

Preliminary communication

THE PREPARATION OF η^5 -CYCLOPENTADIENYLVANADIUM DIHALIDE COMPLEXES

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Summary

Reaction of $VX_3 \cdot 3THF$ ($X = Cl, Br$) with Cp_2Mg and PR_3 ($R = Me, Et$) gives the complexes $CpVX_2 \cdot 2PR_3$. These complexes are convenient starting materials for the preparation of CpV complexes e.g. $CpV(acac)_2$, $CpV(CO)_3PEt_3$ and $(CpVCl \cdot PEt_3)_2$.

Growing interest in low-valent CpV compounds ($Cp = \eta^5-C_5H_5$) led us to investigate the synthesis of useful new appropriate starting materials. The known monocyclopentadienylvanadium compounds $CpV(CO)_4$ and $CpVCl_3$ 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 $CpVCl_3$ is difficult and poorly reproducible, while the yields are low to moderate [3, 4].

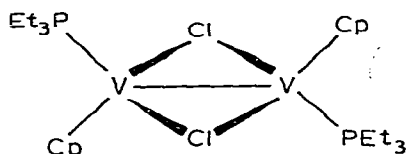
We began by exploring the synthesis of tervalent vanadium compounds $CpVX_2$ ($X = Cl, Br$). Since these complexes are coordinatively highly unsaturated, it is likely that stabilizing ligands will be needed to give stable products. Reaction of $VX_3 \cdot 3THF$ in THF with cyclopentadienylating agents $CpNa$, $CpTi$, $CpSnBu_3$ or Cp_2Mg gave deep purple, very air-sensitive mixtures. Work up led to isolation of $CpVX$ and $VX_3 \cdot 3THF$ instead of the expected $CpVX_2 \cdot 2THF$. Addition of donor ligands ($L = PR_3, RCN, R_3N$) to the reaction mixtures gave only Cp_2VX and $VX_3 \cdot 3THF$.

More successful were the low-temperature reactions of $VX_3 \cdot 3THF$, Cp_2Mg and PR_3 ($R = Et, Me$) in THF. From these mixtures the compounds $CpVX_2 \cdot 2PR_3$ are formed during warming from $-78^\circ C$ to room temperature. They were recrystallized from n-pentane as dark blue very air-sensitive needles. The spectral properties (IR: Cp and PR_3 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 $CpVX_2 \cdot 2PR_3$.

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 acetylacetonone the new trivalent complex $\text{CpV}(\text{acac})_2$ 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 $\text{CpVCl}_2 \cdot 2\text{PEt}_3$ under CO or N_2 .

Under CO, mixtures of $\text{CpV}(\text{CO})_4$ and $\text{CpV}(\text{CO})_3\text{PEt}_3$ are formed; the compounds were identified by vanadium analyses, IR and ^1H 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 $\text{CpVCl}_2 \cdot 2\text{PEt}_3$, and the dimer $(\text{CpVCl} \cdot \text{PEt}_3)_2$ is formed. The compound is a purple, very air-sensitive 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 susceptibility 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 addition reactions. Reaction with CO (1 atm) gives a product with the formula $[\text{Cp}_2\text{V}_2\text{Cl}_2(\text{PEt}_3)_2(\text{CO})_3]$; 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 $(\text{CpVCl} \cdot \text{PEt}_3)_2\text{O}_2$.

These results indicate that the complexes $\text{CpVX}_2 \cdot 2\text{PR}_3$ are very promising starting materials for a range of new monocyclopentadienylvanadium compounds. The synthesis of $\text{CpVCl}_2 \cdot 2\text{PEt}_3$ is given below.

Preparation of $\text{CpVCl}_2 \cdot 2\text{PEt}_3$ (N_2 atmosphere)

$\text{VCl}_3 \cdot 3\text{THF}$ (4.4 g, 11.7 mmol) in 100 ml of THF was cooled to -78°C . A THF solution of Cp_2Mg (8.1 ml, 0.72 M) was added with rapid stirring, followed by 2.8 g (23.4 mmol) of PEt_3 . After slowly warming to room temperature 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 vacuum, and isolated. Yield 3.3 g (7.8 mmol, 67%).

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