

## OXIDATIVE ADDITION OF $\text{HN}_3$ AND $\text{NCN}_3$ TO DICYCLOPENTADIENYL-VANADIUM AND -CHROMIUM

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### Summary

The reactions of  $\text{HN}_3$  and  $\text{NCN}_3$  with dicyclopentadienylvanadium and dicyclopentadienylchromium,  $(\eta\text{-C}_5\text{H}_5)_2\text{M}$  ( $\text{M} = \text{V}$  and  $\text{Cr}$ ) give  $(\eta\text{-C}_5\text{H}_5)_2\text{M}(\text{N}_3)_2$  and  $(\eta\text{-C}_5\text{H}_5)_2\text{MN}_3(\text{CN})$ , respectively. The products are characterized by their elemental analysis, magnetic moments, and EPR and IR spectra.

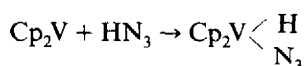
### Introduction

In previous papers [1,2] we have described the synthesis of pseudohalogen derivatives of dicyclopentadienyl-titanium, -vanadium and -chromium of the type  $(\eta\text{-C}_5\text{H}_5)_2\text{MLL}'$  ( $\text{L} = \text{L}' = \text{SCN}$ ,  $\text{SeCN}$ ;  $\text{L} = \text{CN}$ ,  $\text{L}' = \text{SCN}$ ,  $\text{SeCN}$ ;  $\text{M} = \text{Ti}$ ,  $\text{V}$ ,  $\text{Cr}$ ) by oxidative addition of the relevant pseudohalogen to the appropriate dicyclopentadienyls. In the present work we present the results obtained with reactions of the same type but using hydrogen azide and cyanazide.

### Results and discussion

Addition of an ethereal solution of  $\text{HN}_3$  to solutions of  $(\eta\text{-C}_5\text{H}_5)_2\text{M}$  ( $\text{M} = \text{V}$ ,  $\text{Cr}$ ) under  $\text{N}_2$  causes loss of hydrogen and formation in high yield of solids which were shown to be  $\text{Cp}_2\text{V}(\text{N}_3)_2$  (already known [3]) and the new  $\text{Cp}_2\text{Cr}(\text{N}_3)_2$ . The initial purple colour due to  $\text{Cp}_2\text{V}$  changes to blue after addition of  $\text{HN}_3$  and a brown solid precipitates. It is probable that this reaction involves two steps:

(a) Oxidative addition of  $\text{HN}_3$  to  $\text{Cp}_2\text{V}$  to afford the blue intermediate:



(b) Hydrogen elimination between  $\text{Cp}_2\text{V}(\text{H})\text{N}_3$  and  $\text{HN}_3$  to yield  $\text{Cp}_2\text{V}(\text{N}_3)_2$

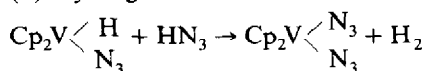


TABLE 1  
 EPR SPECTRA OF PRODUCTS

Compounds <sup>a</sup>	$g_{\text{iso}}$	$A_{\text{iso}}(10^{-4} \text{ cm}^{-1})$	$\Delta m = 1$		$\Delta m = 2$	
			$g$	$H$	$g$	$H$
$\text{R}_2\text{V}(\text{N}_3)_2$	1.990	66.85				
$\text{R}_2\text{VN}_3(\text{CN})$	1.984	60.39				
$\text{R}_2\text{Cr}(\text{N}_3)_2$			1.996	3275	3.938	1660
$\text{R}_2\text{CrN}_3(\text{CN})$			1.999	3270	3.915	1670

<sup>a</sup>  $\text{R} = \eta\text{-C}_5\text{H}_5$ .

It has not been possible to isolate the intermediate, probably because reaction b is very fast. Similar results are obtained in the reaction between  $\text{Cp}_2\text{Cr}$  and  $\text{HN}_3$ .

The mixed cyanoazide complexes  $(\eta\text{-C}_5\text{H}_5)_2\text{M}(\text{CN})\text{N}_3$  ( $\text{M} = \text{V}, \text{Cr}$ ) are easily obtained by mixing ethereal solutions of  $\text{N}_3\text{CN}$  and the corresponding dicyclopentadienyls.

The solutions of the chromium(IV) derivatives are unstable, probably due to instability of this oxidation state of chromium relative to others.

The EPR spectra of the vanadium(IV) complexes in chloroform at room temperature show eight lines, due to the coupling of the non-paired electron with the  $^{51}\text{V}$  ( $I = 7/2$ ) nucleus. These spectra can be explained using the spin Hamiltonian

$$\hat{H} = gH \cdot \hat{S}_z + AI_z \hat{S}_z \quad (1)$$

for systems with  $S = 1/2$ , and applying the 2nd order correction [4]. The parameters of the spin Hamiltonian (eq. 1) are shown in Table 1. The hyperfine coupling constant  $A$  values can be used as a measurement of the metal–ligand bond covalency [5], because  $A$  decreases when covalency increases; this means that when we replace

 TABLE 2  
 IR SPECTRA DATA FOR THE COMPLEXES<sup>a</sup>

$\text{R}_2\text{V}(\text{N}_3)_2$	$\text{R}_2\text{VN}_3(\text{CN})$	$\text{R}_2\text{Cr}(\text{N}_3)_2$	$\text{R}_2\text{CrN}_3(\text{CN})$	Assignment
2069vs	2170vs	2100vs	2150vs	
2028vs		2050vs		$\nu_{\text{as}}(\text{N}_3)$
1990sh		1995sh		
	2110m		2080s	$\nu(\text{CN})$
1280m	1205m	1275m	1205m	$\nu_s(\text{N}_3)$
642w	640w	642w	665w	$\delta(\text{N}_3)$
590w		590w	560w	$\gamma(\text{N}_3)$
435s	510m	400m	462s	$\nu_a(\text{MN}_3)$
392m	395m	412m	425m	$\nu_a(\text{MR})$
340m		312m		$\nu_s(\text{MN}_3)$
	352m		400m	$\nu(\text{MC})$
303m	323m	370m		$\nu_s(\text{MR})$
220w	210w	220w		$\delta(\text{MN}_3)$
190w				$\delta_a(\text{NMN})$

<sup>a</sup> In  $\text{cm}^{-1}$ ,  $\text{R} = \eta\text{-C}_5\text{H}_5$ .

a  $N_3$  ligand in  $(\eta-C_5H_5)V(N_3)_2$  by a CN ligand, the covalent character of the bond increases (see Table 1).

The EPR spectra of the chromium complexes, in chloroform solution at  $-160^\circ C$  show an intense signal at about 3300 G, corresponding to the  $\Delta m = 1$  transition, and a very weak signal at lower values of the magnetic field (1600 G) corresponding to the forbidden transition  $\Delta m = 2$ . The  $g$  values are given in Table 1. These spectra are similar to those observed for chromium(IV) complexes [6,7].

The IR spectra show the characteristic bands of the cyclopentadienyl ligands at 3100, 1400, 1100, 1000 and 800  $cm^{-1}$  [8,9]. In Table 2 the bands assigned to the cyanide and azide ligands are reported, along with those for the metal–ligand bonds. The range of the stretching vibrations  $\nu(CN)$  and  $\nu(N_3)$  is characteristic of terminal ligands [10]. The bands for  $\nu_{as}(MR)$  appear between 420–390  $cm^{-1}$  (Table 2) displaced towards frequencies higher than those of the original dicyclopentadienyl compounds owing to increase of the oxidation level of the metal and the larger number of electrons surrounding it.

## Experimental

The hydrogen azide [11] and the cyanoazide [12] were obtained by published methods, and the experimental techniques used have been described previously [1,2]. *The compounds described below are explosive and should be handled with extreme care.*

### Preparation of $(\eta-C_5H_5)_2V(N_3)_2$

Freshly sublimed  $(\eta-C_5H_5)_2V$  (1 g, 5.5 mmol) was dissolved in  $Et_2O$  (40  $cm^3$ ) under a  $N_2$  atmosphere in a 100 ml two-necked flask provided with a  $N_2$  inlet, magnetic stirrer and pressure-equalized dropping funnel. The solution was cooled to  $0^\circ C$  and through the funnel was added an ethereal  $HN_3$  solution, prepared from  $NaN_3$  (6 g, 92 mmol) and conc.  $H_2SO_4$  (12  $cm^3$ ). A brown solid separated immediately and a gas was evolved, and was identified as hydrogen. Stirring was continued for 1 h at  $0^\circ C$  and the solid was filtered off, washed several times with  $Et_2O$ , and dried in vacuo at room temperature. This solid, when dry, explodes readily upon heating or shock. It is only slightly soluble in the common solvents. Yields 90%. (Found: C, 45.1; H, 3.9; N, 31.2; V, 18.7.  $C_{10}H_{10}N_6V$  calcd.: C, 45.3; H, 3.8; N, 31.8; V, 19.2%).  $\mu_{eff}$  1.67 BM.

### Preparation of $(\eta-C_5H_5)_2Cr(N_3)_2$

This compound was obtained by the method described above using  $(\eta-C_5H_5)_2Cr$  (1.5 g, 8.2 mmol) and an ethereal  $HN_3$  solution obtained from  $NaN_3$  (8 g, 120 mmol) and conc.  $H_2SO_4$  (14  $cm^3$ ). The violet solid which separates readily explodes upon heating or shock. Yield 80%. (Found: C, 46.7 H, 3.4; N, 30.0; Cr, 18.2.  $C_{10}H_{10}N_6Cr$  calcd.: C, 47.4; H, 3.5; N, 30.2; Cr, 18.7%).  $\mu_{eff}$  2.52 BM.

### Preparation of $(\eta-C_5H_5)_2VN_3(CN)$

The  $(\eta-C_5H_5)_2V$  (1 g, 5.5 mmol) was dissolved in  $Et_2O$  (40  $cm^3$ ) in a 100 ml two-necked flask provided with a  $N_2$  inlet, magnetic stirrer and pressure equalizing dropping funnel. The flask was cooled to  $-20^\circ C$  and a  $N_3CN$  solution in ether,

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