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Preliminary communication

SYNTHESIS, X-RAY STRUCTURE AND REACTIONS OF PHENYLIMIDODECAMETHYLVANADOCENE

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Summary

The synthesis and X-ray structure of phenylimidodecamethylvanadocene are described. Its reactions with electrophiles, including isocyanides, which lead to loss of one pentamethylcyclopentadienyl ring (Cp*) are reported.

Nitrene chemistry has attracted much interest among organometallic chemists in the past decade. Metal coordinated nitrenes have been suggested to be active intermediates in the reactions of some organic azides with several substrates [1] including copper(I) catalyzed processes [2] and reactions with CO leading to the corresponding isocyanates, which is a field of considerable interest from an industrial viewpoint [3]. Furthermore, transition metal organo-imido moieties appear to be plausible intermediates in some enzymatic nitrogen fixation processes, and recently a bridging dinuclear nitrene species was identified as an intermediate in model dinitrogen activation studies [4].

Synthetic methods and physico-chemical properties were thoroughly reviewed by Nugent and Haymore a few years ago [5]. Surprisingly, the literature provides little information on the structural determination and on the chemistry of mononuclear metallocene-nitrene derivatives.

Fluorinated and silylated azides are useful reagents in the synthesis of stable nitrene derivatives, the first vanadocene bonded mononuclear nitrene being obtained by use of silylated derivatives [6]. We now describe the synthesis, structural analysis, and chemical reactions of mononuclear phenylimidodecamethyl-

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vanadocene. Polymethylation of cyclopentadienyl rings is well known to lead to better crystallinity and to improve the stability of early transition metallocene derivatives [7].

Decamethylvanadocene shows some peculiar chemical behaviour and it can promote radical breakdown of several substrates and trap unstable moieties [8]. Low temperature reaction of decamethylvanadocene with phenylazide gives a dark brown insoluble crystalline solid (I), which loses nitrogen at room temperature to give a deep green solution, from which crystals of II can be isolated in good yield on cooling [9].

$$\mathrm{Cp}^{\star}_2\mathrm{V} + \mathrm{PhN}_3 \xrightarrow[\text{n-hexane}]{-20^{\circ}\mathrm{C}} \underset{\text{(I)}}{\mathrm{Cp}^{\star}_2\mathrm{VN}_3\mathrm{Ph}} \xrightarrow[-\mathrm{N}_2]{\text{room temperature}} \underset{\text{(II)}}{\mathrm{Cp}^{\star}_2\mathrm{V{=}NPh}} \qquad (1)$$

The coordination of organic azides in their intact form is an intriguing problem and coordinated azides have never been fully characterized by X-rays analysis. Unfortunately the characterization of crystalline I was unsuccessful because it loses nitrogen above 0°C.

The nature of complex II, which is paramagnetic and whose spectrum IR shows a strong band at 1158 cm^{-1}, has been further elucidated by X-ray diffraction [10]. The crystal structure (Fig. 1) shows that the V—N bond length is rather short (1.730(5) Å) and the V—N—C angle is nearly linear (178.2(6)°). This suggests some triple-bond character in V≡NR [11], in agreement with the N—C bond length (1.345(9) Å), which is intermediate between a single and a double bond, implying *sp* hybridization of the N atom orbitals with delocalization of the N lone pair both on to the V atom and into the phenyl ring:

$$\mathrm{V}\overset{..}{=}\mathrm{N}\overset{..}{-}\mathrm{Ph}$$

If, as usual, the cyclopentadienyl rings are considered as monodentate ligands, the coordination around vanadium is trigonal and strictly planar. The phenylimido ligand is planar and nearly perpendicular to the coordination plane (93.8(2)°). The strong interaction of vanadium with the phenylimido ligand significantly influences the $\mathrm{Cp}^{\star}_2\mathrm{V}$ geometry, the V—Cp* bond lengths (2.058(8), 2.049(8) Å) being longer than those observed in other $\mathrm{Cp}^{\star}_2\mathrm{V}$ complexes [8]. As a consequence of this strong interaction, the Cp* rings are bent, and the angle subtended at the V atom by two Cp* rings is narrower (138.4(3)°) than those observed in the other complexes mentioned above.

The methyl carbon atoms are bent away from the ring planes to reduce methyl—methyl steric interactions. The displacements of the methyl carbons from the respective ring planes are: C(11) 0.315(9), C(12) 0.019(9), C(13) 0.222(11), C(14) 0.037(9), C(15) 0.174(10) and C(16) 0.106(8), C(17) 0.089(9), C(18) 0.134(8), C(19) 0.348(8), C(20) 0.107(8) Å.

Because of the powerful electron donating ability of methylated Cp rings and the large steric hindrance we thought it of interest to investigate the chemical behaviour of complex II towards electrophiles. The highly moisture sensitive II, which is stable in refluxing hexane, reacts under mild conditions as summarized in the Scheme 1.

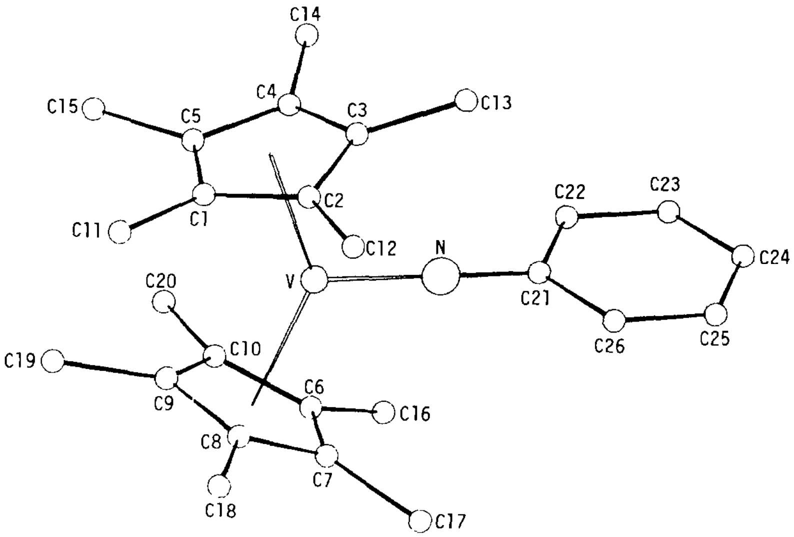
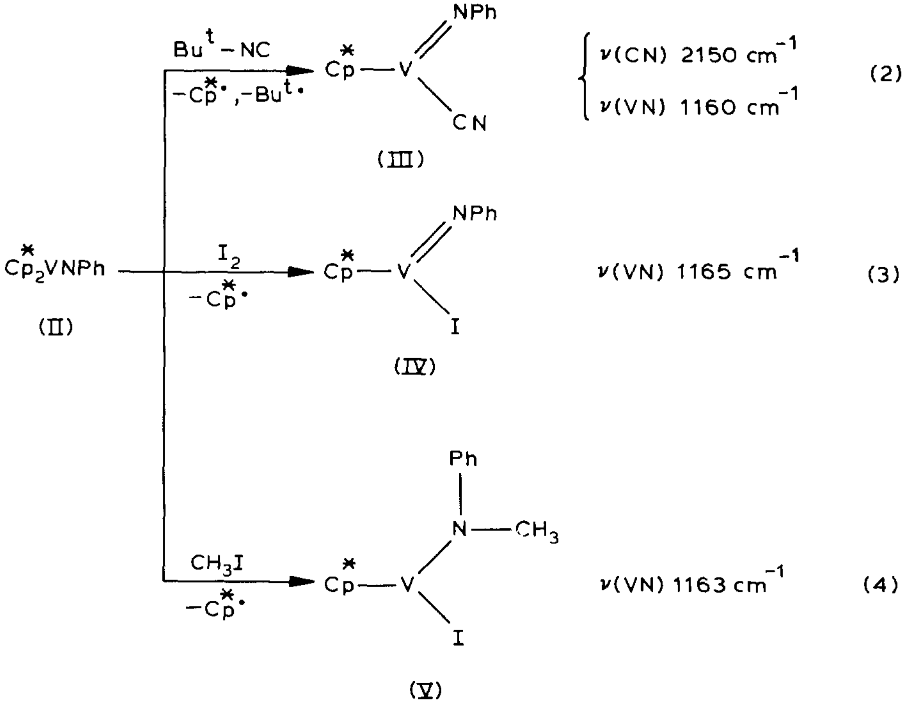


Fig. 1. A molecular view of $Cp_2V(NPh)$.



SCHEME 1

The removal of one Cp* ring was demonstrated by the usual methods. The behaviour towards Bu^{t}NC in reaction 2 is not a surprisingly reaction for polymethylated metallocene [8]. The V=N bond thus seems to be quite stable except towards hydrolysis or electrophilic addition, as CH_3I. Investigations of the mechanism of the reaction of complex II with CO are in progress.

Tables of atomic coordinates, bond lengths, and angles for this work are available on request from the Director of the Cambridge Crystallographic Data Center, University Chemical Laboratories, Lensfield Road, Cambridge CB2 1EW (Great Britain). Any request should be accompanied by the full literature citation for this communication.

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9 2.5 ml of pure azide were added to a stirred solution cooled at 0°C of 5.27 g of decamethylvanadocene in 50 ml of dry hexane. A plentiful crystalline brown solid separated almost immediately and no gas evolution was observed. Reaching room temperature, the suspension loses N_2 helped by a gentle heating. The solid desolves and the solution turned deep green. On cooling at 30 °C, 4.82 g of deep green crystalline solid separated. Analysis: C, 75.88 (75.70); H, 8.77 (8.55); N, 3.35 (3.39).

10 *Crystal data.* $C_{26}H_{35}NV$, $M = 412.5$, monoclinic, space group $P2_1/c$, a 13.951(5), b 12.199(4), c 13.845(5) Å, β 103.92(4)°, U 2287(1) Å^3, D_c 1.198 g cm^{-3}, $Z = 4$, $F(000)$ 884, λ(Mo-K_α) 0.71069 Å, μ(Mo-K_α) 4.29 cm^{-1}. 4020 reflections measured on a Philips PW 1100 diffractometer. Structure solved by the heavy atom method and refined by full-matrix least-squares to $R = 0.054$ and $R_w = 0.053$ for 1577 observed reflections ($I > 3\sigma(I)$).

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