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Preliminary communication

Crystal structure of $[V(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2]AlCl_4$, the primary product of the reduction of VCl_3 by $Al/AlCl_3/1,3,5\text{-}Me_3C_6H_3$, and its further reduction to $V(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2$ *

Fausto Calderazzo *, Guido Pampaloni, Lucia Rocchi and Fabio Marchetti
Dipartimento di Chimica e Chimica Industriale, Sezione di Chimica Inorganica, Università di Pisa, Via Risorgimento 35, I-56126 Pisa (Italy)

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Abstract

The $VCl_3/Al/AlCl_3$/mes (mes = $1,3,5\text{-}Me_3C_6H_3$) system gives, after treatment with THF, the bismesitylenevanadium(I) tetrachloroaluminate, $[V(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2]AlCl_4$, $[Vmes_2]AlCl_4$, the structure of which has been determined by an X-ray diffraction study. The crystal consists of the discrete $AlCl_4^-$ and $[Vmes_2]^+$ ions, the former tetrahedral and the latter having eclipsed arene ligands. The iodide $[Vmes_2]I$ is reduced by biscyclopentadienylcobalt(II), $CoCp_2$, in THF in excellent yields.

It is known [1] that the reaction of titanium(IV) halides with Al/AlX_3 in the parent hydrocarbon as medium (the Fischer–Hafner reductive system [2]) affords η^6-arene derivatives of titanium(II) of formula $Ti(\eta^6\text{-arene})[(\mu\text{-}X)_2AlX_2]_2$ containing bridging tetrahaloaluminato groups. Recently, some of us showed [3] that the initial products formed during the reaction of zirconium(IV) [3a], hafnium(IV) [3a] and niobium(V) [3b,3c] halides with the Al/AlX_3 system are the mono-η^6-arene derivatives of the metal in the oxidation state II. On the basis of spectroscopic and chemical evidence, the η^6-arene derivatives of zirconium(II), hafnium(II) and niobium(II) were suggested to have a molecular structure similar to that of the titanium(II)η^6-arene derivatives [1c–e].

As far as Group 5 metals are concerned, earlier chemical evidence [4a] had indicated that a bis(η^6-mesitylene)vanadium(I) complex [4b,4c] was produced in the $VCl_3/Al/AlCl_3$/mes system, but the precise nature of the reduction product remained to be clarified. We have now isolated $[Vmes_2]AlCl_4$ and determined its crystal and molecular structure; moreover, we have found that $Vmes_2I$ can be conveniently reduced to $Vmes_2$ by biscyclopentadienylcobalt(II), $CoCp_2$.

Dropwise addition of the red-brown oil obtained by reduction of VCl_3 with $Al/AlCl_3$/mes in THF at room temperature, afforded a brown solid [5*] of

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* Dedicated to the memory of Professor Piero Pino.

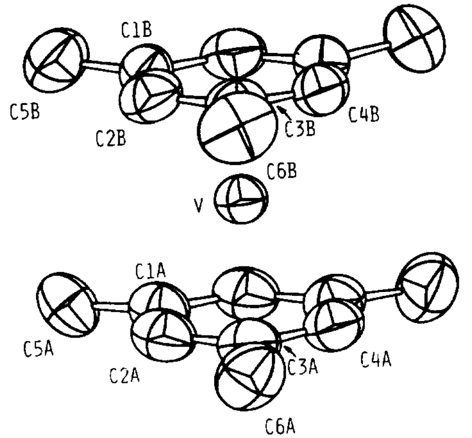

Fig. 1. View of the $[\mathrm{Vmes}_2]^+$ cation in $[\mathrm{Vmes}_2]\mathrm{AlCl}_4$. Relevant bond distances (Å) and angles (deg) are: V–C (mean value): 2.231(10); C–C (mean value): 1.395(12); V–ring centroids (mean value): 1.729 (11); (ring 1)–V–(ring 2): 179.3(5); C–C–C (ring, mean value): 119.8(6).

composition $[\mathrm{Vmes}_2]\mathrm{AlCl}_4$, which, on recrystallization from $\mathrm{CH_2Cl_2}$/heptane, gave large red-brown crystals suitable for an X-ray diffraction study [6*]. The structure consists of discrete $[\mathrm{Vmes}_2]^+$ cations and $\mathrm{AlCl_4}^-$ anions. The cation (Fig. 1) contains symmetrically bonded, substantially parallel 1,3,5-trimethylbenzene rings. The aromatic ligands are planar and eclipsed, within experimental error. The vanadium–carbon distance [2.231(10) Å, average] is not significantly different from that reported for the neutral species Vmes_2 [11].

Some aspects of the results, considered along with those obtained earlier for Group 4 (Ti, Zr, Hf) and Group 5 (Nb) metal halides, are worthy of discussion. The demonstration of the existence of the discrete $[\mathrm{Vmes}_2]^+$ cation has shown that vanadium(I) is reluctant to expand its coordination sphere by covalently bonding a bridging chloride from the $\mathrm{AlCl_4}$ moiety to give $\mathrm{Vmes_2}(\mu\text{-Cl})\mathrm{AlCl_3}$. This is in keeping with the failure to observe the formation of the $[\mathrm{Vmes_2(CO)}]^+$ cation in the $\mathrm{Vmes_2/V(CO)_6/CO}$ system that yields $[\mathrm{Vmes_2}][\mathrm{V(CO)_6}]$ [3c]. On the other hand, that vanadium(I) is the lowest thermodynamically stable oxidation state in the $\mathrm{VCl_3/Al/AlCl_3}$/mes system, is consistent with the observed reduction of $\mathrm{AlCl_3}$ by $\mathrm{Vmes_2}$, the $[\mathrm{Vmes_2}]^+$ cation being the corresponding oxidation product. This observation has a precedent in the similar finding by Fischer and Seeholzer for $\mathrm{Cr}(\eta^6\text{-benzene})_2$ [12].

The following stoichiometries were previously observed in the $\mathrm{MX}_n/\mathrm{Al}/\mathrm{AlX_3}$/arene systems for metal halides of Groups 4 and 5: mixed valence trimeric compounds of formula $[\mathrm{M_3}(\eta^6\text{-hexamethylbenzene})_3\mathrm{X_6}]^{n+}$, $n = 1, 2$; M = Ti [13a], Zr[13a,13b], Nb[13a,13c], Ta[13a,13c]; a mixed-valence titanium derivative containing a bridging benzene ring of stoichiometry $(\mu_2\text{-I})_3\mathrm{Ti_3}\{1,3,5\text{-}[\mu_2\text{-I-Al(I)}_2]_3\mathrm{C_6H_3}\text{-}\mu^3,\eta^6;\eta^6\}\mathrm{Ti}(\eta^6\text{-C}_6\mathrm{H}_6)$ [14]; $(\mu_2\text{-Br})_3\{(\eta^6\text{-C}_6\mathrm{H}_6)\mathrm{Zr}[(\mu\text{-Br})_2\text{-AlBr}_2]\}_2$ [15]; $\{\mathrm{Zr}(\eta^6\text{-C}_6\mathrm{H}_6)_2[(\mu\text{-I})_2\mathrm{AlI}_2]\}\mathrm{Al_3I_{10}}$ [15]; $\mathrm{M}(\eta^6\text{-arene})[(\mu\text{-Cl})_2\mathrm{AlCl_2}]_2$ for titanium(II) [1], zirconium(II) [3a,16*] and hafnium(II) [3a,16*] of d^2 configuration and for

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* Reference number with asterisk indicates a note in the list of references.

niobium(II) [3b,3c,16*] of d^3 configuration; [M(η^6-arene)$_2$]AlCl$_4$ for vanadium(I) of d^4 configuration. Thus, the reduction to the +I oxidation state is possible for vanadium only, which is consistent with the higher tendency of 3*d* transition elements to undergo reduction with respect to their 4*d* and 5*d* congeners [17].

In agreement with the results reported in a patent [18] we have found that the product obtained by the $VCl_3/Al/AlCl_3$/mes system is not reduced by alkali metals or zinc even in refluxing mesitylene. On the other hand, as noted earlier [19], [Vmes$_2$]I is a useful precursor for Vmes$_2$. We have found that [Vmes$_2$]I reacts readily with $CoCp_2$ in THF to give Vmes$_2$ in excellent yields [20*].

Further reductions of the [Vmes$_2$]$^+$ cation are under investigation.

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References and notes

1 (a) G. Natta, G. Mazzanti and G. Pregaglia, Gazz. Chim. Ital., 89 (1959) 2065; (b) H. Martin and F. Vohwinkel, Chem. Ber., 94 (1961) 2416; (c) U. Thewalt and F. Österle, J. Organomet. Chem., 172 (1979) 317; (d) U. Thewalt and F. Stollmaier, J. Organomet. Chem., 228 (1982) 149; (e) S.I. Troyanov and V.B. Rybakov, Metalloorg. Khim., 1 (1988) 1280; (f) P. Biagini, F. Calderazzo and G. Pampaloni, J. Organomet. Chem., 355 (1988) 99.

2 E.O. Fischer and W. Hafner, Z. Naturforsch., 10B (1955) 665.

3 (a) F. Calderazzo, P. Pallavicini and G. Pampaloni, J. Chem. Soc., Dalton Trans., (1990) 1813; (b) F. Calderazzo, G. Pampaloni, L. Rocchi, J. Strähle and K. Wurst, Angew. Chem., Int. Ed. Engl., 30 (1991) 102; (c) idem, J. Organomet. Chem., JOM 21756, in press.

4 (a) F. Calderazzo, Inorg. Chem., 3 (1964) 810; (b) E.O. Fischer and H.P. Kögler, Chem. Ber., 90 (1957) 250; (c) E.O. Fischer, G. Joos and W. Meer, Z. Naturforsch., 13b (1958) 456.

5 A mixture of $AlCl_3$ (3.1 g, 23.0 mmol), Al (0.62 g, 23.2 mmol), VCl_3 (3.62 g, 23.0 mmol) in mesitylene (50 ml) was heated at 120–130 °C for 2 h. The reaction mixture was filtered when hot, cooled at room temperature and added dropwise to THF (50 ml) within 1 h at room temperature. Formation of a brown solid was observed. The suspension was stirred for 15 h at room temperature, filtered and the solid was dried *in vacuo* affording 5.1 g (48% yield) of [Vmes$_2$] AlCl$_4$ in the form of a hygroscopic microcrystalline solid. Anal. Found Cl, 30.8; V, 11.0; $C_{18}H_{24}AlCl_4V$ calc.: Cl, 30.8, V, 11.1%.

6 *Crystal data*: $C_{18}H_{24}AlCl_4V$; $M = 460.1$; orthorhombic, space group *Pnnm*, $a = 15.078(5)$; $b = 14.391(3)$; $c = 10.481(3)$ Å; $V = 2274(1)$ Å^3; $Z = 4$; $D_c = 1.344$ g cm^{-3}; $\lambda(\text{Mo-}K_{\alpha_1}) = 0.70930$ Å; $\mu = 0.93$ mm^{-1}; $F(000) = 944$; $T = 294$ K, Ital Structures automatic diffractometer. Anisotropic thermal parameters were refined for all non-hydrogen atoms using the SHELX-76 programme [7]. $R/ = \Sigma \Delta F/\Sigma|F_o| = 0.057$, $R' = [\Sigma wF^2/\Sigma wF_0^2]^{1/2} = 0.073$ for 143 parameters. The atomic scattering factors were from ref. 8. The calculations were carried out on an IBM 3081 computer (C.N.U.C.E., Pisa) and the programmes PARST [9] and ORTEP II [10] were also used. The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, UK. Any request should be accompanied by a full literature citation for this communication.

7 G.M. Sheldrick, SHELX-76, Program for Crystal Structure Determination, University of Cambridge, 1976.

8 International Tables for X-ray Crystallography, Kynoch Press, Birmingham, Vol., 4 1974.

9 M. Nardelli, Comput. Chem., 7 (1983) 95.

10 G.K. Johnson, ORTEP II, Report ORNL 5138, Oak Ridge National Laboratory, Tennessee, 1976.

11 D. Braga and P. Sabatino, Acta Crystallogr., C46 (1990) 2308.

12 E.O. Fischer and J. Seeholzer, Z. Anorg. Allg. Chem., 312 (1961) 244.

13 (a) E.O. Fischer and F. Röhrscheid, J. Organomet. Chem., 6 (1966) 53; (b) F. Stollmaier and U. Thewalt, J. Organomet. Chem., 208 (1981) 327; (c) R.B. King, D.M. Braitsch and P.N. Kapoor, J. Am. Chem. Soc., 97 (1975) 60.

14 S.I. Troyanov and V.B. Rybakov, Metalloorg. Khim., 1 (1988) 1061.

15 S.I. Troyanov and V.B. Rybakov, Metalloorg. Khim., 2 (1989) 1382.

16 Not established crystallographically, deduced from spectroscopic and chemical properties.

17 F.A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, 5th ed., Wiley Interscience, New York, 1988, p. 776; D.J. Cardin, M.F. Lappert and C.L. Raston, Chemistry of Organo-Zirconium and -Hafnium Compounds, Ellis Horwood, Chichester, 1986, p. 11; J.O. Hill, I.G. Worsley and L.G. Hepler, Chem. Rev., 71 (1971) 127.

18 D.G. Pillsbury, U.S. Patent No. 4,526,724 (1983); Chem. Abstr., 103 (1985) 178457n.

19 T. Aviles and J.H. Teuben, J. Organomet. Chem., 253 (1983) 39.

20 A solution of $CoCp_2$ (2.24 g, 11.8 mmol) in THF (50 ml) was treated with $[Vmes_2]I$ (5.03 g, 12.0 mmol). After 1 h stirring at room temperature a yellow solid {identified as $[CoCp_2]I$} was presented along with a red solution. The solvent was removed *in vacuo* at room temperature and the residue was treated with heptane (50 ml). The solution was filtered and the filtrate combined with heptane (3 × 10 ml) washings of the insoluble material, and the volume was reduced to ca. 30 ml. The solution was kept at ca. −78 °C to yield large crystals of $Vmes_2$ (2.92 g, 83% yield). See also: F. Calderazzo, G. Pampaloni, F. Masi, A. Moalli and R. Invernizzi, Eur. Pat. 90200953.9 (to ENIChem ANIC SpA) (April 18, 1990).