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ON THE REACTIVITY OF $V(\eta\text{-}C_6H_3Me_3\text{-}1,3,5)_2I$

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Summary

$V(\eta\text{-}C_6H_3Me_3\text{-}1,3,5)_2I$ reacts with reducing agents such as MeLi, $Na[AlH_2(OCH_2CH_2OCH_3)_2]$ or Na to yield the neutral complex $V(\eta\text{-}C_6H_3Me_3\text{-}1,3,5)_2$ in 70–75% yield. Reaction of $V(\eta\text{-}C_6H_3Me_3\text{-}1,3,5)_2I$ with compounds containing suitable donor atoms such as THF, $P(OMe)_3$, CH_3CN or Py yields $V(\eta\text{-}C_6H_3Me_3\text{-}1,3,5)_2$ in 40–45% yield via disproportionation. The complex $V(\eta\text{-}C_5H_5)_2I$ was isolated in low yield, together with $V(\eta\text{-}C_6H_3Me_3\text{-}1,3,5)_2$ from the reaction of $V(\eta\text{-}C_6H_3Me_3\text{-}1,3,5)_2I$ with Cp_2Mg in toluene. Reaction of $V(\eta\text{-}C_6H_3Me_31,3,5)_2I$ or $V(\eta\text{-}C_6H_3Me_3\text{-}1,3,5)_2$ with allyl chloride leads to oxidation of the metal and loss of both mesitylene ligands.

Introduction

Bent bis-η-arene complexes of Zr, Hf and W have been recently reported [1]. They represent the first examples of this type of compound and their stability suggests that additional representatives of this class may exist. We were interested in developing the arene chemistry of vanadium, and it was hoped that similar types of complexes could be made by treatment of $V(\eta\text{-}C_6H_3Me_3\text{-}1,3,5)I$ [2] with nucleophiles such as Me^- or H^-, involving nucleophilic addition to the metal center to yield 18 electron complexes.

Likewise only a few examples of mono-arene-vanadium complexes are known, e.g. the cation $[V(CO)_4(\eta\text{-arene})]^+$ [3], the anion $[V(CO)_3(\eta\text{-}C_6H_3Me_3\text{-}1,3,5)]^-$ [4] and the neutral complex $[V(CO)_3(\eta\text{-}C_6Ph_6)]$ [5] or derivatives of these complexes like $[V(CO)_3(\eta\text{-}C_6H_3Me_3\text{-}1,3,5)I]$ and $[V(CO)_3(\eta\text{-}C_6H_3Me_3\text{-}1,3,5)H]$ [4]. The very unstable $V(\eta\text{-}C_5H_5)(\eta\text{-}C_6H_6)$ [6] has also been reported. We were interested in the chemistry of mono-arene-vanadium with ligands different from CO. (A very exten-

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sive mono-arene-molybdenum chemistry has been developed from the bis-η-arene-molybdenum by treating it with PR_3 or $P(OR)_3$ ligands which resulted in removal of one of the arene rings [7,8,9].) We describe below the reactions of cationic $V(\eta\text{-}C_6H_3Me_3\text{-}1,3,5)_2I$ and neutral $V(\eta\text{-}C_6H_3Me_3\text{-}1,3,5)_2$ with nucleophiles and ligands containing suitable donor atoms, the results were different from those we had expected.

Results and discussion

Treatment of $V(\eta\text{-}C_6H_3Me_3\text{-}1,3,5)_2I$ (I) with MeLi in pentane at −80°C gave on warming to room temperature a red solution from which $V(\eta\text{-}C_6H_3Me_3\text{-}1,3,5)_2$ (II) was isolated in 75% yield. GLC of the gas phase showed that ethane was formed. Reaction of I in toluene with $Na[H_2Al(OCH_2CH_2OCH_3)_2]$ at room temperature for 24 h gave similar yields of $V(\eta\text{-}C_6H_3Me_3\text{-}1,3,5)_2$.

Complex I was reduced to $V(\eta\text{-}C_6H_3Me_3\text{-}1,3,5)_2$ by treatment with Na sand in toluene for 24 h at 100°C. No replacement of mesitylene by toluene was observed.

When I was treated with reagents containing donor atoms, complex II was isolated, in lower yields 40–45%. Thus a suspension of I in THF was stirred for 24 h. After this time the THF had a red colour and II was isolated in 45% yield. GLC investigation of the mother liquor showed free mesitylene to be present, in about 1/1 molar ratio with respect to I taken. When I was treated with $P(OMe)_3$, CH_3CN or Py at room temperature, a rapid reaction took place and was completed after 2 h stirring, in each case II was isolated in 40–45% yield. GLC on the mother liquor showed free mesitylene to be present. It seems that I undergoes disproportionation in the presence of ligands containing donor atoms in a manner similar to that described for reaction with water [2], as depicted in equation 1.

$$nV(\eta\text{-}C_6H_3Me_3\text{-}1,3,5)_2I \xrightarrow{L} (n-1)V(\eta\text{-}C_6H_3Me_3\text{-}1,3,5)_2 + VI_nL_{6-n} + 2C_6H_3Me_3\text{-}1,3,5 \quad (1)$$

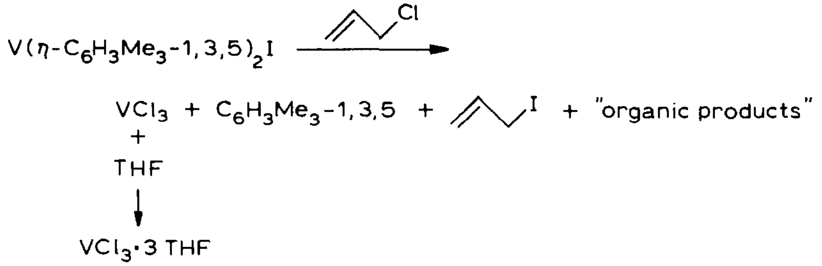
(L = THF, $P(OMe)_3$, Py, CH_3CN)

Presumably vanadium iodide forms a coordination complex with L. Since we were interested only in the organometallic chemistry of vanadium, no attempts were made to identify the higher oxidation state vanadium species. When (I) was treated with Cp_2Mg in toluene, $V(\eta\text{-}C_5H_5)_2I$ was isolated in low yield together with (II). Free mesitylene was found in the mother liquor. The isolation of $V(\eta\text{-}C_5H_5)_2I$ is a clear indication of the occurrence of disproportionation.

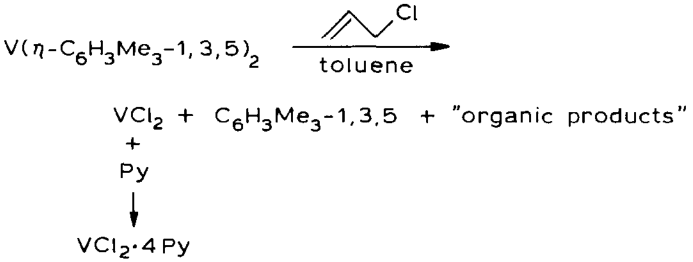
When II was treated with $P(OMe)_3$ under more drastic conditions for 24 h at 100°C no reaction took place.

Treatment of either I or II with allyl chloride caused oxidation of the vanadium, which was recovered as $VCl_3 \cdot 3THF$ and $VCl_2 \cdot 4Py$ respectively, and loss of both mesitylene groups.

Investigation by GC-MS or GLC of the mother liquor showed the presence of free mesitylene and halogenated organic compounds. In reaction 2a, allyl iodide was formed, produced by replacement of Cl^- in allyl chloride by I^- from I, together with 1,2-dichloropropane, and two isomers of chloroiodopropane as the main components and traces of chlorinated species produced by dimerization and trimerization of allyl chloride.



(2a)



(2b)

It is evident that we have developed a high yield synthesis of the neutral V(η-$C_6H_3Me_3$-1,3,5)$_2$. The complex [V(η-$C_6H_3Me_3$-1,3,5)$_2$]I has a high tendency to give V(η-$C_6H_3Me_3$-1,3,5)$_2$ under a variety of conditions, whereas [V(η-$C_6H_3Me_3$-1,3,5)$_2$] has no tendency, under the conditions employed to form bent bis-η-arene complexes of formula V(η-$C_6H_3Me_3$-1,3,5)$_2$R (R = H, Me) despite the fact that they would be 18 electron systems.

Experimental

All reactions and manipulations were carried out under dinitrogen or in vacuo. All solvents were dried and distilled before use. Elemental analyses were performed in the Microanalytical Department of this University under supervision of Mr. A.F. Hamminga. Infrared spectra were recorded as mulls on a JASCO-IRA-2 or a Pye Unicam SP3-300 spectrophotometers. Mass spectra were determined using a A.E.I.M.S. 9 spectrometer. GLC analyses were carried out with a Packard–Becker 428 GC apparatus, a Hewlett–Packard 7620 A Research Chromatograph using a 25 mm × 0.24 mm i.d. WCOT glass capillary column coated with SE-30 (Chrompack) and a porapack Q 6ft × 1.8″ column. GC-MS analyses were performed on a Finnigan 3300 system interfaced to a Finnigan 6110 computer by Dr. A.P. Bruins at the Department of Pharmacy of this University using a WCOT glass capillary column, coated with CP Sil 5 (Chrompack).

Reaction of V(η-$C_6H_3Me_3$-1,3,5)$_2$I (I) with MeLi

A suspension of I (1.1 g, 2.6 mmol), prepared as described in ref. 2, in pentane (20 cm^3) was cooled to -78°C and MeLi (2.75 mmol, 5 cm^3 of a 0.55 *M* ether solution) was added. The mixture was allowed to warm to room temperature with stirring. After 2 h the reaction was completed. GLC on the gas phase showed the presence of ethane. The solvent was removed under reduced pressure and the residue sublimed, to give red crystals. These were redissolved in pentane and crystallized out at $-78°C$, yield 75%. The crystals were identified as $V(\eta\text{-}C_6H_3Me_3\text{-}1,3,5)_2$ (II) by mass spectrometry, elemental analyses, and comparison of the infrared spectrum with that of an authentic sample.

Reaction of $V(\eta\text{-}C_6H_3Me_3\text{-}1,3,5)_2I$ with $Na[H_2Al(OCH_2CH_2OCH_3)_2]$

A suspension of I (0.60 g, 1.4 mmol) in pentane (25 cm^3) was cooled to $-78°C$ and $Na[H_2Al(OCH_2CH_2OCH_3)_2]$ (0.4 cm^3 of a 70% toluene solution) was added. The mixture was allowed to reach room temperature and stirred for 24 h. The mixture was then cooled to ca. $-40°C$ and water (5 cm^3) was added. The solvent was removed under reduced pressure and the residue extracted with pentane. Cooling to $-78°C$ gave red needles of $V(\eta\text{-}C_6H_3Me_3\text{-}1,3,5)_2$; yield 75%.

Reaction of $V(\eta\text{-}C_6H_3Me_3\text{-}1,3,5)_2I$ with Na

Complex I (0.69 g, 1.6 mmol) was suspended in toluene (20 cm^3) and Na sand (0.15 g, 6.5 mmol) added. The mixture was stirred at 100°C for 12 h, and the solvent was then removed under reduced pressure. Pentane extraction gave $V(\eta\text{-}C_6H_3Me_3\text{-}1,3,5)_2$; yield 70%.

Reaction of $V(\eta\text{-}C_6H_3Me_3\text{-}1,3,5)_2I$ with L ligands

A suspension of I in L (10 cm^3) (L = THF, $P(OMe)_3$, Py, or CH_3CN) was stirred at room temperature for ca. 2 h, except that in the case of THF ca. 24 h was required for completion. The solution was red coloured, and a solid remained in suspension. The solvent was distilled off under reduced pressure, GLC showed the presence of mesitylene in the destillate. The residue was partially extracted with pentane, and the extract was filtered and concentrated. Cooling to $-78°C$ afforded red needles of $V(\eta\text{-}C_6H_3Me_3\text{-}1,3,5)_2$; yield 40–45%.

No attempts were made to identify the component of the residue which not extracted into pentane.

Reaction of $V(\eta\text{-}C_6H_3Me_3\text{-}1,3,5)_2I$ with Cp_2Mg

Complex I (3.8 g, 9.0 mmol) was suspended in toluene (30 cm^3) and Cp_2Mg (2.8 g, 18.1 mmol) added. The mixture was stirred at room temperature for 4 days, during which it became red. The solvent was distilled off under reduced pressure, and GLC showed the presence of free mesitylene in the destillate. Extraction with pentane (5×30 cm^3) gave $V(\eta\text{-}C_6H_3Me_3\text{-}1,3,5)_2$ and some white crystals. The IR spectrum of the white crystals showed them to be Cp_2Mg.

The residue which was insoluble in pentane was treated with toluene (30 cm^3), to give a green solution. After filtration addition of pentane and cooling to $-78°C$ it gave green crystals, which were identified as $V(\eta\text{-}C_5H_5)_2I$ by elemental analyses, mass spectrometry (m/e 308), and comparison of their IR spectrum with that of an authentic sample; yield ca. 6%.

When the residue insoluble in toluene was treated with more Cp_2Mg (1.4 g, 9 mmol) in toluene (20 cm^3) more $V(\eta\text{-}C_6H_3Me_3\text{-}1,3,5)_2$ was isolated. Total yield 35%.

Reaction of $V(\eta\text{-}C_6H_3Me_3\text{-}1,3,5)_2$ with $P(OMe)_3$

A solution of II (0.3 g, 1.0 mmol) in $P(OMe)_3$ (5 cm^3) was stirred at 100°C for 20 h. After this time II was recovered unreacted.

Reaction of $V(\eta\text{-}C_6H_3Me_3\text{-}1,3,5)_2I$ *with allyl chloride*

A suspension of I (2.89 g, 6.9 mmol) in anhydrous allyl chloride (20 cm^3) was stirred at room temperature. After 3 h the orange colour of the suspended solid had turned to brown.

The mother liquor had a brownish colour. It was filtered and the more volatile components of the mother liquor were removed by distillation under reduced pressure to leave a thick oil. GC-MS on the volatile components showed the presence of allyl iodide, traces of mesitylene, two isomers of 1,2-dichloropropane, two isomers of chloroiodopropane, and traces of chlorinated products from the dimerization and trimerization of allyl iodide. The brown solid was dissolved in THF to give a brown-pink solution. This was filtered and concentrated to give pink crystals on cooling. They were identified as $VCl_3 \cdot 3THF$ by comparison of their infrared spectrum with that of an authentic sample; yield 45%.

Reaction of $V(\eta\text{-}C_6H_3Me_3\text{-}1,3,5)_2$ *with allyl chloride*

A solution of II (1 g, 3.4 mmol) in toluene (10 cm^3) was treated with dry allyl chloride (1 cm^3). The mixture was stirred at room temperature for 24 h, after which there was a colourless solution and a pale brown precipitate. The mother liquor was filtered and GC-MS showed the presence of mesitylene (yield 75%) and organic compounds, products of the reaction of allyl chloride with either toluene or mesitylene. The pale brown precipitate was dissolved in pyridine (50 cm^3) to give a deep purple solution, which was filtered and concentrated to give purple crystals. They were identified as $VCl_2 \cdot 4Py$ by comparison of their infrared spectrum with that of an authentic sample; yield 75%.

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