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Review

Aromatic hydrocarbons as ligands. Recent advances in the synthesis, the reactivity and the applications of bis(η^6-arene) complexes

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Contents

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Dedicated to Professor Fausto Calderazzo, an admired and esteemed “maestro”, on the occasion of his 80th birthday.

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ABSTRACT

Synthetic procedures for bis(η^6-arene) metal derivatives and aspects of their reactivity are reviewed. Attention is focused on early transition metals (Groups 4–6) but, when necessary, reference will be made to arene derivatives of Groups 7–10, lanthanides and actinides.

After a short historical presentation of bis(η^6-arene) derivatives, aimed at illustrating the relevance of this class of compounds to the origin and the evolution of organometallic chemistry, the synthetic procedures to bis(η^6-arenes) will be discussed in the light of the most recent results. As far as the reactivity of bis(η^6-arene) compounds is concerned, particular attention is given to the electron transfer reactions occurring with or without arene displacement; data are reported for the use of low-valent bis(η^6-arene) compounds as a useful entry into the inorganic and coordination chemistry of the corresponding metal in non aqueous systems.

The use of bis(η^6-arene) derivatives of transition metals in low oxidation states (0, +1) as precursors to catalytic systems for the oligomerisation and polymerization of unsaturated monomers and as starting compounds for the preparation of molecule-based magnets, ordered crystals and new materials and supports is described.

1. Introduction

The new coordination chemistry of transition elements was initiated in 1951 when bis(cyclopentadienyl)iron(II), Fe(η^5-C_5H_5)$_2$, $FeCp_2$, was discovered independently by two research groups [1]. In order to make the iron atom obey the 18-electron rule, *i.e.* to reach

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the electronic configuration of the next inert gas, krypton, Geoffrey Wilkinson [2] and Ernst Otto Fischer [3] independently suggested that the entire π-electron system of each cyclopentadienyl group (six electrons) was involved in a symmetric bond to iron. Thus, the new compound could be correctly interpreted within the general theory of coordination compounds introduced by Alfred Werner some decades before [4], and later developed by Sidgwick [5], with the new important idea that the set of ligand donor atoms known to give coordination compounds with transition elements (at that time mainly confined to nitrogen, oxygen, sulfur and halogens) could be extended to carbon.

After the discovery of ferrocene, it was readily realized that, in addition to the six electron π-system of the planar cyclopentadienyl ligand, aromatic hydrocarbons also could act as ligands for transition metals. In 1955 Fischer and Hafner obtained the prototype of these compounds, $Cr(\eta^6\text{-}C_6H_6)_2$, isoelectronic with bis(cyclopentadienyl)iron(II), by reduction of anhydrous $CrCl_3$ with $Al/AlCl_3$ in benzene [6]. It soon became clear that compounds containing a carbon–carbon unsaturated bond could, at least in principle, behave as a ligand for a transition element: $Fe(\eta^5\text{-}C_5H_5)_2$ and $Cr(\eta^6\text{-}C_6H_6)_2$ should be therefore regarded as two milestones in the development of modern inorganic chemistry. An exhaustive and fascinating review on the discovery of $Cr(\eta^6\text{-}C_6H_6)_2$ and the solution to the problem of “Hein’s phenylchromium compounds” has appeared [7].

The chemistry of π-arene complexes has developed considerably in the last 50 years. It is interesting that these compounds, initially believed to be stable only when in combination with low-valent transition metals, were found to be isolable for transition elements in their usual oxidation states and for Main Group elements [8] as well.

Arene complexes are interesting compounds for several reasons: (i) Since the arene ligand is uncharged, vacant coordination positions can be more easily generated than with negatively charged ligands such as the cyclopentadienyl anion. (ii) The hapticity of the arene ligand may be changed (η^6-, η^4-, η^2-) by changing the nature of the ancillary ligands. (iii) The change of the hapticity of the arene ligands may create vacant coordination positions; arene derivatives therefore fulfill the primary requisite to be catalytic precursors. (iv) If the arene ligand is part of a zerovalent system, its displacement can generate the metal in an active form. If a redox reaction occurs, metal arene derivatives may be the precursors of inorganic and coordination compounds. (vi) The relatively high vapour pressures usually associated with zerovalent arene complexes make them good candidates for the Metal Organic Chemical Vapour Deposition (MOCVD).

Reviews have been published concerning synthesis, properties and reactivity of arene complexes of transition metals, Main Group elements and lanthanides [8,9]. In particular, in 1994 and 1995 two reviews appeared [8a,9e] dealing with the synthesis of arene derivatives of early transition metals. The present review will pay attention to the recent advances obtained by ourselves and by other research groups on the reactivity of derivatives of the elements of Groups 4–6. The discussion will be limited to bis(η^6-arene) derivatives of transition metals: compounds containing π-acceptors such as cyclopentadienyls, carbon monoxide and phosphines as additional ligands will not be considered.

2. Synthesis

2.1. General methods

There are several ways to generate a $M(\eta^6\text{-arene})L$ species and they depend on the nature of L which can be a σ-donor such as a halide or a labile ligand (a solvent molecule), or a π-acid such as carbon monoxide or cyclopentadienyl [8,9]. The synthetic procedures to bis(η^6-arene) derivatives are less abundant and can be substantially limited to the following reactions: (i) cyclotrimerization of alkynes, (ii) reductive complexation, (iii) halide elimination, (iv) Metal Vapour Synthesis and (v) Fischer–Hafner synthesis [10]. Having a less general character, the procedures (i)–(iii) will be shortly described, while Sections 2.2 and 2.3 will detail the Metal Vapour Synthesis and the Fischer–Hafner reaction.

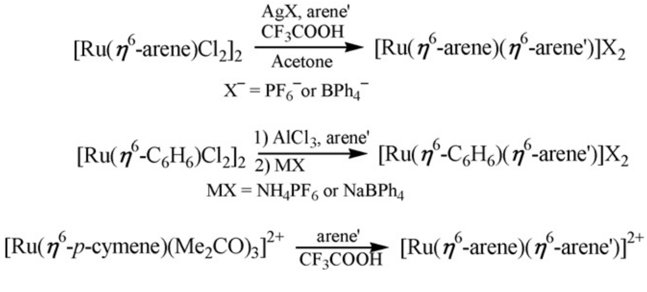
The transition metal-catalyzed cyclotrimerization of alkynes is well known as a useful method for the construction of substituted benzenes in one step [11]. In the case the reaction involves transition metal complexes, the reaction may occur stoichiometrically to give an arene metal complex rather than the free arene, thus providing a route to arene transition metal compounds that has found occasional application. For example, the reaction of 2-butyne with $Ti(\eta^6\text{-}MeC_6H_5)[(\mu\text{-}Br)_2AlBr_2]_2$ gives C_6Me_6 and the titanium(II) hexamethylbenzene complex $Ti(\eta^6\text{-}C_6Me_6)[(\mu\text{-}Br)_2AlBr_2]_2$ [12]. The zirconium(II) arene derivative $Zr(\eta^6\text{-}C_6H_6)Al_2Cl_8$ behaves similarly [13]. Analogously, the cations $[Co(\eta^6\text{-}C_6Me_6)_2]^+$ and $[Mn(\eta^6\text{-}C_6Me_6)(\eta^6\text{-}C_6H_6)]^+$ were prepared from $Co(1,3,5\text{-}Me_3C_6H_2)_2$ or $Mn(C_6H_5)_2$ and 2-butyne [14]. The stoichiometric alkyne cyclotrimerization has been used also for the preparation of mixed C_6H_6-arene derivatives of ruthenium(0) starting from $Ru(\eta^6\text{-}C_6H_6)\,\eta^4$-1,3-cyclohexadiene) under UV irradiation [15], Eq. (1).

$$Ru(\eta^6\text{-}C_6H_6)(\eta^4\text{-}1,3\text{-}C_6H_8) + 3RC \equiv CR \xrightarrow{h\nu} Ru(\eta^6\text{-}C_6H_6)(\eta^6\text{-}C_6R_6) + 1,3\text{-}C_6H_8 \quad (1)$$

In view of their catalytic applications [16], several synthetic routes have been developed for the preparation of ruthenium(II) complexes [9b], the most used being the removal of the chloride from $[Ru(\eta^6\text{-arene})Cl_2]_2$ in the presence of arenes [17], or the substitution of three two-electron donor species L such as acetone or acetonitrile in $[Ru(\eta^6\text{-arene})L_3]^{2+}$ by an arene molecule [18], Scheme 1.

Synthetic reactions starting from metal powders via activation by microwave irradiation have been proposed by Whittaker and Mingos [19]. The bis(η^6-arene) derivatives of titanium(0), $Ti(\eta^6\text{-arene})_2$, previously accessible only by the metal vaporization technique, have been prepared by reduction of $TiCl_4$ with $KBEt_3H$ in arene (arene = C_6H_6, MeC_6H_5, $p\text{-}Me_2C_6H_4$, $1,3,5\text{-}Me_3C_6H_3$) under ultrasonic irradiation [20] or with arene (4,4′-di-*tert*-butylbiphenyl) anions in THF [21]. Neodymium(II) and dysprosium(II) iodides in boiling benzene have been recently used to prepare $V(\eta^6\text{-}C_6H_6)_2$ from $V(\eta^5\text{-}C_5H_5)_2$, Eq. (2) [22]:

$$2LnI_2 + V(\eta^5\text{-}C_5H_5)_2 + 2C_6H_6 \rightarrow V(\eta^6\text{-}C_6H_6)_2 + 2Ln(\eta^5\text{-}C_5H_5)I_2, \quad Ln = Nd, Dy \quad (2)$$



Scheme 1. Synthesis of ruthenium arene derivatives.

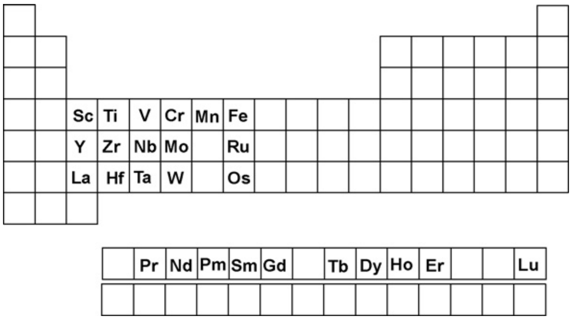


Fig. 1. Elements for which bis(η^6-arene) derivatives are prepared via the MVS technique.

2.2. The metal vapour synthesis

The metal vapour technique for the preparation of arene derivatives was introduced by Timms in 1969 [23], as applied to $Cr(\eta^6\text{-}C_6H_6)_2$. Since then, this technique was used successfully in several other cases due to its unique advantage of removing the thermodynamic barrier connected with the vaporization of the metal. Fig. 1 reports the elements for which bis(η^6-arene) complexes are prepared via MVS techniques.

In spite of some difficulties connected with the availability of the apparatus for metal vaporization, this technique has proved to be necessary for the synthesis of those compounds which cannot be obtained by conventional methods, such as bis(η^6-arene) complexes of zirconium(0), hafnium(0), tantalum(0), tungsten(0), manganese(I) and lanthanides(0) [8a,24,25], or compounds containing halogenated aromatic hydrocarbons [8a,26], aromatic amines, esters, nitriles [27], polynuclear aromatics [8a,28], biphenyl [29], poly-methylphenylsiloxanes [30] or cyclophanes [8a]. Other compounds accessible up to now only via MVS are the transition metal derivatives of heteroarenes such as pyridines [31], tetramethylpyrazine [32], phosphabenzene, C_5H_5P [31b,33], arsabenzene C_5H_5As [34].

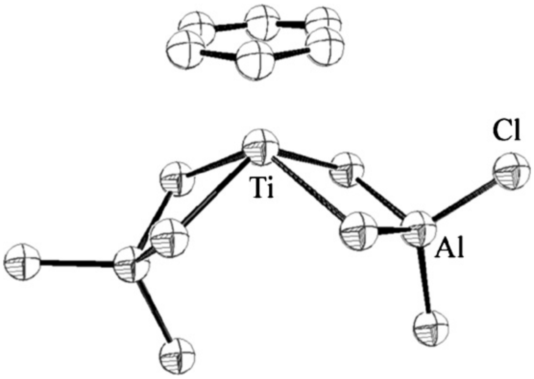


Fig. 3. Molecular structure of $Ti(\eta^6\text{-}C_6H_6)[(\mu\text{-}Cl)_2AlCl_2]_2$ [42].

2.3. The Fischer–Hafner method

The reaction of metal halides with AlX_3 in the presence or absence of aluminium in aromatic hydrocarbons has been widely used for the synthesis of η^6-arene derivatives of typical *d*-transition elements, lanthanides and actinides in their typical oxidation states or in reduced form, see Fig. 2. Examples of the first type are the η^6-arene derivatives of Fe(II), Ru(II) [35], Co(II), Rh(II) [36], Ni(II) [37] of general formula $[M(\eta^6\text{-arene})_2]^{2+}$, and U(IV), $\{[U(\eta^6\text{-}C_6Me_6)Cl_2]_2(\mu\text{-}Cl)_3\}AlCl_4$ [38], Eq. (3), while the η^6-arene derivatives of Cr(I), V(I), Mo(I) and U(III), have been obtained in the presence of aluminium [8a,26d,39,40]:

$$2UCl_4 + AlCl_3 + 2\,C_6Me_6 \rightarrow \{[U(\eta^6\text{-}C_6Me_6)Cl_2]_2(\mu\text{-}Cl)_3\}AlCl_4 \tag{3}$$

A different behaviour is observed with the halides of Group 4 metals, MX_4, and of niobium and tantalum, MX_5 [8a,9e,41]. They react with the Fischer–Hafner reducing system, producing mono-arenes of general formula $M(\eta^6\text{-arene})[(\mu\text{-}X)_2AlX_2]_2$ with bridging tetrahaloaluminato groups. This type of structure is well established for the titanium(II) halo complexes, $Ti(\eta^6\text{-arene})[(\mu\text{-}X)_2AlX_2]_2$; Fig. 3 reports the structure of the prototype, $Ti(\eta^6\text{-}C_6H_6)[(\mu\text{-}Cl)_2AlCl_2]_2$ [42]. Similar structural properties are observed for the lanthanide derivatives $Ln(\eta^6\text{-arene})[(\mu\text{-}X)_2AlX_2]_3$ formed when LnX_3 reacts with AlX_3 in arenes [8a,43].

The arene synthesis via the Fischer–Hafner methods often produces biphasic liquid systems, the dark-coloured lower layer generally containing most of the metal. A similar phenomenon was reported by Atwood [44] for tetraalkylammonium derivatives of large, aluminium-containing anions. These systems were named “liquid clathrates” [44] to indicate the formation of *non-stoichiometric liquid inclusion* complexes. Some years ago, we studied [45] the biphasic system obtained from the reaction $VX_3/Al/AlX_3/1,3,5\text{-}Me_3C_6H_3$ system and verified that the $1,3,5\text{-}Me_3C_6H_3$/vanadium molar ratio is an important factor in determining the formation of the bilayer system.

Recently, successful crystallizations of $[M(\eta^6\text{-arene})_2]^+$ species directly from the liquid phase obtained from the Fischer–Hafner reduction of MCl_3 (M = V, arene = MeC_6H_5 [46], M = Cr, arene = C_6H_6) [47] have definitely confirmed the presence of cationic species as primary products of the process.

Although the Fischer–Hafner synthesis requires less expensive and common laboratory glassware, it suffers from some limitations related to the reactivity of both aluminium (which explosively

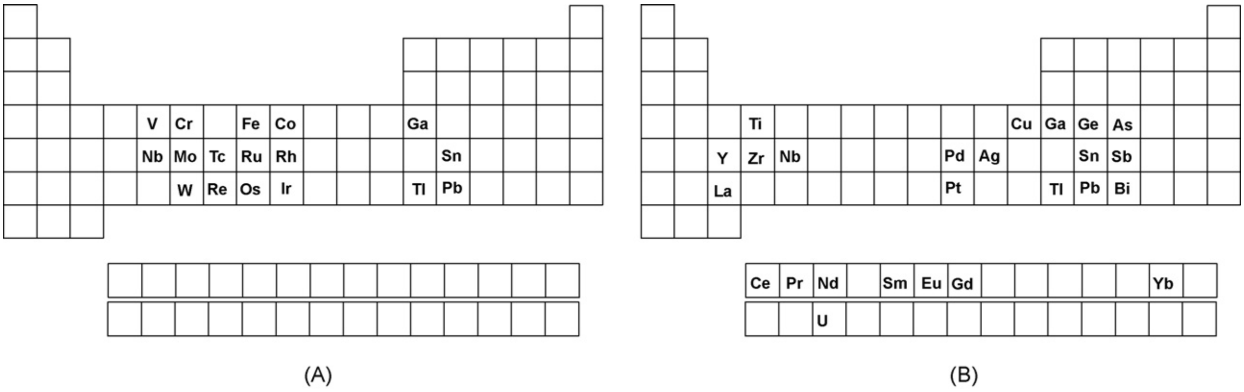


Fig. 2. Elements for which arene derivatives are prepared via the Fischer–Hafner method: (A) bis-arenes; (B) mono-arenes.

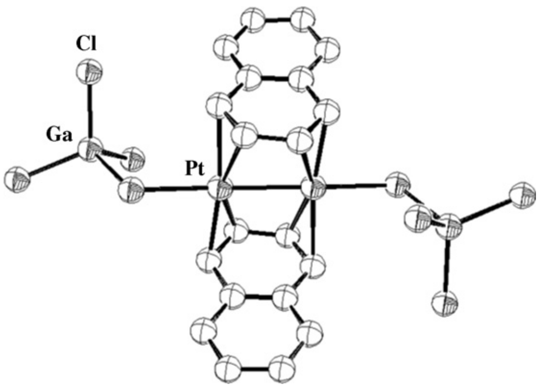


Fig. 4. Molecular structure of $Pt_2(GaCl_4)_2(C_{10}H_8)_2$ [50a].

reacts with halogenated hydrocarbons) and aluminium halides. The latter are in fact strong Lewis acids which give Lewis adducts (thus causing deactivation) with *O*- or *N*-containing arenes or cause Friedel–Crafts trans-alkylation reactions when the arene contains secondary or tertiary alkyl groups [48]. Moreover, methyl substituents on the arene can undergo migration or to be lost under the reaction conditions.

The Fischer–Hafner reduction was applied to $PdCl_2$ by Allegra et al. for the preparation of the palladium(I) dimers $Pd_2X_2(C_6H_6)_2$ ($X = AlCl_4^-$, $Al_2Cl_7^-$), containing the Pd_2^{2+} core and showing two benzene rings π-bonded to both palladium(I) centers [49]. Recently, gallium halides in combination with palladium(II) and platinum(II) halides and arenes have been used to prepare similar compounds of palladium(I) and platinum(I), see Fig. 4 [50]. The authors suggested that the reduction of palladium(II) or platinum(II) halides occurs via halogenation of the arene [50b]. A platinum(0)–gallium(III) (Pt–Ga) chrysene complex has been also prepared and structurally characterized [51].

3. Reactivity

An aromatic hydrocarbon may assume many roles when coordinated to a metal. It can be a labile ligand which temporarily occupies vacant coordination sites, or a spectator ligand so that the reactivity of the complex occurs on the metal. Alternatively, it can be a substrate for either catalytic or stoichiometric transformations. Whatever the role it plays, complexation of an arene molecule to a metal causes profound changes in its chemical properties. The electronic distribution of the aromatic molecule is a parameter largely influenced by coordination to a metal fragment. In 1976 Graves and Lagowski reported a ^{13}C NMR study on Cr(η^6-arene)$_2$ compounds showing [52] that the delocalized π-electron system of a complexed arene is essentially quenched, thus explaining why these complexes fail to undergo electrophilic aromatic substitution [53]. Upon coordination to [Cr(η^6-arene)]$^+$, as well as to [Cr(CO)$_3$] fragments the arene ligand is depleted of its usual electron density, becoming susceptible of nucleophilic aromatic substitution [54]. For example, the rate of nucleophilic substitution of chloride by [OMe]$^-$ is enhanced by up to 10^{15} times with respect to the uncoordinated arene when chlorobenzene is coordinated to a [Cr(η^6-arene)]$^+$ fragment [55].

Studies on the shielding of the benzene ligand as a function of the nature of the polycyclic aromatic hydrocarbons (PAH) in Cr(η^6-benzene)(η^6-PAH) [56] and structural effects in Cr(η^6-arene)$_2$ compounds containing CN groups in the aromatic ring [57] have been reported.

The reactivity of the iron derivatives [Fe(η^6-arene)$_2$] and [Fe(η^6-arene)$_2$]$^{2+}$ has been studied in some detail in view of their possibility to act as electron reservoir (the neutral, 20-e compound) [58] or substrate for nucleophilic substitution (the 18-e cationic species), which can occur on a single or on both aromatic rings according to the nucleophile [59].

In contrast to the well developed use of Cr(η^6-arene)(CO)$_3$ as intermediate of organic transformations at the chromium-coordinated aromatic ring [9a,60], relatively few reactions have been reported for bis(η^6-arene) metal complexes [9b,59b,c]. A reason for this relative paucity of studies is probably due to the difficulties of their synthesis and handling compared to the tricarbonyl derivative. Moreover, bis(η^6-arene) metal complexes tend to decompose under the conditions normally required for the aromatic nucleophilic, electrophilic and radical substitution. For example, Cr(η^6-MeC$_6$H$_5$)$_2$ reacts with RCOCl/AlCl$_3$, with acylation of the aromatic ring but the π-complex does not survive the reaction conditions and uncomplexed acylated rings are obtained [53].

In this Section aspects of the reactivity of bis(η^6-arene) compounds will be considered, namely the arene ligand displacement reactions without redox processes, the redox reactions occurring with or without aromatic ligand release, and the metalation reactions of the rings, a useful route to polymetallic compounds.

3.1. *Arene displacement without redox processes*

The exchange of a free ligand in solution for one coordinated to a metal is a fundamental reaction in organometallic chemistry. This reaction is a key step for many catalytic and stoichiometric transformations which occur in the presence of transition-metal complexes [9]. For arene complexes, the coordinated arene may be displaced by a new arene or by another type of ligand (carbon monoxide, phosphines, nitrogen bases) which will be referred to as "arene exchange" and "arene displacement", respectively [91].

Although most of the work on arene ligand exchange reactions has been performed on chromium and ruthenium, it has been reported that Ti(η^6-C$_6$H$_6$)[(μ-Cl)$_2$AlCl$_2$]$_2$ [61] reacts with 1,2,4,5-Me$_4$C$_6$H$_2$, C$_6$Me$_5$H and C$_6$Me$_6$ to give the corresponding exchange products: the observed stability being higher on increasing the methylation degree of the aromatic ring [62].

In 1979, Connor et al. reported a detailed thermochemical study on the mean bond dissociation energy of the Cr–arene bond showing that it decreases according to arene = $C_6H_6 > EtC_6H_5 > 1,3,5\text{-}Me_3C_6H_3 > C_6Me_6 > C_{10}H_8$ [63]. They also found that C$_{10}$H$_8$ is displaced by monocyclic arenes and that C$_6$H$_6$ displaces any other arene from Cr(η^6-arene)$_2$, see Eq. (4) [63]. This conclusion, which conflicts with the generally observed increase of stability of the M-arene bond on increasing the methyl substitution [64] (vide infra), was supported by the observation that the displacement of C$_6$H$_6$ in Cr(η^6-C$_6$H$_6$)$_2$ by 1,3,5-Me$_3$C$_6$H$_3$ can be brought about

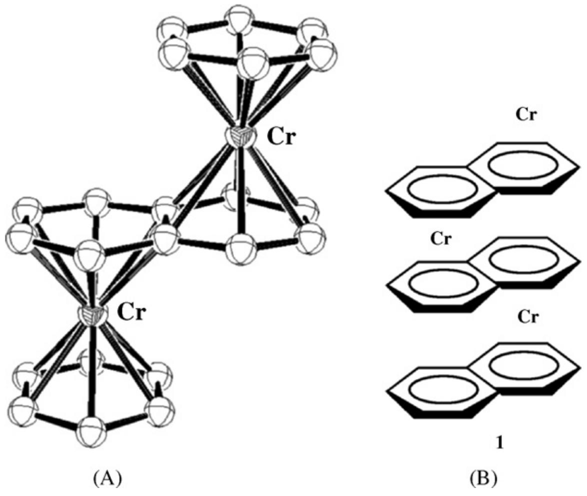


Fig. 5. Structure of Cr$_2$(μ, η^6, η^6-C$_{10}$H$_8$)(η^6-C$_6$H$_6$)$_2$ [70b].

only in the presence of $AlC1_3$ and that $Cr(\eta^6\text{-}C_6H_6)_2$ is formed by refluxing $Cr(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2$ in benzene [65]. Subsequent investigations showed that the displacement of $1,3,5\text{-}Me_3C_6H_3$ from $Cr(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2$ by C_6H_6 did not occur at 240 °C for 12 h [66].

$$Cr(\eta^6\text{-arene})_2 + 2\text{arene}' \rightarrow Cr(\eta^6\text{-arene}')_2 + 2\text{arene} \tag{4}$$

It is well-established that η^5-indenyl complexes undergo substitution reactions more readily than corresponding η^5-cyclopentadienyl complexes, probably as a consequence of the stabilization of a η^3-indenyl transition state or intermediate [67]. In view of the fact that a similar effect probably operates in naphthalene complexes, studies have been devoted to the preparation and the reactivity of this class of compounds.

Chromium(0) bis(naphthalene), $Cr(\eta^6\text{-}C_{10}H_8)_2$ [68,69] was described by Timms as *a thermally stable but very reactive compound* [68c]: at least one of the ligands can be exchanged under mild conditions (THF, 80 °C) to give $Cr(\eta^6\text{-arene})(\eta^6\text{-}C_{10}H_8)$ [66]. However, forcing the conditions in the same solvent, the formation of the mono-substituted product is accompanied by that of the bis-substituted derivative $Cr(\eta^6\text{-arene})_2$ and by the dinuclear $Cr_2(\mu,\eta^6,\eta^6\text{-}C_{10}H_8)(\eta^6\text{-arene})_2$, containing a bridging naphthalene, Fig. 5A, arene = C_6H_6 [70a]. Also the extended polymer **1**, Fig. 5B, containing repeating eclipsed naphthalene units, has been isolated from the exchange reaction [70b].

The *astonishingly* [68a] mild conditions necessary for substitution of the π-bonded naphthalene ligand are reflected also in the fact that $Cr(\eta^6\text{-}C_{10}H_8)_2$ reacts smoothly with CO at 1 atm and 20 °C to give first $Cr(\eta^6\text{-}C_{10}H_8)(CO)_3$ and then $Cr(CO)_6$ [68b,c], whereas $Cr(\eta^6\text{-}C_6H_6)_2$ gives the hexacarbonyl only under drastic conditions (300 atm of CO/200 °C) [71]. Analogously, 2,2′-bipyridyl does not react with $Cr(\eta^6\text{-}C_6H_6)_2$ at ca. 210 °C [72], while the formation of the red-brown $Cr(2,2'\text{-bipyridyl})_3$ is instantaneous at room temperature starting from the bis(naphthalene) derivative [68a].

Mixed arene/naphthalene ruthenium(II) cations [9i] undergo ligand exchange to give dicationic complexes of general formula $[Ru(\eta^6\text{-}C_6H_6)(\eta^6\text{-}C_6H_5(CH_2)_nX)][BF_4]_2$ (n = 3, X = vinyl, CO_2Et; n = 2, X = Br, OH; n = 1, X = OH) [73]. If the starting material is not a naphthalene derivative, the exchange requires the two-stage method reported in Eq. (5) [73]: treatment of the 18-e dication with $NaBH_4$ to produce the 18-e Ru(0) derivative **2** containing a η^4-bonded cyclohexadienyl, which easily undergoes ligand substitution and reoxidation to Ru(II).

$$[Ru(\eta^6\text{-}C_6H_6)(\eta^6\text{-}R_nC_6H_{6-n})]^{2+}\begin{array}{l}\xrightarrow[\text{THF}]{NaBH_4}\ \underset{\mathbf{2}}{[Ru(\eta^4\text{-}(C_6H_8)(\eta^6\text{-}R_nC_6H_{6-n})]}\\ \xrightarrow[CF_3COOH]{R'_nC_6H_{6-n}}\ [Ru(\eta^6\text{-}R'_nC_6H_{6-n})(\eta^6\text{-}R_nC_6H_{6-n})]^{2+}\end{array}\tag{5}$$

$$V(\eta^6\text{-arene})_2 + n\,L \rightarrow V(L)_n + 2\ \text{arene}$$

arene = C_6H_6, L = 2,2',2''-terpyridyl, n = 2
arene = $C_{10}H_8$, L = 2,6-dimethylphenylisocyanide, n = 6

$$Cr(\eta^6\text{-}C_6H_6)_2 + 6\,PF_3 \rightarrow Cr(PF_3)_6 + 2\,C_6H_6$$

$$Mo(\eta^6\text{-}C_6H_6)_2 + \text{azulene} \rightarrow Mo(\eta^6\text{-}C_6H_6)(\eta^6\text{-azulene}) + C_6H_6$$

$$M(\eta^6\text{-arene})_2 + n\,P \rightarrow M(\eta^6\text{-arene})P_n + \text{arene}$$

M = Nb, Mo, W; arene = C_6H_6, MeC_6H_5, $C_6H_5SiMe_3$; P = mono-, bi- or tridentate phosphine

$$Fe(\eta^6\text{-}C_6Me_6)_2 + n\,L \rightarrow Fe(\eta^6\text{-}C_6Me_6)L_n + C_6Me_6$$

L = CO, n = 2; L = 1,3-cyclohexadiene, n = 1

Scheme 2. Partial- or total arene displacement in the reactions of arene derivatives with C-, N- or P-donors.

The easy formation of $Ru(\eta^6\text{-arene})(\eta^4\text{-}1,5\text{-cyclooctadiene})$ by reaction of alkynes with $Ru(\eta^6\text{-}C_{10}H_8)(\eta^4\text{-}1,5\text{-cyclooctadiene})$ at room temperature [74] constitutes an additional example of the liability of the naphthalene ligand.

Visible light irradiation of the cyclohexadienyl complex $[Fe(\eta^6\text{-}C_6H_6)(\eta^4\text{-}C_6H_7)]^+$ in the presence of alkyl-substituted benzenes results in arene exchange forming $[Fe(\eta^6\text{-}R_nC_6H_{6-n})(\eta^4\text{-}C_6H_7)]^+$ species which can be transformed into unsymmetrical $[Fe(\eta^6\text{-}R_nC_6H_{6-n})(\eta^6\text{-}C_6H_6)]^{2+}$ dication by hydride abstraction, Eq. (6) [75]:

$$\begin{array}{l}[Fe(\eta^6\text{-}C_6H_6)(\eta^4\text{-}C_6H_7)]^+ \xrightarrow[R_nC_6H_{6-n}]{h\nu} [Fe(\eta^6\text{-}R_nC_6H_{6-n})(\eta^4\text{-}C_6H_7)]^+ \xrightarrow{CPh_3^{\,+}} [Fe(\eta^6\text{-}R_nC_6H_{6-n})(\eta^6\text{-}C_6H_6)]^{2+}\\ R_nC_6H_{6-n} = MeC_6H_5,\ \ 1,4\text{-}Me_2C_6H_4,\ \ 1,3,5\text{-}Me_3C_6H_3,\ \ 1,2,4,5\text{-}Me_4C_6H_2\end{array}\tag{6}$$

The ligand exchange reactions offer a valuable alternative to the metal vapour synthesis of η^6-alkylbenzenes (the Fischer–Hafner synthesis does not apply due to extensive transalkylation reactions, see Section 2.3). Working in vacuo at ca. 160 °C, several alkylbenzene derivatives of Mo(0) have been prepared starting from $Mo(\eta^6\text{-}C_6H_6)_2$ [76]. The cerium(III) derivative $Ce(\eta^6\text{-}MeC_6H_5)_2(GaCl_4)_3$ exchanges the arene at 80–90 °C with polycyclic aromatic hydrocarbons such as naphthalene and pyrene [77].

The arene ligand of a bis(η^6-arene) derivative can be displaced by a variety of π-acids such as CO [71,78], phosphines [79], phosphites [79g], isocyanides [80], some examples being reported in Scheme 2. Additional examples are the reaction of $V(\eta^6\text{-}C_6H_6)_2$ with 2,2′,2″-terpyridyl [81], and the formation of molybdenum(0) derivatives containing η^6-azulene [82], 1-oxa-1,3-dienes [83], α,β-unsaturated amides and esters [84], pyridine [85] from $Mo(\eta^6\text{-arene})_2$ and the corresponding ligand.

In contrast to $Nb(\eta^6\text{-}MeC_6H_5)_2$, which promptly reacts at room temperature with the tridentate phosphine $CH_3Si(CH_2PMe_2)_3$ to give $Nb(\eta^6\text{-}MeC_6H_5)_2[CH_3Si(CH_2PMe_2)_3]$ [79f], the trimethyl-substituted compound $Nb(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2$ reacts only at 70 °C in vacuo. Under these conditions, both the arene ligands are displaced and the bis-phosphino derivative $Nb[CH_3Si(CH_2PMe_2)_3]_2$ is obtained in moderate yields [86].

The 20e-compound $Fe(C_6Me_6)_2$ acts as a productive source of $Fe(C_6Me_6)$ fragments: upon treatment with the cyclopentadienyl dicarbonyl derivatives of the cobalt triad, $MCp(CO)_2$, it affords heterodinuclear Fe/Co, Fe/Rh, and Fe/Ir complexes [87].

Photochemically- [88] or electrochemically induced [89] loss of both the arene ligands from $[Fe(\eta^6\text{-arene})_2]^{2+}$ dications provides an attractive route to cationic Lewis acids that can function as initiators for polymerization reactions or substrates for the formation of charge transfer complexes. For example, the active species initiating the ring opening polymerization of epoxides is a cationic Lewis acid resulting from the removal of arene upon photolysis of $Fe(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2]^{2+}$ cations, Eq. (7) [88b].

$$[Fe(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2]^{2+} + 6CH_3CN \xrightarrow{h\nu,\ CH_3CN} [Fe(CH_3CN)_6]^{2+} + 2\,1,3,5\text{-}Me_3C_6H_3 \quad (7)$$

3.2. *Redox processes*

Since they contain a metal atom in oxidation state zero, neutral $M(\eta^6\text{-arene})_2$ derivatives may undergo redox reactions affording cationic or anionic species of general formula $[M(\eta^6\text{-arene})_2]^{n+/-}$. One of the systems most studied is the redox couple $Cr(\eta^6\text{-arene})_2/[Cr(\eta^6\text{-arene})_2]^{+/-}$ [90], but also iron(II) and ruthenium(II) species have been examined from a chemical and an electrochemical point of view [17d,17e,91]. Because of the low oxidation state of the metal, the bis(η^6-arene) derivatives generally behave as reducing agents with a reducing power which can be modulated by changing the nature of the ligands.

As a general introduction to the oxidation reactions involving bis(η^6-arene) metal species, it can be stated that the arene-metal bond does not survive the loss of more than two electrons from the metal, the net charge of the resulting cation depending on the nature of the metal: +1 for the early transition elements (V, Cr, Mo) and +2 for iron, ruthenium and cobalt. Further removal of electrons causes complete loss of the π-acid ligands and formation of classical coordination compounds such as carboxylates, acetylacetonates, halides, etc. Thus, a distinction will be made between the redox reactions which occur without loss of the arene {formation of $[M(\eta^6\text{-arene})_2]^-$ anions or $[M(\eta^6\text{-arene})_2]^+$ cations} and reactions taking place with partial or total loss of the aromatic ligands.

3.2.1. *Reactions without arene displacement*

3.2.1.1. Reductions. In spite of the large number of electrochemical studies involving the oxidation of $Cr(\eta^6\text{-arene})_2$ to the $[M(\eta^6\text{-arene})_2]^+$ cations, few examples are reported on the corresponding reduction to the −1 charged anion [90f]. Quantum chemical calculations [92] carried out on C_6H_6 and $C_{10}H_8$ derivatives of chromium(0) showed that the redox processes occur with participation of a molecular orbital, the main contribution to which comes from the π-orbital of the aromatic ligand. The calculations are confirmed by the similarity of the half wave potentials $E_{1/2}$ for the electrochemical reduction of uncoordinated arenes and the metal bonded ones [90f].

The first report on the chemical reduction of a bis(η^6-arene) species dates back to 1970 when Henrici–Olivé and Olivé identified spectroscopically two bis(naphthalene) complexes of chromium with an oxidation state lower than zero [93]. Some years later, Elschenbroich and Gerson noticed that $Cr(\eta^6\text{-}C_6H_6)_2$ does not react with potassium in DME at −80 °C [94] but slowly gives some reaction upon contact with a potassium mirror in HMPA at room temperature [95]. The same authors found that the reducing system was efficient for the reduction of the paramagnetic 17-e species $V(\eta^6\text{-}C_6H_6)_2$: the diamagnetic 18-e anion $[V(\eta^6\text{-}C_6H_6)_2]^-$ was characterized by a sharp NMR resonance at δ 3.28 ppm [95]. Some years later, the vanadium(-I) derivative $[K(THF)_{1.5}][V(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2]$ was isolated and characterized by X-ray diffraction [96].

Solutions of the vanadium(-I) derivatives are quickly re-oxidized by either CO or CO_2 to the vanadium(0) complex $V(\eta^6\text{-arene})_2$ with formation of C_1 and C_2 species (formate, hydrogen carbonate and oxalate), the relative yields depending on the reaction conditions [97]. Similarly, reduction of $M(\eta^6\text{-}C_6H_6)_2$, M = Cr, Mo, with finely divided potassium in dme produces a species, probably the radical anion $[M(\eta^6\text{-}C_6H_6)_2]^{\bullet -}$, which acts as a dehydrogenation catalyst transforming 1,4-cyclohexadiene into benzene and dihydrogen [98].

Potassium (as a film or as hydride in THF) has been used to reduce $Ti(\eta^6\text{-}RC_6H_5)_2$, R = H, Me, to the dark blue anions $[Ti(\eta^6\text{-}RC_6H_5)_2]^-$, which have been characterized by EPR spectroscopy [99]. The same reducing systems afford the diamagnetic $[Nb(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2]^-$ anion (isolated as 18-crown-6-stabilized potassium salt) which promptly reacts with CO to give the hexacarbonylniobate anion, $[Nb(CO)_6]^-$ [100].

The electrochemical reduction of $Ti(\eta^6\text{-}MeC_6H_5)_2$ shows a reversible peak at 2.49 V (*vs.* Ag/AgCl/LiCl 4 M) attributed to the formation of the $[Ti(\eta^6\text{-}MeC_6H_5)_2]^-$ anion which is stable in the −80 and 20 °C range [101].

The chemical reduction of bis(η^6-arene) metal cations is much more developed than that of the neutral species. The paper where Fischer and Hafner described the synthesis of $Cr(\eta^6\text{-}C_6H_6)_2$ [6], reports that the $[Cr(\eta^6\text{-}C_6H_6)_2]^+$ cation is reduced to the neutral compound using a basic, aqueous solution of sodium dithionite [6,7], Eq. (8a). Similar reductions have been also described for vanadium, molybdenum and tungsten, the reducing agents being alkali metals, aluminium, $Na[AlH_2(OCH_2CH_2OCH_3)_2$, LiMe, $Co(\eta^5\text{-}C_5R_5)_2$, R = H, Me [8,102]. Noteworthy is the case of $V(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2$, which now can be prepared in high yields by the *in situ* reduction of the readily available $[V(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2]^+$ cation by addition of an ethereal solvent to the crude reaction mixture still containing the excess of aluminium metal, Eq. (8b) [45,103]. Almost quantitative yields of $Cr(\eta^6\text{-}MeC_6H_5)_2$ were obtained with chromium by the same method, although more severe reaction conditions (8 h, ca. 80 °C) are required. For molybdenum, the best yield obtained by the new procedure is 39% in the case of $Mo(\eta^6\text{-}MeC_6H_5)_2$ [45]:

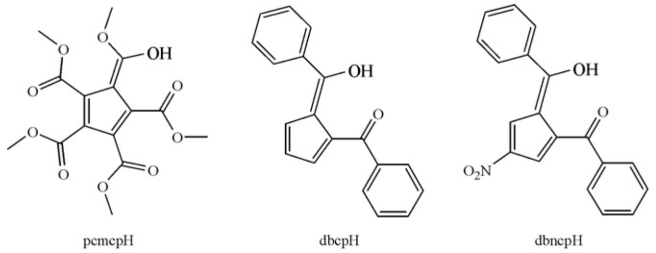
$$2[Cr(\eta^6\text{-}C_6H_6)_2]^+ + S_2O_4{}^{2-} + 4OH^- \rightarrow Cr(\eta^6\text{-}C_6H_6)_2 + 2SO_3{}^{2-} + 2H_2O \quad (8a)$$

$$VCl_3 \xrightarrow[\text{(2) ethereal solvent, room temperature}]{\text{(1) Al/AlCl}_3\text{/1,3,5-Me}_3\text{C}_6\text{H}_3\text{, 120–130 °C, 2 h}} \underset{95\%}{V(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2} \quad (8b)$$

In this context, the $[M(\eta^6\text{-}C_6Me_6)_2]^{2+}$, M = Fe, Ru, undergo sodium-reduction to the zerovalent derivatives. In the case of iron, the very reactive, 20-e, $Fe(\eta^6\text{-}C_6Me_6)_2$ is obtained, while a 18-e species containing a η^4-bonded C_6Me_6 is isolated in the case of ruthenium [35d,104,105]. A mechanism for the electrochemical reduction of the ruthenium(II) cation has been proposed [106].

3.2.1.2. Oxidations. While the reduction of the metal in a coordination compound containing π-acid ligands may reinforce the metal–ligand bond, the oxidation of the metal often causes loss of the arene ligands and formation of naked metal ions which have particular reactivities. This topic will be discussed in Section 3.2.2. The discussion will be now limited to the oxidation of bis(η^6-arene) derivatives which occurs without loss of arenes and formation of mono- or dications of general formula $[M(\eta^6\text{-arene})_2]^{n+}$.

Soon after the discovery of $Cr(\eta^6\text{-}C_6H_6)_2$, it was observed that $[Cr(\eta^6\text{-}C_6H_6)_2]^+$ salts could be obtained from the zerovalent metal complex by air oxidation in the presence of water followed by treatment of the aqueous solution with the appropriate anion source. Most of the $[Cr(\eta^6\text{-}C_6H_6)_2]^+$ salts were stable in neutral and basic solution [7]. Since then (1955), the reducing properties of $Cr(\eta^6\text{-arene})_2$ have been widely studied and many oxidizing agents have been tested [64]. For example, Elschenbroich reported that $Cr(\eta^6\text{-}C_6H_6)_2$ reacts with SO_2 with formation of a black solid consisting of $[Cr(\eta^6\text{-}C_6H_6)_2]_2[S_4O_{10}]$ [107]. On the basis of the S–O distances the $[S_4O_{10}]^{2-}$ structural unit can be viewed either as a Lewis adduct with two extremely long S–O bonds or as a charge transfer complex $S_2O_6{}^{2-}$ $2SO_2$ of a dithionate ion with two molecules of SO_2 [107].



Scheme 3. Sterically hindered fulvenes.

Recently, it has been reported that $Cr(\eta^6\text{-}MeC_6H_5)_2$ reacts with the fulvenes reported in Scheme 3, with evolution of dihydrogen and formation of the ionic derivatives $[Cr(\eta^6\text{-arene})_2][X]$ where arene = toluene, 1,3,5-$Me_3C_6H_3$; X^- = *pentakis*(methoxycarbonyl)cyclopentadienyl, $[pcmcp]^-$, 1,2-dibenzoylcyclopentadienyl, $[dbcp]^-$, 1,2-dibenzoyl-4-nitro-cyclopentadienyl, $[dbncp]^-$ [26d, 108]. The analysis of the molecular structures of the cations leads to the conclusion that the conformation of the arene rings in the solid state depends on the steric demand of the anion and it tends toward the staggered conformation [109] as the anion decreases in size.

In 1977, Broderick et al. reported that fullerene C_{60} reacts with $Cr(\eta^6\text{-arene})_2$ (arene = C_6H_6, MeC_6H_5, 1,3,5-$Me_3C_6H_3$) to give ionic species of formula $[Cr(\eta^6\text{-arene})_2][C_{60}]$ [110], which showed interesting magnetic and electric properties. Since then, several chromium(I) derivatives containing the fulleride anion have been described including hexasubstituted arene species [111]. Spectroscopic and magnetic evidence indicated that, at temperatures below 250 K, the C_{60}^- anion in $[Cr(\eta^6\text{-arene})_2][C_{60}]$, arene = MeC_6H_5, 1,3,5-$Me_3C_6H_3$, dimerizes to the $[C_{60}^-]_2$ species [112]. Additional examples of chromium(I) salts containing single bonded $[C_{60}^-]_2$ [113] and $[C_{70}^-]_2$ dimers [114] have been characterized by X-ray diffraction methods.

Interesting charge-transfer stacked crystals form by oxidation of $M(\eta^6\text{-arene})_2$, M = Cr, Fe, arene = C_6H_6, 1,3,5-$Me_3C_6H_3$, C_6Me_6, with C_6F_6 [115], 2,4,6-tricyano-1,3,5-triazine [116], tetracyanoquinodimethane [117] and of $Mo(\eta^6\text{-}MeC_6H_5)_2$ with di-iodine followed by treatment with NEt_4FeBr_4 [118]. Similar charge transfer complexes containing iron and ruthenium have been prepared by reduction of tetracyanoquinodimethane in the presence of a bis(η^6-arene) dication [119].

Two noteworthy systems have been obtained by oxidation of bis(η^6-arene) compounds: the first one is a rare example of a well defined titanium(I) compound, $[Ti(\eta^6\text{-}1,3,5\text{-}{}^iPr_3C_6H_3)_2][B(aryl)_4]$, **3**, Fig. 6, obtained by treatment of $Ti(\eta^6\text{-}1,3,5\text{-}{}^iPr_3C_6H_3)_2$ with $FeCp_2[B(aryl)_4]$, aryl = C_6H_5, p-C_6H_4F, 3,5-$C_6H_3(CF_3)_2$ [120]. Before the isolation of **3**, the only evidence for the existence of a bis(η^6-arene) titanium(I) derivative consisted of an anodic peak at −0,63 V (*vs.* Ag/AgCl/LiCl 4 M) observed during the electrochemical oxidation of $Ti(\eta^6\text{-}MeC_6H_5)_2$ [101]: the irreversibility of the process was associated with the instability of the $[Ti(\eta^6\text{-}MeC_6H_5)_2]^+$ cation [101]. This observation is in agreement with the generally accepted rule that the stability of the arene derivatives increases on increasing the steric hindrance of the aromatic ligand [121].

The second system comes from the monoelectronic oxidation of $Nb(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2$ with $[FeCp_2][B(aryl)_4]$, in the presence of a π-donor ligand, to the niobium(I) adduct **4**, Scheme 4 [122]. When L = CO or diphenylacetylene, the ionic compound is stable whereas, with L = 2-butyne, **4** thermally rearranges with loss of both the original aromatic ligands affording **5**, the first example of a compound containing the tetraphenylborato anion behaving as a 12-e donor [122].

The knowledge of the chemistry of Group 5 bis(η^6-arene) derivatives has largely expanded after the discovery of conventional, high yield synthetic procedures to $M(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2$, M = V, Nb [8a]. These compounds are easily oxidized to the metal(I) cations by a variety of agents such as silver tetrafluoborate [100], metal carbonyls, ferrocenium salts, *N*,*N*′-dimethyl-4,4′-dipyridinium cations [45,103,122,123], borane adducts of nitriles [124].

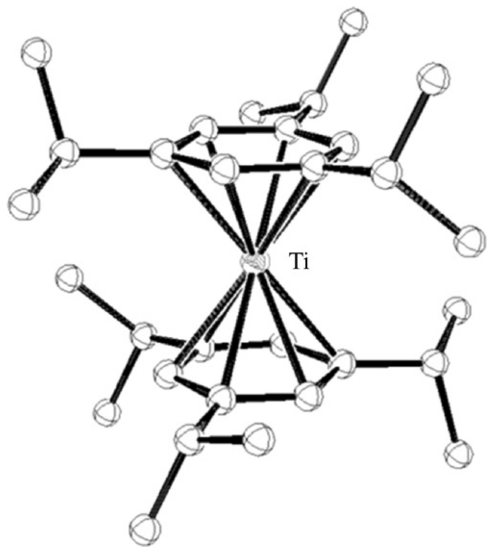


Fig. 6. View of the $[Ti(\eta^6\text{-}1,3,5\text{-}{}^iPr_3C_6H_3)_2]^+$ cation in $[Ti(\eta^6\text{-}1,3,5\text{-}{}^iPr_3C_6H_3)_2][B(p\text{-}C_6H_4F)_4]$ [120].

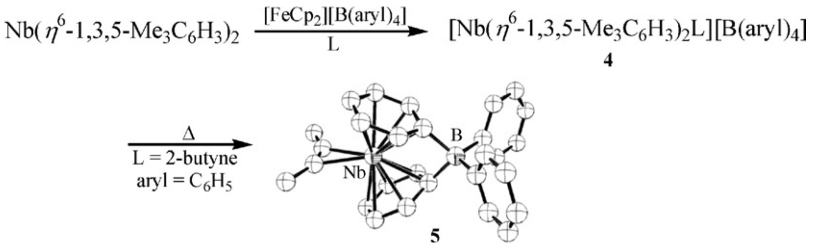
The reaction of $Nb(\eta^6\text{-arene})_2$ with one equivalent of allyl- (arene = toluene [79f]) or *N*,*N*′-dimethyl-4,4′-dipyridinium (arene = 1,3,5-$Me_3C_6H_3$ [125]) halides occurs with oxidation to $Nb(\eta^6\text{-arene})_2X$ (X = Br, I). When arene = MeC_6H_5, the compound can be transformed into $Nb(\eta^6\text{-}MeC_6H_5)_2R$, R = Me, Ph, upon treatment with lithium organyls at low temperature [79f].

Like their chromium analogues, vanadium(0) bis-arenes react with carbon monoxide under drastic conditions (100 atm, 35 °C, 20 h) [126], but the products are different for the two metals: in the case of $Cr(\eta^6\text{-}C_6H_6)_2$, $Cr(CO)_6$ is formed through the intermediacy of $Cr(\eta^6\text{-}C_6H_6)(CO)_3$ [71,127], whereas the ionic $[V(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2][V(CO)_6]$, **6**, is obtained from the reaction of $V(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2$ with CO. The formation of **6** has been explained [126] by assuming that $V(CO)_6$, formed upon carbonylation of $V(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2$, undergoes a redox process with the still unreacted bis(arene) derivative affording the hexacarbonylvanadate(-I) salt **6**, Scheme 5. Compound **6** is in fact formed in high yields from the room temperature reaction of $V(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2$ with $V(CO)_6$ [126].

The reaction of $Nb(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2$ with CO [128] gives $[Nb(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2CO][Nb(CO)_6]$, **7**, where, at variance to **6**, the cation is a 18-e species, Eq. (9) [123b]. The different behaviour between the vanadium and the niobium cations has been attributed to the instability of heptacoordinated low-valent vanadium species with respect to the niobium and tantalum ones. For example, it is known that $V(CO)_6$ exists as a monomer in the solid state [129a–c] and in solution [129d,e], and that the heptacoordinated compounds $MX(CO)_4L_2$, X = halide, L = P- or N-donor ligand, are stable only for niobium and tantalum [130]:

$$2Nb(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2 + 7CO \rightarrow \underset{\mathbf{7}}{[Nb(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2CO][Nb(CO)_6]} + 2\ \ 1,3,5\text{-}Me_3C_6H_3 \qquad (9)$$

The formation of compound **7** via the reaction reported in Eq. (9), together with the formation of $[Nb(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2CO][V(CO)_6]$ from $Nb(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2$ and $V(CO)_6$, represents strong evidence about the possible existence of an unsta-



Scheme 4. Oxidation of $Nb(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2$ and formation of $Nb(\eta^2\text{-}C_2Me_2)[\eta^{12}\text{-}(C_6H_5)_2B(C_6H_5)_2]$.

ble hexacarbonyl derivative of niobium(0), whose existence has not proved hitherto.

The marked reducing properties of the early transition metal derivatives have been demonstrated by the reaction of $Ti(\eta^6\text{-}MeC_6H_5)_2$ with CO_2 (resulting in the formation of the low-valent titanium oxalate [131]) and of $M(\eta^6\text{-arene})_2$, M = Ti, V, Cr, with $AlCl_3$. The latter reaction, which is fast in toluene medium, produces aluminium metal and the covalent tetrachloroaluminates of titanium(II) $Ti(\eta^6\text{-}MeC_6H_5)[(\mu\text{-}Cl)_2AlCl_2]_2$ [132] or the vanadium or chromium bis(η^6-arene) cations, see Eqs. (10) and (11) [45,65,133]. Boron trifluoride or phosphorous trichloride oxidize $Cr(\eta^6\text{-}C_6H_5C_6H_5)_2$ to $[Cr(\eta^6\text{-}C_6H_5C_6H_5)_2]BF_4$ and $[Cr(\eta^6\text{-}C_6H_5C_6H_5)_2]Cl$, respectively [134]:

$$3Ti(\eta^6\text{-}MeC_6H_5)_2 + 8AlCl_3 \rightarrow 3Ti(\eta^6\text{-}MeC_6H_5)[(\mu\text{-}Cl)_2AlCl_2]_2 + 2Al + 3MeC_6H_5 \qquad (10)$$

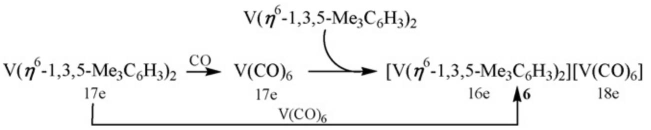
$$3V(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2 + 4AlCl_3 \rightarrow 3[V(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2][AlCl_4] + Al \qquad (11)$$

3.2.2. *Reactions with arene displacement*

Redox reactions occurring with partial or total loss of arenes are typical of early transition metal derivatives. Niobium bis(η^6-arene) reacts with iodine, $ReX(CO)_5$, X = Br, I, arene = $1,3,5\text{-}Me_3C_6H_3$ [123e,135], or dialkyldisulfides, arene = toluene [79f], to give $Nb_2(\mu\text{-}I)_4(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2$, $(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)(CO)_2Nb(\mu\text{-}X)_2Re(CO)_3$, Fig. 7, and $Nb_2(\mu\text{-}SR)_4(\eta^6\text{-}MeC_6H_5)_2$, respectively. Molybdenum and tungsten arenes give monoarene compounds by reaction with 6,6-diorganylfulvene [136] or with allyl chloride [137].

In contrast to the behaviour of chromium(0) and molybdenum(0), see Section 3.2.1.2, the reaction of titanium(0), vanadium(0) and niobium(0) bis(η^6-arene) derivatives with the fulvene species reported in Scheme 3, proceeds with loss of aromatic ligands and formation of compounds of titanium(III), vanadium(II) or niobium(III) with *O,O′*-coordinated cyclopentadienyl rings [138], Eq. (12). This trend has been related to the particular high oxygen affinity of the Groups 4–5 elements, and to their greater tendency to undergo oxidation (with consequent loss of the π-acid arene ligands) with respect to the Group 6 congeners:

$$M(\eta^6\text{-arene})_2 + nLH \rightarrow M(O,O'\text{-}L)_n + (n/2)H_2 + 2\text{arene}$$
$$LH = \text{pcmcpH, dbcpH, dbncpH},\ M = V,\ n = 2;\ M = Ti, Nb,\ n = 3 \qquad (12)$$



Scheme 5. The $V(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2/V(CO)_6/CO$ system.

Another reaction, which strongly depends on the metal, occurs between the Group 4 and 5 bis-arenes and the tetra- or the pentahalides of the corresponding Groups of the periodic table. As shown in Scheme 6, $Ti(\eta^6\text{-}MeC_6H_5)_2$ or $V(\eta^6\text{-arene})_2$, arene = C_6H_6, $1,3,5\text{-}Me_3C_6H_3$, and $Nb(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2$ react with $TiCl_4$ with formation of solid compounds of general formula MTi_nCl_m, with n and m depending on the $M(\eta^6\text{-arene})_2/TiCl_4$ molar ratio [132,139]. On the other hand, the chromium and molybdenum toluene derivatives $M(\eta^6\text{-}MeC_6H_5)_2$ undergo a one electron transfer with formation of $[M(\eta^6\text{-}MeC_6H_5)_2][M'X_4(THF)_2]$, M = Cr, Mo, M′ = Ti, V; X = Cl, Br, Scheme 6 [132,140]. Formation of $[Cr(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2][MCl_5(THF)]$ is observed when $Cr(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2$ is treated with $MCl_4(THF)_2$, M = Zr, Hf, in THF. The isolation of a Cr(I) bis(η^6-arene) cation suggests that reduction of zirconium(IV) or hafnium(IV) may have occurred in the system, but no evidence of the formation of reduced species was obtained [140]. In this context, it is noteworthy that $Cr(\eta^6\text{-arene})_2$ is oxidized by alkyl halides to the monocation $[Cr(\eta^6\text{-arene})_2]^+$ [141], and only the irradiation in a chlorinated solvent causes the Cr(0) → Cr(III) process and formation of $CrCl_3$ [142].

The titanium(0), vanadium(0) and niobium(0) bis(η^6-arene) derivatives react with alcohols [143], carboxylic acids [144,145], diketones [132], quinones [146,147], hydrogen- or alkyl halides or halogens [132,148], with formation of metal alcoholates, carboxylates, diketonates, diolates or halides of the metals in the oxidation states 2 or 3.

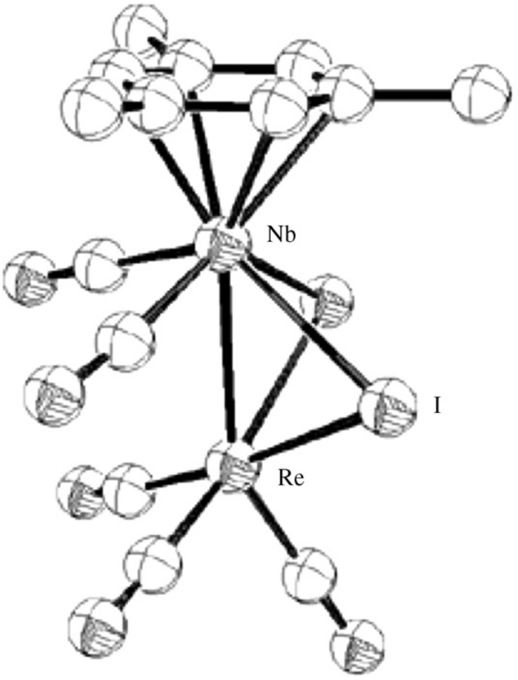
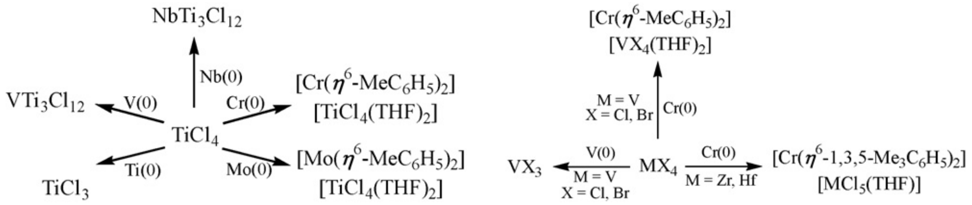


Fig. 7. Molecular structure of $(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)(CO)_2Nb(\mu\text{-}I)_2Re(CO)_3$ [123e].



Scheme 6. Reactions of metal halides with bis(η^6-arene) derivatives.

The reaction of the titanium(II) derivatives Ti(η^6-C$_6$H$_6$)[(μ-Cl)$_2$AlCl$_2$]$_2$ with cyclopentadiene [149] or tricyclo-[5.2.1.0^{2,6}]deca-2,5-diene, isodicyclopentadiene [150], produces the corresponding titanium(III) TiCp$^\#$[(μ-Cl)$_2$AlCl$_2$]$_2$ species, Cp$^\#$ = cyclo- or isodicyclopentadienyl anion, and dihydrogen.

Vanadium, molybdenum and tungsten bis(η^6-arene) cations easily disproportionate in polar solvents with simultaneous formation of the zerovalent complex and of the high valent metal ion. As a matter of fact, Cr(C$_6$H$_6$)$_2$ was obtained from the corresponding cation [6] by using an alkaline solution of dithionite, but a simple treatment with an aqueous alkaline solution was used to obtain the corresponding compounds of vanadium(0) [151], molybdenum(0), and tungsten(0) [152], Scheme 7.

Disproportionation of isolated [Cr(η^6-arene)$_2$]$^+$ cations occurs in the presence of strong bases (pyridine, 2,2′-dipyridyl) in anhydrous systems, with formation of Cr(0) and Cr(II)/Cr(III) species [153]. The hexafluorophosphate [Cr(η^6-C$_6$H$_6$)$_2$]PF$_6$ disproportionates in pyridine at 75 °C affording Cr(η^6-C$_6$H$_6$)$_2$ and three products of chromium in higher oxidation state, namely Cr(pyridine)$_4$(PF$_6$)$_2$, [Cr(pyridine)$_5$F]PF$_6$, and *trans*-[Cr(pyridine)$_4$F$_2$]PF$_6$ [153b].

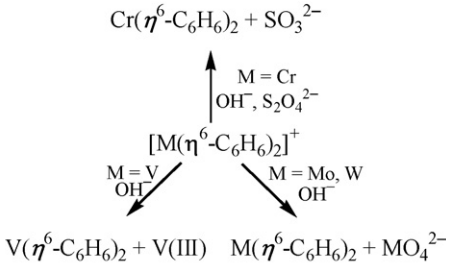
A similar situation occurs with vanadium, Eqs. (13) and (14), but the [V(η^6-arene)$_2$]$^+$ cations undergo disproportionation much more easily than the corresponding chromium derivatives. The iodide [V(η^6-1,3,5-Me$_3$C$_6$H$_3$)$_2$]I [123a] disproportionates in aqueous solution or in the presence of Lewis bases at room temperature according to Eq. (15) [148d]:

$$2[\mathrm{V}(\eta^6\text{-arene})_2]^+ \rightarrow \mathrm{V}(\eta^6\text{-arene})_2 + \mathrm{V}^{2+} + 2\text{arene}\,(\textit{neutral medium}) \tag{13}$$

$$[\mathrm{V}(\eta^6\text{-arene})_2]^+ + \mathrm{V}^{2+} \rightarrow \mathrm{V}(\eta^6\text{-arene})_2 + \mathrm{V}^{3+}\,(\textit{alkaline medium}) \tag{14}$$

$$\begin{aligned} &n[\mathrm{V}(\eta^6\text{-1,3,5-Me}_3\mathrm{C}_6\mathrm{H}_3)_2)_2]\mathrm{I} \\ &\xrightarrow{\mathrm{L}} (n-1)\mathrm{V}(\eta^6\text{-1,3,5-Me}_3\mathrm{C}_6\mathrm{H}_3)_2 + \mathrm{VI}_n\mathrm{L}_{6-n} \\ &\quad + 2\ \ 1,3,5\text{-Me}_3\mathrm{C}_6\mathrm{H}_3, \\ &\quad \mathrm{L} = \mathrm{THF},\ \mathrm{P(OMe)}_3,\ \text{acetonitrile or pyridine};\ n = 2 \text{ or } 3 \end{aligned} \tag{15}$$

The disproportionation of the vanadium(I) derivatives was conclusively demonstrated by Calderazzo et al. [154] with the isolation of V(η^6-arene)$_2$ and [V$_2$(μ-Cl)$_3$(THF)$_6$]$^+$ from the reaction between [V(η^6-arene)$_2$]$^+$ cations, arene = C$_6$H$_6$, MeC$_6$H$_5$, 1,3,5-Me$_3$C$_6$H$_3$, and ether solvents such as THF or 1,2-dimethoxyethane. It was also demonstrated that the extent of disproportionation depends on the nature of both the counteranion and the arene ligand. In the case of [V(η^6-MeC$_6$H$_5$)$_2$]Al$_2$Cl$_7$, the overall disproportionation reaction is reported in Eq. (16):



Scheme 7. Formation of M(η^6-C$_6$H$_6$)$_2$, M = V, Cr, Mo, W, from the corresponding [M(η^6-C$_6$H$_6$)$_2$]$^+$ cations.

$$\begin{aligned} &4[\mathrm{V}(\eta^6\text{-MeC}_6\mathrm{H}_5)_2]\mathrm{Al}_2\mathrm{Cl}_7 + 20\mathrm{THF} \\ &\rightarrow 2\mathrm{V}(\eta^6\text{-MeC}_6\mathrm{H}_5)_2 + [\mathrm{V}_2(\mu\text{-Cl})_3(\mathrm{THF})_6]\mathrm{AlCl}_4 \\ &\quad + 7\mathrm{AlCl}_3(\mathrm{THF})_2 + 4\text{toluene} \end{aligned} \tag{16}$$

3.3. Metalation of the aromatic rings

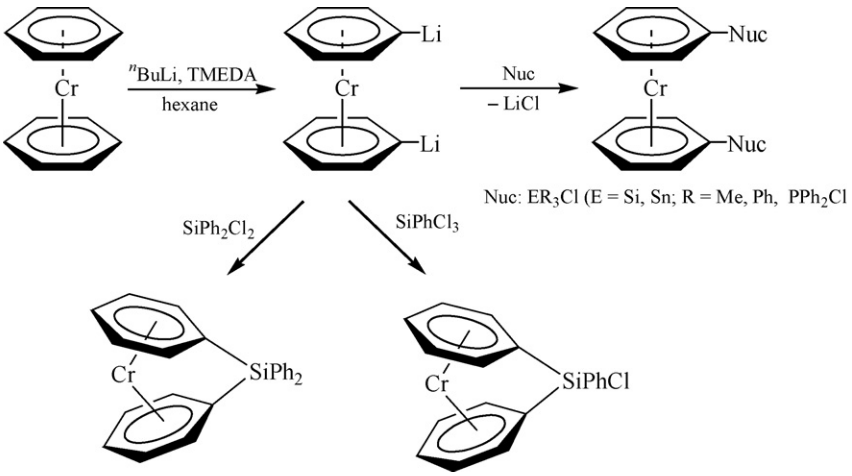
The first metalation of a metal-ligated benzene ring was achieved by Fischer and Brunner by reacting Cr(η^6-C$_6$H$_6$)$_2$ with amylsodium in hexane solution [155], but complications arising from multiple metalation restricted the synthetic utility of the reaction. Some years later, Cr(η^6-C$_6$H$_6$)$_2$ was dilithiated with ^{n}BuLi in cyclohexane in the presence of TMEDA [156] and it was demonstrated that the π-bonded benzene is metalated preferentially with respect to uncoordinated benzene and that the presence of lithium on a benzene ring strongly activates the molecule to further metalation [156]. In fact, the lithiation of Cr(η^6-C$_6$H$_6$)$_2$ with ^{n}BuLi/TMEDA affords a mixture of mono- and dilithiated derivatives which can be separated in view of the low solubility of Cr(η^6-C$_6$H$_6$)(η^6-C$_6$H$_5$Li) [156b]. Examples of sandwich compounds of chromium derived from the lithiation of the two aromatic rings are reported in Scheme 8 [157].

Some years after that the preparation of the chromium derivative, the ^{n}BuLi/TMEDA system was used to prepare the first bis(metalated) arene of vanadium(0), V(η^6-C$_6$H$_5$Li)$_2$ [158], which chemistry parallels that of the chromium derivative. In 1986, Green et al. used the same metalating system to obtain Mo(η^6-C$_6$H$_5$Li)$_2$, which reacts with D$_2$O, SiMe$_3$Cl and SiMe$_2$Cl$_2$ to give Mo(η^6-C$_6$H$_5$D)$_2$, Mo(η^6-C$_6$H$_5$SiMe$_3$)$_2$, and Mo(η^6-C$_6$H$_5$SiMe$_2$Cl)$_2$, respectively [159].

Because there is a relatively acidic proton in the fluorinated ring, Cr(η^6-C$_6$H$_6$)(η^6-C$_6$F$_5$H), **8**, prepared by co-condensing benzene, C$_6$F$_5$H and chromium vapours at −196 °C, reacts with ^{n}BuLi affording Cr(η^6-C$_6$H$_6$)(η^6-C$_6$F$_5$Li), **9** [160], which can be used as starting material for the preparation of asymmetric sandwiches, see Scheme 9 [161].

Quite recently, the mixed-metal [(TMEDA)M(μ-Bu)(μ-TMP)Mg(TMP)], M = Na, K; TMP = 2,2,6,6-tetramethylpiperidide, have been used as monometalating agents for Cr(η^6-C$_6$H$_6$)$_2$ [162], Fig. 8A, and for the regioselective *para* monodeprotonation of Cr(η^6-MeC$_6$H$_5$)$_2$, Fig. 8B [163], thus opening a new route, which does not make use of the MVS technique, to chromium compounds containing different substituents on the two aromatic rings.

On consideration that one of the most versatile, general methods of generating heterobimetallic compounds involves the use of



Scheme 8. Sandwich compounds of chromium derived from the lithiation of the aromatic rings.

ER_2-substituted sandwich complexes (E = P, As) as organometallic chelating ligands [59b,c], the chromium and vanadium bis(η^6-diphenylphosphinobenzene) derivatives M(η^6-$C_6H_5PPh_2$)$_2$ offered the possibility of fixing two metals at a well defined intramolecular distance, and to study the extent of metal···metal interaction as a function of intermetallic separation and conformation flexibility. These topics have been studied in detail by electrochemical and spectroscopic (EPR) methods by Elschenbroich et al. [164]; examples are in Scheme 10.

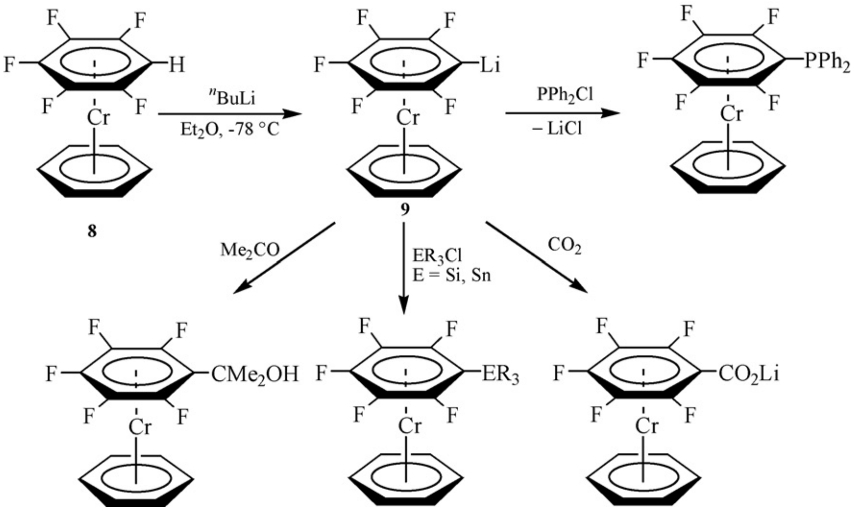
Although vanadium, chromium and molybdenum metalated arenes are known since decades and their reactivity is well established, the first unequivocal characterization of a dimetalated compound occurred in 2007, when Braunschweig et al. reported the structural data of [Mo(η^6-C_6H_5Li)$_2$]$_2$(thf)$_6$ [165]. This dilithiated molybdenum(0) derivative exhibits a symmetrical dinuclear structure in which both molecules are connected by two pairs of bridging lithium atoms bound to the *ipso* carbons of each C_6H_5 moiety. Each unsaturated lithium centre is stabilized by coordination of six oxygen atoms of tetrahydrofuran, Fig. 9.

4. Applications

Bis(η^6-arene) derivatives of transition metals have found applications not only in fields typical of organometallic compounds such as olefin oligo- or polymerization reactions, but in materials chemistry too. They have been used by crystal engineers as building blocks for the growth of desired crystal structures in appropriate forms in order to obtain novel or improved physico-chemical properties. By reaction with appropriate electron acceptors, transition metal arenes produced molecule-based magnets (molecular magnets), a class of magnetic materials that expands the properties typically associated with magnets, to include low density, transparency, electrical insulation, and low-temperature fabrication. Moreover, new mesoporous materials, metal carbonitride films, and organometallic polymers have been obtained starting from metal bis(η^6-arene) species. The last part of the review deals with these aspects of the reactivity.

4.1. Oligomerization and polymerization reactions

Following the discovery of the Phillips catalysts (chromium oxide supported on silica) for the polymerization of ethylene [166], several silica supported chromium organometallic systems including chromium bis(η^6-arene) complexes were tested as precursors [167]. These opened the way to the utilization of transition metal arene derivatives as catalytic precursors: Ti(0), Zr(0), Hf(0) and Ti(II) arene derivatives have been studied [168]. Later studies showed that the combination of V(η^6-arene)$_2$ or Ti(η^6-MeC_6H_5)[(μ-Cl)$_2$AlCl$_2$]$_2$ with MCl_4 (M = Ti, V) affords active α-olefin polymerization catalysts [139,169].



Scheme 9. Preparation of asymmetric sandwiches starting from Cr(η^6-C_6H_6)(η^6-C_6F_5Li).

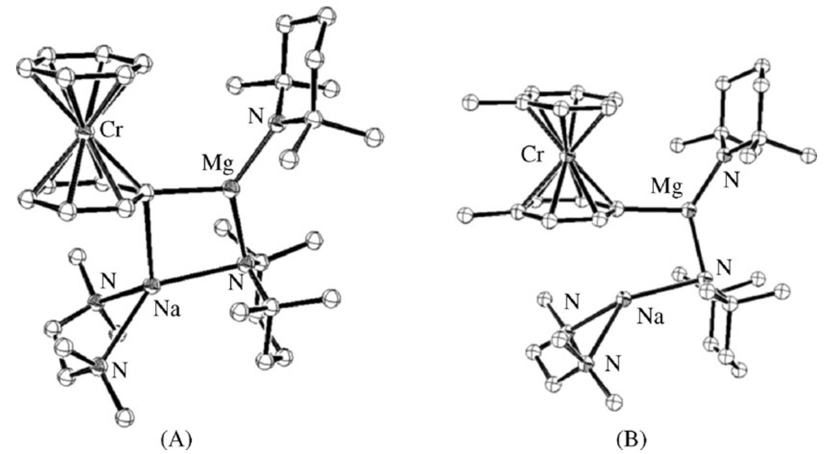
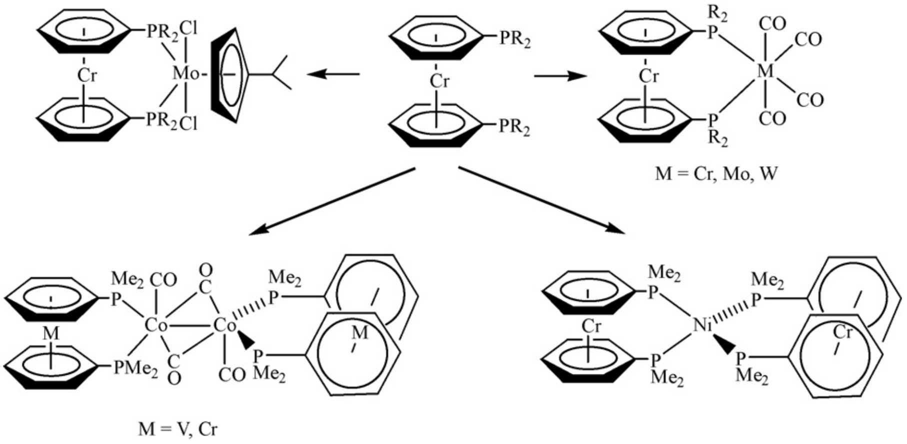


Fig. 8. Molecular structure of (A) [(TMEDA)Na(μ-TMP){μ-(p-C_6H_5)Cr(C_6H_6)}Mg(TMP)] and (B) [(TMEDA)Na(μ-TMP){μ-(p-C_6H_4Me)Cr(C_6H_5Me)}Mg(TMP)] [162,163].



Scheme 10. Generation of heterobimetallic compounds via ER_2-substituted sandwich complexes.

Operating under specific experimental conditions, the titanium(II) derivatives Ti(η^6-MeC_6H_5)[(μ-Cl)$_2$AlCl_2]$_2$, in combination with aluminium alkyls [170] or methylaluminoxane [171], give stereoregular polypropylene and polystyrene. Moreover, crystalline polyisobutylvinyl ether is obtained from isobutyl vinyl ether in the presence of the Cr(η^6-C_6H_6)$_2$/TiCl_4 combination (*i.e.* [Cr(η^6-arene)$_2$][TiCl_4], see Section 3.2.2) [172]. Butadiene, isoprene and *trans*-piperylene are polymerized by surface vanadium hydrides obtained by the thermal reaction of V(η^6-C_6H_6)$_2$ with silica (Areosil A-300) [173]. The polymerization of R_FC≡CCN, R_F = perfluoroalkyl, catalyzed by Cr(η^6-C_6H_6)$_2$ has also been carried out [174].

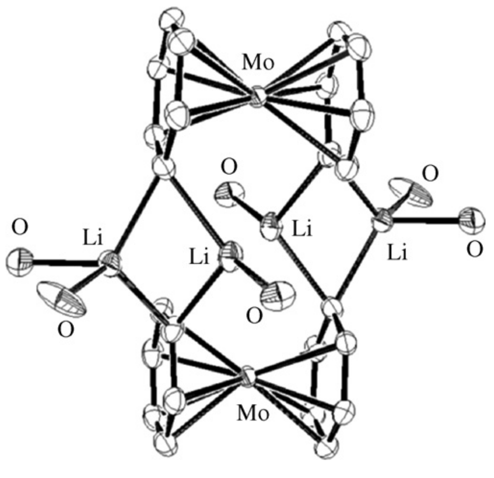
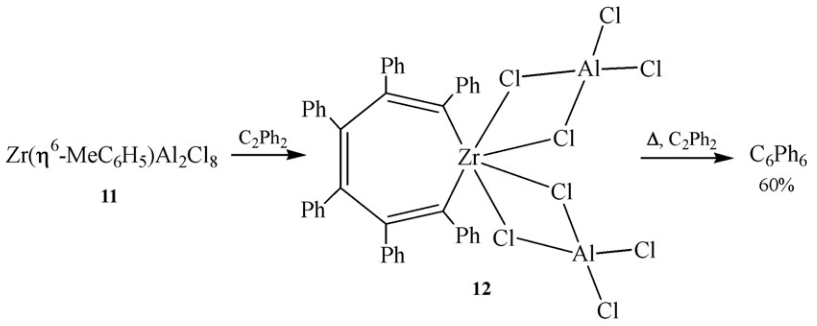


Fig. 9. Molecular structure of [Mo(η^6-C_6H_5Li)$_2$]$_2$(thf)$_6$ [165]. The carbon atoms of the thf rings have been omitted for clarity.

The bis(η^6-arene) complexes Cr(η^6-arene)$_2$, arene = C_6H_6, C_6H_5-C_6H_5, 1,3,5-$Me_3C_6H_3$, C_6Me_6, catalyze the oligomerization of perfluoropropene to dimers and trimers [175]; defluorinated trimers are also formed, probably through "Cr–H" species formed via activation of an aromatic ligand within the catalytic precursor [175c].

Butadiene is cyclotrimerized to (*Z*,*E*,*E*)-cyclododecatriene by a variety of transition metal compounds [176] including Ti(η^6-arene)$_2$, arene = C_6H_6, MeC_6H_5 [177] and Ti(η^6-arene)[(μ-X)$_2$AlX_2]$_2$ [178]. The addition of ethylaluminium compounds to Ti(η^6-arene)[(μ-X)$_2$AlX_2]$_2$ to form Ti(η^6-C_6H_6)$Al_2Cl_{8-n}Et_n$, n = 0–2, **10**, derivatives, further improves the catalytic properties and the kinetics of butadiene cyclotrimerization. It has also been observed that the activity and the selectivity depend on the number of ethyl groups present in **10** [178].

Strictly related to the higher stability of the titanium(II) arenes on increasing the methyl-substitution on the arene [62], the butadiene cyclotrimerization catalysed by Ti(η^6-C_6H_6)[(μ-Cl)$_2$AlCl_2]$_2$ is prevented by the presence of 1,3,5-$Me_3C_6H_3$ or more alkylated arenes. An elegant paper by Mach and coworkers [178] reports that Ti(η^6-C_6Me_6)[(μ-Cl)$_2$AlCl_2]$_2$, which does not cyclotrimerize butadiene, becomes active after treatment with AlEt_3. This fact has been attributed [178] to the formation of Ti(η^6-C_6Me_6)[(μ-Cl)$_2$AlClEt]$_2$ (X-ray structure) and products of further alkylation (identified in



Scheme 11. Reactivity of $Zr(\eta^6\text{-}MeC_6H_5)Al_2Cl_8$ with diphenylacetylene.

solution): the introduction of ethyl groups on aluminium destabilizes the titanium–C_6Me_6 bond so that the replacement of hexamethylbenzene by butadiene in the first steps of the catalytic cycle becomes more feasible.

Detailed studies [179] on the reaction between $Zr(\eta^6\text{-}MeC_6H_5)Al_2Cl_8$, **11**, and internal alkynes have shown that **11** catalyzes the cyclotrimerization of 2-butyne to hexamethyldewarbenzene and hexamethylbenzene at room temperature, the former being the predominant initial product, followed by the isomerization to the aromatic arene. The reaction of diphenylacetylene with **11** affords the metallacyclic compound **12**, which undergoes decomposition to hexaphenylbenzene only under drastic conditions (boiling decalin, 6 h, 60% C_6Ph_6), Scheme 11. A seven-membered metallacycle of formula $\overline{\mathrm{CPh(CPh)_4CPhTi}}\mathrm{Br_2}$ is formed in the reaction of $Ti(\eta^6\text{-}C_6H_6)[(\mu\text{-}Cl)_2AlCl_2]_2$ with diphenylacetylene in the presence of $AlEt_3$ [180].

4.2. Molecule-based magnets

One of the more intriguing developments in the field of molecule-based magnets has been the discovery in 1991 that the reaction of $V(\eta^6\text{-}C_6H_6)_2$ with tetracyanoethylene (TCNE) affords an insoluble amorphous black solid of composition $V(TCNE)_2\cdot 1/2(CH_2Cl_2)$ [181]. This solid has an ordering temperature higher than 400 K: this means that spontaneous magnetization of the material in the absence of an externally applied magnetic field is observed at about room temperature, a property that gives to this species numerous potential applications [182]. The room temperature magnetic ordering of the material has been recently confirmed by X-ray magnetic circular dichroism [183]. The mechanism of formation of $V(TCNE)_2\cdot 1/2(CH_2Cl_2)$ has been studied [184] and the first step is an electron transfer forming $[V(\eta^6\text{-}C_6H_6)_2]^+$ and $[TCNE]^{\bullet -}$, followed by disproportionation of V(I) to V(0) and V(II), the latter present in solution in the form of the solvento-species $[V(solvent)_6]^{2+}$; substitution of the solvent molecules by TCNE affords the final compound.

By taking into consideration that the stability to disproportionation of vanadium bis(η^6-arene) compounds increases with the steric demand of the arene ligands [120,121], the reaction was repeated with $V(\eta^6\text{-}1,3,5\text{-}{}^tBu_3C_6H_3)_2$. By using a V/TCNE = 1 molar ratio, $[V(\eta^6\text{-}1,3,5\text{-}{}^tBu_3C_6H_3)_2][TCNE]$ was isolated and converted (upon addition of TCNE) into $V(TCNE)_x\cdot y(CH_2Cl_2)$ magnets, which show ordering temperatures between 260 and 205 K. It has also been demonstrated that, in the case of sterically demanding ligands, the disproportionation reaction is not an important step of the reaction [184].

Other magnetic ordered materials, based on the use of vanadium arenes of general formula $VL_2\cdot y(CH_3CN)$, were obtained by reaction of $V(\eta^6\text{-}C_6H_6)_2$ with pentafluorophenyl-tricyanoethylene, *m*-di(tricyanovinyl)benzene, α,α'-dicyanoperfluorostilbene [185].

Thin-films of magnetic materials have been grown from the gas phase at room temperature [186] or at 350 K [187], but in the former case the more volatile $V(CO)_6$ was used because no reaction was observed by employing $V(\eta^6\text{-}C_6H_6)_2$. Furthermore, the chemical vapour deposition technique allowed the preparation of $Mo(TCNE)_x$ magnets from $Mo(\eta^6\text{-}MeC_6H_5)_2$ and TCNE [188].

In contrast to the reaction of $V(\eta^6\text{-arene})_2$ and TCNE to form $V(TCNE)_x\bullet y(solvent)$ species, but in agreement with the fact that $[Cr(\eta^6\text{-arene})_2]^+$ cations are more resistant to disproportionation than the corresponding $V(\eta^6\text{-arene})_2$ complexes, see Section 3.2.2, the reaction of TCNE and $Cr(\eta^6\text{-arene})_2$, arene = C_6H_6, 1,3,5-$Me_3C_6H_3$, C_6Me_6, produces the stable $[Cr(\eta^6\text{-arene})_2][TCNE]$ [184]. Only by substitution of benzene with the more labile naphthalene ligands, see Section 3.1, the chromium compound $Cr(TCNE)_x\cdot y(toluene)$ was obtained [184]. It is worth mentioning that the chromium-based materials have an ordering temperature below 10 K [184,189].

4.3. Crystal engineering

Although the idea of attaining collective crystal properties via an adequate choice of the building blocks and the growth of desired crystal structures in appropriate forms is more than thirty years old, it has evolved considerably in recent times towards the interface between the supramolecular and solid state sciences [190].

Much effort has been devoted to so-called organometallic crystal engineering, i.e., the modelling, synthesis, characterization and evaluation of crystalline materials constituted by organometallic molecules and ions [190c]. The utilization of organometallic building blocks, whether molecules or ions, allows one to take advantage of the valence and spin states of transition metal atoms as well as of metal–ligand bonding [190d]. Although the most studied systems are cyclopentadienyl derivatives, Braga et al. at the University of Bologna made a large contribution to crystal engineering with the study of chromium bis(η^6-arene) derivatives either in the 0 or the +I oxidation state. Recently, Braga has reported that hydrogen oxalate anions, obtained by partial deprotonation of oxalic acid, can be used as building blocks in the engineering of crystals containing columns of cationic $[Cr(\eta^6\text{-}C_6H_6)_2]^+$ sandwiches, the anionic chain developing parallel to the cationic piles and containing twisted hydrogen oxalate units, Fig. 10A [191].

Selected examples of building blocks for the construction of crystal architectures containing bis(η^6-arene) metal units are: $[Cr(\eta^6\text{-}C_6H_6)_2]_2[C_4O_4]\cdot H_2O$, Fig. 10B [192], $Cr(\eta^6\text{-}C_6H_6)_2,CrO_3(OCH_3)]$, obtained during attempts to crystallize $[Cr(\eta^6\text{-}C_6H_6)_2][OH]$ from methanol [193], $Cr(\eta^6\text{-arene})_2]_2[(1,3\text{-cyclohexadienone})_n]$, arene = C_6H_6, $n = 4$; arene = MeC_6H_5, $n = 2$ [194], and the chromium(0) derivative $Cr(\eta^6\text{-}C_6H_5COOH)_2$ [195].

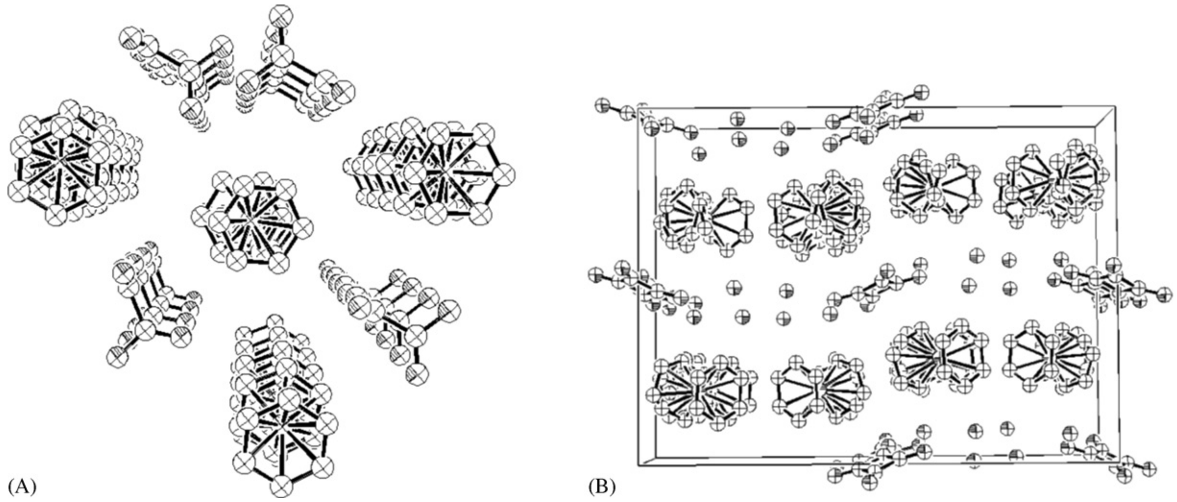
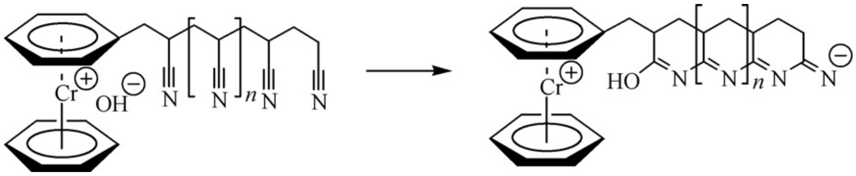


Fig. 10. (A) Projection of $[Cr(\eta^6\text{-}C_6H_6)_2][HC_2O_4]H_2O$ along the cation pile showing the anionic chain in between. (B) Projection of $[Cr(\eta^6\text{-}C_6H_6)_2]_2[C_4O_4]H_2O$ showing the alternating layers of squarate dianions [191,192].



Scheme 12. Formation of CN-conjugated ladder-structured polynaphthyridine-type polymers.

4.4. New materials

In this section, I will give examples of the use of bis(η^6-arene) derivatives to obtain organometallic materials with regular pore structures on the nanometer or micrometer scale and thin films.

In 1999, Douglas and coworkers reported [196] that polyacrylonitrile covalently bonded to bis(η^6-arene) chromium units is readily obtained by the room temperature polycyanomethylation reaction between acrylonitrile and $Cr(\eta^6\text{-arene})_2$, arene = C_6H_6, EtC_6H_5, $Et_2C_6H_4$ and $Et_3C_6H_3$. The ability of the arene ligand to undergo cyanoethylation increases in the order: $C_6H_6 < EtC_6H_5 < Et_2C_6H_4 < Et_3C_6H_3$. The reaction was later extended to vanadium [197]; in this case, the process was activated by the presence of tetracyanoethylene, which formed cationic bis(η^6-arene) derivatives and radical anions which started the polycyanoethylation [197b]. The polymeric species consist of a central $M(\eta^6\text{-arene})_2$ compound with up to four polyacrylonitrile arms, each composed of ca. 63 acrylonitrile units, Fig. 11.

Novel and interesting polymeric film-producing nanocomposites, based on bis(η^6-arene) chromium derivatives incorporated into CN-containing matrices, have been developed. The formation of the film involves the hydrolysis of polyacrylonitrile (promoted by strongly alkaline $[Cr(\eta^6\text{-arene})_2]OH$ species); the hydrolytic process causes the cyclization of the CN groups giving ladder-structured polynaphthyridine-type polymers with conjugated CN bonds, see Scheme 12 [198].

In 2004, Berenbaum and Manners reported the first homopolymer with main chains consisting of bis(η^6-arene) chromium and organosilane units [199], Scheme 13, demonstrating that metal catalyzed ring opening polymerization (ROP) permits the polymerization of strained metal-containing rings which are difficult to polymerize using other initiation methods.

Metallorganic chemical vapour deposition (MOCVD) allows the low temperature deposition of a large variety of thin films. Due to the fact that chromium coatings are of interest for their resistance to corrosion and high hardness, studies have been performed to identify suitable precursor for MOCVD of chromium metal thin films which avoid carbon incorporation (in the form of carbides which are thermodynamically stable under the experimental conditions) [200].

As suggested in Section 1, the decomposition of transition metal arenes generates a thermodynamically stable molecule (the arene) which can be removed rapidly from the deposition zone after cleavage of the metal–ligand bond [201]. On the other hand, when films containing more than one element are needed, either high temperature MOCVD or co-deposition may be the useful technique, as in the case of the deposition of chromium carbide films from $Cr(\eta^6\text{-arene})_2$, arene = C_6H_6, MeC_6H_5, $p\text{-}Me_2C_6H_4$, at 300–600 °C [202,203], or of niobium nitride and carbonitride films from $Nb(\eta^6\text{-}MeC_6H_5)_2$ and hydrazine at high temperature [204]. Addition of $Cr(\eta^6\text{-}C_6H_6)_2$ to acid solutions derived from 4,4′-oxydianiline and either 1,2,4,5-benzenetetracarboxylic acid dianhydride or 3,3′,4,4′-benzophenonetetracarboxylic acid dianhydride, followed by thermal curing, gives polyimide films containing a homogeneous dispersion of nanoclusters (4–1.5 nm) of Cr_2O_3 [205].

In order to prevent aggregation of metal particles after the deposition of metal colloid particles on solid supports such as carbon,

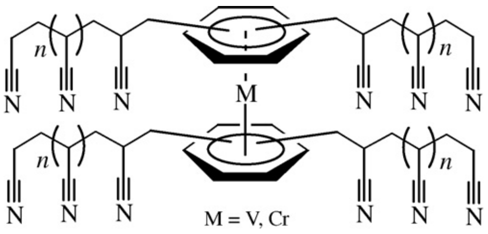
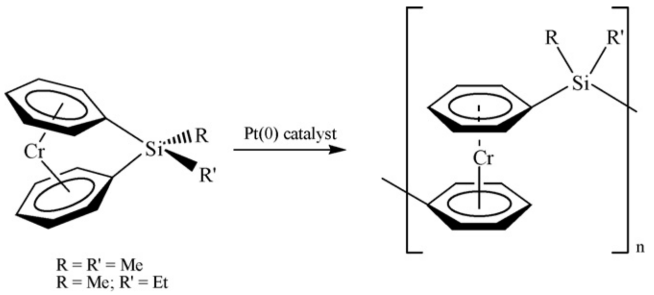


Fig. 11. Polyacrylonitrile covalently bonded to bis(η^6-arene) chromium derivatives.



Scheme 13. Polymerization of silicon-bridged bis(benzene) chromium complexes.

Bönnemann et al. doped the support with small amounts of Ti(η^6-arene)$_2$ derivatives prior to deposition of the metal colloids: a considerable increase of the activity of the resulting hydrogenation catalyst was observed [20b], due to a more diffused uniformity of the dispersion.

Highly reactive sandwich complexes such as M(η^6-MeC$_6$H$_5$)$_2$, M = Ti, Fe, have been used for the synthesis of TiO$_2$ and of nanosized iron/iron oxide fine particles, respectively, in confined nanosized compartments of mesoporous alumina. The iron/iron oxide particles can be reduced by hydrogen at high temperature affording catalysts for the formation of multiwalled carbon nanotubes [206].

A review has appeared in 2002 [207] dealing with the synthesis and application of organometallic reagents as reductants of mesoporous molecular sieves. It has been observed that mesoporous niobium, tantalum and titanium oxides can act as stoichiometric electron acceptors and hosts for a variety of electron-donating guest species such as M(η^6-arene)$_2$, M = Ti, V, Nb, Cr, arene = C$_6$H$_6$, MeC$_6$H$_5$. For example, the treatment of mesoporous niobium oxide with M(η^6-C$_6$H$_6$)$_2$, M = V, Cr, forms paramagnetic materials with conductivity values as high as $10^{-5}\,\Omega^{-1}\,\mathrm{cm}^{-1}$ [208], which retain the mesostructure and contain both M(η^6-C$_6$H$_6$)$_2$ and [M(η^6-C$_6$H$_6$)$_2$]$^+$ species within the pores of the materials, Fig. 12A. The Cr(η^6-C$_6$H$_6$)$_2$ content of the material can be increased by doping the walls of the niobium oxide material with vanadium(V) species [from VO(O^{i}Pr)$_3$] [209]. This observation is consistent with an electron transfer between the bis(η^6-arene) and the walls of the mesostructure and with the higher oxidizing power of vanadium(V) with respect to niobium(V) [210].

The treatment of mesoporous niobium oxide with Nb(η^6-MeC$_6$H$_5$)$_2$ leads to a mesopouros material that exhibits metallic properties: the metallic behaviour has been attributed to niobium atoms which have been deposited on the walls of the structure, Fig. 12B. This material causes room temperature dinitrogen cleavage leaving a thin nitride coat on the reduced niobium oxide surface [211]. Formation of ammonia, via nitride intermediates, was observed when mesoporous titanium [212] or tantalum oxides [213] were reacted with Ti(η^6-MeC$_6$H$_5$)$_2$ under nitrogen atmosphere.

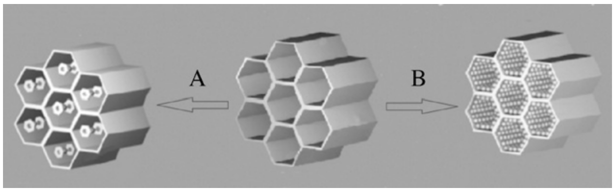


Fig. 12. Reactions of mesoporous oxides with M(η^6-C$_6$H$_6$)$_2$, M = V, Cr (path A) and with M(η^6-MeC$_6$H$_5$)$_2$, M = Ti, Nb (path B) [207].

5. Conclusions

Fifty years after the first bis(η^6-arene) metal derivative was characterized, complexes containing η^6-bonded aromatic ligands are still a research area of interest. Studies in this field have shown the possibility that the arenes can stabilize both normal and low oxidation states, suggesting that these ligands may modulate their σ-donor or π-acceptor properties.

The metal atom/arene vapour co-condensation technique and the Fischer-Hafner, AlCl$_3$-mediated, syntheses are still the principal pathways to obtain these compounds. The discovery of conventional, high-yielding syntheses of M(η^6-1,3,5-Me$_3$C$_6$H$_3$)$_2$, M = V, Nb, derivatives, together with the long-standing preparative method of the bis(arene) species of chromium and molybdenum, has allowed their chemistry to be explored in some detail. The use of metal bis(η^6-arene) complexes as precursors to classical coordination compounds has developed. Generally speaking, metal arenes can be converted into metal halides, carboxylato or β-diketonato derivatives by hydrogen halides, carboxylic acids or substituted β-diketones, respectively, via redox reactions, which are high-yielding and produce arenes and hydrogen only as by-products, thus favouring the recovery of the metal-containing product.

The reaction of bis(η^6-arene) derivatives of titanium(0), vanadium(0), and niobium(0) easily proceeds with oxidation of the metal to titanium(III), vanadium(II), and niobium(III) respectively, and loss of the aromatic ligand. The isolation of compounds in a different oxidation state for vanadium with respect to titanium and niobium (+2 instead of +3), while operating under the same experimental conditions, confirms the general rule [210] stating that the stability of the higher oxidation states decreases from left to right within a period and increases on descending a vertical sequence of transition elements. This reactivity has to be compared with that of the bis(η^6-arene) derivatives of chromium(0) and molybdenum(0) which afford compounds containing the [M(η^6-arene)$_2$]$^+$ cation under the same experimental conditions. This behaviour is related to the much higher tendency to undergo oxidation with consequent loss of the π-acid arene ligands of the elements of Groups 4 and 5 with respect to those of Group 6.

Recent work has shown that bis(η^6-arene) derivatives of transition metals are useful starting materials for the production of thin metal film, organometallic nanomaterials for non linear optics and materials with regular pore structures on the nanometer or micrometer scale.

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