SYNTHESIS AND CHARACTERISATION OF A SERIES OF VANADIUM ISONITRILE COMPLEXES

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Summary

The reaction between $(\eta^5\text{-}C_5H_5)V(CO)_4$ and RNC in the presence of PdO as catalyst to give $(\eta^5\text{-}C_5H_5)V(CO)_{4-n}(CNR)_n$ ($n = 1$–3) is reported. The complexes have been characterized by IR and ^{51}V and ^1H NMR spectroscopy.

Introduction

The use of the isonitrile ligand (RNC) in organometallic chemistry is well documented [1]. The small size of the ligand [2] as well as the ability to vary the electronic (and steric) properties of the isonitrile by varying the R group make this a versatile ligand for stabilizing metals in both high and low oxidation states. [1] In this publication we wish to report on the catalysed thermal reaction between $(\eta^5\text{-}C_5H_5)V(CO)_4$ and RNC and the stereochemistry of the resulting products $(\eta^5\text{-}C_5H_5)V(CO)_{4-n}(CNR)_n$ ($n = 1$–3). In particular the exploitation of ^{51}V NMR spectroscopy to determine the geometry of the substituted products is discussed.

Only a limited number of vanadium isonitrile complexes have been reported in the literature and these complexes have been synthesized by a variety of routes e.g. $VCl_3(CNR)_3$ from VCl_3 and RNC [3,4]; $(\eta^5\text{-}C_5H_5)_2V(CNR)$ from $(\eta^5\text{-}C_5H_5)_2V$ and RNC [5]; $[V(CO)_5(CNR)]^-$ from $[V(CO)_5NH_3]^-$ [6] or $[V(CO_5)THF]^-$ [7] and RNC and $(\eta^5\text{-}C_5H_5)V(CO)_3(CNR)$ from $(\eta^5\text{-}C_5H_5)V(CO)_3CS$ and RNH_2 [8].

It is to be noted that the direct reaction between $(\eta^5\text{-}C_5H_5)V(CO)_4$ and RNC to give $(\eta^5\text{-}C_5H_5)V(CO)_3(CNR)$ has not previously been mentioned in the literature and that the direct reaction between $(\eta^5\text{-}C_5H_5)V(CO)_4$ and simple 2 electron donors is usually achieved by photochemical procedures [9]. The role of a catalyst in the chemistry of $[(\eta^5\text{-}C_5H_5)V(CO)_3H]^-$ has been described [10].

Experimental

(η^5-C$_5$H$_5$)V(CO)$_4$ was purchased from Strem Chemicals. The isonitrile ligands were either synthesized (MeNC) [11] or purchased from Fluka AG ('BuNC, 2,6-Me$_2$C$_6$H$_3$NC) Strem ('PrNC) or Merck (C$_6$H$_{11}$NC, C$_6$H$_5$CH$_2$NC). All solvents were routinely dried and degassed prior to use. Degassed Celite (Celite 521, Aldrich Chemicals) was used for separating the catalyst from the reaction products. IR spectra were recorded on a Jasco IRA1 and ^{1}H NMR spectra on a Bruker WP80 FT NMR spectrometer. ^{51}V NMR spectra were recorded on a Bruker WH90 PFT spectrometer operating at 23.66 MHz. Elemental analyses were determined by the Microanalytical Laboratories, CSIR, Pretoria or the Chemical Laboratories, University of Hamburg.

Synthesis of (η^5-C$_5$H$_5$)V(CO)$_3$(CNR) (R = Me, 'Bu, C$_6$H$_5$CH$_2$, 'Pr, C$_6$H$_{11}$, 2,6-Me$_2$C$_6$H$_3$)

(η^5-C$_5$H$_5$)V(CO)$_4$ (226 mg, 1 mmol) and PdO (30 mg) were added to degassed toluene (10 ml) and the solution brought to reflux. RNC (1.05 mmol) was added to the solution and the reaction monitored by IR spectroscopy. On completion of the reaction (10 min) the solution was filtered through Celite and the orange to red solutions collected under nitrogen. Solvent was removed under vacuum, the complex redissolved in hexane and the pure material obtained as red or orange crystals after standing at $-5°$C for 24 h.

Synthesis of (η^5-C$_5$H$_5$)V(CO)$_2$(CNR)$_2$ (R = 'Bu, 2,6-Me$_2$C$_6$H$_3$)

(η^5-C$_5$H$_5$)V(CO)$_4$ (226 mg, 1 mmol) and PdO (30 mg) were added to degassed toluene (10 ml) and the solution brought to reflux. RNC (2.05 mmol) was added to the solution and the reaction monitored by IR spectroscopy. During the course of the reaction the solution turned dark red. When all the monosubstituted intermediate had been consumed the reaction solution was cooled and filtered through Celite under nitrogen. Solvent was removed on a vacuum pump and the crude product crystallised from toluene/hexane at $-5°$C.

Discussion

The thermal reaction between (η^5-C$_5$H$_5$)V(CO)$_4$ and t-BuNC in refluxing toluene was monitored by IR spectroscopy and after 4 h IR intensity data suggested 20% formation of (η^5-C$_5$H$_5$)V(CO)$_3$(CNBu^t) (see below). Previous success using transition metal catalysts to induce CO replacement by RNC in transition metal carbonyl chemistry [12] suggested that this might be a feasible approach to obtaining the required vanadium complex more rapidly and in higher yield. A brief survey of a number of catalysts indicated that PdO would be a suitable catalyst for further investigation [13].

Using a PdO/V ratio of 1/5, a range of monosubstituted isonitrile derivatives (η^5-C$_5$H$_5$)V(CO)$_3$(CNR) (R = Me, 'Bu, 'Pr, C$_6$H$_{11}$, CH$_2$C$_6$H$_5$, 2,6-Me$_2$C$_6$H$_3$) were obtained in less than 10 min under the experimental conditions as detected by IR spectroscopy. A lower PdO/V ratio also results in complete reaction but with longer reaction time. The use of alternate reaction solvents to aid in eventual product purification was also attempted, but toluene was found to be the solvent of choice. It

TABLE 1

IR AND ^{1}H NMR SPECTRAL DATA FOR THE VANADIUM ISONITRILE COMPLEXES

	IR (cm^{-1}) ^{a,b}		^{1}H NMR (δ) ^{c}		
	ν(NC)	ν(CO)	η^5-C_5H_5	CH_3 or CH_2	C_6H_5
(η^5-C_5H_5)V(CO)$_3$(CNMe) ^{d}	2130m	1974ms 1900sh 1894s	4.57	2.10	
(η^5-C_5H_5)V(CO)$_3$(CN^{i}Pr)	2100m	1972ms 1900sh 1889s	4.58	3.1 ^{e}, 0.71 ^{d}	–
(η^5-C_5H_5)V(CO)$_3$(CNBu^t)	2094m	1973ms 1898sh 1890s	4.58	0.90	–
(η^5-C_5H_5)V(CO)$_3$(CNC$_6$H$_{11}$)	2100m	1971ms 1896sh 1885s	4.62	1.0–1.2	–
(η^5-C_5H_5)V(CO)$_3$(CNCH$_2$C$_6$H$_5$)	2114m	1977ms 1903sh 1894s	4.55	3.90	6.8–7.1
(η^5-C_5H_5)V(CO)$_3$(CNC$_6$H$_3$Me$_2$-2,6)	2075m	1968ms 1906sh 1896s	4.59	2.10	6.3–6.7
(η^5-C_5H_5)V(CO)$_2$(CNBu^t)$_2$ ^{g}	$\begin{cases}2090m \\ 2010w\end{cases}$	– 1880s 1831s	4.84	1.08	–
(η^5-C_5H_5)V(CO)$_2$(CNC$_6$H$_3$Me$_2$-2,6)$_2$	$\begin{cases}2060m \\ 2000sh \\ 1990m\end{cases}$	– 1903s 1868ms	4.88	2.28	6.8
(η^5-C_5H_5)V(CO)(CNC$_6$H$_3$Me$_2$-2,6)$_3$ ^{g}	1974s, br	– – 1840m	5.07	2.31	6.8

^{a} Recorded in hexane unless otherwise stated. ^{b} m = medium, s = strong, sh = shoulder. ^{c} Recorded in C$_6$D$_6$ relative to TMS. ^{d} Lit. values [8]: IR (CH$_2$Cl$_2$) 2139, 1935, 1920 cm^{-1}; NMR 4.53, 2.13 (δ, ppm). ^{e} Heptet for CHMe$_2$ proton ($J \sim 6.5$ Hz). ^{f} Doublet (J 6.5 Hz). ^{g} IR recorded in C$_6$D$_6$.

is to be noted that the use of heptane resulted in highly erratic reactions which gave product yields varying from 30–60%. The monosubstituted products were readily purified by passage through a celite column to remove catalyst followed by crystallisation at $-5°C$.

The products were readily characterized by IR spectroscopy (data similar to that found for other (η^5-C_5H_5)V(CO)$_3$L derivates [14], see Table 1), ^{1}H NMR spectroscopy (correct intensity ratio of RNC and cyclopentadienyl ring, see Table 1) and elemental analyses (Table 2). The ^{51}V NMR data (Table 3) are consistent with the known bonding characteristics of the RNC ligands [1]. In particular the data indicate that the values lie between those observed for (η^5-C_5H_5)V(CO)$_3$L where L = P(OMe)$_3$ (1496 ppm) a strong acceptor ligand and L = P(^{i}Bu)$_3$ (1377 ppm), a

TABLE 2

ANALYTICAL DATA FOR THE VANADIUM ISONITRILE COMPLEXES

Complex	M.p. (°C)	Analyses (Found (calcd.) (%))		
		C	H	N
(η^5-C_5H_5)V(CO)$_3$(CNMe)	^{a}	49.4 (49.79)	3.2 (3.34)	5.7 (5.81)
(η^5-C_5H_5)V(CO)$_3$(CN^{i}Pr)	42–43	53.2 (53.54)	4.4 (4.50)	5.2 (5.21)
(η^5-C_5H_5)V(CO)$_3$(CNBu^t)	81–82	55.4 (55.11)	5.2 (4.98)	5.1 (4.95)
(η^5-C_5H_5)V(CO)$_3$(CNC$_6$H$_{11}$)	58–59	57.7 (58.26)	5.3 (5.22)	4.6 (4.56)
(η^5-C_5H_5)V(CO)$_3$(CNCH$_2$C$_6$H$_5$)	76–78	59.6 (60.58)	3.6 (3.82)	4.4 (4.42)

^{a} Lit. value [8]: 88–90°C.

TABLE 3

^{51}V NMR SPECTRAL DATA FOR THE VANADIUM ISONITRILE COMPLEXES

Complex	δ ^{a}(ppm)	$W_{1/2}$ ^{b} (Hz)
$(\eta^5\text{-}C_5H_5)V(CO)_3(CNPr^i)$	-1403	38
$(\eta^5\text{-}C_5H_5)V(CO)_3(CNBu^t)$	-1404	38
$(\eta^5\text{-}C_5H_5)V(CO)_3(CNC_6H_{11})$	-1401	45
$(\eta^5\text{-}C_5H_5)V(CO)_3(CNCH_2C_6H_5)$	-1407	38
$(\eta^5\text{-}C_5H_5)V(CO)_3(CNC_6H_3Me_2\text{-}2,6)$	-1430	42
$(\eta^5\text{-}C_5H_5)V(CO)_2(CN^tBu)_2$	$-1268s, -1301m$	61, 58
$(\eta^5\text{-}C_5H_5)V(CO)_2(CNC_6H_3Me_2\text{-}2,6)_2$	$-1327m, -1342s$	71, 71
$(\eta^5\text{-}C_5H_5)V(CO)(CNC_6H_3Me_2\text{-}2,6)_3$	-1235	

^{a} Relative to VOCl$_3$ (δ 0 ppm) at 300(1) K in 7.5 mm vials recorded in toluene (error ± 1 ppm).
^{b} Half-width of resonance signal.

medium accepting ligand [14]. Also of note is the upfield shift of 25 ppm for the aromatic compared to the aliphatic isonitrile. This effect is not unexpected and indicates the better accepting ability of the former complex.

The piano-stool geometry of $(\eta^5\text{-}C_5H_5)V(CO)_4$ [15] and its substituted derivatives [16] have been well established. Since this geometry should be maintained for the monosubstituted isonitrile derivatives (isonitriles are sterically undemanding ligands [2]) only one isomer is possible for the $(\eta^5\text{-}C_5H_5)V(CO)_3RNC$ complexes.

In an attempt to synthesize disubstituted isonitrile derivatives the RNC/V molar ratio was increased for the isonitrile with R = ^{t}Bu and 2,6-Me$_2$C$_6$H$_3$. The reaction was monitored by IR spectroscopy and readily indicated that new products were formed in the reaction. After catalyst removal the products were crystallised at $-5°$C (toluene/hexane). The new complexes were characterized by IR, ^{1}H and ^{51}V spectroscopy and the spectroscopic data are completely in keeping with data available for other $(\eta^5\text{-}C_5H_5)V(CO)_2L_2$ complexes [17].

Use of the ν(CO) intensity data [18] together with the ^{1}H NMR spectral data (one C$_5$H$_5$ resonance) suggested that the complex existed as one isomer only (e.g. cis-isomer for t-BuNC). However ^{51}V NMR spectral data clearly indicate the presence of two isomers (with different intensity ratios) for the R = ^{t}Bu and 2,6-Me$_2$C$_6$H$_3$ derivatives. It is thus apparent that care must be used in assessing the stereochemistry of complexes containing small ligands on the basis of IR intensity data alone.

The trisubstituted derivatives (R = ^{t}Bu, 2,6-Me$_2$C$_6$H$_3$) can also be synthesized by use of a large excess of ligand. Thus the reaction between a four-fold excess of 2,6-Me$_2$C$_6$H$_3$NC and $(\eta^5\text{-}C_5H_5)V(CO)_4$ was monitored by IR spectroscopy and the reaction was terminated when only minor changes were observed in the IR spectrum (6 h). The IR spectrum at this stage suggested that the reaction mixture contained predominantly $(\eta^5\text{-}C_5H_5)V(CO)(CNC_6H_3Me_2\text{-}2,6)_3$. IR, ^{1}H NMR and ^{51}V NMR spectral data of the isolated complex are consistent with this proposal (Tables 1 and 2) although surprisingly only one Me resonance was detected in the ^{1}H NMR spectrum. As expected only one ^{51}V NMR signal was observed for the new complex. Trisubstitution of $(\eta^5\text{-}C_5H_5)V(CO)_4$ with Group V donor ligands has been achieved previously by photochemical procedures [15,19].

Long reaction times ($>$ 36 h) during which a 10 fold excess of ^{t}BuNC is added in

portions to $(\eta^5\text{-}C_5H_5)V(CO)_4$ did give the expected changes in the IR spectrum consistent with formation of $(\eta^5\text{-}C_5H_5)V(CO)(CNBu^t)_3$. ($\nu(CO)$ absorption in C_7H_{16} at 1835 cm^{-1}). However, no further attempt was made to characterize this complex.

An attempt was also made to extend the reaction procedure to the synthesis of Group V donor ligand complexes viz. $(\eta^5\text{-}C_5H_5)V(CO)_3PR_3$. However, reaction of PMe_2Ph with $(\eta^5\text{-}C_5H_5)V(CO)_4$ in the presence of PdO and in either heptane or toluene as solvent gave no indication (IR spectral changes) of product formation (24 h).

Substitution of RNC for CO results in an increase in electron density at the central metal atom. Chemical oxidation of the resulting isonitrile derivatives described above should result in new high oxidation state vanadium isonitrile complexes [20]. Attempted reactions with I_2 and tetracyanoethylene did indeed result in the formation of new complexes but attempts to isolate and characterize these complexes have so far met with little success.

Acknowledgements

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