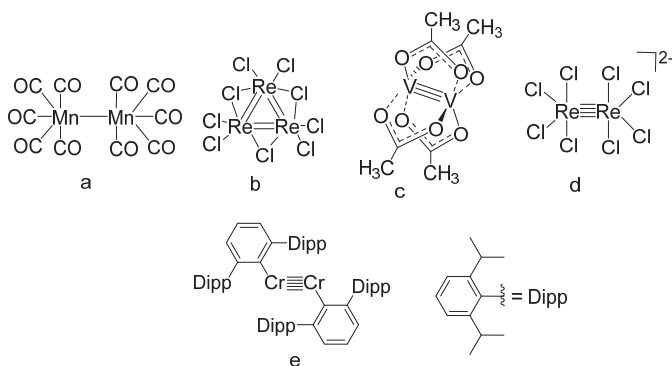


Figure 1.4: Selected examples of metal complexes with a metal-metal bond order from one to five.^[10,14]



energy of the molecular orbitals can be determined using the Hückel concept *i.e.* the more the overlap, the lower the energy of the bonding molecular orbital. The overlap strength is increasing in the order $\delta < \pi < \sigma$, resulting in the following order in the energy of the molecular orbitals: $\sigma < \pi < \delta < \delta^* < \pi^* < \sigma^*$. The bond order corresponds to half of the difference between the numbers of bonding and antibonding electrons. In case of the $[\text{Re}_2\text{Cl}_8]^{2-}$ ion, eight electrons occupy bonding orbitals (excluding the Cl ions) and no electron is present in antibonding orbitals, resulting in a quadruple bond between the two Re atoms.^[10] In 2006, Power and co-workers raised the bar for the maximum number of bonds possible between two elements by making the first quintuple bond in a chromium complex (e, Figure 1.4).^[14]

1.2.2 Multinuclear complexes *via* bridging ligands

Using a bridging ligand is a common approach to make multinuclear complexes, the key aspect of this approach is ligand design rather than considerations of possible metal-orbital overlaps. In addition, this approach allows an easy inclusion of different types of metals in one complex. Multinuclear complexes can be classified into two groups a) homometallic complexes: two or more identical metals in one complex b) heterometallic complexes: two or more different metals in one complex.^[15] Homometallic complexes can be conveniently synthesized by using multidentate ligands having similar coordination sites. On the other hand, the synthesis of heterometallic complexes requires specifically designed ligands having donor sites for binding to specific metals. Heterometallic complexes present the additional possibility of a synergistic reactivity, which is different than that observed for complexes containing only one type of metal.^[16] Several types of heterometallic complexes have been reported in the literature and a very broad spectrum of ligands is available to synthesize them. In this section, only bidentate ligands featuring both a soft and a hard donor centre, in respect with the “hard and soft acids and bases” (HSAB) principle, are discussed. The most frequently used hard donor functional groups include carboxylates, alkyl or aryloxides, and amides, while typical soft donor groups involve thiols, phosphines, and carbenes. In the periodic table, early transition metals are classified as relatively hard acids, in comparison to the softer nature of late transition metals. Ligands with hard and soft donor groups within the same framework have been successfully employed to access early-late heterobimetallic (ELHB) complexes.

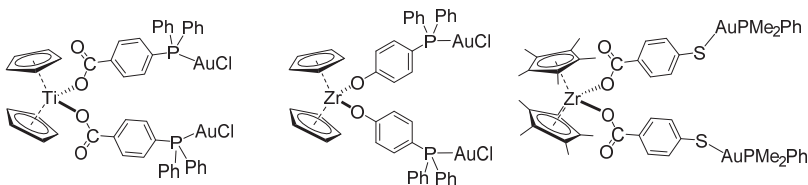


Figure 1.5: Selected examples of group-4 and [Au] heterobimetallic complexes.^[17]

Apart from being fundamentally interesting, ELHB complexes have shown potential applications in catalysis, small molecule activation and medicinal chemistry.^[18] Notably, P-N based ligands have been successfully employed for the synthesis of several ELHB complexes,^[18-19] which have also been further used in various small-molecule activation. Especially, Ti/Zr-Co complexes supported by phosphinoimide ligands have been used to activate H₂,^[20] CO₂,^[21] organoazides,^[22] and diazo reagents.^[23] Very recently, a Zr-Co complex was used to activate dry oxygen and pyridine-*N*-oxide, and the obtained complexes were further tested for the ring opening of thf in the presence of Lewis acids. The use of P-N ligands to access heterometallic complexes is not only limited to transition metals as these ligands have also been used to synthesize lanthanide-transition metal complexes.^[24] On the basis of the HSAB principle, hydroxy or carboxy group substituted phosphine ligands, that can be conveniently synthesized, are also promising supporting ligands for the selective preparation of heterometallic complexes. Corresponding heterometallic complexes of group 4 metals and gold have been synthesized and have shown interesting properties such as photoluminescence and anti-cancer properties (Figure 1.5).^[17]

1.3 Divalent lanthanides

1.3.1 General

Lanthanides (Ln) belong to f-block elements and their most common oxidation states are 0 and +3, although the oxidation states +2 and +4 are also known depending on the Ln element.^[25] The chemistry of trivalent lanthanides is very well explored and the corresponding complexes have found applications in various fields ranging from material science to bioinorganics.^[25] In comparison, divalent lanthanides (Ln^{II}) are far less studied because the +2 oxidation state of lanthanides is not naturally occurring. Divalent lanthanide complexes are classified into two



classes *i.e.* classical and non-classical. Among the lanthanides, Eu, Yb, and Sm are the most stable in divalent oxidation state and are categorized as classical divalent lanthanides.^[26] The remaining lanthanides are classified as non-classical divalent lanthanides. Among the non-classical Ln^{II}, halides of only Tm, Dy, and Nd have been isolated in the solid state.^[27] However, stable organometallic complexes of all the non-classical divalent lanthanides have also been successfully synthesized by employing bulky cyclopentadienyl ligands.^[28] Apart from numerous applications of Ln^{II}, the use of [Sm^{II}X₂] (X = Cl, Br, I) as a single-electron reductant in several organic reactions is a standout application.^[29]

In 1964, Fischer reported the synthesis of the first organometallic complexes of divalent Eu and Yb by reaction of elemental Eu or Yb and cyclopentadiene in liquid ammonia.^[30] Five years later, the first organometallic complex of divalent samarium, [Cp₂Sm^{II}] (Cp = C₅H₅), was also obtained by reduction of [Cp₃Sm^{III}] with potassium-naphthalene in thf.^[31] However, at that time, the interest in this field kept rather limited because of the insolubility of [Cp₂Ln^{II}] (Ln = Sm, Eu, Yb) in common organic solvents. In 1981, Evans *et al.* synthesized the hydrocarbon-soluble divalent lanthanide complex [Cp*₂Sm^{II}(thf)₂] (Cp* = C₅Me₅) by vaporization of elemental Sm into a hexane solution of pentamethylcyclopentadiene.^[32] Later on, a simple synthesis of [Cp*₂Sm^{II}(thf)₂] in solution was reported by reaction of [Cp*K] with [SmI₂] in a 2:1 molar ratio in thf.^[33] As of now, a substantial amount of research has been done on divalent lanthanocenes due to their easy accessibility, and especially on samarocene due to its highly reductive nature. It should be noted that [Cp*₂Sm^{II}(thf)₂] is a stronger reducing agent than [Sm^{II}I₂] because Cp* ligands are more electron donating compared to iodides.^[34] Sublimation of [Cp*₂Sm^{II}(thf)₂] at elevated temperature leads to the loss of the two thf molecules, resulting in the unsolvated samarocene, [Cp*₂Sm^{II}].^[35] The most striking reactivity of [Cp*₂Sm^{II}] is the activation of dinitrogen at room temperature. The reaction of two molecules [Cp*₂Sm^{II}] with one molecule of N₂ occurs *via* single-electron reduction steps, resulting in the oxidation of Sm from +2 to +3, and the formation of a di-reduced N₂²⁻ dianion which is trapped in between two [Cp*₂Sm^{III}]⁺ moieties.^[36] Roesky and co-workers have synthesized the first molecular f-block polyphosphide by activation of white phosphorous with [Cp*₂Sm^{II}].^[37] However, no reaction was observed with the heavier pnictogens

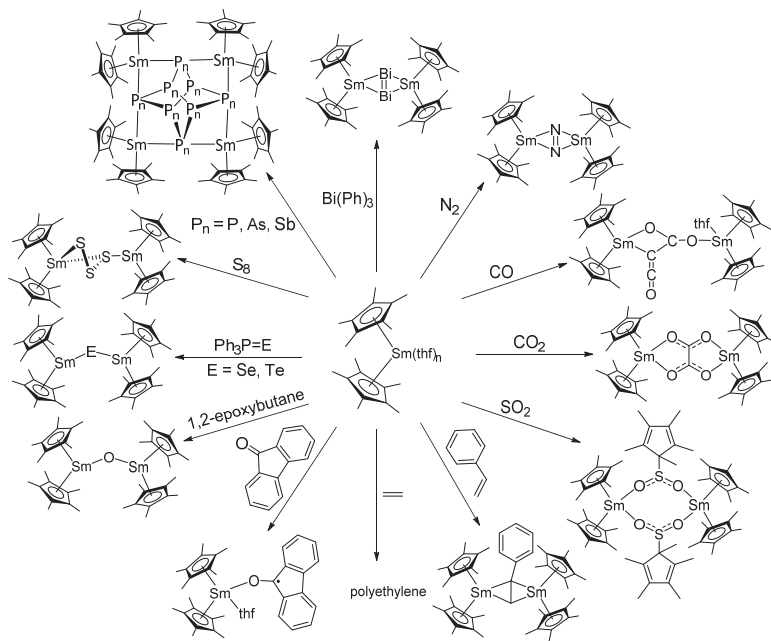


Figure 1.6: Reactivity of $[\text{Cp}^*_2\text{Sm}^{\text{II}}(\text{thf})_n]$ towards different organic and inorganic species (or elements).

such as elemental arsenic and antimony. Synthesis of the largest polyarsenides and polystibides of samarium was nevertheless possible by reaction of $[\text{Cp}^*_2\text{Sm}^{\text{II}}]$ with highly reactive nanoscale arsenic^[38] or nanoscale antimony,^[39] respectively. The strong reductive ability of samarocene has also allowed the activation of small molecules such as CO_2 ,^[40] CO ,^[41] SO_2 ,^[42] and N_2 .^[41] Miscellaneous reduction reactions of main group species and elements by samarocene resulted in the isolation of several elusive anions such as $(\text{P}_n)_8^{4-}$ ($\text{P}_n = \text{P}, \text{As}, \text{Sb}$),^[37-39] Bi_2^{2-} ,^[43] $[\text{OC}_3\text{O}_2]^{2-}$,^[41] S_3^{2-} ,^[44] and N_2^{2-} .^[36] The reduction chemistry of samarocene has also been extended to organic molecules containing unsaturated bonds such as styrene and ethene (Figure 1.6).^[45]

The chemistry of divalent lanthanides is dominated by the use of cyclopentadiene as a supporting ligand. The metal-ligand interaction involving f-block metals is more ionic in nature, compared to that with transition metals. Indeed, Wilkinson showed that the reaction of $[\text{Cp}_3\text{Sm}^{\text{III}}]$ with FeCl_2 resulted in the formation of ferrocene and samarium(III) chloride.^[25] Due to this fact, it was long



electronic environments around the lanthanide metal centre, resulting in a different stabilization of possible intermediates.

1.3.2 Lanthanide-Transition metal carbonyl complexes

f-block elements can be characterized by their strong Lewis acidity, as well as specific photoluminescence and magnetism properties.^[25,51] Transition metal carbonyl complexes, on the other hand, are well known for their catalytic properties.^[6] Therefore, heterometallic complexes of the type Ln-TM (TM = transition metal) carbonyl are interesting from both fundamental and application points of view.^[52] Understanding the metal-metal interaction between d- and f-block elements is especially desirable. Ln-TM carbonyl complexes can be divided into three major categories: (i) isocarbonyl linkage between both metals, (ii) direct Ln-TM bond, and (iii) solvent-separated ion pairs.^[52] Owing to the oxophilic nature of lanthanides and the stabilization of the anionic charge on the TM due to π -acceptor nature of the CO ligands, isocarbonyl bridged Ln-TM complexes are predominant over the two other systems.^[53] Depending on the oxidation state of the lanthanide metal centre, two types of Ln-TM carbonyl complexes have been synthesized: i) Ln^{III}-TM carbonyl complexes and ii) Ln^{II}-TM carbonyl complexes. Ln^{III}-TM carbonyl complexes have been synthesized either by a salt metathesis reactions between trivalent lanthanide complexes and alkali-salts of TM carbonyls^[54] or through redox reactions between divalent lanthanides and TM carbonyls.^[55] In contrast, Ln^{II}-TM carbonyl complexes have been accessed by reaction of elemental lanthanides (Sm, Yb, Eu) with TM carbonyls in the presence of mercury.^[52-53,56]

Anderson and co-workers reported the first structurally characterized Ln^{III}-TM carbonyl complex, $[(Cp^*_2Yb^{III})_2(\mu_2-\eta^2-CO)_4\{(CO)_7Fe_3\}]$, obtained by reduction of $[Fe_2(CO)_9]$ with $[Cp^*_2Yb^{II}(OEt_2)]$.^[55a] This strategy to reduce TM carbonyl complexes with highly reductive divalent lanthanide complexes was further applied to other TM metal complexes such as $[Mn_2(CO)_{10}]$, $[Co_2(CO)_8]$, and $[(Cp^*Fe(CO)_2)_2]$ (Figure 1.8).^[55a-d,57] In such reactions, the divalent lanthanide complexes are oxidized from the +2 to +3 oxidation state *via* a single-electron transfer to the TM carbonyl moiety. As a result, formation of the $[TM(CO)_x]^-$ anion occurs, along with TM-TM bond cleavage. However, in some cases, instead of TM-TM bond cleavage, formation of new TM-TM bonds or new anionic TM carbonyl clusters is observed. For example, Deacon and co-workers isolated the

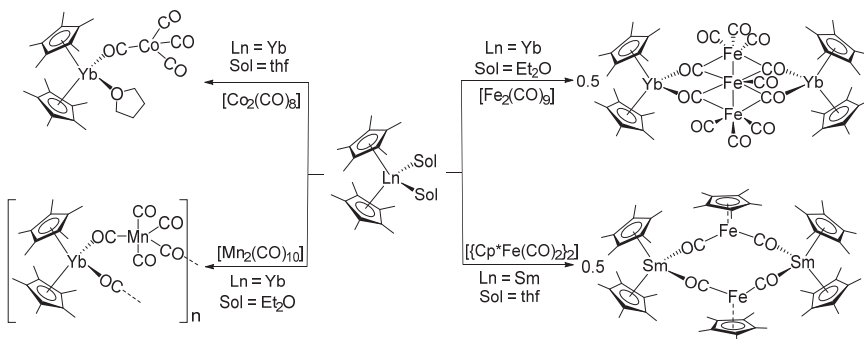


Figure 1.8: Ln^{II}-TM carbonyl complexes via reduction of TM carbonyls by divalent lanthanocenes.^[55a-d]

elusive $[W_2(CO)_{10}]^{2-}$ anion, featuring an unsupported W-W bond in a mixed-valent Sm^{II/III} calix[4]pyrrolide sandwich by reduction of $[W(CO)_6]$ with a divalent samarium *meso*-octaethylcalix[4]pyrrolide.^[58] The reduction of TM carbonyls by using different ligands around Ln^{II} have also been investigated. The reaction of $[(Tp^{Me,Me})_2Sm^{II}]$ ($Tp^{Me,Me}$ = hydro-tris-(3,5-dimethyl)pyrazolylborate) with $[Re_2(CO)_{10}]$ resulted in the formation of $[(Tp^{Me,Me})_2Sm^{III}][HRe_4(CO)_{17}]$ featuring a novel rhenium carbonyl cluster, $[HRe_4(CO)_{17}]^-$ (Figure 1.9).^[59] It should be noted that divalent lanthanides have been also used in the reduction of TM carbonyl sulfides or polyphosphides. For example, the reduction of $[Fe_2(\mu-S_2)(CO)_6]$ by $[Cp^*_2Ln^{II}(thf)_2]$ (Ln = Sm, Yb) resulted in a wheel-shaped Ln-Fe sulfide cluster, $\{[Cp^*_2Ln^{III}]_2\{(\mu-S)_6(CO)_{12}Fe_6\}$.^[60]

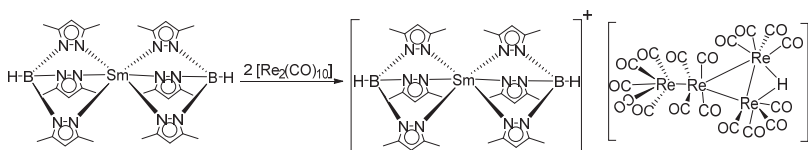


Figure 1.9: Synthesis of rhenium-carbonyl cluster by reduction of $[Re_2(CO)_{10}]$ with $[(Tp^{Me,Me})_2Sm^{II}]^+$.^[59]

The first Ln^{II}-TM carbonyl complex, $[(NH_3)_nYb^{II}((\mu-CO)_4Fe)]$, has been obtained by Shore and co-workers by reduction of $[Fe_3(CO)_{12}]$ with elemental Yb in liquid ammonia. A ladder-type polymeric complex, $\{[(CH_3CN)_3Yb^{II}((\mu-CO)_4Fe)]_2(CH_3CN)\}_n$, with a direct Yb^{II}-Fe bond was obtained after crystallization from acetonitrile.^[61] This Yb^{II}-Fe carbonyl complex can be considered as a lanthanide analogue of Colman's reagent, $[Na_2\{Fe(CO)_4\}]$. Several other Ln^{II}-TM carbonyl