

NOTIZEN

**Substitution of CO for CN⁻
in Cyclopentadienyl Carbonyl Vanadium
Compounds**

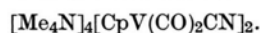
DIETER REHDER

Institut für Anorganische und Angewandte Chemie
der Universität Hamburg

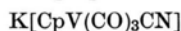
(Z. Naturforsch. **31b**, 273-274 [1976]; received October 22, 1975)

Cyclopentadienyl Carbonyl Vanadium Compounds,
⁵¹V NMR, UV, IR

UV irradiation of [Me₄N][VCp(CO)₃] and [Me₄N]CN results in the formation of a complex with zero-valent vanadium which possibly has to be formulated as



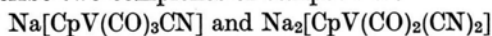
A new method of preparation of



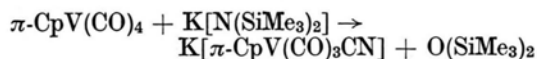
is described; ⁵¹V NMR results and a complete IR spectrum are presented and discussed.

Investigation of CN⁻ substituted carbonyls and carbonylates of transition elements in low oxidation states provides information on the extent and variation of π-acceptor and σ-donor abilities of the CN⁻ and CO ligand and their mutual influence and interaction *via* the central metal ion.

Cyclopentadienyl carbonyl vanadium compounds containing the cyanide ligand were first prepared by FISCHER and SCHNEIDER by cleavage of the V-V bond in Cp₂V₂(CO)₅ with NaCN¹. The authors describe two complexes of composition



which, however, remain incompletely characterized. The mono-substituted product was now obtained in a more direct way through reaction between π-CpV(CO)₄ and potassium bis(trimethylsilyl)-amide:



following the original work of WANNAGAT and SEYFFERT². The silylamide is most conveniently prepared from hexamethyldisilazane and potassium

in liquid ammonia under catalytic induction of platinum black. The above reaction is carried out with equimolar amounts of the starting products dissolved in benzene with strict enclosure of air and moisture. The yield after three days of reaction is about 70%. (Excess of K[N(SiMe₃)₂] does not result in the formation of a disubstituted product.) The complex is obtained as an air-sensitive, diamagnetic, orange-brown powder which is insoluble in benzene but well soluble in THF and CH₃CN.

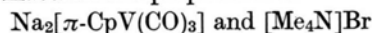
In Table I, the complete IR spectrum is recorded and compared with the CpV(CO)₄ spectrum (DURIG *et al.*³). The CN/CO regions of the solvent spectra are consistent with an assumed C_s symmetry of the V(CO)₃CN moiety. Substitution of CO for the weak π-acceptor CN⁻ implies a stronger π-interaction between vanadium and the remaining three CO ligands; hence a considerable decrease of the CO stretching frequencies and simultaneously an increase of the V-CO stretching modes. The treatment of the V(CO)₃CN moiety as an isolated structural unit seems also justified by the fact that only the out-of-plane CH-deformation mode of the cyclopentadienyl ring system is strongly influenced by introduction of CN⁻, *i.e.* split and shifted towards lower wave numbers, whereas all in-plane frequencies remain almost uninfluenced.

The absolute value for the ⁵¹V-chemical shift in K[CpV(CO)₃] dissolved in CH₃CN is -1.218% (regarding a calculated absolute value for [V(CO)₆]⁻ = -1.950%, see ref. 4; the chemical shift relative to a standard [V(CO)₆]⁻ is +0.712%) as compared to -1.228% for π-CpV(CO)₄ in CH₃CN. Hence, substitution of CO for the weaker CN⁻ decreases the chemical shift, an effect which was observed previously in monosubstituted hexa-carbonyl-vanadates⁴ and⁵, and apparently accounts for (i) the lesser ligand strength of the CN⁻ with respect to the CO-ligand (ii) the change in symmetry.

Attempts to apply a similar reaction to Na₂[π-CpV(CO)₃] were not successful. CO substitution in this anion, however, was carried out by UV irradiation of a solution containing



This reaction proceeds with simultaneous photo-induced oxidation of vanadium(-I) to vanadium(0). Starting material are prepared from



in liquid ammonia, and from [Me₄N]Cl and KCN in absolute methanol, respectively. [Me₄N]CN is soluble in methanol. From the evaporated solution,

Requests for reprints should be sent to D. REHDER, Institut für Anorganische und Angewandte Chemie der Universität, D-2000 Hamburg 13, Martin-Luther-King-Platz, FRG.

Table I. IR Spectrum of $[\pi\text{-CpV}(\text{CO})_3\text{CN}]^-$.

THF	K $[\pi\text{-CpV}(\text{CO})_3(\text{CN})]$		Na $[\pi\text{-CpV}(\text{CO})_3\text{CN}]$ KBr (see ref. ¹)	$\pi\text{-CpV}(\text{CO})_4$	
	CH ₃ CN	Nujol mull		Nujol (ref. ³)	
		3100 vw		3120 w	ν_{CH}
2075		2063 s	2092		ν_{CN}
1955	1953	1945 vs	1938	2027 vs	ν_{CO}
1845	1847	1840 vs	1825	1917 vs	ν_{CO}
1830	1830	1820 vs	1782		ν_{CO}
		1425 m		1435 m	ν_{CC}
		1005 m		1015 m	ip- δ_{CH}
		840 (sh), 831			
		825 (sh), 815		840 s	op- δ_{CH}
		800 s			
		629 m		625 s	δ_{VCO}
		600 s		600 s	δ_{VCO}
		546 s		496 s	$\nu_{\text{V-CO}}$
		511, 505 m		430 m	$\nu_{\text{V-CO}}$
		478 w, 455 vw			δ_{VCN}
		435 w, 422 vw			$\nu_{\text{V-CN}}$
		385, 360, 330 (all vw)		325 vw	$\nu_{\text{V-Cp}}$

it can be extracted with hot (near to b.p.) acetonitrile (from which it crystallizes in transparent flakes). The hot extract is filtered into a solution of $[\text{Me}_4\text{N}]_2[\pi\text{-CpV}(\text{CO})_3]$ in CH_3CN and irradiated for about 35 hours at room temperature. During the reaction (carried out in inert gas atmosphere) a weak N_2 -stream is bubbled through the solution. The solution is filtered, evaporated to about 5 ml, decanted from excess $[\text{Me}_4\text{N}]\text{CN}$ and evaporated to dryness. Finally, the greasy red-brown product is washed with liquid ammonia. The remaining air-sensitive, red crystals are diamagnetic. The compound was thereupon formulated as a binuclear complex $[\text{Me}_4\text{N}]_4[\pi\text{-CpV}(\text{CO})_2\text{CN}]_2$. The empirical composition is analytically confirmed.

$\text{C}_{16}\text{H}_{29}\text{N}_3\text{O}_2\text{V}$

Calcd C 55.48 H 8.44 N 12.13 V 14.71,
Found C 55.6 H 8.6 N 12.0 V 14.8.

The IR spectrum in CH_3CN shows one ν_{CN} (2070 cm^{-1}) and two ν_{CO} (1790 and 1679 cm^{-1}). Thus, the CO-stretching modes are above those of the starting product $[\text{Me}_4\text{N}]_2[\pi\text{-CpV}(\text{CO})_3]$ ($\nu_{\text{CO}} = 1742$ and 1630 cm^{-1} in CH_3CN). This seems to prove that the stretching frequency for the CO group is

more distinctly influenced by a change in oxidation number [$\text{V}(\text{-I}) \rightarrow \text{V}(\text{O})$] than by replacement of CO for CN^- . 1659 cm^{-1} is, however, quite an unusual low wave number for a carbonyl complex with zero-valent vanadium. This suggests bridging carbonyl groups between $\pi\text{-CpV}(\text{CO})(\text{CN})$ moieties. For $\text{Cp}_2\text{V}_2(\text{CO})_5$, FISCHER and SCHNEIDER report a $\nu_{\text{CO}} = 1828\text{ cm}^{-1}$ for the bridging carbonyl groups¹. Taking into account a decrease in ν_{CO} by approximately 130 cm^{-1} when decreasing the formal oxidation number of the central metal atom by one unit, there is appropriate accordance between predicted and experimentally detected ν_{CO} for a possible bridging CO in $[\pi\text{-CpV}(\text{CO})_2\text{CN}]^{4-}$. Assuming C_{2h} symmetry for a CO-bridged, binuclear anion in a first approximation, two IR active bands (A_u and B_u) and one ν_{CN} (B_u) are expected which again agrees with the experimental data. It should be pointed out, however, that the low ν_{CO} can also be interpreted in terms of increased V-CO interaction due to introduction of CN^- into the complex.

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¹ E. O. FISCHER and R. J. SCHNEIDER, Chem. Ber. **103**, 11 [1970].

² U. WANNAGAT and H. SEYFFERT, Angew. Chem. **77**, 457 [1965].

³ J. R. DURIG, A. L. MARSTON, R. B. KING, and

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⁴ D. REHDER, J. Organometal. Chem. **37**, 303 [1972].

⁵ D. REHDER and J. SCHMIDT, J. Inorg. Nucl. Chem. **36**, 333 [1974].