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Published in:
Journal of Organometallic Chemistry

DOI:
10.1016/S0022-328X(00)93830-0

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Document Version
Publisher's PDF, also known as Version of record

Publication date:
1980

Link to publication in University of Groningen/UMCG research database

Citation for published version (APA):

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Preliminary communication

THE PREPARATION OF $\eta^5$-CYCLOPENTADIENYLVANADIUM DIHALIDE COMPLEXES

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(Received November 27th, 1979)

Summary

Reaction of VX₃ .3THF (X = Cl, Br) with Cp₂ Mg and PR₃ (R = Me, Et) gives the complexes CpVX₂ .2PR₃. These complexes are convenient starting materials for the preparation of CpV complexes e.g. CpV(acac)₂, CpV(CO)₃ PET₃ and (CpVCl.PET₃)₂.

Growing interest in low-valent CpV compounds (Cp = $\eta^5$-C₅H₅) led us to investigate the synthesis of useful new appropriate starting materials. The known monocyclopentadienylvanadium compounds CpV(CO)₄ and CpVCl₃ are not the most convenient to start with. With CpV(CO)₄ substitution of the CO ligands is not easy and usually only partial [1, 2]. The synthesis of CpVCl₃ is difficult and poorly reproducible, while the yields are low to moderate [3, 4]. We began by exploring the synthesis of tervalent vanadium compounds CpVX₂ (X = Cl, Br). Since these complexes are coordinatively highly unsaturated, it is likely that stabilizing ligands will be needed to give stable products. Reaction of VX₃ .3THF in THF with cyclopentadienylationating agents CpNa, CpTl, CpSnBu₃ or Cp₂ Mg gave deep purple, very air-sensitive mixtures. Work up led to isolation of CpVX and VX₃ .3THF instead of the expected CpVX₂ .2THF. Addition of donor ligands (L = PR₃, RCN, R₃N) to the reaction mixtures gave only Cp₂ VX and VX₃ .3THF.

More successful were the low-temperature reactions of VX₃ .3THF, Cp₂ Mg and PR₃ (R = Et, Me) in THF. From these mixtures the compounds CpVX₂ .2PR₃ are formed during warming from —78° C to room temperature. They were re-crystallized from n-pentane as dark blue very air-sensitive needles. The spectral properties (IR: Cp and PR₃ present, UV-vis: maxima at 580 and 700 nm), magnetic moments (2 unpaired electrons per V atom), molecular weight determination and elemental analyses are in agreement with the formulation as monomeric CpVX₂ .2PR₃.

The chemical properties of these compounds are very interesting. The halide
and phosphine ligands are labile and can easily be replaced. In the reaction with
acetylacetone the new tervalent complex CpV(acac)$_2$ is formed. The brown,
air-sensitive, but thermally very stable compound (subl. 120° C, 0.4 mmHg)
was identified by elemental analysis and IR spectroscopy (the characteristic Cp
and acac absorptions are present). With reducing agents (Na, Mg, Al, Zn)
smooth reactions take place with complete or partial removal of the halide and/
or phosphine ligands. The products depend on the conditions used. We have
started a study of the reduction of CpVCl$_2$.2PEt$_3$ under CO or N$_2$.

Under CO, mixtures of CpV(CO)$_4$ and CpV(CO)$_3$PEt$_3$ are formed; the com-
ounds were identified by vanadium analyses, IR and $^1$H NMR spectroscopy
and by comparison with literature data on related complexes [5]. Under N$_2$, 
reduction with Na and Mg in THF gives complex mixtures, but with Al or Zn
one chlorine and phosphine are removed per molecule of CpVCl$_2$.2PEt$_3$, and
the dimer (CpVCl.PEt$_3$)$_2$ is formed. The compound is a purple, very air-sensi-
tive solid (m.p. 130° C) which can be crystallized from pentane. It was identified
by elemental analyses, IR spectra (Cp and PEt$_3$ absorptions are at the expected
values), and molecular weight determination (dimer in benzene). A possible
structure for this complex is given below.

Evidence for the metal—metal interaction comes from the magnetic suscepti-
bility measurements (200—300 K temperature independent paramagnetic $\chi =$
$1.64 \times 10^{-3}, 100—200$ K slowly increasing to $\chi = 1.88 \times 10^{-3}$). The dimer is
 coordinatively unsaturated and is expected to show a variety of interesting ad-
dition reactions. Reaction with CO (1 atm) gives a product with the formula
$[\text{Cp}_2 \text{V}_2 \text{Cl}_2 (\text{PEt}_3)_2 (\text{CO})_1]$; the structure of which is under investigation. It also
reacts with one mole of dioxygen to give an intensely coloured violet complex,
which is tentatively formulated as (CpVCl.PEt$_3$)$_2$O$_2$.

These results indicate that the complexes Cp VX$_2$.2PR$_3$ are very promising
starting materials for a range of new monocyclopentadienylvanadium com-
ounds. The synthesis of CpVCl$_2$.2PEt$_3$ is given below.

Preparation of CpVCl$_2$.2PEt$_3$ (N$_2$ atmosphere)

VCl$_3$.3THF (4.4 g, 11.7 mmol) in 100 ml of THF was cooled to $-78°$ C. A
THF solution of Cp$_2$Mg (8.1 ml, 0.72 M) was added with rapid stirring, fol-
lowed by 2.8 g (23.4 mmol) of PEt$_3$. After slowly warming to room tempera-
ture the mixture was stirred for 2 hours. The solvent was then pumped off and
the residue extracted with 100 ml of n-pentane. Blue crystals separated on
cooling to $-78°$ C. The product was washed with cold n-pentane, dried in vacu-
um, and isolated. Yield 3.3 g (7.8 mmol, 67%).

Acknowledgements

This investigation was supported by the Netherlands Foundation for Chemi-
cal Research (SON) with financial aid from the Netherlands Organization for the advancement for Pure Research (ZWO). The authors thank Dr. H.J. de Liefde Meijer and Prof. Dr. F. Jellinek for their stimulating interest.

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