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One-electron redox reactions involving chromium(0) and molybdenum(0) bis-1,3,5-trimethylbenzene derivatives

Ulli Englert [a], Guido Pampaloni [b,*], Filippo Puccini [b], Manuel Volpe [b,1]

[a] *Institut für Anorganische Chemie der RWTH Aachen, Landoltweg 1, D-52074 Aachen, Germany*
[b] *Università di Pisa, Dipartimento di Chimica e Chimica Industriale, Via Risorgimento 35, I-56126 Pisa, Italy*

Abstract

The reaction of $M(\eta^6$-1,3,5-$Me_3C_6H_3)_2$, M = Cr, Mo, with the tetrahalides of Groups 4 and 5 elements proceeds with the monoelectronic oxidation of the metal bis-arene to the $[M(\eta^6$-$Me_3C_6H_3)_2]^+$ cation. In the case of MX_4, M = Ti, X = Cl, Br, M = V, X = Cl, and of Nb_2Cl_{10} the reduction products are the titanium(III), vanadium(III) halides and the niobium(IV) chloride, isolated as the solvate anions $[MCl_4(THF)_2]^-$ and $[NbCl_4(CH_3CN)]^-$. The reaction of the tetrachloro complexes $MCl_4(THF)_2$, M = Zr, Hf, with $Cr(\eta^6$-1,3,5-$Me_3C_6H_3)_2$ in THF produces the ionic $[Cr(\eta^6$-1,3,5-$Me_3C_6H_3)_2][MCl_5(THF)]$, which has been characterized by single-crystal X-ray diffraction in the case of hafnium.
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1. Introduction

It is known that metal carbonyls such as $V(CO)_6$, $Cr(CO)_6$ and $Mo(CO)_6$ react with $TiCl_4$ to afford binary chlorides of general formula $MCl_n \cdot nTiCl_3$ [1]. Some of us have extended this reaction to $M(\eta^6$-1,3,5-$Me_3C_6H_3)_2$, M = V, Nb, showing the formation of solid compounds of general formula MTi_nCl_m, with *n* and *m* depending on the $M(\eta^6$-1,3,5-$Me_3C_6H_3)_2$/$TiCl_4$ molar ratio [2a]. As far as the arene derivatives of Group 6 are concerned, it has been recently reported that $M(\eta^6$-$MeC_6H_5)_2$, M = Cr, Mo, reacts with $TiCl_4$ to give $[Cr(\eta^6$-$MeC_6H_5)_2][$-$TiCl_4(THF)_2]$ after treatment of the primary product with THF [3]. On the other hand, the reactivity of the cited toluene derivatives with the tetrachlorides of zirconium(IV) and hafnium(IV) did not allow the isolation of well-defined compounds due to partial loss of the arene rings.

In view of the increased reducing power [4] and stability [5] of the bis-arenes derivatives on increasing the methyl substitution on the aromatic rings, and aiming to find out new synthetic procedures to bimetallic compounds which may act as olefin polymerization catalytic precursors [1,2], we decided to study the reactivity of the trimethylbenzene derivatives of Cr(0) and Mo(0), $M(\eta^6$-1,3,5-$Me_3C_6H_3)_2$, with Groups 4 and 5 metal halides.

2. Results and discussion

The study of the reactivity of $M(\eta^6$-1,3,5-$Me_3C_6H_3)_2$, M = Cr, Mo, with metal halides was preceded by experiments aimed to elucidate some difficulties recently encountered in the synthesis of the bis-trimethylbenzene compounds of chromium [6]. As a matter of fact, $M(\eta^6$-1,3,5-$Me_3C_6H_3)_2$, M = Cr, Mo, could be obtained in 60% (Cr) and 30% (Mo) yields by a modification of the original Fischer–Hafner procedure used to prepare $Cr(\eta^6$-$C_6H_6)_2$ [7]. All attempts to increase the yields of the chromium(0) compound were unsuccessful. On the other hand, the same procedure applied to the vanadium/1,3,5-trimeth-
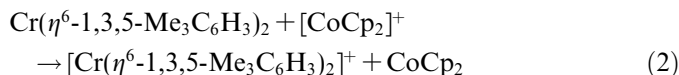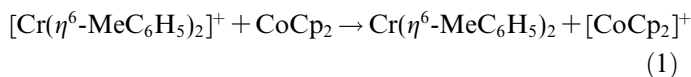

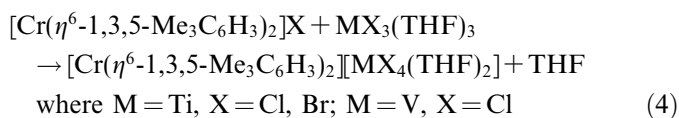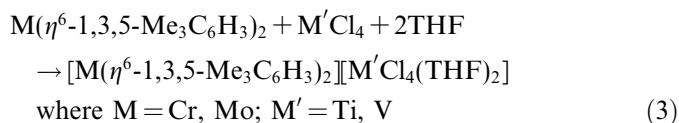ylbenzene- and to the chromium/toluene systems gave almost quantitative yield of $M(\eta^6\text{-arene})_2$ [8].

Although the lower yields in the case of molybdenum might be due to the instability of the bis(η^6-arene) derivatives of molybdenum(0) (which may react with loss of one or two aromatic rings [3]), the question remained open in the case of chromium bis(1,3,5-trimethylbenzene).

A reason for this different behaviour could be the higher stability of the $[Cr(\eta^6\text{-}1,3,5\text{-Me}_3C_6H_3)_2]^+$ cation with respect to $[V(\eta^6\text{-}1,3,5\text{-Me}_3C_6H_3)_2]^+$. Therefore, we decided to compare the redox properties of the chromium bis-arene species with those of the vanadium derivatives under reaction conditions as similar as possible to those typical of the second step of the Fischer–Hafner synthesis [8]. We used cobaltocene, a species which has widely been used in organometallic chemistry as a monoelectronic reducing reagent in aprotic media [8,9], to test the redox properties of chromium(I) compounds, and we found that *only* the reactions reported in Eqs. (1) and (2) (and not the reverse ones) take place.
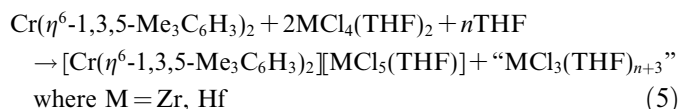
$$[Cr(\eta^6\text{-MeC}_6H_5)_2]^+ + CoCp_2 \rightarrow Cr(\eta^6\text{-MeC}_6H_5)_2 + [CoCp_2]^+ \tag{1}$$

$$Cr(\eta^6\text{-}1,3,5\text{-Me}_3C_6H_3)_2 + [CoCp_2]^+$$
$$\rightarrow [Cr(\eta^6\text{-}1,3,5\text{-Me}_3C_6H_3)_2]^+ + CoCp_2 \tag{2}$$

These results are in agreement with the redox potentials measured for the couples $[CoCp_2]^+/CoCp_2$ ($E^\circ = -0.93$ V vs. SCE in THF) [9c], $[Cr(\eta^6\text{-MeC}_6H_5)_2]^+/Cr(\eta^6\text{-MeC}_6H_5)_2$ ($E^\circ = -0.86$ V vs. SCE in DMSO) [4d], and $[Cr(\eta^6\text{-}1,3,5\text{-Me}_3C_6H_3)_2]^+/Cr(\eta^6\text{-}1,3,\ 5\text{-Me}_3C_6H_3)_2$ ($E^\circ = -0.98$ V vs. SCE in DMSO) [4d]. Taking into account that both $[V(\eta^6\text{-arene})_2]^+$, arene = toluene, 1,3,5-trimethylbenzene, are reduced by cobaltocene [8] and considering that the M(I) → M(0) reduction is a pivotal step in the Fischer–Hafner synthesis, the higher tendency to reduction of vanadium with respect to chromium, and of $[Cr(\eta^6\text{-MeC}_6H_5)_2]^+$ with respect to $[Cr(\eta^6\text{-}1,3,5\text{-Me}_3C_6H_3)_2]^+$, may explain the lower yields generally observed for the latter compound.

The tetrachloro derivatives of titanium(IV) and vanadium(IV) readily react with $M(\eta^6\text{-Me}_3C_6H_3)_2$ in THF to give the products shown in Eq. (3), two of which can also be obtained by chloride addition reaction to $MX_3(THF)_3$ [10], according to Eq. (4):

$$M(\eta^6\text{-}1,3,5\text{-Me}_3C_6H_3)_2 + M'Cl_4 + 2THF$$
$$\rightarrow [M(\eta^6\text{-}1,3,5\text{-Me}_3C_6H_3)_2][M'Cl_4(THF)_2]$$
$$\text{where } M = Cr, Mo; M' = Ti, V \tag{3}$$

$$[Cr(\eta^6\text{-}1,3,5\text{-Me}_3C_6H_3)_2]X + MX_3(THF)_3$$
$$\rightarrow [Cr(\eta^6\text{-}1,3,5\text{-Me}_3C_6H_3)_2][MX_4(THF)_2] + THF$$
$$\text{where } M = Ti, X = Cl, Br; M = V, X = Cl \tag{4}$$

The reactions of $ZrCl_4$ or $HfCl_4$ with $Cr(\eta^6\text{-}1,3,5\text{-Me}_3C_6H_3)_2$ have a different outcome. Treatment of $ZrCl_4$ or $HfCl_4$, in the form of their tetrahydrofuran adducts,

with $Cr(\eta^6\text{-}1,3,5\text{-Me}_3C_6H_3)_2$ led to the slow formation of slightly soluble yellow solids containing zirconium(IV) [or hafnium(IV)] and chromium(I) that analyzed as $[Cr(\eta^6\text{-}1,3,5\text{-Me}_3C_6H_3)_2][MCl_5(THF)]$. The reaction was usually carried out with a 1/1 metal/$Cr(\eta^6\text{-}1,3,5\text{-Me}_3C_6H_3)_2$ molar ratio and the yields, based on the tetrachloro-complex introduced, never exceeded 50%, the remaining unaccounted metal probably being in a reduced form in solution. Thus, the reaction can be represented as in the following equation:
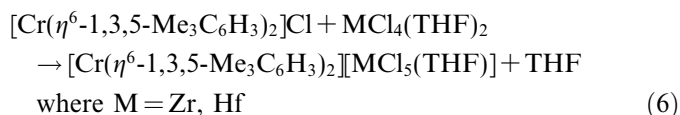
$$Cr(\eta^6\text{-}1,3,5\text{-Me}_3C_6H_3)_2 + 2MCl_4(THF)_2 + nTHF$$
$$\rightarrow [Cr(\eta^6\text{-}1,3,5\text{-Me}_3C_6H_3)_2][MCl_5(THF)] + \text{``}MCl_3(THF)_{n+3}\text{''}$$
$$\text{where } M = Zr, Hf \tag{5}$$

The different behaviour of $MCl_4(THF)_2$ with respect to $[Cr(\eta^6\text{-}1,3,5\text{-Me}_3C_6H_3)_2]$, see Eqs. (3) and (5), can be related to the higher tendency of TiX_4 to undergo reduction with respect to the heavier congeners [11]. Data from the literature suggest that the reduction of zirconium(IV) and hafnium(IV) complexes is generally a less favourable process than that of the corresponding titanium species. For example, the bis(cyclopentadienyl) derivatives MCp_2Cl_2 (M = Zr, Hf) undergo reduction at a more negative potential than the corresponding titanium analogue [12]. Besides, the M–halogen bond strengths increase from titanium to zirconium and hafnium [11].

Thus, if the halogen abstraction process is slow for zirconium and hafnium, formation of $[Cr(\eta^6\text{-}1,3,5\text{-Me}_3C_6H_3)_2]Cl$ will occur in the presence of unreacted MCl_4 thus leading to the occurrence of reaction (6), with formation of the observed product.

We did several attempts to isolate a Zr(III) or Hf(III) species but we did not succeed. In order to explain this result, we can admit that a transient formation of "$MCl_3(THF)_n$" is followed by the homolytic cleavage of the C–O of THF and formation of a metal-coordinated butoxy radical; this species may evolve with radical coupling, the metal regaining the +IV oxidation state. Formation of an uranium(IV) butoxy derivative has been observed in the reactions of UCl_3 with NaCp in THF [13]. Attempts have been made in order to verify the presence in solution of compounds deriving from the THF activation, but the only product we observed was 1,3,5-$Me_3C_6H_3$ clearly deriving from the bis(arene) cation.

The products arising from the $Cr(\eta^6\text{-}1,3,5\text{-Me}_3C_6H_3)_2/MCl_4$ system could also be prepared from $[Cr(\eta^6\text{-}1,3,5\text{-Me}_3C_6H_3)_2]Cl$ and the $MCl_4(THF)_2$, see the following equation:

$$[Cr(\eta^6\text{-}1,3,5\text{-Me}_3C_6H_3)_2]Cl + MCl_4(THF)_2$$
$$\rightarrow [Cr(\eta^6\text{-}1,3,5\text{-Me}_3C_6H_3)_2][MCl_5(THF)] + THF$$
$$\text{where } M = Zr, Hf \tag{6}$$

This is a quite general reaction for the tetrahalo complexes of Group 4 metals: for example, the tetrachlorides of the Group 4 give the $[MCl_5(THF)]^-$ anion by reaction with $[CoCp_2]Cl$, see the following equation [9a]:

$$[CoCp_2]Cl + MCl_4(THF)_2 \rightarrow [CoCp_2][MCl_5(THF)] + THF \tag{7}$$
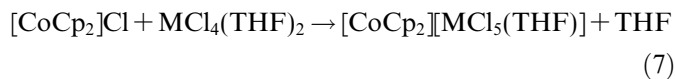
The compound $[Cr(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2][HfCl_5(THF)]$ was characterized by X-ray single-crystal diffraction and its structure is shown in Fig. 1; a selection of bond distances and angles is collected in Table 1. The precision of the structural model is limited due to non-merohedral twinning and the presence of two crystallographically independent, discrete $[Cr(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2]^+$ cations and $[HfCl_5(THF)]^-$ anions. The conformations in these independent species are quite similar; Fig. 2 provides an overlay of the cations.

The average chromium–mesitylene geometry is characterized by a Cr(1)–centroid distance of 1.610(6) Å, with Cr–C bond lengths ranging from 2.124(15) to 2.166(14) Å [average 2.140 Å]. Similar values have been observed in $[Cr(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2][E]$, E = TCNE (2.16 Å) [15], TCNQ (2.154 Å) [16], pcmcp (pentacarbometoxycyclopentadienyl anion) [2.154(4) Å] [6] and in $[Cr(\eta^6\text{-}MeC_6H_5)_2][pcmcp]$ [2.145(5) Å] [17].

The chromium atom is sandwiched between two staggered mesitylene rings, see Fig. 2. The methyl groups of the two rings form a dihedral angle of 59.1(6)° (average) in cation 1 and of 57.3(5)° (average) in cation 2 (theoretical value should be 60°). It is interesting to observe that the recently reported $[Cr(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2][pcmcp]$ [6] crystallizes with four independent cations and anions in the unit cell differing with respect to the relative disposition of the two mesitylene rings (the dihedral angles between methyl groups of different rings are 2.6°, 9.9°, 19.3°, and 22.3°).

We have recently observed that the solid state orientation of the two methyl groups on the two toluene rings of $[M(\eta^6\text{-}MeC_6H_5)_2]^+$ cations, M = V [18], Cr [17,19], depends on the steric hindrance of the anion. For example, sterically demanding anions, such as $[pcmcp]^-$, [1,2-dib-
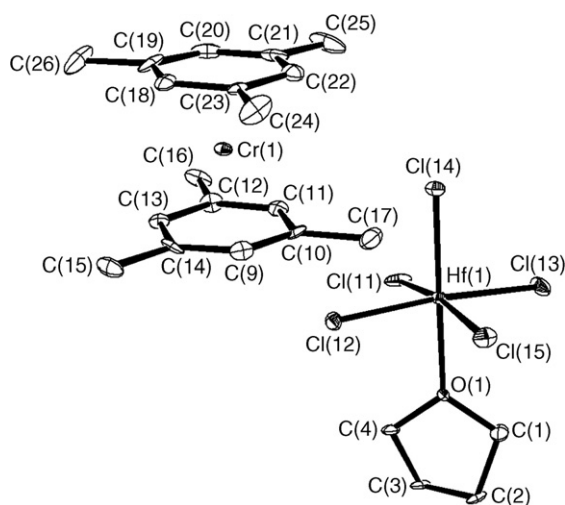
enzoylcyclopentadienyl]⁻ and [1,2-dibenzoyl-4-nitrocyclopentadienyl]⁻, seem to induce stabilization of the more compact *cis*-eclipsed conformation of the methyl groups, i.e., dihedral angles close to 0°, in crystallographically quite different solids.

As far as the $[HfCl_5(THF)]^-$ anion is concerned, the average Hf–Cl (2.419(2) Å) bond distance is comparable to that reported for the same anion in the $[Co(C_5Me_5)_2]^+$ derivative [2.425(4) Å] [9a].

Table 1
Selected bond distances (Å) and angles (°) for $[Cr(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2][HfCl_5(THF)]$

Cr(1)–C(9)	2.124(15)	Cr(2)–C(27)	2.119(14)
Cr(1)–C(12)	2.127(14)	Cr(2)–C(38)	2.120(13)
Cr(1)–C(23)	2.128(13)	Cr(2)–C(36)	2.133(14)
Cr(1)–C(11)	2.130(13)	Cr(2)–C(40)	2.139(14)
Cr(1)–C(21)	2.134(15)	Cr(2)–C(31)	2.142(13)
Cr(1)–C(20)	2.135(15)	Cr(2)–C(41)	2.147(13)
Cr(1)–C(18)	2.136(14)	Cr(2)–C(28)	2.149(14)
Cr(1)–C(10)	2.147(13)	Cr(2)–C(29)	2.159(14)
Cr(1)–C(13)	2.147(14)	Cr(2)–C(32)	2.162(14)
Cr(1)–C(14)	2.148(13)	Cr(2)–C(37)	2.163(13)
Cr(1)–C(22)	2.157(15)	Cr(2)–C(30)	2.164(13)
Cr(1)–C(19)	2.166(14)	Cr(2)–C(39)	2.167(14)
Hf(1)–O(1)	2.196(9)	Hf(2)–O(2)	2.202(8)
Hf(1)–Cl(3)	2.400(4)	Hf(2)–Cl(9)	2.391(4)
Hf(1)–Cl(4)	2.408(3)	Hf(2)–Cl(7)	2.414(4)
Hf(1)–Cl(2)	2.409(3)	Hf(2)–Cl(8)	2.418(3)
Hf(1)–Cl(1)	2.438(4)	Hf(2)–Cl(6)	2.434(4)
Hf(1)–Cl(5)	2.444(4)	Hf(2)–Cl(10)	2.437(3)
O(1)–Hf(1)–Cl(3)	87.7(3)	O(2)–Hf(2)–Cl(9)	178.7(3)
O(1)–Hf(1)–Cl(4)	178.5(3)	O(2)–Hf(2)–Cl(7)	86.1(3)
Cl(3)–Hf(1)–Cl(4)	92.3(1)	Cl(9)–Hf(2)–Cl(7)	93.7(1)
O(1)–Hf(1)–Cl(2)	86.0(2)	O(2)–Hf(2)–Cl(8)	87.0(3)
Cl(3)–Hf(1)–Cl(2)	173.6(1)	O(2)–Hf(2)–Cl(8)	87.0(3)
Cl(4)–Hf(1)–Cl(2)	94.0(1)	Cl(9)–Hf(2)–Cl(8)	93.2(1)
O(1)–Hf(1)–Cl(1)	85.5(3)	Cl(7)–Hf(2)–Cl(8)	172.8(1)
Cl(3)–Hf(1)–Cl(1)	89.6(2)	O(2)–Hf(2)–Cl(6)	83.8(3)
Cl(4)–Hf(1)–Cl(1)	95.9(1)	Cl(9)–Hf(2)–Cl(6)	94.9(1)
Cl(2)–Hf(1)–Cl(1)	88.7(1)	Cl(7)–Hf(2)–Cl(6)	92.1(1)
O(1)–Hf(1)–Cl(5)	84.6(3)	Cl(8)–Hf(2)–Cl(6)	89.4(1)
Cl(3)–Hf(1)–Cl(5)	90.4(2)	O(2)–Hf(2)–Cl(10)	85.9(3)
Cl(4)–Hf(1)–Cl(5)	94.0(1)	Cl(9)–Hf(2)–Cl(10)	95.4(1)
Cl(2)–Hf(1)–Cl(5)	90.2(1)	Cl(7)–Hf(2)–Cl(10)	89.1(1)
Cl(1)–Hf(1)–Cl(5)	170.1(1)	Cl(8)–Hf(2)–Cl(10)	88.2(1)

Fig. 1. View of one of the two independent $[Cr(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2]^+$ cations and of one of the two $[HfCl_5(THF)]^-$ anions in the structure of $[Cr(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2][HfCl_5(THF)]$. Atoms are represented by their 30% probability ellipsoids.

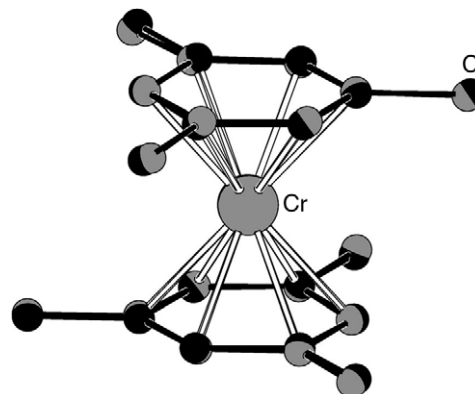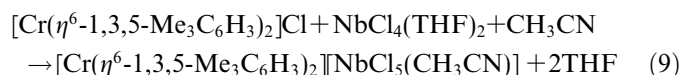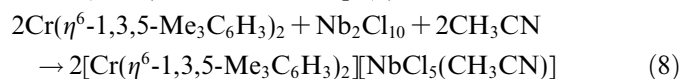

Fig. 2. Overlay [14] of the symmetrically independent but conformationally similar cations in $[Cr(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2][HfCl_5(THF)]$.

The reaction between $Cr(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2$ and Nb_2Cl_{10} is dependent on the reaction medium: when the reaction was performed in hydrocarbon solvent at room temperature or in THF even at low temperature, impure compounds were obtained. On the other hand, the reaction in acetonitrile afforded a microcrystalline red solid which was identified as $[Cr(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2][NbCl_5(CH_3CN)]$, Eq. (8). This compound, as the others of this series, was also obtained by chloride addition to $NbCl_4(THF)_2$ in CH_3CN, Eq. (9):

$$2Cr(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2 + Nb_2Cl_{10} + 2CH_3CN$$
$$\rightarrow 2[Cr(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2][NbCl_5(CH_3CN)] \qquad (8)$$

$$[Cr(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2]Cl + NbCl_4(THF)_2 + CH_3CN$$
$$\rightarrow [Cr(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2][NbCl_5(CH_3CN)] + 2THF \qquad (9)$$

The IR spectrum in the solid state shows the absorptions typical of the cation at 3053, 1039 and 1004 cm^{-1}: the band at 2279 cm^{-1} has been assigned to the CN stretching vibration of the coordinated acetonitrile. The higher wavenumber shift with respect to free acetonitrile (2245 cm^{-1}) is typical of coordinated nitrile species [20].

3. Conclusions

In this paper, the reactivity of $M(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2$, M = Cr, Mo, towards metal halides of Groups 4 and 5 has been examined. It has been shown that both chromium and molybdenum derivatives are monoelectronically oxidized to the respective $[M(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2]^+$ cations with formation of reduced, solvent-stabilized, anionic metal halides of general formula $[MX_nL_m]^-$. The reactivity of the bis-1,3,5-$Me_3C_6H_3$ derivatives parallels that of the reported bis-toluene compounds $M(\eta^6\text{-}MeC_6H_5)_2$, M = Cr, Mo.

On the other hand, the bis-mesitylene derivative $Cr(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2$ reacts with $MCl_4(THF)_2$, M = Zr, Hf, in THF with formation of $[Cr(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2][MCl_5(THF)]$, which have been isolated and characterized in the solid state via X-ray structural analysis for M = Hf. The isolation of a Cr(I) bis-arene cation suggests that reduction of zirconium(IV) or hafnium(IV) may occur in the system, although we have not been able as yet to isolate the product of the reduction, probably due to its instability in THF.

The crystal structure of $[Cr(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2][HfCl_5(THF)]$ has confirmed the conclusions drawn in previous papers of this series [6,17–19]: the conformation of the arene rings in the chromium(I) cations in the solid state depends on the steric demand of the anion and it tends toward the staggered conformation as the dimensions of the anion get smaller.

4. Experimental

4.1. General procedures

Unless otherwise stated, all of the operations were carried out under an atmosphere of prepurified argon. Solvents were dried by conventional methods prior to use. $TiCl_4$ was distilled prior to use. Commercial VCl_4 was used as heptane solution (stored at $-30\,°C$) and analyzed for its chloride content prior to use. Triphenylmethyl halides were used as received. The compounds $Cr(\eta^6\text{-}MeC_6H_5)_2$ [8], $M(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2$, M = Cr [6], Mo [6], $MCl_4(THF)_2$, M = Zr, Hf, Nb [21], $MCl_3(THF)_3$, M = Ti, V [21], $TiBr_3(THF)_3$ [22], $CoCp_2$ [23], were prepared according to the literature. IR spectra were recorded on a FT-1725X instrument on Nujol or polychlorotrifluoroethylene (PCTFE) mulls or on a FTIR-spectrometer equipped with a Perkin–Elmer UATR sampling accessory.

4.2. Treatment of $Cr(\eta^6\text{-}arene)_2$ with $[CoCp_2]Br$

4.2.1. Arene = toluene

A well stirred solution of $Cr(\eta^6\text{-}MeC_6H_5)_2$ (0.18 g, 0.77 mmol) in THF (30 mL) was treated with solid $[CoCp_2]Br$ (0.20 g, 0.76 mmol). After 15 h stirring at room temperature. The yellow solid was recovered by filtration, washed with THF (2 × 5 mL) and identified as $[CoCp_2]Br$ (0.16 g, 78% yield, IR spectroscopy). The volume of the mother liquor was reduced to 2 mL, added of heptane (5 mL) and the solid was recovered by filtration, dried in vacuo and identified as $Cr(\eta^6\text{-}MeC_6H_5)_2$ (0.15 g, 82% yield).

4.2.2. Arene = $1,3,5\text{-}Me_3C_6H_3$

A well stirred solution of $Cr(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2$ (0.39 g, 1.3 mmol) in THF (25 mL) was treated with solid $[CoCp_2]Br$ (0.35 g, 1.3 mmol). After 12 h stirring at room temperature some yellow solid was present which was removed by filtration. The yellow solid was recovered by filtration, washed with THF (2 × 5 mL) and dried in vacuo at room temperature affording 0.45 g (93% yield) of $[Cr(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2]Br$ identified by IR spectroscopy. The volume of the mother liquor was reduced to 2 mL, added of heptane (5 mL) and the solid was recovered by filtration and dried in vacuo. It was identified as $CoCp_2$ (0.21 g, 85% yield).

4.3. Treatment of $[Cr(\eta^6\text{-}arene)_2]Br$ with $CoCp_2$

4.3.1. Arene = toluene

A well stirred solution of $[Cr(\eta^6\text{-}MeC_6H_5)_2]Br$ (0.15 g, 0.48 mmol) in THF (30 mL) was treated with solid $CoCp_2$ (0.090 g, 0.48 mmol). After 15 h stirring at room temperature the yellow solid was recovered by filtration, washed with THF (2 × 5 mL) and dried in vacuo at room temperature affording 0.11 g (91% yield) of $[CoCp_2]Br$ identified by IR spectroscopy. The volume of the mother liquor was reduced to 2 mL, added of heptane (5 mL) and the solid was recovered by filtration and dried in vacuo. It was identified as $Cr(\eta^6\text{-}MeC_6H_5)_2$ (0.089 g, 78% yield).

4.3.2. Arene = 1,3,5-Me$_3$C$_6$H$_3$

A well stirred yellow suspension of [Cr(η^6-1,3,5-Me$_3$C$_6$H$_3$)$_2$]Br (0.37 g, 1.0 mmol) in THF (25 mL) was treated with solid CoCp$_2$ (0.18 g, 0.96 mmol). After 12 h stirring at room temperature some yellow solid was present which was removed by filtration. The yellow solid was recovered by filtration, washed with THF (2 × 5 mL) and dried in vacuo at room temperature affording 0.27 g (74% yield) of [Cr(η^6-1,3,5-Me$_3$C$_6$H$_3$)$_2$]Br identified by IR spectroscopy. The volume of the mother liquor was dried in vacuo at room temperature and the residue was sublimed at 60 °C/ 0.05 mmHg, obtaining 0.12 g (67% yield) of CoCp$_2$.

4.4. Reactions of Cr(η^6-1,3,5-Me$_3$C$_6$H$_3$)$_2$ with triphenylmethyl halides

Only the reaction of Cr(η^6-1,3,5-Me$_3$C$_6$H$_3$)$_2$ with CPh$_3$Cl is described in detail, the reaction with CPh$_3$Br being performed in a similar way. A solution of Cr(η^6-1,3,5-Me$_3$C$_6$H$_3$)$_2$ (0.91 g, 3.1 mmol) in THF (50 mL) was treated dropwise with a solution of CPh$_3$Cl (0.87 g, 3.1 mmol) in THF (50 mL). An orange bright suspension was obtained. The suspension was stirred for 6 h and the solid was recovered by filtration, washed with THF and dried in vacuo at room temperature affording 0.85 g (84% yield) of [Cr(η^6-1,3,5-Me$_3$C$_6$H$_3$)$_2$]Cl as an orange microcrystalline solid. Anal. Calc. for C$_{18}$H$_{24}$ClCr: C, 66.0; H, 7.3. Found: C, 65.9; H, 7.5%. IR (solid state): $\tilde{v}$/cm^{-1}: 3045 m, 1607 w, 1533 m, 1510 w, 1306 w, 1159 m, 1039 s, 1019 m, 887 m, 834 w, 722 w.

[Cr(η^6-1,3,5-Me$_3$C$_6$H$_3$)$_2$]Br (bright orange, 78% yield). Anal. Calc. for C$_{18}$H$_{24}$BrCr: C, 58.1; H, 6.5. Found: C, 57.9; H, 6.0%. IR (solid state): $\tilde{v}$/cm^{-1}: 3046 m, 1533 m, 1510 w, 1305 w, 1163 w, 1038 s, 1015 m, 1006 w, 995 w, 886 m, 721 mw, 668 m.

4.5. Preparation of [M(η^6-1,3,5-Me$_3$C$_6$H$_3$)$_2$] [M'Cl$_4$(THF)$_2$], M = Cr, Mo; M' = Ti, V

Only the reaction of Cr(η^6-1,3,5-Me$_3$C$_6$H$_3$)$_2$ with TiCl$_4$ is described in detail, the reaction with VCl$_4$ being performed in a similar way. A well stirred solution of Cr(η^6-1,3,5-Me$_3$C$_6$H$_3$)$_2$ (0.63 g, 2.2 mmol) in heptane (50 mL) was treated dropwise with a solution of TiCl$_4$ (0.23 mL, 2.1 mmol) in heptane (5 mL). The solution became immediately cloudy and changed to a bulky suspension within 5 min. The solid was filtered, washed with heptane and dried in vacuo. The heptane solution did not contain appreciable amounts of chloride ions (test with silver nitrate). The extremely air sensitive solid was treated with THF (50 mL) and an orange solid was obtained which was recovered by filtration. After drying in vacuo, [Cr(η^6-1,3,5-Me$_3$C$_6$H$_3$)$_2$][TiCl$_4$(THF)$_2$] (0.68 g, 49% yield) was isolated as a air sensitive, orange microcrystalline solid. Anal. Calc. for C$_{26}$H$_{40}$Cl$_4$CrO$_2$Ti: C, 49.9; H, 6.4; Cl, 22.6. Found: C, 49.5; H, 6.8; Cl, 22.1%. IR (Nujol), $\tilde{v}$/cm^{-1}: 3058 m, 1610 m, 1334 w, 1061 m, 1034 s (THF), 1023 m, 920 w, 868 s (THF), 721 w, 668 w, 445 m.

[Cr(η^6-1,3,5-Me$_3$C$_6$H$_3$)$_2$][VCl$_4$(THF)$_2$] (air sensitive, yellow microcrystalline solid, 63% yield). Anal. Calc. for C$_{26}$H$_{40}$Cl$_4$CrO$_2$V: C, 49.6; H, 5.1; Cl, 22.5. Found: C, 49.9; H, 5.2; Cl, 22.3%. IR (Nujol), $\tilde{v}$/cm^{-1}: 3052 m, 1608 m, 1330 w, 1060 m, 1034 s (THF), 1021 m, 917 w, 868 s (THF), 721 w, 442 m.

[Mo(η^6-1,3,5-Me$_3$C$_6$H$_3$)$_2$][TiCl$_4$(THF)$_2$] (air sensitive, green microcrystalline solid, 38% yield). Anal. Calc. for C$_{26}$H$_{40}$Cl$_4$MoO$_2$Ti: C, 46.6; H, 6.0; Cl, 21.1. Found: C, 46.7; H, 6.2; Cl, 21.5%. IR (Nujol), $\tilde{v}$/cm^{-1}: 3047 m, 1516 m, 1339 w, 1060 m, 1037 s (THF), 865 s (THF), 722 w, 492 w, 430 w.

[Mo(η^6-1,3,5-Me$_3$C$_6$H$_3$)$_2$][VCl$_4$(THF)$_2$] (air sensitive, green microcrystalline solid, 39% yield). Anal. Calc. for C$_{26}$H$_{40}$Cl$_4$MoO$_2$V: C, 46.4; H, 6.0; Cl, 21.1. Found: C, 46.2; H, 6.2; Cl, 21.3%. IR (Nujol), $\tilde{v}$/cm^{-1}: 3045 m, 1514 m, 1341 w, 1064 m, 1035 s (THF), 869 s (THF), 721 w, 490 w, 427 w.

4.6. Preparation of [Cr(η^6-1,3,5-Me$_3$C$_6$H$_3$)$_2$] [MCl$_4$(THF)$_2$], M = Ti, V, from [Cr(η^6-1,3,5-Me$_3$-C$_6$H$_3$)$_2$]Cl and MCl$_3$(THF)$_3$

Only the reaction of [Cr(η^6-1,3,5-Me$_3$C$_6$H$_3$)$_2$]Cl with TiCl$_3$(THF)$_3$ is described in detail, the reaction with VCl$_3$(THF)$_3$ being performed in a similar way. A well stirred suspension of [Cr(η^6-1,3,5-Me$_3$C$_6$H$_3$)$_2$]Cl (0.26 g, 0.80 mmol) in THF (50 mL) was treated with solid TiCl$_3$(THF)$_3$ (0.29 g, 0.80 mmol). The pale green suspension was stirred for 2 h at room temperature obtaining a orange suspension. The solid was recovered by filtration, washed with THF (2 × 2 mL) and dried in vacuo affording [Cr(η^6-1,3,5-Me$_3$C$_6$H$_3$)$_2$][TiCl$_4$(THF)$_2$] (0.45 g, 90% yield) identified on the basis of the analytical data and the IR spectrum.

4.7. Preparation of [Cr(η^6-1,3,5-Me$_3$C$_6$H$_3$)$_2$] [TiBr$_4$(THF)$_2$] from [Cr(η^6-1,3,5-Me$_3$C$_6$H$_3$)$_2$]Br and TiBr$_3$(THF)$_3$

A well stirred suspension of [Cr(η^6-1,3,5-Me$_3$C$_6$H$_3$)$_2$]Br (0.42 g, 1.1 mmol) in THF (70 mL) was treated with solid TiBr$_3$(THF)$_3$ (0.57 g, 1.1 mmol). The suspension was stirred for 4 h at room temperature obtaining a orange suspension. The solid was recovered by filtration, washed with THF (2 × 2 mL) and dried in vacuo affording [Cr(η^6-1,3,5-Me$_3$C$_6$H$_3$)$_2$][TiBr$_4$(THF)$_2$] (0.75 g, 85% yield) as a dark orange microcrystalline solid. Anal. Calc. for C$_{26}$H$_{40}$Br$_4$CrO$_2$Ti: C, 38.8; H, 5.0; Br, 39.7. Found: C, 39.4; H, 4.7; Br, 39.5%. IR (Nujol), $\tilde{v}$/cm^{-1}: 3060 m, 1592 m, 1328 w, 1063 m, 1030 s (THF), 1025 m, 921 w, 859 s (THF), 720 w, 665 w, 442 m.

4.8. Reaction of [Cr(η^6-1,3,5-Me$_3$C$_6$H$_3$)$_2$] with MCl$_4$(THF)$_2$, M = Zr, Hf

Only the reaction of Cr(η^6-1,3,5-Me$_3$C$_6$H$_3$)$_2$ with HfCl$_4$ is described in detail, the reaction with ZrCl$_4$ being per-

formed in a similar way. A well stirred solution of $Cr(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2$ (0.73 g, 2.5 mmol) in THF (25 mL) was treated dropwise with a solution of $HfCl_4(THF)_2$ (1.1 g, 2.4 mmol) in THF (25 mL). A small amount of orange yellow solid was present after 2 h from mixing the reagents. The suspension was stirred for 48 h at room temperature and refluxed for 4 h. The orange solid was recovered by filtration, washed with THF (2×3 mL) and dried in vacuo at room temperature affording 0.48 g of an exceedingly air sensitive solid. Another crop of product (0.29 g) was obtained from the mother liquor after 48 h at room temperature. The two solid were combined and identified as $[Cr(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2][HfCl_5(THF)]$ (0.77 g, 43% yield). Anal. Calc. for $C_{22}H_{32}Cl_5CrHfO$: C, 36.7; H, 4.5; Cl, 24.6. Found: C, 36.9; H, 4.3; Cl, 24.1%. IR (Nujol), $\tilde{v}/cm^{-1}$: 3058 m, 1608 m, 1507 w, 1305 w, 1035 m (THF), 1003 m, 858 s (THF), 722 m-w, 688 w, 520 m-w, 446 m-s.

The mother liquor was refluxed for 3 h but no additional solid was obtained. The solvent was partially removed in vacuo and toluene was added which caused the formation of a dark oily solid which was not investigated further.

A GC–MS analysis of the mother liquor revealed only detectable amounts of $1,3,5\text{-}Me_3C_6H_3$.

The reaction was repeated by using a Cr/Hf molar ratio of 1/2, but unreacted $HfCl_4(THF)_2$ was identified in the mother liquor by IR spectroscopy.

$[Cr(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2][ZrCl_5(THF)]$ (yellow, 44% yield). Anal. Calc. for $C_{22}H_{32}Cl_5CrOZr$: C, 41.7; H, 5.1; Cl, 41.7. Found: C, 41.1; H, 5.0; Cl, 42.1%. IR (Nujol), $\tilde{v}/cm^{-1}$: 3056 m, 1605 m, 1510 w, 1309 w, 1033 m (THF), 1008 m, 862 s (THF), 722 m-w, 685 w, 520 m-w, 446 m-s.

4.9. X-ray structure determination of $[Cr(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2][HfCl_5(THF)]$

Crystals of $[Cr(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2][HfCl_5(THF)]$ were grown from THF at ca. 4 °C and the data were collected at 110(2) K with Mo Kα radiation ($\lambda = 0.71073$ Å) on a CCD area detector diffractometer equipped with a graphite monochromator, on a crystal of approximate dimensions $0.34 \times 0.31 \times 0.19$ mm. Details for the X-ray data collections are listed in Table 2. An empirical absorption correction (min. trans. 0.29, max. trans 0.45) was applied before averaging symmetry equivalent data ($R_{int} = 0.1054$). After merging 12024 independent reflections remained for structure solution by direct methods [24]. The structure model was completed by Fourier difference synthesis and refined with full-matrix least-squares on F^2 [25]. Convergence was reached for 12024 reflections and 554 variables at agreement factors of $R_1 = 0.079$ [observations with $I > 2\sigma(I)$] and $wR_2 = 0.216$ (all data).

4.10. Preparation of $[Cr(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2][HfCl_5(THF)]$ from $[Cr(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2]Cl$ and $HfCl_4(THF)_2$

A well stirred suspension of $[Cr(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2]Cl$ (0.42 g, 1.3 mmol) in THF (50 mL) was treated with solid

Table 2
Crystallographic data for $[Cr(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2][HfCl_5(THF)]$

Empirical formula	$C_{22}H_{32}Cl_5CrHfO$
Formula weight	720.22
Crystal system	Monoclinic
Space group	$P2_1/n$
a (Å)	20.892(5)
b (Å)	13.601(3)
c (Å)	21.053(5)
β (°)	118.140(7)
V (Å^3)	5275(2)
Z	8
D_{calc} (g cm^{-3})	1.814
$F(000)$	2824
μ (cm^{-1})	4.864
Reflections collected	68982
θ Range (°)	1.13–27.63
Limiting indices	$-27 \leqslant h \leqslant 23$, $-17 \leqslant k \leqslant 16$, $-9 \leqslant l \leqslant 27$
Independent reflections (R_{int})	12024 (0.1054)
Data/restraints/parameters	12024/94/554
Goodness-of-fit on F^2	1.082
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.079$, $wR_2 = 0.201$
Final R indices (all data)	$R_1 = 0.104$, $wR_2 = 0.216$

$R_1 = \sum \lVert F_o \rvert - \lvert F_c \rVert / \sum (F_o)$, $wR_2 = [\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]]^{1/2}$.

$HfCl_4(THF)_2$ (0.56 g, 1.2 mmol). The pale yellow suspension was stirred for 2 h at room temperature obtaining a orange suspension. The solid was recovered by filtration, washed with THF (3×2 mL) and dried in vacuo affording $[Cr(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2][HfCl_5(THF)]$ (0.88 g, 93% yield) identified on the basis of the analytical data and the IR spectrum.

4.11. Reaction of $[Cr(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2]Cl$ with Nb_2Cl_{10}

A well stirred solution of $Cr(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2$ (0.36 g, 1.2 mmol) in CH_3CN (25 mL) was treated with solid Nb_2Cl_{10} (0.33 g, 0.60 mmol). The brown solution turned reddish. After 1 h stirring at room temperature, a bright red microcrystalline solid was present which was recovered by filtration and dried in vacuo at room temperature affording 0.080 g of red solid. The volume of the mother liquor was reduced to ca. 5 mL and toluene (15 mL) was added. The red solid which formed was recovered by filtration, washed with toluene and dried in vacuo affording 0.50 g of $[Cr(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2][NbCl_5(CH_3CN)]$ (0.58 g, 80% total yield). Anal. Calc. for $C_{20}H_{27}Cl_5CrNNb$: C, 39.8; H, 4.5; N, 2.3; Cl, 29.4. Found: C, 39.3; H, 4.3; N, 2.1; Cl, 29.8%. IR (Nujol), $\tilde{v}/cm^{-1}$: 3053 m, 2277 m, 1506 w, 1408 m, 1303 w, 1039 m, 1004 w, 896 w, 879 m, 824 w, 721 m-w, 521 m-w, 447 m-s.

4.12. Reaction of $[Cr(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2]Cl$ with $NbCl_4(THF)_2$

A well stirred suspension of $[Cr(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2]Cl$ (0.37 g, 1.1 mmol) in CH_3CN (30 mL) was treated dropwise with a solution of $NbCl_4(THF)_2$ (0.42 g, 1.1 mmol) in CH_3CN (25 mL). The colour of the solution changed

to dark brown. After 12 h stirring at room temperature some yellow solid was present which was removed by filtration. The volume of the solution was reduced to ca. 10 mL and toluene (20 mL) was added. The red solid which formed was recovered by filtration and dried in vacuo at room temperature affording 0.50 g (75% yield) of [Cr(η^6-1,3,5-Me$_3$C$_6$H$_3$)$_2$][NbCl$_5$(CH$_3$CN)] identified on the basis of the analytical data and the IR spectrum.

Acknowledgments

Appendix A. Supplementary material

CCDC 627010 contains the supplementary crystallographic data for [Cr(η^6-1,3,5-Me$_3$C$_6$H$_3$)$_2$][HfCl$_5$(THF)]. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.01.044.

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