INORGANOMETALLIC CHEMISTRY

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Contents

Summary

The aim of this chapter is to introduce the area called inorganometallic chemistry as a specific field of non-metal (other then H, C, N, O, S and halogen) and metalloid – metal element chemistry with potential significance to the organometallic chemistry observed in the second half of the 20th century. However, in order to make the rational choice of the main group element in this chapter we focus on the d-block - p-block elements bonding involving predominately the TM elements of the groups 3 – 12 including lanthanides and main group 13 - 16 (excluding C, O and essentially S, N and P) elements. Procedures for synthesis, structure and reactivity of such inorganometallics of the general formulas TM_m-E_n (where $m = 1, 2$ and $n = 1 - 7$) (subchapter 2) inorganometallic clusters (subchapter 3) the role of inorganometallics containing TM-E bonds in catalytic transformations of compounds E (mainly of group 13, 14 and exemplary reaction of group 15 and 16) – (subchapter 4) as well as selected applications of inorganometallics as precursors of optoelectronic and ceramic materials (Section 5), constitute contents of the chapter.

1. Definition of Inorganometallic vs. Organometallic Chemistry

Organometallic compounds (organometallics) are defined as materials which possess direct ionic or covalent localized or delocalized bond between one or more carbon atoms of an organic group or molecule and the atom from the main group, transition, lanthanide or actinide metals. According to the IUPAC rules, organometallic compounds are those in which the carbon atoms are bonded to any other element with exception of H, C, N, O, F, Cl, Br, I and At. Some difficulties arise in defining the metal of the main group (*p*-block) elements. Usually organometallic compounds are comprised not only of compounds of typical metals, but also of metalloids such as boron, silicon, arsenic, selenium, etc. In compounds of metals as well as in those of metalloids, the bond is generally polarized as follows: $M^{\delta+}$ - $C^{\delta-}$. Consequently, M will be susceptible to nucleophilic attack, while the carbon atom to electrophilic attack. So, organometallic compounds contain carbon atoms bonded to elements which are more electropositive than carbon itself. Organophosphorous compounds in which element is slightly less electronegative then carbon, and to some extend organoselenium compounds are not generally included in organometallic chemistry. However, editors of the Journal of Organometallic Chemistry write “Papers dealing with those aspects of organophosphorous and organoselenium chemistry that are of interest to the organometallic chemist will also be considered.”

In most organometallic compounds, the metal-carbon bond has predominantly covalent character except for the alkali and alkaline earth metals. The ionic or covalent contribution to the bond depends on ionization potential of the metal, the size of a resulting ion, the ratio of the ionic charge to its radius, and σ–donor, σ-acceptor, π-donor and π-acceptor properties of ligands and their structure. The main group elements have four valence orbitals *ns* and *np*, while the transition metals have nine valences orbitals (*n*-1)*d*, *ns*, and *np*. Therefore, the compounds of the main group elements with bonds of considerably covalent character obey the octet rule (they form 8e compounds) while the transition metals can form 18e complexes since all their valence orbitals can be used to form molecular orbitals. On the other hand, if such a metalloid (p-block elements, i.e. main groups 13, 14, except C, 15, except N and Se and Te from 16) replaces the carbon atom in the metal-carbon bond, then they really form a metal-nonmetal bonding and, for the main part, *p*-block – *d*-block and *f*-block element bonding. Such compounds are the subject of a new field of study called “inorganometallic chemistry”.

Consequently, per analogy to the definition of “organometallics”, the “inorganometallic compounds” can be defined as materials with a bonding interaction (ionic or covalent, localized or delocalized) between one or more *p*-block elements (except carbon and other nonmetal like H, C, N, O, F, Cl, Br, I, At) of a fragment or a molecule with a transition, lanthanide or actinide metal atom (or atoms). Phosphorous and selenium including ligands are formally not excluded but in the “inorganometallics” more complex and often new types of bonding interaction are emphasized. The diversity in the bonding in particular in the transition metal - main group metal (TM-E) bonding, leads to a considerable variation in physical and chemical properties being quite different than in the classical coordination compounds.

In conclusion, the term “inorganometallics”, (in particular involving compounds containing bonds of *d*-block and/or *f*-block element with *p*-block elements) ties together much nonmetal-metal chemistry that is closely related to organometallic chemistry yet is distinctly different from the former. This can be illustrated by the triangular relationship shown in Figure 1, where the connection to p-block group element (E) – carbon chemistry (C) and transition metal (TM) chemistry is implied, Figure 1.

The main application of organometallic chemistry is the use of metals, mostly transition metals in low oxidation state capable of complex carbon-metal interactions, for activation of carbon-hydrogen and carbon-carbon bonds, generally and finally for facilitation of transformations of organic moieties. The application of organometallic reagents in organic synthesis is a convenient way for controlling of the reactivity of the organic fragment. Such a feature is expected to be much more important for related behavior of *p*-block (*E*) elements other than carbon to expect activation of inorganic fragments and finally promote new transformations of these inorganics. Besides, inorganometallic chemistry may change the intrinsic reactivity that lead to chemistry determined by equilibrium (thermodynamic control) rather than kinetics, which is a feature to carbon chemistry.

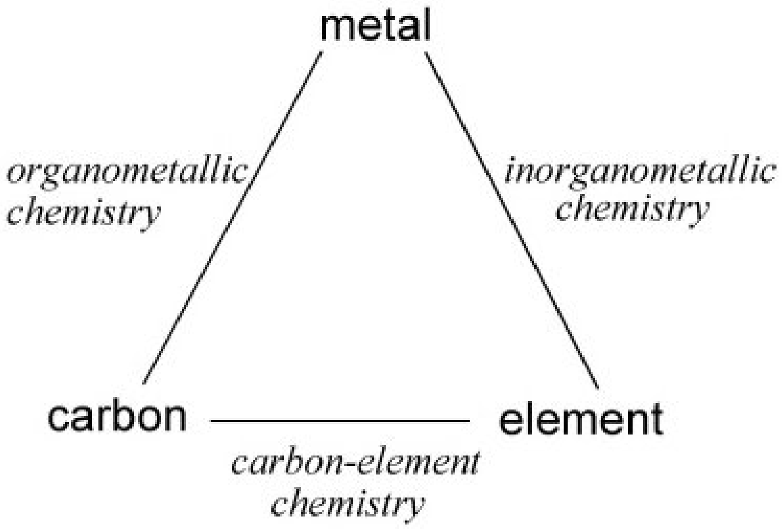


Figure 1: Illustration of the relationships between metal, carbon and nonmetal element chemistry formed which serves to define the cross-disciplinary field

Consequently, in this chapter a comparison of inorganometallic compounds with organometallic species will be strongly emphasized. Yet, the major theme of this chapter is the nonmetal – metal bond and the division between metal and nonmetals is commonly accepted (see Figure 2a). However, in order to make the rational choice of the main group element in this chapter we focus on the *d*-block – *p*-block element bonding involving predominantly the TM elements of the 3-12 groups including lanthanides and main group 13-16 presented in Figure 2b (excluding C, O and essentially S, N and P elements).

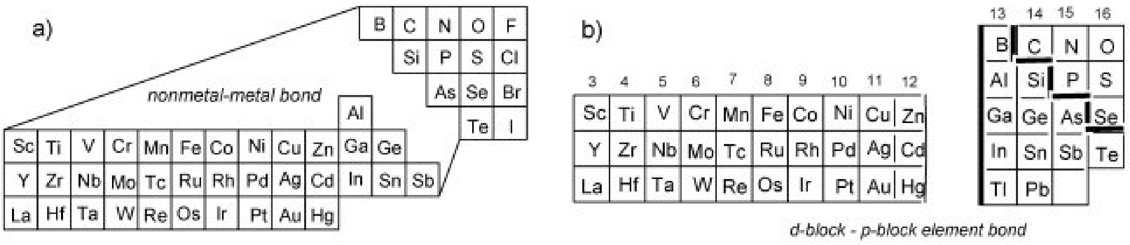


Figure 2: The division between: a) metal and non-metal bond; b) *d*-block – *p*-block element bond

A consequence of this decision is also to include partially compounds containing main group (metal) – main group (metalloid) compounds. Clusters and polynuclear complexes containing TM-metal – TM-metal bonds are the subject of the next (6.100.10) chapter so here only the clusters including TM-E bonds besides TM-TM ones are presented.

The aim of this chapter is to introduce the area called inorganometallic chemistry as a specific field of non-metal (other than H, C, N, O and halogens) – and metalloids metal element chemistry with potential significance of the organometallic chemistry observed in the second half of the 20th century.

2. Inorganometallic Compounds Containing Transition Metal (TM) – Main Group Metal (E) Bond – Synthesis, Structure and Reactivity

In order to demonstrate the fundamental modes of metal – nonmetal binding, predominantly transition metal TM – *p*-block element (E) bonds, a number of relatively uncomplicated compounds containing TM-E interactions are discussed in this section. Procedures for synthesis, structure and reactivity of such inorganometallics of the general formula TM_m-E_n (where m = 1, 2 and n = 1-7) are presented. We expect these modes of TM-p-block element bonds to be competitive to more complicated modes and structurally more complex TM_m-E_n compounds discussed in the Section 3 - Inorganometallic clusters.

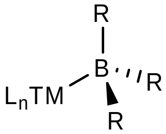
2.1. Inorganometallic Complexes of TM with Group 13 Elements

2.1.1. Inorganometallic Complexes of TM with Boron

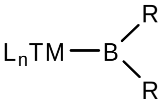
Boron shows unique structural variety in its combinations with transition metals. In contrast to borides, metallaboranes, metallaheteroboranes and π-complexes with boron-containing ligands (such as borole, diborolene, borazine or borabenzene), transition metal (TM) complexes of boron contain a conventional covalent two-center, two-electron bonds between boron and metal center. Despite very early investigation in this area (1960s), the first structurally authentic TM complex of boron was obtained only in 1990.

Boron-containing transition metal complexes can be systematically classified according to the coordination number of boron and multiplicity of the TM-B bonds.

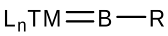
• Borane complexes containing tetra-coordinated boron atoms. These complexes can be understood as Lewis acid-base adducts of acidic boranes (BR_3) with basic TM centers giving rise to four-fold coordination of the boron atom.

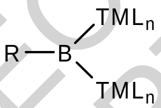


- Boryl complexes, in which sp^2-hybridized boron atoms (from $-BR_2$ groups) are linked to a TM center,



- Borylene complexes containing terminal or bridging borylene (=BR) ligands

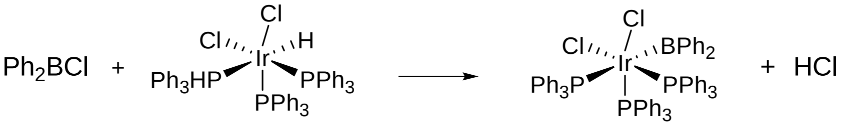




Although, many neutral and anionic TM complexes containing BR_3 fragments (e.g. $[Rh(BCl_3)(CO)(Cl)(PPh_3)_2]$, $[Co(BH_3)(CO)_4]^-$, $[CpFe(CO)_2(BPh_3)]$) have been described, their structures have been mostly confirmed on the basis of spectroscopic data and only few X-ray structures of simple derivatives have been reported. The first structurally authentic borane complex: $[Ru(Bmt_3)(CO)(PPh_3)_2]$ (mt = 2-sulfanyl-1-methylimidazol) was reported in 1999.

Among the TM complexes of boron, the group of boryl complexes of the general formula $L_nTM\text{-}BR_2$ is the largest one, comprising more than one hundred structurally characterized examples. The main synthetic approaches applied to the preparation of TM-boryl complexes are:

- Oxidative addition of haloboranes (BR_2X), hydridoboranes (BR_2H) or diboranes ($R_2B\text{-}BR_2$) to a low-valent, low-coordinate TM species with vacant coordination sites and containing readily dissociating ligands. This route can be used for elements of all of the transition metal groups, Equations (1)-(3).



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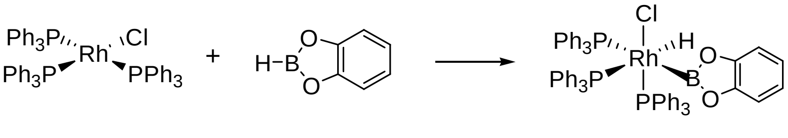

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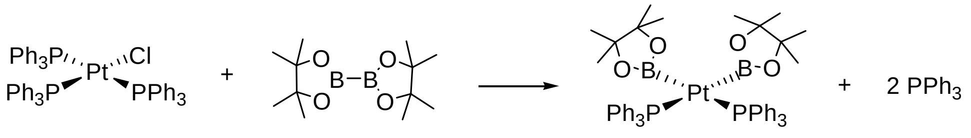
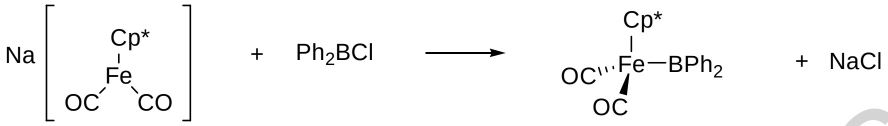


(3)

- Salt elimination reaction between an anionic TM fragment and a suitable haloborane precursor, Equations (4)-(5). This method is a popular synthetic route for generation of TM boryl complexes of group 5-8 metals.



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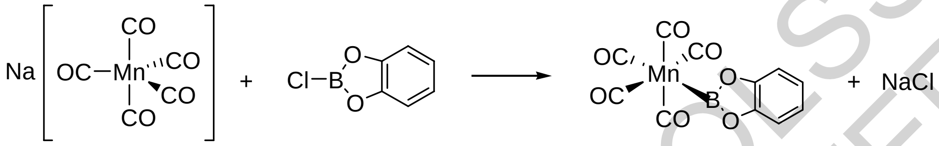


(5)

The bonding model of TM complexes containing boryl ligands assumes that the sp^2-hydridized boron atom adopts a trigonal planar coordination and forms σ-bonds with the metal fragment L_nTM (formed with an empty TM-based orbital of σ-symmetry) and with both boryl substituents R. To compensate for the electron deficiency at boron, the competitive π-donation from a metal based frontier orbital of the appropriate symmetry or from a filled non-bonding orbital on the R substituents, into the empty boron *p* orbital, takes place. Covalent bonding in TM-boryl complexes as well as stabilization of the vacant *p* orbital on boron is presented below.

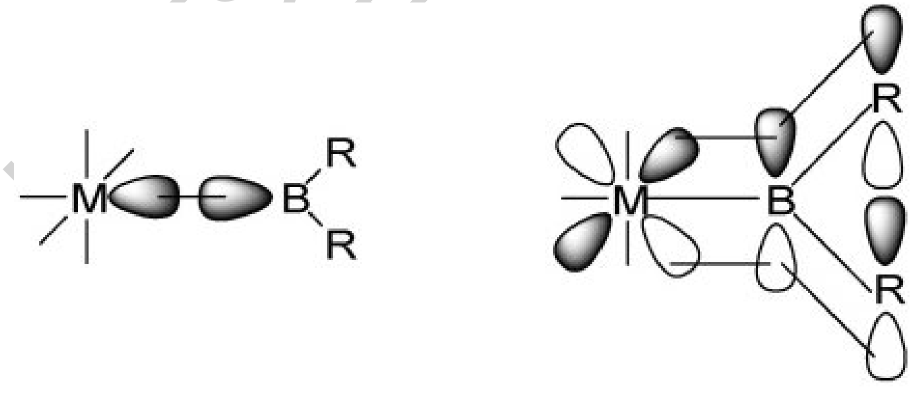
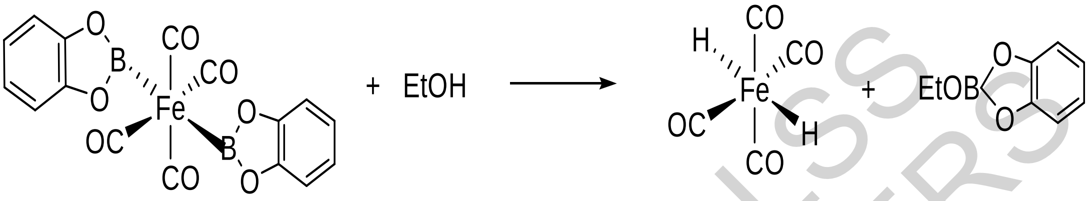


Figure 3: Covalent bonding in TM-boryl complexes

In view of the bonding relationships described above, TM complexes bearing boryl ligands are stabilized by low-valent, late transition metal centers possessing good σ-donor ligands and π-donating R substituents (e. g. catechol group or related cyclic ligands) on boron atom. However, transition metal boryl complexes are thermodynamically much more stable than those containing metal-carbon bonds, the former being quite reactive compounds. Many of them are rather labile and readily accessible to nucleophilic attack with cleavage of the TM-B bond.

There has been significant interest in the reactivity of TM complexes of boron due to their implication in many catalytic processes leading to the selective functionalization of alkanes, alkenes and arenes. Most of the TM boryl complexes exhibit instability in the presence of air and moisture, leading to decomposition of the boryl groups. Similarly, reactions with other protic reagents (e. g. alcohols, amines and hydrohalogens) proceed via TM-B cleavage with formation of respective alkoxy-, amino- or haloborane derivatives. A few examples for reactions of boryl complexes with non-polar substrates such as H_2 or halogens have been reported. These processes occur with cleavage of TM-B linkage and formation of the corresponding boranes and haloboranes, Equations (6)-(8).



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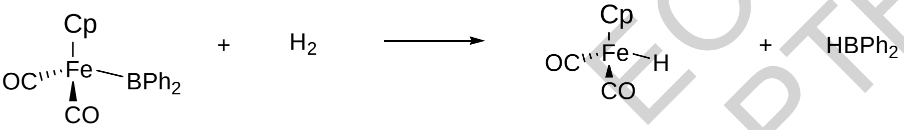

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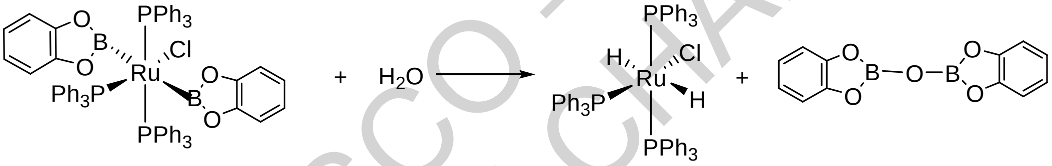
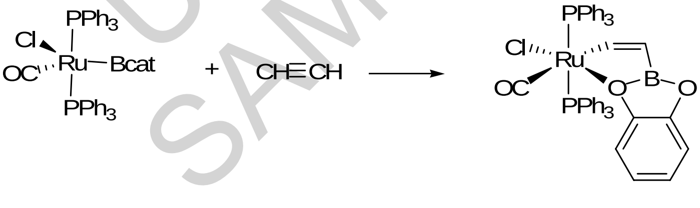


(8)

TM boryl complexes (especially those containing late TM) have also been shown to undergo insertion reactions with alkenes and alkynes (Equation (9)) to generate catalytically important boryl derivatives.



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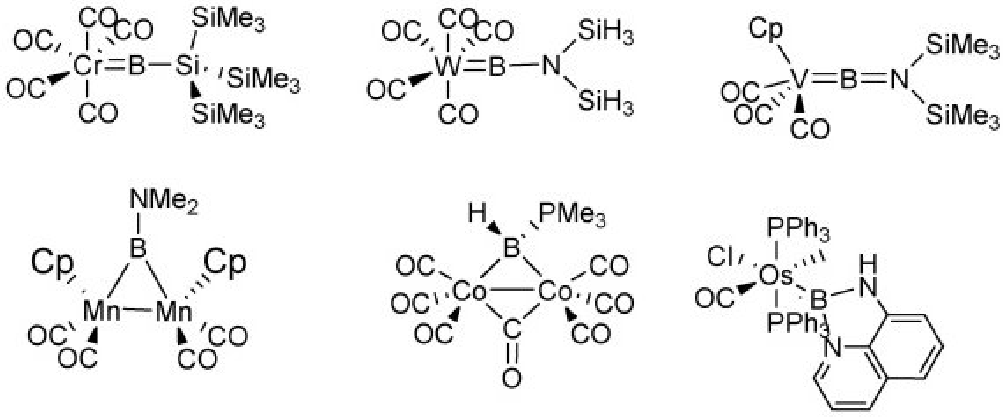


Figure 4: Selected examples of borylene complexes

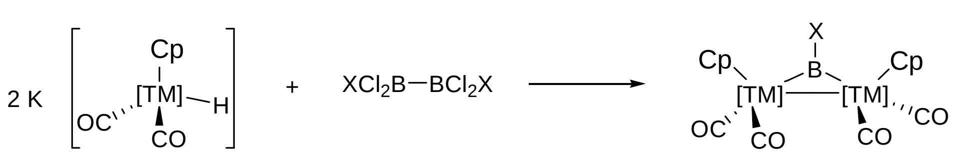
TM complexes containing borylene ligands (BR) can adopt two different coordination modes: either terminal (BR group terminally bonded to one metal atom and boron assuming a coordination number 2) or bridging (borylene group adopting bridging position between two metal centers with a threefold-coordinated boron). In comparison to boryl complexes, TM compounds bearing borylene ligands are relatively rare. Both terminal and bridging complexes have been synthesized recently, e.g., the first terminal borylene complex: [Cp*BFe(CO)$_4$], was reported in 1998. The boron center in borylene complexes require stabilization by a sterically demanding and electron-releasing ligands, Figure 4:

In view of the fact that the low-coordinated boron center in these complexes displays some Lewis acidic character, there is a possibility to add a suitable base L which results in the formation of the corresponding adducts of borylene complexes.

Terminal TM borylene complexes can be synthesized via the reaction of anionic TM precursors with dihaloorganoboranes, according to the general equation (10):

$$M'_2[L_nTM(CO)_m] \quad + \quad X_2BR \quad \longrightarrow \quad [L_n(CO)_mTM(=BR)] \quad + \quad 2\ M'X \qquad (10)$$

The reaction of anionic TM precursors with 1,2-dihalodiboranes, Equation (11) or aminodihaloboranes leads to bridging borylene compounds:



X = H, Me, NMe

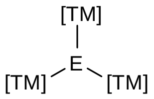
(11)

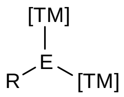
2.1.2. Inorganometallic Complexes of TM with Heavier Elements of Group 13

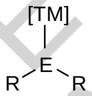
The coordination chemistry of transition metal (TM) complexes with ligands containing heavier atoms of group 13 has made remarkable progress in the last decade. These compounds are potential precursors for applications in material science since they have been found attractive single-sources for generation of special semiconductor layers by the Metalorganic Chemical Vapor Deposition (MOCVD) method. In view of the growing interest in TM-E (E = Al-Tl) species, a range of complexes and clusters have been recently synthesized and structurally characterized.

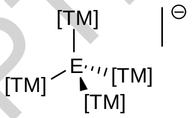
The structures of the complexes containing TM-E bonds (E = Al-Tl) can be catalogued in the following classes:

- Derivatives of the element trihalides (EX_3) or their organometallic analogues (ER_3) in which one, two or three halogen atoms or alkyl groups are substituted by TM as well as their saturated (in the sense of maximum utilization of valence electrons in two-center, two-electron bonding) derivatives



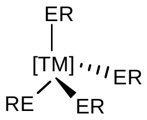






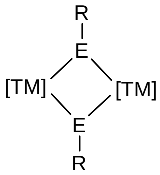
Examples: $[\{Cp(CO)_3Mo\}_3In]$, $[\{Cp(CO)_3Cr\}_3Tl]$, $[\{Cp(CO)_2Fe\}_2AlPh]$, $[Cp(CO)_2FeGa(^tBu)_2]$, $[(PMe_3)_3(H)(Et)Ir(InEt_2)]$, $[\{(CO)_5Cr\}_2TlCl]^{2-}$, $[Cp(CO)_2FeGa(^tBu)_2]$, $[Cp(CO)_2FeAlPh_3]^-$

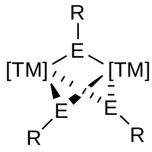
- Mononuclear complexes containing low-valent group 13 organyls (ER) where E exhibits the +1 formal oxidation state



Examples: $[(CO)_5CrGaCp^*]$, $[(CO)_4FeAlN(SiH_3)_2]$, $[Ni\{In(C(SiMe_3)_3\}_4]$, $[Pt\{GaCp^*\}_4]$

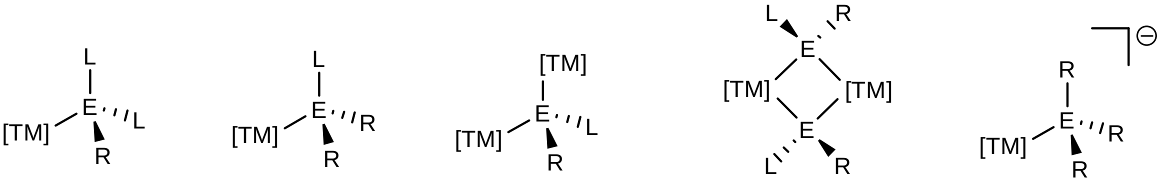
- Dinuclear TM derivatives containing bridged ER groups





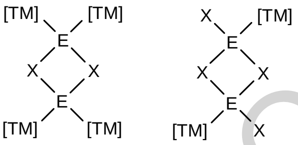
Examples: $[Mn_2(CO)_8\{\mu\text{-}InC(SiMe_3)_3\}_2]$, $[\{CpNiAlCp^*\}_2]$, $[Fe_2(CO)_6\{\mu\text{-}GaSi(SiMe_3)_3\}_3][Mo_2(CO)_6(\mu\text{-}GaCp^*)_3]$

- Complexes possessing tetra-coordinated E centers (containing TM fragments or ligands (L) as Lewis base)



Examples: $[(CO)_5WAl(Et)(tmeda)]$, $[Cp(PPh_3)NiInBr_2(OPPh_3)]$,
$[\{(CO)_4FeGa(C_2H_3)(thf)\}_2]$
$K[Cp(CO)_2FeAlPh_3]$

- Dimeric halide-bridged TM-E complexes containing tetra-coordinated E centers



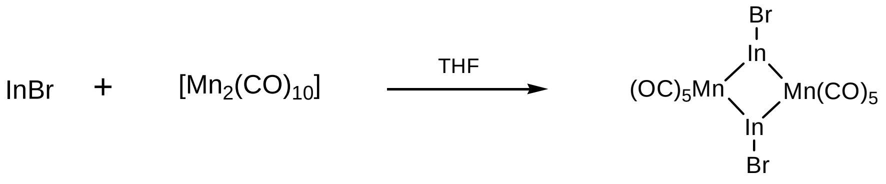
Examples: $[\{[Cp(PEt_3)Ni]_2InCl\}_2]$, $[\{[Cp(CO)_3W]_2InBr\}_2]$

- Compounds possessing triple bonds (the presence of TM≡E bonds in these compounds is still open to question): $[(CO)_4Fe{\equiv}EPh]$ (E = B, Al, Ga, In)

Most of the stable TM-E (E = Al-Tl) compounds can be derived from respective trihalides or trialkyl compounds (EX_3 and ER_3). The TM/E atomic ratio in these compounds typically is $TM/E \geq 1$. The chemistry of indium derivatives is the most complex of group 13 elements. Complexes of gallium and thallium also form considerable families, whereas the crystallographically characterized transition metal-aluminum complexes are relatively infrequent. Moreover, it is worth noting that these kinds of complexes very often contain carbonyl ligands.

Although, the bonding polarity indicates a largely ionic character of the TM-E bond in different types of complexes, the interactions discussed can be described in terms of usual donor/acceptor bond. The stability of the TM-ER bonds measured on the basis of bond dissociation energies is relatively high, decreasing in the sequence $B>Al>Ga\geq In>Tl$. The shortening of the bond lengths in the complexes when compared to those of free ligands as well as the dominant influence of the substituents at both metal center and E center point to a significant covalent contribution, coming from $E\rightarrow TM$ σ-donation and $TM\rightarrow E$ π-back donation. Although, the degree of back bonding of the $M(d_\pi)$ $-E(p_\pi)$ type is still debatable, it is well documented that $TM\rightarrow ER$ interactions play a particularly important role when the ligands contain strong π-donors groups e.g. halogens, NR_2 or cyclopentadienyl (Cp) groups.

Conventional approaches to transition metal complexes with ligands containing heavier atoms of group 13 involve insertion of low-valent halides (EX or E_2X_4) into metal-metal bond, Equation (12) or metal-halide bond, Equation (13), ligand substitution process and salt elimination. Representative examples are presented below, Equations (14)-(15):



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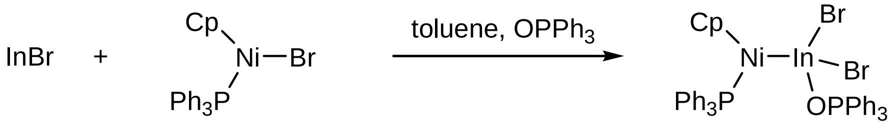

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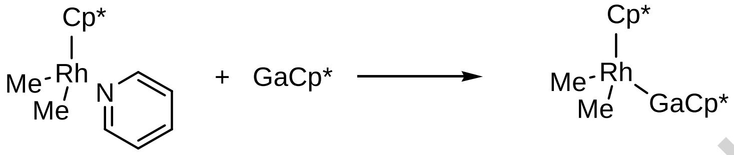

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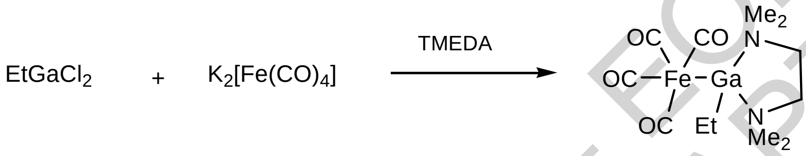
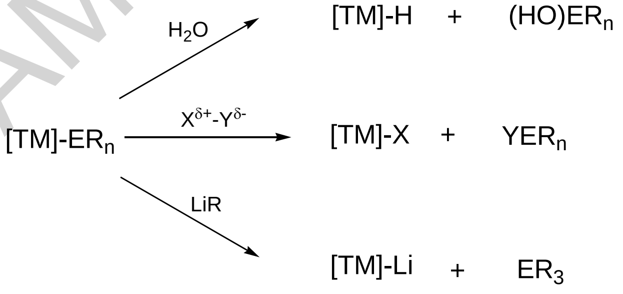
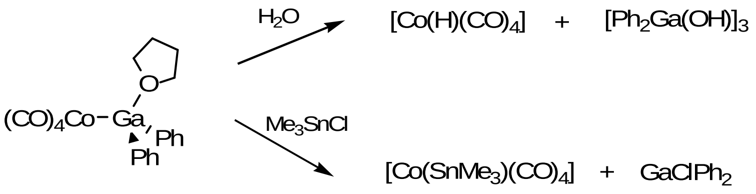


(15)

Substantial degree of ionic character of TM-E bonds affects their reactivity. The $L_nM^{(\delta-)}$-$E^{(\delta+)}R_n$ polarization leads to the formation of a negatively polarized *d*-block metal fragment and positively polarized ER_n group. Thus, the chemical properties of TM complexes containing group 13 ligands are characterized by instability of the TM-E bonds, which can be easily cleaved by electrophilic or nucleophilic reaction partners, e.g. the reaction of TM-E complexes with water provides hydride complex of TM and respective alkylmetal hydroxide. The general scheme of the reactivity of TM-E complexes and representative examples of their reactions are shown below, Schemes 1, 2:

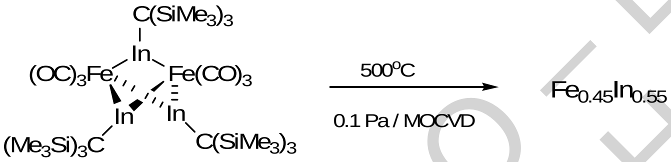


Scheme 1: Reactivity of TM group 13 element complexes



Scheme 2: Reactivity of $[(CO)_4CoGaPh_2(THF)]$

The chemistry of low-valent group 13 metal compounds has received significant attention in the last years. Recent surge in the interest in this area concerns the compounds of the general formula L_nTM-ER, as well as $TM(ER)_n$ (E = Al, Ga, In, Tl). These compounds can be new MOCVD precursors for production intermetallic phases and alloys, which can be used as special III/V type semiconductors. The use of the TM-E compounds as single-source precursors for MOCVD instead of the traditionally used mixture of TM complexes and organometallic derivatives ER_3, facilitates control of the composition of the resulting bimetallic films. For the first time, the concept of the single-source precursors proved to be effective for the deposition of β-CoGa phase of the complex $[(CO)_4CoGaCl_2(thf)]$ using MOCVD technique. An example of the use of such a process is the selective formation of Fe/In films, Equation (16).



(16)

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Professor Bogdan Marciniec, received M. Sc. (1963), Ph.D. (1970) and D.Sc. (1975) from the Adam Mickiewicz University, Poznan, Poland. Member of the Polish Academy of Sciences (1994). Head of the Department of Organometallic Chemistry (1987), President of the Adam Mickiewicz University (1988/1990), Director of Center of Excellence – Center of Silicon Chemistry (2000). He was a post-doctoral associate with Prof. R.C. Schowen, Kansas University (1970/1971).

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He is an author and co-author of 270 publications and 20 book chapters (e.g. *Handbook of Metathesis* (Verlag Chemie, 2003), *Encyclopedia of Catalysis*, (J. Wiley & Sons, Inc. N.Y., 2003), *Applied Homogeneous Catalysis with Organometallic Compounds* (Verlag Chemie, 2002) as well as editor and co-author of 10 books inter alia "*Comprehensive Handbook on Hydrosilylation*" (Pergamon Press, 1993), "*Progress in Organosilicon Chemistry*" (Gordon & Breach Publ.,1995)

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