# NOTIZEN

## Substitution of CO for $CN^-$ in Cyclopentadienyl Carbonyl Vanadium Compounds

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Cyclopentadienyl Carbonyl Vanadium Compounds, $^{51}V$ NMR, UV, IR

UV irradiation of $[Me_4N][VCp(CO)_3]$ and $[Me_4N]CN$ results in the formation of a complex with zero-valent vanadium which possibly has to be formulated as

$$[Me_4N]_4[CpV(CO)_2CN]_2.$$

A new method of preparation of

$$K[CpV(CO)_3CN]$$

is described; $^{51}V$ 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 $\pi$-acceptor and $\sigma$-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 $Cp_2V_2(CO)_5$ with NaCN[1]. The authors describe two complexes of composition

$$Na[CpV(CO)_3CN] \text{ and } Na_2[CpV(CO)_2(CN)_2]$$

which, however, remain incompletely characterized. The mono-substituted product was now obtained in a more direct way through reaction between $\pi$-$CpV(CO)_4$ and potassium bis(trimethylsilyl)-amide:

$$\pi\text{-}CpV(CO)_4 + K[N(SiMe_3)_2] \rightarrow K[\pi\text{-}CpV(CO)_3CN] + O(SiMe_3)_2$$

following the original work of WANNAGAT and SEYFFERT[2]. 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 exclosure of air and moisture. The yield after three days of reaction is about 70%. (Excess of $K[N(SiMe_3)_2]$ 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 $CH_3CN$.

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 $\pi$-acceptor $CN^-$ implies a stronger $\pi$-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 $^{51}V$-chemical shift in $K[CpV(CO)_3]$ dissolved in $CH_3CN$ 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 $\pi$-$CpV(CO)_4$ in $CH_3CN$. Hence, substitution of CO for the weaker $CN^-$ decreases the chemical shift, an effect which was observed previously in monosubstituted hexacarbonyl-vanadates[4] and[5], 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 $Na_2[\pi\text{-}CpV(CO)_3]$ were not successful. CO substitution in this anion, however, was carried out by UV irradiation of a solution containing

$$[Me_4N]_2[\pi\text{-}CpV(CO)_3] \text{ and } [Me_4N]CN.$$

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

$$Na_2[\pi\text{-}CpV(CO)_3] \text{ and } [Me_4N]Br$$

in liquid ammonia, and from $[Me_4N]Cl$ and KCN in absolute methanol, respectively. $[Me_4N]CN$ is soluble in methanol. From the evaporated solution,

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

| THF | $K[\pi\text{-CpV(CO)}_3\text{(CN)}]$ $CH_3CN$ | Nujol mull | $Na[\pi\text{-CpV(CO)}_3\text{CN}]$ KBr (see ref.[1]) | $\pi\text{-CpV(CO)}_4$ Nujol (ref.[3]) | |
|---|---|---|---|---|---|
| | | 3100 vw | | 3120 w | $\nu_{CH}$ |
| 2075 | | 2063 s | 2092 | | $\nu_{CN}$ |
| 1955 | 1953 | 1945 vs | 1938 | 2027 vs | $\nu_{CO}$ |
| 1845 | 1847 | 1840 vs | 1825 | 1917 vs | $\nu_{CO}$ |
| 1830 | 1830 | 1820 vs | 1782 | | $\nu_{CO}$ |
| | | 1425 m | | 1435 m | $\nu_{CC}$ |
| | | 1005 m | | 1015 m | ip-$\delta_{CH}$ |
| | | 840 (sh), 831 | | | |
| | | 825 (sh), 815 | | 840 s | op-$\delta_{CH}$ |
| | | 800 s | | | |
| | | 629 m | | 625 s | $\delta_{VCO}$ |
| | | 600 s | | 600 s | $\delta_{VCO}$ |
| | | 546 s | | 496 s | $\nu_{V-CO}$ |
| | | 511, 505 m | | 430 m | $\nu_{V-CO}$ |
| | | 478 w, 455 vw | | | $\delta_{VCN}$ |
| | | 435 w, 422 vw | | | $\nu_{V-CN}$ |
| | | 385, 360, 330 (all vw) | | 325 vw | $\nu_{V-Cp}$ |

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 $[Me_4N]_2[\pi\text{-CpV(CO)}_3]$ 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 $[Me_4N]CN$ 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 $[Me_4N]_4[\pi\text{-CpV(CO)}_2\text{CN}]_2$. The emperical composition is analytically cornfirmed.

$C_{16}H_{29}N_3O_2V$

| | | | | |
|---|---|---|---|---|
| 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 $\nu_{CN}$ (2070 $cm^{-1}$) and two $\nu_{CO}$ (1790 and 1679 $cm^{-1}$). Thus, the CO-stretching modes are above those of the starting product $[Me_4N]_2[\pi\text{-CpV(CO)}_3]$ ($\nu_{CO}$ = 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 [V(-I) → V(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 $\pi$-CpV(CO)(CN) moieties. For $Cp_2V_2(CO)_5$, FISCHER and SCHNEIDER report a $\nu_{CO}$ = 1828 $cm^{-1}$ for the bridging carbonyl groups[1]. Taking into account a decrease in $\nu_{CO}$ 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 $\nu_{CO}$ for a possible bridging CO in $[\pi\text{-CpV(CO)}_2\text{CN}]^{4-}$. 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 $\nu_{CN}$ ($B_u$) are expected which again agrees with the experimental data. It should be pointed out, however, that the low $\nu_{CO}$ 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 L. W. HOUK, J. Organometal. Chem. **16**, 425 [1969].
[4] D. REHDER, J. Organometal. Chem. **37**, 303 [1972].
[5] D. REHDER and J. SCHMIDT, J. Inorg. Nucl. Chem. **36**, 333 [1974].