*Journal of Organometallic Chemistry*, 295 (1985) 327–331
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

# OLEFIN COMPLEXES OF VANADOCENE

M. MORÁN, J.J. SANTOS-GARCÍA, J.R. MASAGUER and V. FERNÁNDEZ

*Departamento de Química Inorgánica, Facultad de Ciencias, Universidad Autónoma, Canto Blanco, 28049-Madrid (Spain)*

(Received June 5th, 1985)

## Summary

Oxidative addition of the olefins acrylonitrile, acrolein, crotonaldehyde and methyl vinyl ketone to vanadocene leads to formation of the corresponding metallacycle.

## Introduction

Owing to the important role played by derivatives of titanium and vanadium in processes such as polymerization, hydrogenation or hydroformylation [1,2], some olefin and acetylene derivatives of these elements have been characterized [3–5]. However, the only previously known olefin derivative of vanadium was the complex formed by reaction between dimethylfumarate and vanadocene [6]. On the basis of spectroscopic data [6] and on X-ray diffraction studies [7,8], cyclopropanemetal structure have been proposed for these olefin derivatives.

In this paper we describe the synthesis and characterization of several complexes of vanadocene with activated olefins.

## Results and discussion

Complexes of vanadocene with acrylonitrile, acrolein, crotonaldehyde and methyl vinyl ketone can be readily obtained by addition of the corresponding olefin to an ethereal solution of vanadocene under an inert atmosphere; brown air-sensitive solids immediately separate out. The IR spectra of the products show the characteristic bands of the $\eta^5$-$C_5H_5$ rings at 3100–2900m, 1500–1430m, 1300–1250m, 1040m, 860–820s $cm^{-1}$ [9,10] and the characteristic bands of the CN and CO groups of the coordinated olefins are also observed, as shown in Table 1.

In all cases, the $\nu$(C=C) band, which is in the range 1608–1640 $cm^{-1}$ in the free olefin, disappears upon coordination to the vanadium atom, indicating the formation of a metallacycle. This coordination mode is confirmed in the case of the acrylonitrile by shift of the $\nu$(CN) band to lower frequencies, upon coordination to

TABLE 1

IR ($cm^{-1}$) DATA FOR THE NEW OLEFIN COMPLEXES

| Compound | Olefin | | Complex | |
|---|---|---|---|---|
| | $\nu(C=C)$ | $\nu(CO)$ or $\nu(CN)$ | $\nu(C=C)$ | $\nu(CO)$ or $\nu(CN)$ |
| $Cp_2V(CH_2CHCN)$ | 1608 | 2230 | – | 2162 |
| $Cp_2V(CH_2CHCHO)$ | 1620 | 1702 | – | 1643, 1630 |
| $Cp_2V(CH_3CHCHCHO)$ | 1641 | 1697 | – | 1658, 1614 |
| $Cp_2V(CH_2CHCOCH_3)$ | 1618 | 1683 | | 1640 |

the metal [11]. In the other complexes there is also a shift to lower frequencies of the $\nu(CO)$ bands when the olefin is coordinated to metal. The small shifts (40–50 $cm^{-1}$) observed in these bands relative to those for the free olefin indicate that the CN and CO groups are not directly involved in the coordination to metal. The doublet observed for some of these bands (Table 1) is probably due to solid state interactions [6].

Metallacycle formation is also indicated by a reduction in the number of the unpaired electrons from 3 in the vanadocene to 1 in the synthesized complexes, as shown by the EPR spectra. This decrease can be accounted for in terms of the bonding model presented by Lauher and Hoffman [12] for this type of complex. In this the $\pi$-occupied orbital of the olefin provides a donor orbital which interacts with the $2a_1$ orbital of the metal, while the two electrons which are in the $b_2$ orbital of the metal can be transfered by back donation into the $\pi^*$ empty orbital of the olefin. This back donation interaction results in oxidation of the metal from $V^{II}$ in vanadocene to $V^{IV}$ in the olefin complexes, in which the olefin is bonded to the metal through two $\sigma$ bonds, thus forming the metallacycle. On this picture the unpaired electron is localized in the $a_1$ nonbonding orbital of the metal.

The EPR spectra recorded for $CHCl_3$ solutions at room temperature show eight signals arising from coupling between the unpaired electron with the $^{51}V$ ($I = 7/2$) nucleus. The small $A_{iso}$ values found for these complexes ($41-43 \times 10^{-4}$ $cm^{-1}$) (Table 2), compared with those observed for other complexes of the type $Cp_2VX_2$ (X = Cl, Br, CN, SCN) [13], reflect a higher electronic delocalization in the former series, which is consistent with their metallacycle nature. This decrease in the $A_{iso}$ values is consistent with the high values observed for $g_{iso}$ (see Table 2), in the light of the decrease in the spin-orbit contribution when the electronic delocalization is increased. The narrow range observed for the values of the isotropic hyperfine coupling constants in the complexes we have studied indicates that the olefin is bonded in a similar way to the vanadocene in all cases.

The EPR spectra obtained at liquid nitrogen temperature in frozen solutions of mixtures of $CHCl_3$/EtOH, are anisotropic, and present two groups of eight well defined signals and a third set which is poorly resolved, but which can be calculated using the following expressions: $g_{iso} = 1/3\,(g + g_y + g_z)$ and $A_{iso} = 1/3\,(A_x + A_y + A_z)$. The calculated values for the three components of the $g$ and $A$ tensors, are indicated in Table 2.

Because of the close similarity between these EPR spectra and those found in other vanadium complexes, such as $Cp_2VL_2$ [13], of $C_{2v}$ symmetry, we used the same coordinate system, in which $A_x$ is directed to the olefin molecule and $A_y$ is

TABLE 2

EPR PARAMETERS FOR THE $Cp_2V$(olefin) COMPLEXES (hyperfine coupling, $kP$, and $P$ in units of $10^4$ $cm^{-1}$)

| Compound | $A_{iso}$ | $g_{iso}$ | $-A_x$ | $-A_y$ | $-A_z$ | $g_x$ | $g_y$ | $g_z$ | $a^2$ | $b^2$ | $kP$ | $P$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $(\eta\text{-}C_5H_5)_2V(CH_2CHCN)$ | 41.9 | 1.996 | 58.3 | 71.2 | 18 | 2.006 | 1.981 | 2.002 | 0.994 | 0.01 | 43 | 74 |
| $(\eta\text{-}C_5H_5)_2V(CH_2CHCHO)$ | 43.3 | 1.997 | 61.3 | 71.4 | 20 | 2.007 | 1.982 | 2.002 | 0.997 | 0.01 | 45 | 76 |
| $(\eta\text{-}C_5H_5)_2V(CH_3CHCHCHO)$ | 41.6 | 1.996 | 55.3 | 71.6 | 18 | 2.007 | 1.981 | 2.002 | 0.992 | 0.008 | 47 | 80 |
| $(\eta\text{-}C_5H_5)_2V(CH_2CHCOCH_3)$ | 41.5 | 1.997 | 56.3 | 71.6 | 18 | 2.007 | 1.982 | 2.002 | 0.993 | 0.007 | 46 | 79 |

perpendicular to the plane of the metallacycle. In agreement with the bond scheme previously indicated, the fundamental electronic state consists of a mixture of two or more $d$ orbitals, and can be represented by $\psi_0 = a\, d_{z^2} + b\, d_{x^2-y^2}$, where $a$ and $b$ are the mixture coefficients.

The parameters of the low temperature EPR spectra can be analyzed by the equations described by Evans [14], which give the $a$, $b$, $P$ and $K$ values. The hyperfine parameter $P = g_0\ g_n\ \gamma_e\ \gamma_n\ \langle r^{-3} \rangle$ gives direct information about the electronic delocalization and the covalency; $K$ is the spin polarization parameter which is related to $A_{\text{iso}}$ by the equation $A_{\text{iso}} = -KP + (g_{\text{iso}} - g_e)P$. The calculated values for $a$, $b$, $P$ and $K$ are listed in Table 2 and it will be seen that the $P$ values vary between $74$–$80 \times 10^{-4}\ \text{cm}^{-1}$, compared with the $P$ value of $172 \times 10^{-4}\ \text{cm}^{-1}$ for a free $V^{4+}$ ion, indicating that the unpaired electron is 42–46% localized on the metal; this suggests that there is extensive electronic delocalization or a large degree of covalent character in the vanadium–olefin bonds.

The observed values for $a^2$ and $b^2$ indicate that the unpaired electron is localized in a $d_{z^2}$ orbital. Furthermore, the $a^2$ value for the complexes is significantly higher than the one obtained for $Cp_2VCl_2$ ($a^2 = 0.96$, $b^2 = 0.25$ [15]), which indicates that the contributions of the $d_{z^2}$ and $d_{x^2-y^2}$ orbitals to the ground state depend on the type of ligand. Thus with $\pi$-acceptor ligands such as the olefins we have studied, higher values of $a^2$, such as those found with $\sigma$ type halide ligands, are observed. This is consistent with a greater overlap between the $\pi$-acceptor orbitals of the ligand and the $d_{z^2}$ orbital, which facilitates the back donation from the metal to the olefin in agreement with the proposed bonding scheme, and also leads to delocalization of the electrons of the vanadium–olefin bond, which contributes to the low values obtained for $P$.

The influence of the various olefin substituents is noteworthy; the largest variations are found in the $A_x$ values ($A_x$ is directed to the coordinated olefin), while $A_y$ and $A_z$ remain practically constant (Table 2). However it is at present not possible to correlate the influence of the olefin substituents with the electronic distribution in the complexes.

## Experimental

All manipulations were carried out under purified nitrogen using Schlenk techniques. Vanadocene was prepared by the usual method [16].

The IR spectra were recorded at 4000–200 $\text{cm}^{-2}$ on a Nicolet 5DX FT-IR spectrophotometer using Nujol and Hostaflon mulls between CsI windows. The EPR spectra were recorded on a Varian E-12 spectrometer at a microwave frequency of 9 GHz (X-band) equipped with a HP 5342 A frequencemeter and a Bruker NMR Gaussmeter. The spectra at low temperature were recorded in a variable temperature cell.

### *Preparation of compounds*

*$(\eta^5\text{-}C_5H_5)_2V(CH_2CHCN)$.* Freshly sublimed $(\eta^5\text{-}C_5H_5)_2V$ (1 g, 5.5 mmol) was dissolved in $Et_2O$ (30 $\text{cm}^3$) under an $N_2$ atmosphere in a 100 ml two-necked flask provided with an $N_2$ inlet, magnetic stirrer, and pressure-equalized dropping funnel, and a solution of acrylonitrile (0.32 g, 6 mmol) in $Et_2O$ (10 $\text{cm}^3$) was added. A brown solid separated immediately. Stirring was continued for 1 h and the solid was

filtered off, washed several times times with $Et_2O$, and dried in vacuo at room temperature. The product is air-sensitive. (Found: C, 65.8; H, 5.3; N, 5.6; V, 21.0. $C_{13}H_{13}NV$ calcd.: C, 66.6; H, 5.5; N, 5.9; V, 21.8%).

*$(\eta^5\text{-}C_5H_5)_2V(CH_2CHCHO)$.* This compound was obtained by the method described above from $(\eta^5\text{-}C_5H_5)_2V$ (1 g, 5.5 mmol) and acrolein (0.33 g, 6 mmol). The brown solid which separates is more air-sensitive than that described above. (Found: C, 65.0; H, 5.1; V, 19.9. $C_{13}H_{14}OV$ calcd.: C, 65.8; H, 5.9; V, 21.5%).

*$(\eta^5\text{-}C_5H_5)_2V(CH_3CHCHCHO)$.* This compound was prepared by a similar procedure from $(\eta^5\text{-}C_5H_5)_2V$ (1 g, 5.5 mmol) and crotonaldehyde (0.42 g, 6 mmol). After the addition of the olefin the violet vanadocene solution turned brown. Subsequent addition of pentane gave a brownish-green precipitate, which was filtered off, washed several times with pentane, and dried in vacuo at room temperature. The compound was air-sensitive. (Found: C, 66.0; H, 6.0; V, 19.8. $C_{14}H_{16}OV$ calcd.: C, 66.9; H, 6.3; V, 20.3%).

*$(\eta^5\text{-}C_5H_5)_2V(CH_2CHCOCH_3)$.* Similarly, 1 g, 5.5 mmol of $(\eta^5\text{-}C_5H_5)_2V$ was dissolved in 40 $cm^3$ of $Et_2O$ and a solution of 0.42 g (6 mmol) of methyl vinyl ketone in 10 $cm^3$ of $Et_2O$ was added. A very air-sensitive dark green, solid was obtained. (Found: C, 65.8; H, 6.0; V, 19.7. $C_{14}H_{16}OV$ calcd.: C, 66.9; H, 6.3; V, 20.3%).

## Acknowledgements

We thank the CAICYT for financial support of this work.

## References

1 R. Tsumara and N. Hagihara, Bull. Chem. Soc. Jpn., 38 (1965) 861.
2 S.D. Ittel and J.A. Ibers, Adv. Organomet. Chem., 14 (1976) 33.
3 G. Fachinetti, C. Floriani, F. Marchetti and M. Meltini, J. Chem. Soc. Dalton Trans., (1978) 1398.
4 H.J. de Liefde Meijer and J. Fellinek, Inorg. Chim. Acta, 4 (1970) 651.
5 D.F. Foust, M.D. Rausch, W.E. Hunter, J.L. Atwood and E. Samuel, J. Organomet. Chem., 197 (1980) 217.
6 G. Fachinetti, S. Del Nero and C. Floriani, J. Chem. Soc. Dalton Trans., (1976) 1046.
7 G. Fachinetti, C. Floriani, A. Chiesa-Villa and C. Guastini, Inorg. Chem., 18 (1979) 2282.
8 J.L. Petersen and L. Griffith, Inorg. Chem., 19 (1980) 1852.
9 H.P. Fritz, Adv. Organomet. Chem., 1 (1964) 239.
10 V.T. Aleksanyan and B.V. Lokshin, J. Organomet. Chem., 131 (1977) 113.
11 S.Y. Bryan, P.G Huggett, K. Wade, J.A. Daniels and J.R. Jenning, Coord. Chem. Rev., 44 (1982) 149.
12 J.L. Lauher and R. Hoffman, J. Am. Chem. Soc., 98 (1976) 1729.
13 A.T. Casey and J.B. Raynor, J. Chem. Soc. Dalton Trans., (1983) 2057.
14 A.G. Evans, J.C. Evans, D.J.C. Espley, P.H. Morgan and J. Mortimer, J. Chem. Soc. Dalton Trans., (1978) 57.
15 J.L. Petersen and L.F. Dahl, J. Am. Chem. Soc., 97 (1975) 6422.
16 R.B. King, Organometallic Synthesis, Vol. 1, 1961, p. 64.