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Journal of Organometallic Chemistry 500 (1995) 47–60

Journal of Organometallic Chemistry

Invited review

Aromatic hydrocarbons, carbocyclic ligands spanning several oxidation states in both Main Group and transition elements. Recent advances with early transition d elements

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Received 22 February 1995

Abstract

In this paper some synthetic procedures to obtain (η^6-arene)metal derivatives are reviewed. The metal-atom–arene-vapour co-condensation technique is the most appropriate to generate complexes of polycyclic aromatic hydrocarbons or heterocycles. As far as the aluminium halide-mediated synthesis is concerned, two classes of reaction are observed. When AlX_3 is used with a metal halide in the presence of an aromatic hydrocarbon in the absence of any reducing agent, AlX_3 can function as a dehalogenating agent, to give ionic compounds of general formula $[M(\eta^6\text{-arene})n](AlX_4)_m$, or it can add across the M–X bond with formation of $M(\mu\text{-X})_nAlX_{4-n}$ systems. In both cases the metal displays its typical oxidation state. However, the use of AlX_3 in combination with aluminium (the Fischer–Hafner reducing system) affords ionic or covalent low-oxidation-state metal(η^6-arene) complexes. Attention is focused on our most recent results concerning the synthesis, properties and reactivity of η^6-arene derivatives of Group 4 and 5 elements, showing, inter alia, the first example of a tetraarylborate anion behaving as a 12-electron donor to one metal atom and low-valent η^6-arene compounds as useful reagents in the inorganic and coordination chemistry of the corresponding metal in nonaqueous systems.

Keywords: Arene complexes; Transition metals; Vanadium; Niobium

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1. Introduction

Metal complexes of six-membered aromatic carbocycles ligands have attracted the interest of inorganic chemists since Fischer and Hafner [1] characterized the prototype of these compounds, $[Cr(\eta^6\text{-benzene})_2]$, obtained by reduction of anhydrous $CrCl_3$ with $Al/AlCl_3$ in the aromatic hydrocarbon as solvent. This accomplishment also closed a long debate in the literature concerning the nature of the Hein's "polyphenyl" derivatives [2], which were proposed [3] and finally confirmed [4] to be π-arene complexes of chromium in the zero or I oxidation state.

The chemistry of π-arene complexes has developed considerably in the last forty years. While this chemistry was believed initially to be confined to low-oxidation-state transition metals, it has now been proved that stable and isolatable π-arene metal complexes can also exist for transition elements in their usual oxidation states, and also for Main Group elements. For aromatic hydrocarbons as ligands we are therefore witnessing a situation which is similar to that encountered with alkyl and aryl derivatives of transition elements, which were initially believed to require the simultaneous presence of π-acids such as carbon monoxide and tertiary phosphines to stabilize the lower oxidation states. In fact, compounds of this class are now also known for relatively high oxidation states [5]. The predominating factor is actually the coordinative saturation imposed by the ligand environment in the given oxidation state.

There are several reasons for the interest for arene complexes of Main Groups and transition elements. (i) As the arenes are uncharged, and donate an even number of electron, replacement can be carried out by neutral Lewis bases in an organic solvent; vacant coordination positions can be generated more easily than with negatively charged ligands such as the cyclopentadienyl. (ii) The hapticity of the arene ligand can be

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SSDI 0022-328X(95)00505-6

varied ($\eta^6 \rightarrow \eta^4 \rightarrow \eta^2$) by varying the nature of the ancillary ligands [6]. (iii) Because the arene complexes can create vacant coordination sites by changing the hapticity of the ligand, these compounds are appropriate precursors for catalysts, for example in hydrogenation and polymerization processes [6,7]. (iv) If the arene ligand is in a zero-oxidation-state system, its displacement can generate the metal in an active form. (v) Relatively high vapour pressures are usually associated with zero-oxidation-state arene complexes, making them good candidates for the metal organic chemical vapour deposition (MOCVD) [8]. The high stability of the aromatic hydrocarbon set free in the thermal decomposition should minimize the formation of carbon-containing secondary products.

Arene metal complexes are synthesized by three main routes: (1) the co-condensation of the metal vapours with those of the aromatic hydrocarbon at low temperature, the so-called synthesis via metal atoms; (2) the dehalogenation of an anhydrous metal halide by AlX_3 in the presence of an aromatic hydrocarbon; and (3) the reduction of an anhydrous metal halide by AlX_3 with the aromatic hydrocarbon as reactant and medium.

Reviews have been published concerning synthesis, properties and reactivities of arene complexes of transition and Main Group elements [9]. After a brief discussion on the synthesis of arene complexes by the metal vaporization tecnique, this paper will consider the synthesis of arene complexes in relatively high oxidation states, which almost invariably requires the use of aluminium halides as halogen abstractor from anhydrous metal halides in the presence of an aromatic hydrocarbon. The last section of the paper will concern the classical Fischer–Hafner synthesis of arene–metal complexes with the Al/AlX_3 system, which combines the dehalogenating properties of AlX_3 with the reducing power of aluminium. Specific attention will be given to recent advances by other research groups and by ourselves, with specific reference to the elements of Groups 4 and 5. There is an earlier review from this Laboratory on low-oxidation-state η^6-arene complexes of early transition elements [10]; further work on these systems since then is examined in the present article.

2. Synthesis via Metal atoms

This method is most appropriate for arene complexes of elements in their zero oxidation state.

The metal vapour technique for the preparation of arene derivatives was introduced by Timms in 1969 [11], as applied to $[Cr(\eta^6\text{-benzene})_2]$. Since then, this technique has been used successfully in several other cases, due to its unique advantage of removing the thermodynamic barrier connected with the vaporization of the metal. The overall formation of an uncharged bis(η^6-arene) complex of a given element M (see Eq. (1)), can be divided into the two processes of vaporization (Eq. (1a)) and bond formation (Eq. (1b))

$$M_{(s)} \rightarrow M_{(g)} \tag{1a}$$

$$M_{(g)} + 2\ \text{arene}_{(g)} \rightarrow M(\eta^6\text{-arene})_{2\,(g)} \tag{1b}$$

hence

$$M_{(s)} + 2\ \text{arene}_{(g)} \rightarrow M(\eta^6\text{-arene})_{2\,(g)} \tag{1}$$

By this technique, atoms are generated and quenched at low temperature (generally around 70 K) in the presence of the molecularly dispersed arene and several arene derivatives of transition elements [12] and lanthanides [13] have been prepared and characterized in this way.

In spite of some difficulties connected with the availability of the apparatus for metal vaporization, this technique is important in the synthesis of those compounds which cannot be obtained by conventional methods. Examples are complexes with halogenated aromatic hydrocarbons [14], aromatic amines or esters [15], and with polynuclear aromatics such as naphthalene [16], biphenyl [17], polymethylphenylsiloxanes [18] and cyclophanes [19].

Moreover, the metal vaporization technique has allowed the preparation of the zirconium(0) [12f], hafnium(0) [12f], tantalum(0) [12f], tungsten(0) [12f], manganese(I) [20] and lanthanides(0) [13] bis-(arene) complexes, which cannot be synthesised conventially yet (Zr, Hf, Ta, Mn and lanthanides) or in only poor yield (W) [21–25]. Other compounds accessible via the metal vaporization technique only are the transition metal derivatives containing heteroarenes such as 2,6-dimethylpyridine [26], pyridine [27], tetramethylpyrazine [28], phosphabenzene, C_5H_5P [29] and arsabenzene C_5H_5As [30].

3. The AlX_3-mediated synthesis of metal arene derivatives

3.1. Ionic products

Vacating a coordination position is frequently an essential prerequisite for new metal-ligand bond formation. Several reagents may be used when a metal halide is involved and a coordination position around the metal is to be vacated without modifying the metal oxidation state. The most frequently used are silver or thallium(I) salts of poorly coordinating anions such as $AgBF_4$ and $TlPF_6$, or aluminium halides (Eqs. (2) and (3))

$$MX_n + M'^{+} \rightarrow M'X + [MX_{n-1}]^{+} \tag{2}$$

$$MX_n + AlX_3 \rightarrow AlX_4^{-} + [MX_{n-1}]^{+} \tag{3}$$

When stable oxidation states of M are involved, there is no limitation to the use of these reagents. With low oxidation states, only thallium(I) salts or AlX_3 may be used, owing to the oxidizing properties of Ag^+. The use of $AlCl_3$ corresponds to a decrease of the coordination number of aluminium from six in the solid compound to four in the tetrahedral $[AlCl_4]^-$ or $[Al_2Cl_7]^-$ [31], vide infra.

Early examples of the reactivity exemplified in Eq. (3) is the preparation of the hexacarbonyl cations of manganese(I) or rhenium(I), (Eq. (4))

$$[M(CO)_5Cl] + AlCl_3 + CO \rightarrow [M(CO)_6][AlCl_4] \quad (4)$$

M = Mn, Re [32]

A well-known somewhat related case involving a C–X bond, rather than a M–X bond, is the first preparation of a ketenylidene complex by Seyferth et al. [33] (Eq. (5))

$$Co_3(CO)_9C\text{-}Cl + AlCl_3 + CO \rightarrow [Co_3(CO)_9C\text{-}CO]^+ AlCl_4^- \quad (5)$$

The treatment of a metal halide with aluminium trihalide in the presence of an aromatic hydrocarbon has allowed the preparation of bis-(arene) derivatives of transition elements and uranium in their typical oxidation states: Fe(II), $[Fe(\eta^6\text{-arene})_2]^{2+}$ [34], Co(II), $[Co(\eta^6\text{-}Me_6C_6)_2]^{2+}$ [35], Ni(II), $[Ni(\eta^6\text{-}Me_6C_6)_2]^{2+}$ [36] and U(IV), $[\{U(\eta^6\text{-}Me_6C_6)Cl_2\}_2(\mu\text{-}Cl)_3][AlCl_4]$ [37], (Eqs. (6) and (7))

$$MX_2 + 2\ AlX_3 + 2\ \text{arene} \rightarrow [M(\eta^6\text{-arene})_2][AlCl_4]_2 \quad (6)$$

M = Fe; X = Cl, Br, arene = benzene, toluene, $1,2\text{-}Me_2C_6H_4$, $1,3,5\text{-}Me_3C_6H_3$, Me_6C_6;

M = Co, Ni; X = Cl, Br; arene = Me_6C_6

$$2\ UCl_4 + AlCl_3 + 2\ Me_6C_6 \rightarrow \{[U(\eta^6\text{-}Me_6C_6)Cl_2]_2(\mu\text{-}Cl)_3\}AlCl_4 \quad (7)$$

$AlCl_3$ can also abstract chloride ions from non-transition elements. The reaction of $BiCl_3$ or Hg_2Cl_2 with $AlCl_3$ in the presence of aromatic hydrocarbons produces η^6-arene derivatives of Bi(III) [38] or Hg(I) [39] (Eqs. (8) and (9)).

$$BiCl_3 + AlCl_3 + \text{arene} \rightarrow [Bi(\eta^6\text{-arene})Cl_2][AlCl_4] \quad (8)$$

arene = toluene or Me_6C_6

$$Hg_2Cl_2 + 2\ AlCl_3 + 2\ \text{arene} \rightarrow [Hg_2(\eta^6\text{-arene})_2][AlCl_4]_2 \quad (9)$$

arene = toluene, $1,2\text{-}Me_2C_6H_4$, $1,3,5\text{-}Me_3C_6H_3$, $1,2,4,5\text{-}Me_4C_6H_2$ or Me_6C_6

Recent work from our laboratories [40] has extended some earlier work on the reaction between $TiCl_4$ and aromatic hydrocarbons. Krauss and coworkers showed that the deeply coloured solutions of $TiCl_4$ in aromatic hydrocarbons contain aromatic-to-titanium charge transfer complexes. A compound of composition $3\ TiCl_4 \cdot Me_6C_6$ was isolated in the case of hexamethylbenzene [41]. Floriani et al. showed [42] by X-ray diffraction methods that the compound isolated by Krauss is a η^6-arene derivative of titanium(IV) of composition $[Ti(\eta^6\text{-}Me_6C_6)Cl_3][Ti_2Cl_9]$. This ionic product contains the binuclear triply chloride-bridged $[Ti_2Cl_9]^-$ anion. Assuming that equilibria (10) and (11) operate in less methyl-substituted aromatic hydrocarbons than hexamethylbenzene (these are known [43] to give less stable complexes), we reckoned that arene complexation to titanium(IV) could be forced by driving equilibrium (11) to the right by addition of $AlCl_3$. The net result would be the formation of the tetrahaloaluminato complexes (Eq. 12). This was confirmed by experiment.

$$3\ TiCl_4 + \text{arene} \rightleftarrows [Ti(\eta^6\text{-arene})Cl_3]Ti_2Cl_9 \quad (10)$$

$$[Ti(\eta^6\text{-arene})Cl_3]Ti_2Cl_9 + 2\ \text{arene} \rightleftarrows 3\ [Ti(\eta^6\text{-arene})Cl_3]Cl \quad (11)$$

$$3\ [Ti(\eta^6\text{-arene})Cl_3]Cl + 3\ AlCl_3 \rightleftarrows 3\ [Ti(\eta^6\text{-arene})Cl_3]AlCl_4 \quad (12)$$

The ionic η^6-arene complexes of titanium(IV) were formed in the appropriate hydrocarbon and were isolated as analytically pure solids, see Eq. (13). Furthermore, by this method, the synthesis was extended to tetrahalo complexes other than the chloride, though these are less stable.

$$TiX_4 + AlX_3 + \text{arene} \rightarrow [Ti(\eta^6\text{-arene})X_3][AlX_4] \quad (13)$$

arene = $1,3,5\text{-}Me_3C_6H_3$, X = Cl or Br;

$1,2,4,5\text{-}Me_4C_6H_2$, X = Cl;

arene = Me_6C_6, X = Cl, Br or I.

In aromatic hydrocarbons, most of the tetrahaloaluminato complexes give a biphasic liquid system (vide infra). Taking advantage of this property, it was possible to measure the ^{13}C-NMR spectra of the deep-red layer of higher density obtained in the presence of C_6D_6. Arene complexation to titanium(IV) was monitored by the downfield shift of the ^{13}C resonances of both the ring and methyl carbon atoms by about 18 and 3 ppm, respectively, with respect to the uncomplexed hydrocarbon. For toluene and benzene no shift was observed, suggesting that no (or labile with fast exchange in the NMR timescale) arene complexation had occurred.

An interesting feature of the ^{13}C-NMR spectra in C_6D_6 is that the ring carbon atoms carrying the proton appear as triplets, the separation of the components of the signal varying from 25 to 27 Hz, due to coupling between carbon and deuterium (I = 1). This shows that the ring protons undergo a fast H/D exchange process on treatment of the arene derivative of titanium(IV) with C_6D_6 [40].

3.2. Covalent tetrahaloaluminates

In addition to the ionic tetrahaloaluminates described above, the reaction of metal halides with AlX_3 may result in the formation of covalently bonded halide-bridged complexes involving both aluminium and the metal coordinating the aromatic hydrocarbon.

A recent example of this type is represented by the formation of the tetrachloroaluminate η^6-arene complexes of lanthanoid(III), whose synthesis deserves some comment. The procedure initially reported for the preparation of (η^6-arene) compounds of lanthanoids included the use of finely divided aluminium as "activator". Nevertheless, only derivatives of general formula $[Ln(\eta^6\text{-arene})\{(\mu\text{-Cl})_2AlCl_2\}_3]$, containing the lanthanoid(III) ion, were obtained. Some of them had been structurally characterized [44]. Because the lanthanoid does not undergo reduction, two research groups independently demonstrated recently that η^6-arene complexes of neodymium(III) [45], samarium(III) [45b], gadolinium(III) [45] and ytterbium(III) [45] can be obtained according to Eq. (14)

$$LnCl_3 + 3\ AlCl_3 + \text{arene} \rightarrow [Ln(\eta^6\text{-arene})\{(\mu\text{-Cl})_2AlCl_2\}_3] \quad (14)$$

Ln = Nd, Sm, Gd or Yb

Even in the absence of aluminium, the reaction of $EuCl_3$ with $AlCl_3$ and Me_6C_6 results in the formation of a europium(II) arene tetranuclear complex of formula $[\{Eu(\eta^6\text{-}Me_6C_6)(AlCl_4)_2\}_4]$, with terminal bidentate and bridging tetradentate $AlCl_4$ groups [46]. In this system, the reducing agent is not known. It is possibile that some process of HCl elimination involving the methyl groups of coordinated hexamethylbenzene is responsible for the reduction. However, it is known that the oxidation state II is easily accessible for europium.

Covalently bonded tetrahaloaluminato complexes obtained by the use of aluminium halides as dehalogenating agents can also be found outside the lanthanoid series. A number of η^6-arene complexes of Main Group elements, of Tl(I) [47], Pb(II) [48] and Sn(II) [49], have been obtained and structurally characterized, thus showing the ability of Main Group elements to coordinate an arene as η^6 fashion [50].

The dominant factor in determining the coordination mode of the arene group is coordination saturation in any given oxidation state. This is confirmed by the observation that chloride abstraction from CuCl or AgCl by $AlCl_3$ in the presence of arenes affords complexes of general formula $[\{(\eta^2\text{-arene})MAlCl_4\}_n]$. In the copper derivative (arene = benzene), the d^{10} central metal atom is in a distorted tetrahedral environment with three metal-to-chlorine bonds and a π-interaction with benzene [51]. It is worth mentioning that in the benzene complex, $[\{(\eta^2\text{-benzene})AgAlCl_4\}_n]$, the silver cation is five-coordinate due to interaction with four chlorides and one double bond of the aromatic group [51b].

The general conclusion to be drawn from the experimental observations cited in the preceding sections is that the aluminium halides may behave in two different ways in their reactions with metal halides.

They may function as dehalogenating agents thus leaving free coordination sites available for the arene. Additional examples are the $\{M(\eta^6\text{-arene})(CO)_n]^+$ [M = Nb, Ta, $n = 4$ [52]; M = Re, $n = 3$ [53]} obtained from $[M_2(\mu\text{-Cl})_3(CO)_8]^-$, M = Nb or Ta, or from $[ReBr(CO)_5]$ with $AlBr_3$ in the presence of arene (Eqs. (15) and (16))

$$Na[M_2(\mu\text{-Cl})_3(CO)_8] + 4\ AlBr_3 + 2\ \text{arene} \rightarrow 2\ [M(\eta^6\text{-arene})(CO)_4][Al_2Br_6Cl] + NaCl \quad (15)$$

$$[ReBr(CO)_5] + AlBr_3 + \text{arene} \rightarrow [Re(\eta^6\text{-arene})(CO)_3][AlBr_4] + 2\ CO \quad (16)$$

They may also add across the metal-halide bond with formation of $[M(\mu\text{-}X)_nAlX_{4-n}]$ systems as in the case of copper, silver and the lanthanoids. In such cases the aluminum halide is presumably able to reduce the electron density at the metal, increasing the Lewis acidity of M, thus promoting arene coordination.

The interaction of MCl_n with $AlCl_3$ represents a complete structural modification of both partners. Aluminium trichloride in the solid state contains hexacoordinate aluminium with Al–Cl distances ranging from 2.29 to 2.32 Å [54]. The trichlorides of early lanthanides (from praseodymium(III) to gadolinium(III)) are enneacoordinate in a tricapped trigonal prism geometry [55]. However, Ytterbium(III) is octahedrally coordinated in $YbCl_3$ [55]. Thus, the formation of the η^6-arene complex does not appear to depend greatly on the nature of the starting chloride MCl_n, as both lanthanoids in the early part of the series (neodymium, samarium and gadolinium) and ytterbium undergo the reaction with $AlCl_3$ to give the covalently bonded η^6-arene derivatives. The driving force in the reaction of $MCl_n/AlCl_3$ with aromatic hydrocarbons appears to be the formation of the tetrahedral (either ionic or covalent) $AlCl_4$ structure and the coordination of the arene to M, compensating for the partial loss of the original M–Cl bonds.

4. The AlX_3-mediated synthesis of metal arene derivatives in the presence of aluminium: the Fischer–Hafner synthesis

4.1. General features

The reaction of metal halides with the Al/AlX_3 system in aromatic hydrocarbons has been widely used for the synthesis of η^6-arene derivatives of typical d-transition elements [21,35,56] in low oxidation states. In the case of the $CrCl_3/Al/AlCl_3$/arene, the $[Cr(\eta^6\text{-benzene})_2]^+$ cation was shown [1] to be the primary product of the reduction of Cr(III) by aluminium, the counteranion being $[AlCl_4]^-$.

A different behaviour is observed with uranium [44c], with early transition metals such as those of Group 4, and with niobium and tantalum [57]. They react with the Fischer–Hafner system producing mono-arene complexes of general formula $[M(\eta^6\text{-arene})(AlX_4)_n]$ with coordinated tetrahaloaluminato groups. This type of structure is well established for the titanium(II) halo complexes, $[Ti(\eta^6\text{-arene})\{(\mu\text{-}X)_2AlX_2\}_2]$ [57e,g,h,i,l].

In the case of uranium, reduction from uranium(IV) to uranium(III) occurs with formation of the uranium(III) derivative $[U(\eta^6\text{-}Me_6C_6)(AlCl_4)_3]$, which has a structure similar to that of the lanthanide(III) complexes, $[U(\eta^6\text{-}Me_6C_6)\{(\mu\text{-}Cl)_2AlCl_2\}_3]$ [44c].

The reaction conditions appear to be important, especially if the more reactive, less stable metal bromides or iodides are employed. The Fischer–Hafner reduction of TiI_4 or ZrX_4 (X = Br or I) is a good example. When TiI_4 is stirred in the presence of Al/AlI_3 at room temperature, yields as high as 40% of the titanium(II) derivatives of formula $[Ti(\eta^6\text{-arene})\{(\mu\text{-}I)_2AlI_2)\}_2]$ are obtained [57j]. In contrast, prolonged heating of the mixture produces compound **1** (Fig. 1) in which a fragment analogous to dibenzene titanium interacts with a triangular cluster of titanium(II) atoms [58]. The connection between the $Ti(\eta^6\text{-benzene})_2$ group and the triangular titanium cluster is carried out by bridging iodides of three AlI_3 groups which further display an Al–C bond each to three symmetrical positions of one of the six-membered rings. The average oxidation state of titanium in **1** is 1.5. A special feature of this structure is the deformation of one of the benzene rings on coordination to the triangular titanium cluster. The titanium–titanium distance within the cluster is 2.75–2.78 Å, shorter than in titanium metal (2.94 Å) [58].

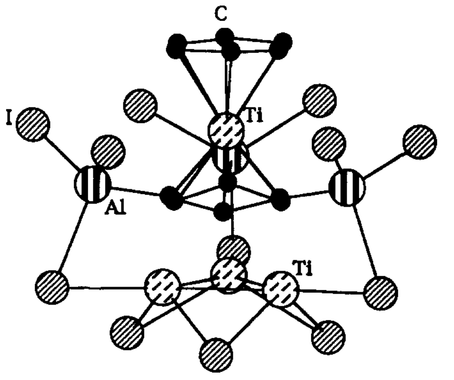


Fig. 1. Schematic representation of the molecular structure of $[(\mu\text{-}I)_3Ti_3\{1,3,5\text{-}[\mu\text{-}I(I_2)Al]_3C_6H_3\text{-}\mu_3,\eta^6,\eta^6\}Ti(\eta^6\text{-}C_6H_6)]$, **1**. Redrawn from published atomic coordinates [58].

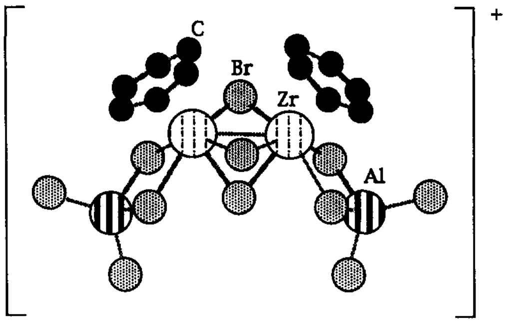


Fig. 2. Schematic representation of the molecular structure of $[\{(\mu\text{-}Br)_3[(\eta^6\text{-}C_6H_6)Zr(\mu\text{-}Br)_2AlBr_2\}_2]^+$, the anion is $[Al_2Br_7]^-$. Redrawn from published atomic coordinates [57k].

In the case of $ZrBr_4$, the zirconium(II) derivative $Zr(\eta^6\text{-arene})[AlBr_4]_2$ is obtained [57m] at room temperature. However, a derivative of zirconium(III), which appears to be an intermediate on the way to the formation of the zirconium(II) complex, has been obtained after 80–100 h at 80–90°C. This cationic compound, has the formula $[(\mu\text{-}Br)_3\{(\eta^6\text{-}C_6H_6)Zr(\mu\text{-}Br)_2AlBr_2\}_2]^+$, and has been isolated as the $[Al_2Br_7]^-$ derivative **2** [57k]. The molecular structure of the benzene cation is shown in Fig. 2. The ionic bis(η^6-arene)tetrahaloaluminates of zirconium(II) of formula $[\{(\eta^6\text{-arene})_2Zr(\mu\text{-}X)_2AlX_2\}]\ [Al_3X_{10}]$ (arene = benzene, X = I) **3**, (Fig. 3) mesitylene, X = Br, have been prepared [57k,n].

The work-up procedure may hinder determination of the nature of the reaction products. Treatment with

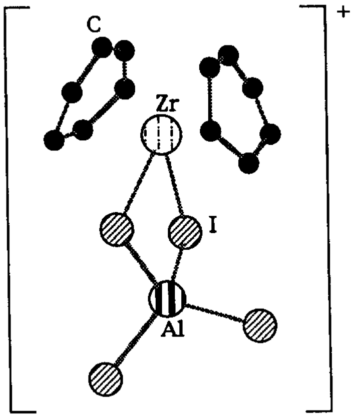


Fig. 3. Schematic representation of the molecular structure of $\{(\eta^6\text{-}C_6H_6)_2Zr(\mu\text{-}I)_2AlI_2]\}^+$, the anion is $[Al_3I_{10}]^-$. Redrawn from published atomic coordinates [57k].

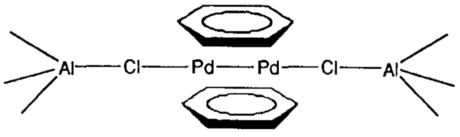
water of the primary reaction product arising from the $MCl_n/Al/AlCl_3/Me_6C_6$ system (M = Ti or Zr, $n = 4$; M = Nb, Ta, $n = 5$), gives trinuclear clusters of general formula $[M_3(\eta^6\text{-}Me_6C_6)_3Cl_6]^{n+}$ (M = Ti, Zr, Nb or Ta; X = Cl, Br; $n = 1$ or 2) [25,58,59]. In this connection, we have recently shown that the primary product of the reaction between MX_n and $Al/AlX_3/Me_6C_6$ is $[M(\eta^6\text{-}Me_6C_6)(AlX_4)_2]$ (M = Zr, $n = 4$, X = Cl [57m]; M = Nb, $n = 5$, X = Cl or Br) [25], which undergo oxidation to $[M_3(\eta^6\text{-}Me_6C_6)_3Cl_6]^+$ on treatment with water. Moreover, if $Nb(\eta^6\text{-arene})(AlBr_4)_2$ (arene = $1,3,5\text{-}Me_3C_6H_3$ or Me_6C_6) was treated with a polar, aprotic solvent such as THF, the niobium(II) dimer $[Nb_2(\eta^6\text{-arene})_2(\mu\text{-}Br)_4]$ (Fig. 4, arene = Me_6C_6) is the product [25].

Considering now the late transition elements, when the Fischer–Hafner procedure is applied to palladium, reduction from palladium(II) to palladium(I) takes place and a new binding mode of the arene to the transition metal is observed. The two diamagnetic crystalline dimers of palladium(I) of formula $[\{PdAl_2Cl_7(C_6H_6)\}]_2$ and $[\{PdAlCl_4(C_6H_6)\}]_2$ show benzene rings π-bonded to both palladium(I) atoms, giving rise to the binuclear sandwich structure 4 [60]. The palladium–palladium distance is 2.57(1) Å, which compares well with the similar distances found in several other palladium(I) dimers [61].

4.2. Bis-arene derivatives of vanadium(0) and niobium(0)

4.2.1. Vanadium, preparation and properties

In the original report by Fischer and Kögler, the preparation of $[V(\eta^6\text{-arene})_2]$ was a two-stage process consisting of treatment of anhydrous vanadium chlorides with $Al/AlCl_3$ in the parent hydrocarbon as medium, followed by reduction of the resulting product with sodium dithionite in alkaline aqueous solution [56c]. Later, $[V(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2]I$ was isolated from the reaction mixture deriving from the reduction of VCl_3 with $Al/AlCl_3$ (or $Al/AlBr_3$) in mesitylene by using LiI in THF. In alkaline solution $[V(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2]$ was obtained by a disproportionation reaction [56f]. The yield of $V(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2$ was poor-to-medium until 1983 when Avilés and Teuben showed that $[V(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2]I$ could be easily converted to $[V(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2]$ by a number of reducing agents such as LiMe, $Na[H_2Al(OCH_2CH_2OCH_3)_2]$, Na or Cp_2Mg in THF [62]. The structure of $[V(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2]$ has been described recently [63].



During our studies on the arene derivatives of the early transition elements we recently re-examined the reduction of VCl_3 to $[V(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2]$ by the Fischer–Hafner procedure and some new observations have been made [64].

(1) The reaction mixture deriving from the treatment of VCl_3 with $Al/AlCl_3$ in mesitylene consists of a biphasic liquid system, the darker lower layer containing most of the vanadium as $[V(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2][Al_xCl_y]$.

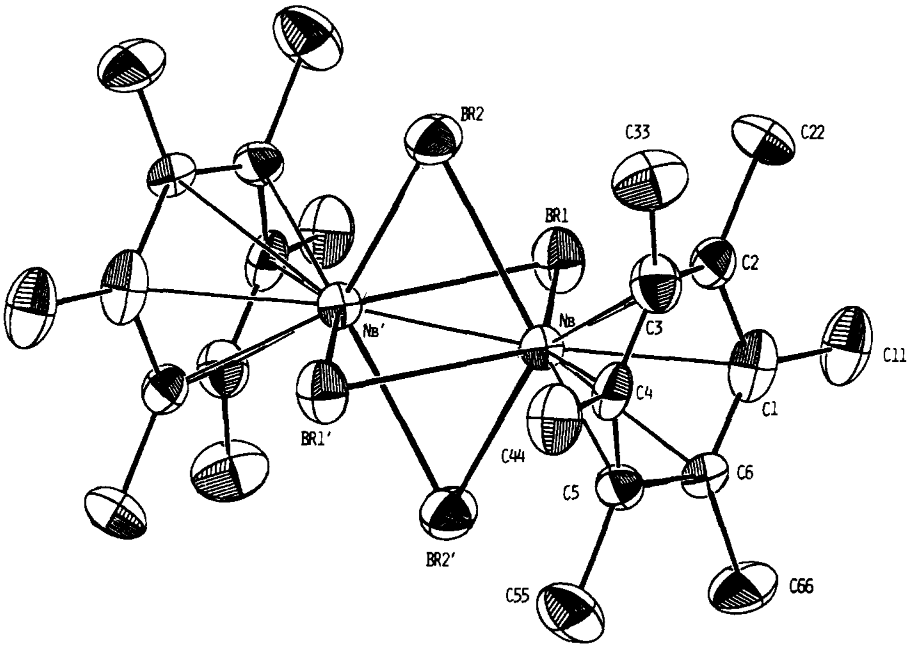


Fig. 4. Schematic representation of the molecular structure of $Nb_2(\eta^6\text{-}Me_6C_6)_2(\mu\text{-}Br)_4$. Reprinted by permission [25].

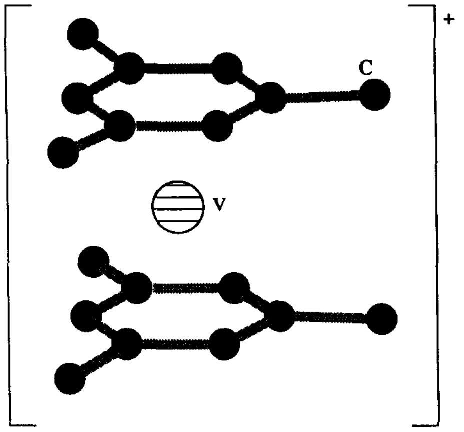


Fig. 5. Schematic representation of the molecular structure of the $[V(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2]^+$ cation in $[V(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2]$-$[AlCl_4]$. Redrawn from published atomic coordinates [64].

(2) Treatment of $[V(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2]$ $[Al_xCl_y]$ with polar, aprotic solvents such as THF and Et_2O, gives $[V(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2][AlCl_4]$, whose molecular structure has been solved (Fig. 5). The $[V(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2]^+$ cation can be described as a sandwich with almost parallel mesitylene rings in a fully eclipsed (both ring and methyl carbon atoms) conformation [64]. The crystal structure of the compound reveals that the ions of the same charge are assembled in pairs (a sequence of four parallel mesitylene groups is shown in Fig. 6) and the distances between pairs of arene groups either the pair linked by the vanadium atom (3.47 Å), or the pairs related by the inversion centre (3.56 Å) are almost equal. Whereas the vanadium-related mesitylene ligands, which are at a shorter distance, are eclipsed, those related by the inversion centre contain staggered methyl groups. The conclusion is that the eclipsed conformation of the vanadium-bonded mesitylene groups is due to an electronic effect and not to packing forces only.

(3) We have verified that the mesitylene/vanadium molar ratio is an important factor in determining the formation of the bilayer system. No bilayer was observed when preformed $[V(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2][AlX_4]$ was treated with mesitylene. However, a viscous solution was obtained on addition of one equivalent of AlX_3 followed by the formation of a bilayer system upon addition of mesitylene, above a specific mesitylene/vanadium molar ratio. It has been shown that the aromatic/vanadium molar ratio necessary for the formation of the bilayer system increases with the dimensions of the halide, from $[AlCl_4]^-$ to $[AlI_4]^-$. For example, the threshold values for the formation of the biphasic system are 2.7, 5.0 and 8.4 for $[AlCl_4]^-$, $[AlBr_4]^-$ and $[AlI_4]^-$, respectively.

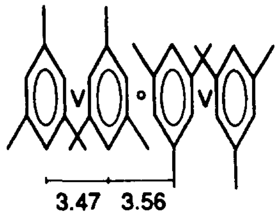


Fig. 6. Cation–cation contacts in the solid state structure of $[V(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2][AlCl_4]$. The small circle represents the inversion centre. Reprinted by permission [64].

These observations led us to conclude that $[V(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2]$ $[Al_2Cl_7]$ is probably the primary product in the reduction of VCl_3 by Al in the presence of $AlCl_3$ in mesitylene. A similar phenomenon has been reported by Atwood [65a] for tetraalkylammonium derivatives of large, aluminium-containing anions. These systems were named "liquid clathrates" [65a] to indicate the formation of non-stoichiometric liquid inclusion complexes. Similar bilayer liquid systems were observed for $[Re(\eta^6\text{-arene})(CO)_3][AlBr_4]$ [53] and $[ZrCp_2Cl(\mu\text{-}Cl)AlCl_2]$ [66] and halocarbonylmetalates of general formula [crown-ether $H]^+[M(CO)_xCl_y]^-$ (M = Cr or W) [65b].

(4) The readily available $[V(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2]^+$ cation can be reduced to the neutral bis(mesitylene) derivative of vanadium(0), $[V(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2]$, on addition of an ethereal solvent to the crude reaction mixture containing the excess of aluminium metal [64b,67]. Yields of crystalline-$[V(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2]$ as high as 95% were obtained by this one-pot procedure (reaction (17))

$$VCl_3 \xrightarrow[\text{2) THF or DME, room temperature}]{\text{1) Al/AlCl}_3\text{/mesitylene, 120–130°C, 2 h}} [V(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2] \qquad (17)$$

This procedure applied to chromium secured quantitative yields of $[Cr(\eta^6\text{-toluene})_2]$ although more severe reaction conditions (8 h, ca. 80°C) had to be used. For molybdenum, the best yield obtained by the new procedure was 39% in the case of $[Mo(\eta^6\text{-toluene})_2]$ [64b].

4.2.2. *Reactivity of vanadium(I) and vanadium(0) compounds*

The stability of the $[V(\eta^6\text{-arene})_2]^+$ cations depends on the arene. Although $[V(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2]AlCl_4$ is stable in THF, the benzene and toluene bis(arene) cations readily disproportionate upon contact with THF, affording good yields of the vanadium(II) and vanadium(0) compounds as in Eq. (18) [68]

$$\begin{aligned} &4\left[V(\eta^6\text{-arene})_2\right]Al_2Cl_7 + 20\ THF \\ &\quad \rightarrow 2\left[V(\eta^6\text{-arene})_2\right] + \left[V_2(\mu\text{-}Cl)_3(THF)_6\right]\left[AlCl_4\right] \\ &\quad + 7\left[AlCl_3(THF)_2\right] + 4\ \text{arene} \qquad (18) \end{aligned}$$

(arene = benzene or toluene)

When the reaction with THF was performed in the presence of LiI, $[V_2(\mu\text{-Cl})_3(THF)_6]I$ and $[V(\eta^6\text{-arene})_2]$ were obtained in good yield [68].

Moreover, we have found that the stability of the bis-(arene) cations in THF is strongly influenced by the nature of the anion. Whereas $[V(\eta^6\text{-1,3,5-}Me_3C_6H_3)_2][AlCl_4]$ is not affected by THF, $[V(\eta^6\text{-1,3,5-}Me_3C_6H_3)_2][AlBr_4]$ is stable at room temperature in that solvent but readily reacts at temperatures above ambient; $[V(\eta^6\text{-1,3,5-}Me_3C_6H_3)_2][AlI_4]$ is stable in THF for short periods even at room temperature and reacts affording $[V(\eta^6\text{-1,3,5-}Me_3C_6H_3)_2]$ and $VI_2 * 0.5$ THF [68].

The availability of large amounts of $[V(\eta^6\text{-1,3,5-}Me_3C_6H_3)_2]$ has allowed us to study its reactivity. The behaviour of the molecule is dependent on the solvent and the counterion: in aromatic or aliphatic hydrocarbons, the $[V(\eta^6\text{-1,3,5-}Me_3C_6H_3)_2]^+$ cation is stable in the presence of large anions [69]. The bis(η^6-mesitylene)-vanadium(I) cation has been isolated in toluene from the reaction of $[V(\eta^6\text{-1,3,5-}Me_3C_6H_3)_2]$ with $[FeCp_2][BPh_4]$ or with $[MnI(CO)_5]$ or $[Co_2(CO)_8]$, according to Eqs. (19)–(21)

$$[V(\eta^6\text{-1,3,5-}Me_3C_6H_3)_2] + [FeCp_2][BPh_4] \rightarrow [V(\eta^6\text{-1,3,5-}Me_3C_6H_3)_2][BPh_4] + [FeCp_2] \quad (19)$$

$$[V(\eta^6\text{-1,3,5-}Me_3C_6H_3)_2] + [MnI(CO)_5] \rightarrow [V(\eta^6\text{-1,3,5-}Me_3C_6H_3)_2]I + 1/2[Mn_2(CO)_{10}] \quad (20)$$

$$2[V(\eta^6\text{-1,3,5-}Me_3C_6H_3)_2] + [Co_2(CO)_8] \rightarrow 2[V(\eta^6\text{-1,3,5-}Me_3C_6H_3)_2][Co(CO)_4] \quad (21)$$

However, in the presence of more polarizing anions such as chloride or bromide, the cation is not stable. A fast reaction occurs between $[V(\eta^6\text{-1,3,5-}Me_3C_6H_3)_2]$ and HX (X = Cl or Br) in heptane or toluene initially affording a brown precipitate, presumably $[V(\eta^6\text{-1,3,5-}Me_3C_6H_3)_2]X$, which quickly transforms into VCl_3 (reaction sequence (22)) or into an intractable mixture of vanadium bromides. A mixture of similar composition was obtained by reaction of $[V(\eta^6\text{-1,3,5-}Me_3C_6H_3)_2]$ with CPh_3Br in toluene [69].

$$[V(\eta^6\text{-1,3,5-}Me_3C_6H_3)] + 3\ HCl \rightarrow [V(\eta^6\text{-1,3,5-}Me_3C_6H_3)_2]X \rightarrow VCl_3 + 2\ \text{mesitylene} \quad (22)$$

Attempts to prepare vanadium(I) derivatives by oxidation of vanadium(0) with HX or CPh_3X failed. The reaction of $[V(\eta^6\text{-1,3,5-}Me_3C_6H_3)_2]$ with one equivalent of either HX or CPh_3X (X = Br or I) in 1,2-dimethoxyethane, DME, afforded products arising from the disproportionation of the formed vanadium(I) salts formed initially to vanadium(II) and vanadium(0). For example [68], on reaction of CPh_3Br with $[V(\eta^6\text{-1,3,5-}Me_3C_6H_3)_2]$ in 1,2-dimethoxyethane, initial formation of a brown solid is observed which quickly changes to a green product in a red-brown solution typical of $[V(\eta^6\text{-1,3,5-}Me_3C_6H_3)_2]$. A 2:1 molar ratio of CPh_3Br and $[V(\eta^6\text{-1,3,5-}Me_3C_6H_3)_2]$ is required to consume the vanadium(0) complex initially present, see Eq. (23) [70]. Similar behaviour has been observed with CPh_3I in DME.

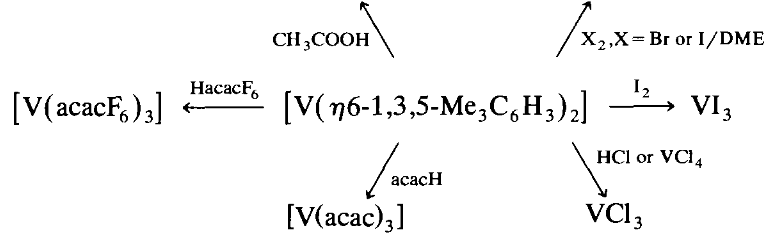
$$[V(\eta^6\text{-1,3,5-}Me_3C_6H_3)_2] + 2\ EX + 2\ DME \rightarrow [VX_2(DME)_2] + E_2 + 2\ \text{mesitylene} \quad (23)$$

X = Br, I; E = H or CPh_3

These observations suggest that reaction (23) proceeds via a one-electron oxidation by the organic bromide, followed by fast disproportionation of the intermediate vanadium(I) bis-(arene) cation to vanadium(0) and vanadium(II) (reaction sequence (24))

$$[V(\eta^6\text{-1,3,5-}Me_3C_6H_3)_2] \xrightarrow{CPh_3Br} [V(\eta^6\text{-1,3,5-}Me_3C_6H_3)_2]Br \xrightarrow{DME} [VBr_2(DME)_2] + [V(\eta^6\text{-1,3,5-}Me_3C_6H_3)_2] \quad (24)$$

$[V(\eta^6\text{-1,3,5-}Me_3C_6H_3)_2]$ is [68,69] a precursor of inorganic and coordination compounds of vanadium(II) and vanadium(III), as reported in (Scheme 1).



Scheme 1.

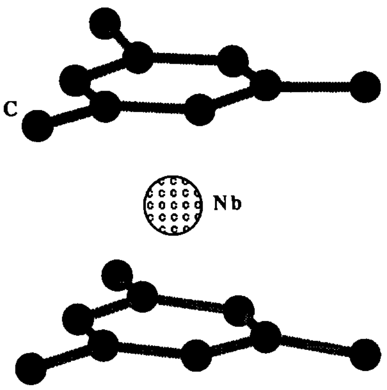


Fig. 7. Schematic representation of the molecular structure of [Nb(η^6-1,3,5-$Me_3C_6H_3)_2$]. Redrawn from published atomic coordinates [71].

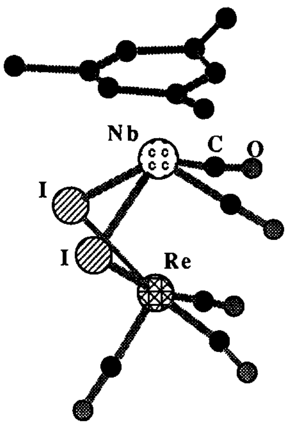


Fig. 8. Schematic representation of the molecular structure of [(η^6-1,3,5-$Me_3C_6H_3$)$Nb(CO)_3(\mu$-$I)_2Re(CO)_3$], **5**. Redrawn from published atomic coordinates [73].

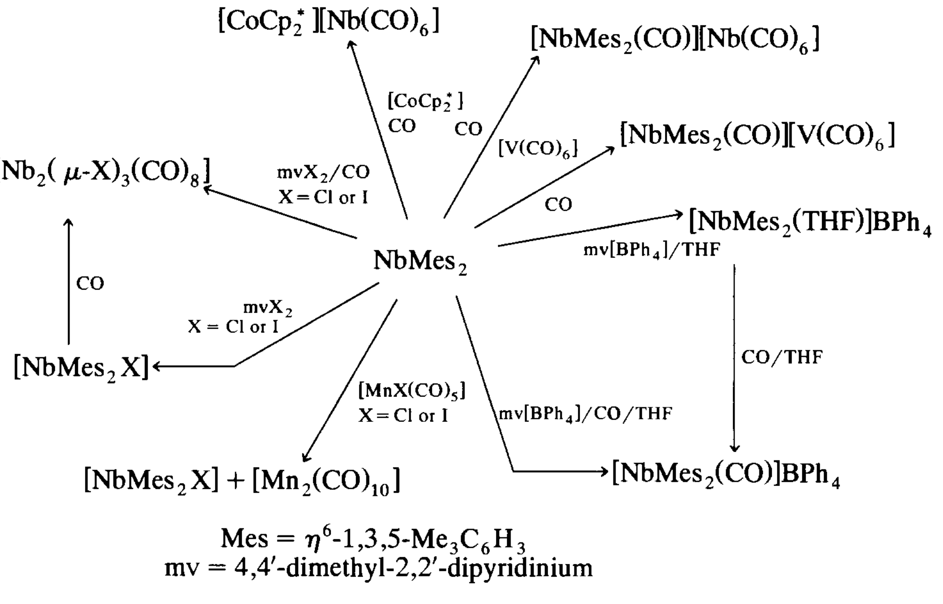
4.2.3. *Niobium*

The primary product of the Fischer–Hafner reduction of $NbCl_5$ being the niobium(II) compound [Nb(η^6-arene)$_2(AlCl_4)_2$], it was supposed that this tetrachloroaluminato derivative could undergo reduction by the excess of aluminium present in the crude reaction mixture, if the polarity of the medium was changed. Addition of THF or DME to the crude reaction mixture afforded the bis(mesitylene) derivative of niobium(0), [Nb(η^6-1,3,5-$Me_3C_6H_3)_2$], the first niobium(0) organometallic derivative to be prepared by a conventional synthetic procedure (vide supra) [25].

The molecular structure of the bis(arene) complex has been found (Fig. 7) to consist of a sandwich molecule with parallel, substantially planar aromatic rings in the fully eclipsed conformation [71]. The compound easily undergoes oxidation to niobium(I); It can also be reduced to [Nb(η^6-1,3,5-$Me_3C_6H_3)_2]^-$ but only with a potassium mirror [72], or to $[Nb(CO)_6]^-$ with potassium [72], or [$CoCp_2^*$] in the presence of carbon monoxide [25]. The redox chemistry of [Nb(η^6-1,3,5-$Me_3C_6H_3)_2$] is partly summarized in Scheme 2.

Oxidation of [Nb(η^6-1,3,5-$Me_3C_6H_3)_2$] by [ReX$(CO)_5$] (X = Br or I) (Scheme 2) proceeds in a different way to that with [MnX$(CO)_5$] [73]. The green products are diamagnetic heterobimetallic complexes with two bridging halides, which can be best described as containing niobium(II) and rhenium(0) of d^3 and d^7 configurations, respectively. Fig. 8 represents schematically the structure of the iodide derivative, **5**.

[Nb(η^6-1,3,5-$Me_3C_6H_3)_2$] is a 17-electron species of a d^5 low-spin system. In an attempt to isolate the 16-electron species [Nb(η^6-1,3,5-$Me_3C_6H_3)_2]^+$ by a one-electron oxidation, a toluene solution of [Nb(η^6-1,3,5-$Me_3C_6H_3)_2$] was treated with [$FeCp_2$][BAr_4] at room temperature. A smooth reaction took place with formation of [Nb(η^6-1,3,5-$Me_3C_6H_3)_2$][BAr_4] and fer-



Mes = η^6-1,3,5-$Me_3C_6H_3$
mv = 4,4′-dimethyl-2,2′-dipyridinium

Scheme 2.

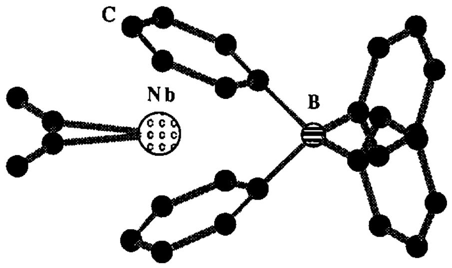


Fig. 9. Schematic representation of the molecular structure of $[Nb(MeC_2Me)(\eta^6\text{-}C_6H_5)_2B(C_6H_5)_2]$, **6**. Redrawn from published atomic coordinates [74].

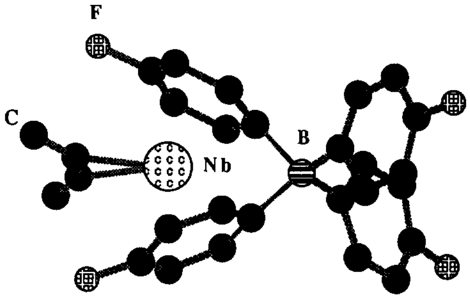


Fig. 10. Schematic representation of the molecular structure of $[Nb(MeC_2Me)(\eta^6\text{-}p\text{-}FC_6H_4)_2B(p\text{-}FC_6H_4)_2]$, **7**. Redrawn from published atomic coordinates [74].

rocene [74]. This class of extremely reactive compounds promptly gives carbonyl and alkyne complexes on reaction with CO or substituted acetylene derivatives, respectively (see Scheme 3). Both compounds are examples of bent bis(arene) derivatives of niobium(I), the other example being $[Nb(\eta^6\text{-toluene})_2(PMe_3)]BF_4$ [72]. The two aromatic rings in the carbonyl derivative adopt a nearly eclipsed conformation, and the aromatic ligands in the diphenylacetylene compound are staggered by 37°.

Electron-withdrawing substituents on the aromatic ring of the tetraarylborate anion stabilize the substituted acetylene compounds with respect to thermal decomposition. Pure $[Nb(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2(MeC_2Me)][BPh_4]$ is obtained at low temperature only, whereas $[Nb(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2(MeC_2Me)][B(p\text{-}FC_6H_4)_4]$ is stable up to ca. 50°C and $[Nb(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2(MeC_2Me)][B(3,5\text{-}(CF_3)_2C_6H_3)_4]$ does not decompose even at 100°C and is stable in air for short periods. The effects of electron-withdrawing substituents on the reactivity of tetraarylborate anions (suppression of electrophilic attack by protons on the phenyl-ring carbon *ipso* to boron [75] and influence on the catalytic [76] and electronic [75b,c] properties of the molecule) are well known phenomena.

The alkyne tetraarylborato complexes of niobium(I) undergo an interesting thermal rearrangement in toluene solution. The disubstituted acetylene derivatives, at temperatures as high as 70°C, give deep red-to-orange solutions from which orange crystals of the neutral $[Nb(RC_2R)(\eta^6\text{-}XC_6H_4)_2B(XC_6H_4)_2]$ were isolated (Eq. (25)).

$$\begin{aligned}&\left[Nb(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2(RC_2R)\right]\left[B(XC_6H_4)_4\right]\\&\quad\rightarrow\left[Nb(RC_2R)(\eta^6\text{-}XC_6H_4)_2B(XC_6H_4)_2\right]\\&\qquad+2\text{ mesitylene}\end{aligned}\tag{25}$$

R = Me, X = H, **6**, *p*-F; **7**; R = Ph, X = H, **8**

This arrangement apparently occurs only when the alkyne is coordinated to niobium. Thermal treatment of $[Nb(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2][BAr_4]$ led to complete decomposition with formation of unidentified pyrophoric materials whereas the carbon monoxide adduct $[Nb(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2CO][BAr_4]$ was recovered unchanged.

The neutral tetraarylborato complexes have been characterized by spectroscopic methods and by crystal structure analyses. The structures of the but-2-yne derivatives containing the unsubstituted and *p*-fluoro-substituted borate anion are reported below. The structure of the tetraphenylborato complex, **6**, (Fig. 9) is highly symmetrical and shows a niobium atom coordinated to two of the four aromatic rings of the tetraphenylborato ligand in a bent fashion: the angle between the perpendiculars to the aryl rings at niobium is 131.6° (147.7° in $[Nb(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2CO][BPh_4]$ [25] and 142.3° in $[Nb(\eta^6\text{-toluene})_2(PMe_3)][BF_4]$ [72]. The mean niobium-ring centroid distance is 1.931 Å. In the *p*-fluoro-substituted complex, **7** (Fig. 10) the metal is encapsulated within the two aromatic rings in an off-*anti* position (mean Nb–C distance: 2.37 Å) and the two η^6-bonded arene rings are bent at an angle of

$$\begin{tikzcd}[column sep=small]
\left[Nb(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)\right]_2+[FeCp_2][BAr_4] \arrow[r] & {} \\
& \left[Nb(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2\right][BAr_4]+[FeCp_2] \arrow[dl, "CO"'] \arrow[dr, "RC_2R"] & \\
\left[Nb(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2CO\right][BAr_4] & & \left[Nb(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2(\eta^2\text{-}RC_2R)\right][BAr_4]
\end{tikzcd}$$

Ar = Ph, *p*-FC_6H_4 or 3,5-$(CF_3)_2C_6H_3$
R = Me or Ph

Scheme 3.

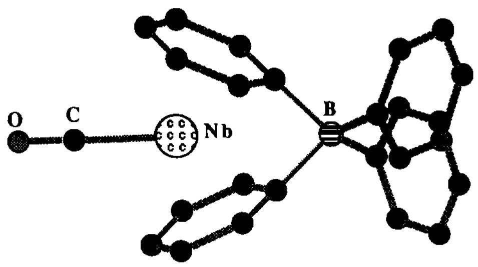


Fig. 11. Schematic representation of the molecular structure of $Nb(CO)(\eta^6\text{-}(C_6H_5)_2B(C_6H_5)_2]$, **9**. Redrawn from the published atomic coordinates [74].

129.1°. In both complexes the bond distances and angles within the alkyne suggest that but-2-yne behaves as a two-electron donor [77].

The neutral carbonyl derivatives **9** and **10** are readily obtained by but-2-yne substitution on **6** and **7** (Eq. 26)

$$\left[Nb(RC_2R)(\eta^6\text{-}XC_6H_4)_2B(XC_6H_4)_2\right] + CO \rightarrow \left[Nb(CO)(\eta^6\text{-}XC_6H_4)_2B(XC_6H_4)_2\right] + RC_2R \quad (26)$$

$R = Me$, $X = H$, **9**, *p*-F; **10**

The compounds indicated in Eqs. (25) and (26) are the first derivatives containing one metal atom bonded to two aryl rings of a tetraarylborate, which behaves as a bent, boron-bridged bis-aryl ligand to a single metal atom. The belief that $[BAR_4]^-$ is a poorly coordinating ligand anion must be reconsidered [78].

The organometallic system with the closest similarity to our niobium(I) derivatives is $[M(\eta^6\text{-}C_6H_5)_2Si(C_6H_5)_2]$ $M = V$ or Cr, isolated by Elschenbroich et al. [79]. The silicon containing ligand is neutral, while the boron systems are formally negatively charged. Substitution of the latter requires anionic ligands or a redox process.

5. Concluding remarks

Forty years after the first bis(η^6-arene) metal derivatives were characterized, complexes containing η^6-bonded aromatic ligands are still a research area of interest. The metal-atom arene–vapour co-condensation technique and the $AlCl_3$-mediated syntheses are the principal pathways to obtain these compounds. Moreover, the 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 primary products of the AlX_3-mediated reduction of metal halides by aluminium have been detected in several instances (titanium, zirconium, hafnium, vanadium and niobium) and the existing procedures for the synthesis of (η^6-arene) derivatives of titanium, zirconium, hafnium and vanadium have been optimized. A conventional synthesis of a niobium(0) bis(η^6-arene) compound has been discovered. Moreover, it has been shown that low-oxidation-state η^6-arene compounds may be an useful synthesis for the inorganic and coordination chemistry of the corresponding metals in non-aqueous systems.

Acknowledgements

The authors wish to thank the Consiglio Nazionale delle Ricerche (C.N.R., Roma) and the Ministero dell'Università e della Ricerca Scientifica e Tecnologica (M.U.R.S.T.) for financial support; they are grateful to all their co-workers, whose names appear in the list of publications, who contributed to the development of this chemistry. We particularly enjoyed our collaboration with Prof. Joachim Strähle and his coworkers of the Universität Tübingen (Germany) and with Dr. Ulli Englert of the Rheinisch-Westfälische Technische Hochschule Aachen (Germany), who joined us in this project.

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