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LETTERS TO THE EDITOR

Synthesis of Cyclopentadienylvanadium Oxydichloride from Vanadium Oxotrichloride

V. D. Makhaev, A. P. Borisov,[†] and P. E. Matkovskii

Institute of Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka, Moscow oblast, Russia

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Vanadium oxotrichloride $VOCl_3$ is one of the available pentavalent vanadium derivatives. It is easily purified by distillation, readily soluble in hydrocarbons and other organic solvents, and, therefore, is quite an attractive starting material for preparing pentavalent vanadium organic compounds and complexes. However, $VOCl_3$ is a strong oxidant and is easily reduced by many organic compounds and, therefore, it has scarcely been used in organometallic synthesis [1]. We expected that using stabilizing multicenter hydrocarbon ligands like the cyclopentadienyl anion would allow us to go around this impediment.

One of the representatives of vanadium compounds with multicenter hydrocarbon ligands, cyclopentadienylvanadium oxychloride $CpVOCl_2$ ($Cp = C_5H_5$), have found application as a component of highly active catalysts of ethylene polymerization and copolymerization [2] and can be used as starting material for preparing other pentavalent vanadium orgaic compounds.

Known methods of synthesis of this compounds are rather intricate. They involve oxidative chlorination of various cyclopetadienyl vanadium compounds with the oxidation degree of the central atom varying from I to IV [$CpV(CO)_4$, Cp_2V, Cp_2VCl_2, etc.] with $O_2 + HCl$ or $O_2 + Cl_2$ mixtures [3–6]. The best results were obtained on treatment of $CpV(CO)_4$ with a mixture of chlorine and oxygen in carbon tetrachloride [6]. The pentamethylcyclopendienyl derivative $(C_5Me_5)VOCl_2$ was obtained in a similar way [7]. Thus, to prepare $CpVOCl_2$ by the referred procedures requires using the corresponding vanadium complexes which are rather difficult to synthesize. $CpVOCl_2$ was also synthesized starting from vanadium oxotrichloride [5, 8]. The first of these two syntheses was performed in two steps: $VOCl_3$ was first treated with magnesiumdicyclopentadienide, and then the reaction products were treated *in situ* with a mixture of hydrogen chloride and oxygen. The yield of $CpVOCl_2$ by this procedure was as low as 21% [5]. The second synthesis was performed by slowly adding a toluene solution of $VOCl_3$ to an equimolar mixture of cyclopentadiene and a base (Et_3N, Et_2NH) at 5–10°C over the course of 5 h. The yield of $CpVOCl_2$ by this procedure was 10–15% [8].

The present work was aimed at developing a more effective method for synthesis of $CpVOCl_2$ from $VOCl_3$, involving no gaseous oxidants.

Our initial attempts to prepare $CpVOCl_2$ by treatment of $VOCl_3$ with various cyclopentadienides (CpLi, CpNa, CpK, CpTl) in various solvents (benzene, toluene, hexane) failed. These reactions gave dark brown precipitates or resulted in the reduction of V^{5+} to V^{4+}, yielding green-colored products.

We suggested that the intermediate complex formation of $VOCl_3$ with a certain Lewis acid that is oxidation-resistant but fairly labile in the coordination sphere of vanadium would attenuate the oxidation power of the metal, thus preventing introduction of more than one cyclopentadienyl group. Unfortunately, $VOCl_3$ oxidizes many ethers and amines. We found that, unlike other ethers, 1,2-dimethoxymethane (DME) is not oxidized with $VOCl_3$ at room temperature. Reactions of solutions of $VOCl_3$ in saturated hydrocarbons (pentane, hexane, heptane, petroleum ether) with excess 1,2-dimethoxyethane give purple crystals whose chemical analysis corresponds to the formula $VOCl_3 \cdot DME$. This compound is soluble in polar solvents, forming red solutions. It can be handled in an inert atmosphere in the dark at room temperature for some months. When exposed to light, $VOCl_3 \cdot DME$ gradually decolorizes (decomposes), and in air it hydrolyzes. The ^1H NMR spectrum of

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[†] Deceased.

coordinated DME contains broadened signals at 3.30 and 3.23 ppm (the respective signals of free DME are at 3.02 and 2.91 ppm). The IR spectrum of $VOCl_3 \cdot DME$ contains, along with DME absorption bands, a broad band of the V=O group at 1000–1050 cm^{-1}, a band at 750 cm^{-1} (1,2-dimethoxyethane V–O), and a broad band at 410–435 cm^{-1}, assignable to V–Cl vibrations.

The reaction of the complex $VOCl_3 \cdot DME$ with CpLi in aromatic hydrocarbons at a 1 : 1 molar ratio resulted in formation of a colorless precipitate of LiCl and a dark blue solution from which we isolated more than 50% of $CpVOCl_2$ as dark blue, almost black crystals.

$$VOCl_3 \cdot DME + CpLi \longrightarrow CpVOCl_2 + LiCl\downarrow + DME$$

The resulting compound was characterized the chemical analysis and spectrally. The ^1H NMR spectrum of a solution of $CpVOCl_2$ in CCl_4 contains as a broadened cyclopentadienyl proton signal at 6.43 ppm (singlet). The IR spectrum displays absorption bands at 970 (V=O), 1455, 1430, 1030, 1005, 835 (cyclopentadienyl ligand) and 460, 410 (V–Cl) cm^{-1}, which is consistent with published data [6].

The synthetic scheme proposed in the present work can be applied for preparing derivatives of $CpVOCl_2$, containing substituents in the cyclopentadienyl rings. For example, the reaction of $(t\text{-}BuC_5H_4)Li$ with $VOCl_3 \cdot DME$ gave a bluish violet solution from which $(t\text{-}BuC_5H_4)VOCl_2$ was isolated as almost black crystals.

Thus, the complex of vanadium oxytrichloride with dimethoxyethane $VOCl_3 \cdot DME$ is a convenient starting material for preparing cyclopentadienyl derivatives of pentavalent vanadium.

The IR spectra were measured on a UR-20 spectrophotometer at 400–4000 cm^{-1} in mineral oil. The ^1H NMR spectrum was obtained on a Bruker AC-200 spectrometer (CCl_4 solutions, external reference residual DMSO-d_6 proton signals).

All operations with air-sensitive compounds were performed in an inert atmosphere. Technical grade $VOCl_3$ was distilled before use (bp 126–127°C). CpLi was prepared by treatment of a solution of cyclopentadiene in diethyl ether with a solution of butyllithium in hexane, after which the solvents were removed by distillation, and the residue was dried in a vacuum. Hexane and benzene were distilled over cetyltrimethylammonium bromide, dimethoxyethane, over lithium aluminum hydride, and methylene chloride and carbon tetrachloride, over phosphoric anhydride.

$VOCl_3 \cdot DME$. A solution of 15 ml of 1,2-dimethoxyethane in 20 ml of hexane was added dropwise at room temperature over the course of 30 min to a magnetically stirred solution of 6.6 g of $VOCl_3$ in 70 ml of hexane. Dark brown crystals formed, and the solution got red. No heat release was observed. The mixture was stirred for an additional 1 h, the precipitate was filtered off, washed with hexane on the filter (2.20 ml), and dried in a vacuum (0.1 mm) at room temperature to obtain 9.7 g (97%) of $VOCl_3 \cdot DME$ as purple crystals. Found, %: Cl 39.5; V 18.8. $C_4H_{10}Cl_3O_3V$. Calculated, %: Cl 40.4; V 19.3.

$CpVOCl_2$. Cyclopentadienyllithium, 0.42 g, was added to a solution of 1.60 g of $VOCl_3 \cdot DME$ in 30 ml of benzene, and the mixture was stirred at 20°C with a magnetic stirrer. The initially red reaction mixture gradually got dark blue. It was stirred for 6 h, after which the colorless solution of LiCl was filtered off, and the filtrate was concentrated in a vacuum to ca. 5 ml. The residue was diluted with 10 ml of hexane to obtain a dark blue, almost black crystals which were separated and dried in a vacuum. Yield 0.61 g (52%). Found, %: Cl 35.1; V 24.9. $C_5H_5 \cdot Cl_2OV$. Calculated, %: Cl 34.94; V 25.10.

REFERENCES

1. *Metody elementoorganicheskoi khimii. Podgruppy medi, skandiya, titana, vanadiya, khroma, margantsa. Lantanoidy i aktinoidy* (Methods of Organoelement Chemistry. Copper, Scandium, Titanium, Vanadium, Chromium, Manganese Subgroups. Lanthanides and Actinides), Nesmeyanov, A.N., Ed., Moscow: Nauka, 1974, pp. 389–428.
2. Chirkov, N.M., Matkovskii, P.E., and D'yachkovskii, F.S., *Polimerizatsia na kompleksnykh metalloorganicheskikh katalizatorakh* (Polymerization on Complex Organometallic Catalysts), Moscow: Khimiya, 1976, pp. 321–328.
3. Fischer, E.O. and Vigoureux, S., *Chem. Ber.*, 1958, vol. 91, no. 6, p. 1342.
4. Fischer, E.O., Vigoureux, S., and Kuzel, P., *Chem. Ber.*, 1960, vol. 93, no. 3, p. 701.
5. de Liefde Meijer, H.J. and van der Kerk, G.J.M., *Recl. Trav. Chim. Pays-Bas*, 1965, vol. 84, no. 11, p. 1418.
6. Herrmann, W.A., Weichselbaumer, G., and Kneuper, H.-J., *J. Organomet. Chem.*, 1987, vol. 319, no. 2, p. C21.
7. Aistars, A., Newton, C., Rubenstahl, T., and Doherty, N.M., *Organometallics*, 1977, vol. 16, no. 9, p. 1994.
8. Magomedov, G.K.-I., Kusainova, K.M., Morozova, L.V., and Beletskaya, I.P., Abstracts of Papers, *IV Vsesouznaya konferentsiya po metalloorganicheskoi khimii* (IV All-Union Conf. on Organometallic Chemistry), Kazan, 1988, p. 14.