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REACTIONS OF VANADOCENE-CARBYLS WITH CARBON MONOXIDE, XYLYLISOCYANIDE AND CARBON DIOXIDE

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Summary

Vanadocene-allyl $Cp_2V(\eta^1\text{-}C_3H_5)$ (**1a**) reacts with strong π-acceptor substrate ligands such as carbon monoxide, carbon dioxide and isonitriles. No reactions are observed with poorer π-acceptor substrates such as alkynes and nitriles. Reaction of **1a** with CO gives $Cp[\eta^4\text{-}C_5H_5(C_3H_5)]V(CO)_2$, showing that migration of the allylic ligand to one of the Cp rings has taken place. The reaction of **1a** with 2,6-xylylisocyanide gave the very stable complex $Cp_2V[\eta^1\text{-}C(C_3H_5){=}N\text{-}2,6\text{-}(CH_3)_2C_6H_3]$. For other Cp_2VR (R = Me, Ph) compounds formation of this type of insertion product with an η^1-iminoacyl ligand was also observed. A carboxylato complex $Cp_2V[\eta^1\text{-}OC(O)C_3H_5]$ was formed in the reaction of **1a** with CO_2.

Introduction

Extensive investigations on the reactions of bent titanocene derivatives of the type Cp_2TiR [1] prompted a study of similar reactions for Cp_2VR. The electronic situation in the vanadium complexes is that there are two unpaired electrons which occupy low-lying valence orbitals [2] and the difference compared with the titanium complexes, Cp_2TiR, is that these have one unpaired electron and one low-lying empty orbital which can be used in initial adduct formation with a substrate molecule. The absence of a comparable low-lying orbital in Cp_2VR has a pronounced effect on the reactivity and product formation.

We describe in this paper the reactions of $Cp_2V(\eta^1\text{-allyl})$ with carbon monoxide, 2,6-xylylisocyanide and carbon dioxide. The analogous reactions of $Cp_2Ti(\eta^3\text{-allyl})$ have been studied by Klei et al. [3]. They observed, after initial adduct formation, insertion of the substrate in the Ti–R bond and formation of titanium acyl, iminoacyl, and carboxylate compounds. In the reaction with carbon monoxide the acyl compound quickly reacts with unchanged $Cp_2Ti(\eta^3\text{-allyl})$ to give triallylmethanol, $(C_3H_5)_3COH$.

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Results and discussion

With carbon monoxide

A smooth reaction was observed when $Cp_2V(\eta^1\text{-}C_3H_5)$ (**1a**) in pentane was treated with carbon monoxide under ambient conditions. Two vanadium complexes were formed, viz. $Cp[\eta^4\text{-}C_5H_5(C_3H_5)]V(CO)_2$ (**2**) and $Cp_2V(CO)$ (**3**). Identification of **2** as $Cp[\eta^4\text{-}C_5H_5(C_3H_5)]V(CO)_2$ was based on IR and ^1H NMR spectra, and by comparison with the related $Cp[\eta^4\text{-}C_5H_5Ph]V(CO)_2$ (**4**) [4]. Strong $\nu(CO)$ bands at 1867, 1907, 1932 and 1970 cm^{-1} indicate terminal CO ligands. The free terminal double bond of the allyl group is indicated by a $\nu(C{=}C)$ band at 1640 cm^{-1} and a $\delta_{o.o.p.}$ band at 910 cm^{-1}. The ^1H NMR spectrum of **2** is shown in Fig. 1; data are given in the experimental part. It shows a singlet for one Cp ligand at 4.22 ppm. The other resonances are assigned as indicated, and are consistent with the presence of an allyl substituted cyclopentadiene ligand. Complex **3** was identified by comparison (IR) with an authentic sample [5], it probably originates from the carbonylation of vanadocene, formed by thermal decomposition of **1a** under the conditions used [6]. This is supported by the presence of 1,5-hexadiene (0.18 mol/V; GLC) in the reaction mixture, and the fact that a carbonylation of the thermally very unstable 1-methallyl analogue $Cp_2V(\eta^1\text{-}1\text{-methallyl})$ produces nearly exclusively **3** and a mixture of octadienes (GC-MS) [6]. The CO uptake (1.65 mol CO/V) in the reaction of **1a** indicates formation of 65% of **2** and 35% of **3**, and this is in agreement with the amount of 1,5-hexadiene formed.

The formation of **2** in the reaction of **1a** with CO shows that the Cp ligands are chemically active in this system. This unusual migration of allyl from the metal atom to a Cp-ring could well involve an intramolecular concerted process with formation of an "*exo*-H-species". The observed reaction is analogous to the phenyl migration and formation of **4** when Cp_2VPh (**1c**) reacts with CO [4]. The phenylcyclopentadiene complex **4** is thermally less stable than the allylcyclopentadiene derivative **2**; **4** decomposes readily at room temperature with elimination of CO and H_2, while **2** is stable at room temperature and decomposes at 105°C (Differential thermal analysis (DTA)). The "*exo*-H" is obviously more labile in the phenylpenta-

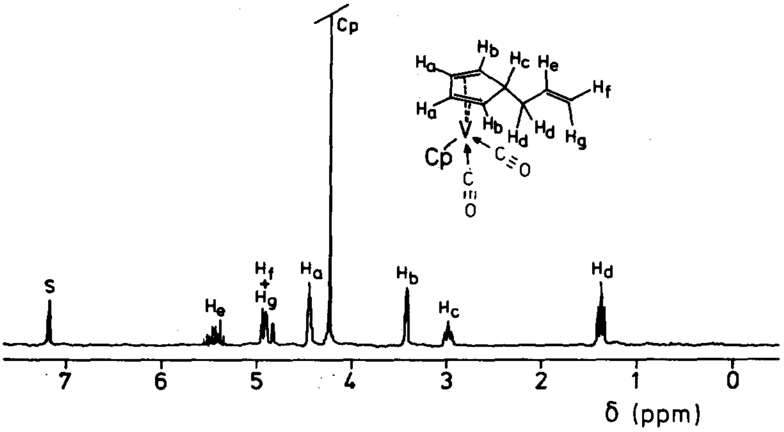


Fig. 1. 200-MHz ^1H NMR spectrum of $Cp[\eta^4\text{-}C_5H_5(C_3H_5)]V(CO)_2$ (**2**) in benzene-d_6 (S).

diene complex **2**, possibly due to formation of a conjugated 12-electron aromatic system $C_5H_4Ph^-$.

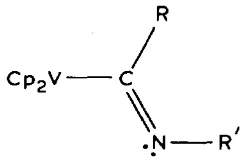
It is noteworthy that a η^1-allyl ligand in this reaction behaves more like a phenyl group than an alkyl group, for there is insertion of CO into the V–C bond and formation of $Cp_2V(COR)(CO)$ complexes [4,7]. The obseved reactivity of **1a** is also quite different from the corresponding titanium complex $Cp_2Ti(\eta^3\text{-}C_3H_5)$. For the latter, insertion of CO to give titanium acyl and subsequent reaction of this species with original titanium allyl bonds results in the formation of triallylmethanol [3].

In a way, the reaction of $CpV(\eta^3\text{-}C_3H_5)_2$ with CO [8] shows a resemblance with the reaction of **1a** with CO. In both reactions diamagnetic V^1 species are formed by a reductive coupling of two ligands, i.e. two allyls to 1,5-hexadiene and Cp with allyl to allylcyclopentadiene, respectively. For $CpV(\eta^3\text{-}C_3H_5)_2$ the 1,5-hexadiene is eliminated, while reaction with excess carbon monoxide leads to $CpV(CO)_4$. In **2** the allylcyclopentadiene remains coordinated, consistent with Fischer's observation that only conjugated dienes and cyclodienes can coordinate in $CpV(diene)(CO)_2$ [9].

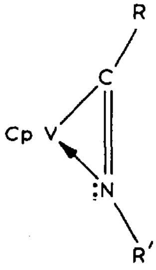
With 2,6-xylylisocyanide (XIC)

Isonitriles, RNC, are iso-electronic with carbon monoxide and often provide good models for the CO reactions. Bulky isonitrile ligands sometimes offer an opportunity to trap intermediate species, so that more information is obtained about the course of the CO reaction.

We investigated the reaction of **1a** with 2,6-xylylisocyanide (XIC). At −80°C in toluene an orange solution was rapidly formed. Upon warming to room temperature the colour gradually changed to brown. After 1 day the IR spectrum revealed the presence of two species in the mixture, viz. a XIC adduct $Cp_2V(\eta^1\text{-}C_3H_5)(XIC)$ (**5a**) and the insertion product $Cp_2V[\eta^1\text{-}C(C_3H_5)\text{=}N\text{-}2,6\text{-}(CH_3)_2C_6H_3]$ (**6a**), which was isolated analytically pure. For the adduct **5a** a strong $\nu(CN)$ band is present at 1965 cm^{-1}, corresponding to a decrease of 150 cm^{-1} relative to the $\nu(CN)$ band of free XIC. This indicates a substantial weakening of the CN bond, caused by an extensive π-back-donation. This effect is apparently smaller than in $Cp_2MR(R'NC)$ ($M = Nb$, Ta; $R =$ alkyl, aryl) where the $\nu(CN)$ band appears in the range 1750–1850 cm^{-1} [10]. These isonitrile complexes are stable towards insertion, probably due to the strong metal–isocyanide bond, i.e. a larger contribution from the carbene resonance structure. For vanadium, slow insertion with formation of the iminoacyl complex **6a** is observed. This result led us to look at the reaction of Cp_2VMe (**1b**) and Cp_2VPh (**1c**) with XIC. Also here iminoacyl complexes of the type $Cp_2V[\eta^1\text{-}C(R)\text{=}N\text{-}2,6\text{-}(CH_3)_2C_6H_3]$ (**6b**, $R = Me$; **6c**, $R = Ph$) were formed, showing the surprisingly identical behaviour of all types of Cp_2VR compounds in this reaction (see Scheme 1).



(A)



(B)

The IR spectra of **6** show a ν(CN) band at 1560 for **6a**, at 1555 for **6b** and at 1556 cm^{-1} for **6c**, a range which is generally considered to be characteristic for η^1-coordination of iminoacyl ligands [11]. Additional evidence for η^1-coordination in the complexes **6** is obtained from ^{1}H NMR spectra, which clearly show them to be paramagnetic. This indicates that the iminoacyl ligands act as one electron ligands resulting in 16-electron species (**A**) with two unpaired electrons, whereas for an η^2-coordinated iminoacyl a diamagnetic 18-electron system (**B**) is expected.

As an example the ^{1}H NMR spectrum (19°C) of **6b** is shown in Fig. 2. The Cp protons are observed at -134.5 ppm, in the range found for trivalent bent-vanadocene derivatives [12]. The α-CH_3 protons appear at -41.6 ppm. The xylyl protons are clearly identified by the changes in their isotropic shift when the temperature is raised to 69°C (see Fig. 2). The aromatic protons *m*-H and *p*-H shift towards their "diamagnetic" position near -7 ppm and the methyl protons shift upfield towards the -2 ppm region. The observed alternation of isotropic shift signs and the comparable magnitudes of these shifts indicate a strong π-delocalization in the xylyl group.

To investigate possible sterical influences in the coordination mode of iminoacyl ligands, we monitored the reaction of **1b** with excess of CH_3NC by NMR spectroscopy. Only one paramagnetic product was observed with a Cp signal at -134 ppm and two CH_3 signals at -91 and -22 ppm. It is clear that again an η^1-iminoacyl ligand is present, and since the $C(CH_3)$=N–CH_3 ligand is small, it is probable that electronic effects are the main influence on the coordination mode. Probably the pairing energy cannot be balanced by the energy gain obtained on coordination of the nitrogen atom of the iminoacyl ligand.

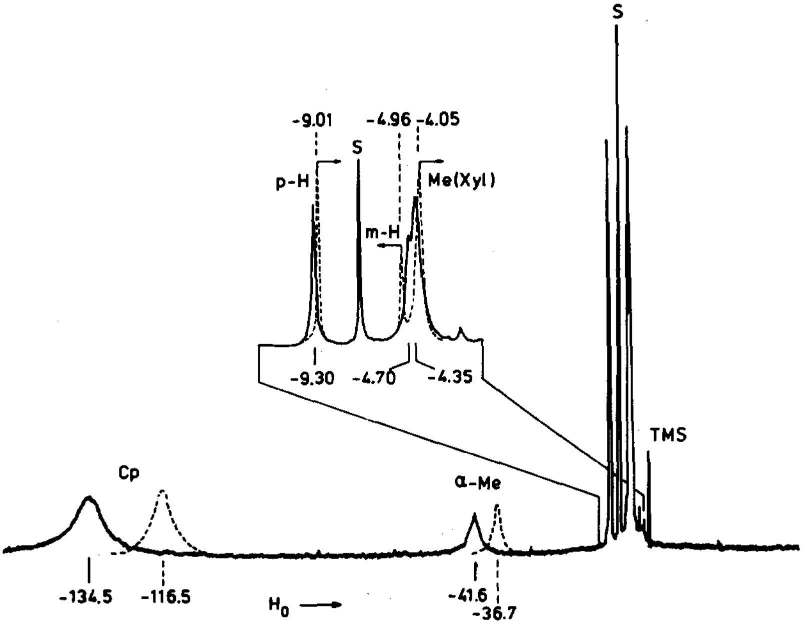


Fig. 2. 200-MHz ^{1}H NMR spectrum of $Cp_2V[\eta^1$-$C(CH_3)$=N-2,6-$(CH_3)_2C_6H_3]$ (**6b** at 19 and at 69°C (dashed line); insert represents expanded version of the spectrum from -0.5 to -11 ppm. S = benzene-d_6.

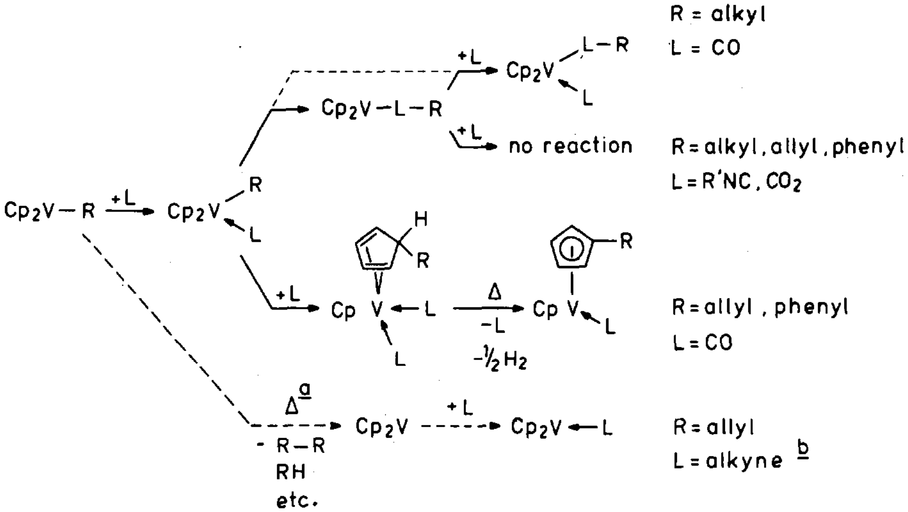
With carbon dioxide

Vanadocene-allyl **1a** reacts slowly with carbon dioxide in toluene under ambient conditions. The blue carboxylato complex $Cp_2V[\eta^1\text{-}OC(O)C_3H_5]$ (7) was formed in about 80% yield; thermal decomposition of **1a** prevented higher yields being obtained.

The IR spectrum shows the terminal double bond absorptions at 1640 and 910 cm^{-1}. The strong and broad asymmetric and symmetric $\nu(OCO)$ bands are observed at 1605 and 1330 cm^{-1}, respectively. This large separation (275 cm^{-1}) indicates an η^1-coordination mode of the carboxylato ligand [13]. The ^{1}H-NMR spectrum is also in agreement with an η^1-coordination mode, i.e. 7 is a paramagnetic 16-electron species, analogous to the iminoacyl compounds, whereas η^2-coordination would give a diamagnetic compound. At 19°C the Cp resonance is observed at -122 ppm. Four remaining resonances are observed in the range -4 to -9 ppm, and are assigned to the allylic protons. It should be noted that, in contrast to the η^1-bonding of the carboxylate group in 7, all known analogous titanium complexes have η^2-carboxylato ligands [1h,i,3,14]. It is also remarkable that the η^3-bonded allyls in the related trivalent vanadium compound $CpV(\eta^3\text{-}C_3H_5)_2$ are much less reactive towards CO_2. A slow reaction was observed at higher pressure (60 bar), mainly resulting in species with bridging carboxylato ligands [8]. This clearly demonstrates the enhanced reactivity of η^1- relative to η^3-bonded allyl ligands.

Concluding remarks

It was shown that vanadocene-allyl **1a** reacts with several small substrate molecules with retention of the allyl ligand in the product. The reaction modes for vanadocene-carbyls $Cp_2V(\eta^1\text{-}R)$ observed up to now are outlined in Scheme 1.



SCHEME 1. [a] See ref. 15; [b] due to thermal lability of **1a** reactions with substrates like alkynes can be considered as reactions with the thermal decomposition product vanadocene; see ref. 16.

Compounds of the type $Cp_2V(\eta^1\text{-}R)$ are 16-electron d^2 systems. They are paramagnetic compounds with a triplet ground state. The two unpaired electrons occupy an essentially non-bonding a_1 orbital and an anti-bonding b_1 orbital with a narrow energy gap of 0.3 to 0.6 eV [2b]. This narrow gap makes spin-pairing in these complexes unfavourable.

Adduct formation with a substrate molecule L to form Cp_2VRL is thought to be the first step in the reactions of Cp_2VR. An empty low-lying orbital must be available for donation of an electron-pair from the substrate molecule to vanadium; this can be provided by spin-pairing of the a_1 and b_1 electron. However, substantial back-donation must occur to make this unfavourable process possible. Carbon monoxide, carbon dioxide and isonitriles clearly possess sufficient acceptor properties. It should be noted that nitriles do not react with Cp_2VR (R = alkyl) [17] and this is clearly related to their limited acceptor properties.

The second step in the reaction can be regarded as migration of R to the substrate (or insertion of substrate into the V–R bond), as observed for isonitriles and carbon dioxide, or for carbon monoxide with R = alkyl. Alternatively activation of Cp and migration of R to Cp occurs for carbon monoxide with R = allyl or phenyl. The species formed are again 16-electron systems, which can be stabilized by unpairing of the a_1 and b_1 electrons. In all CO reactions a second CO molecule can add, again inducing spin-pairing and formation of diamagnetic 18-electron species. No further reactions were observed with an excess of isonitrile or CO_2.

The built-in donor atoms iminoacyl-nitrogen and carboxylato-oxygen clearly lack sufficient acceptor properties to induce spin-pairing and hence η^2-coordination is not observed.

The effect of spin-pairing can also be seen from a comparison with isoelectronic Cp_2TaR systems, where the energy loss by spin-pairing is much smaller than for vanadium. This is reflected in the very strong metal–ligand interactions. Diamagnetic (spin-paired) species are readily formed, e.g. stable nitrile adducts or the diamagnetic hydride-olefin form of Cp_2TaR (R = alkyl) [18].

Experimental

General

All reactions were performed under rigorously oxygen free nitrogen using Schlenk and glove box techniques. All solvents were distilled from sodium or sodium-potassium melts before use. Vanadocene derivatives **1a** [19], **1b** [20], **1c** [20] and **3** [5] were obtained by published procedures. Carbon monoxide and carbon dioxide were purchased from Matheson and were used without purification. The 2,6-xylylisocyanide was prepared as described by Shingaki and Takebayashi [21] and purified by sublimation before use.

Physical measurements

IR spectra were recorded on a JASCO-IRA-2 or a Pye Unicam SP3-300 spectrophotometer. Samples were examined as mulls in Nujol between KBr discs. ^1H NMR spectra were obtained in benzene-d_6 with a Nicolet NT 200 spectrometer, equipped with a Nicolet model 1180 data system. As usual, chemical shifts downfield of Me_4Si internal reference are shown as negative. Differential thermal analysis (DTA) was performed on solid samples using a heating rate of 2–3°C/min. GLC was performed with a Packard-Becker 428 GC instrument, using a 25m × 0.24 mm (i.d.) glass capillary column, coated with SE30. Gas uptakes were measured with a gas burette equipped with a photosensor and an automatic relay control circuit for maintaining constant pressure in the system by use of a motor-driven gastight syringe (50 ml). Elemental analyses were performed at the Micro Analytical Department of the Chemical Laboratories of Groningen University.

$Cp[\eta^4\text{-}C_5H_5(C_3H_5)]V(CO)_2$ (2)

A solution of 0.980 g (4.40 mmol) of **1a** in 75 ml of pentane was stirred under carbon monoxide for 16 h under ambient conditions (uptake 1.65 CO/V). The colour of the solution slowly changed from green to brown-yellow. The solution was concentrated to 10 ml and transferred to a Florisil column. Elution with pentane and ether gave a red solution, from which **2** was crystallized at −20°C (**3** was not eluted). Yield 0.69 g (56%); DTA m.p. 18°C, dec. 105°C; IR ν(CO) at 1867, 1907, 1932 and 1970 cm^{-1}; ^{1}H-NMR (C_6D_6) δ 4.22 (s, $\eta^5\text{-}C_5H_5$), 4.44 (m, $C\mathit{H}{=}CHCHRCHC\mathit{H}$, R = $CH_2CH{=}CH_2$), 3.44 (m, $CH{=}C\mathit{H}CHRC\mathit{H}{=}CH$), 2.98 (t, J(HH) 6.6 Hz, t, J(HH) < 0.5 Hz, $CH{=}CHC\mathit{H}RCH{=}CH$), 1.38 (d, J(HH) 6.6 Hz, d, J(HH) 7.1 Hz, $C_5H_5C\mathit{H}_2CH{=}CH_2$), 5.44 (t, J(HH) 7.1 Hz, d, J(HH) 16.8 Hz, d, J(HH) 10.3 Hz, $C_5H_5CH_2C\mathit{H}{=}CH_2$), 4.9 (overlapping m, $C_5H_5CH_2CH{=}C\mathit{H}_2$), cf. Fig. 1.

$Cp_2V[\eta^1\text{-}C(C_3H_5){=}N\text{-}2,6\text{-}(CH_3)_2C_6H_3]$ (6a)

To a stirred solution of 0.494 g (2.22 mmol) of **1a** in 20 ml of toluene 0.292 g (2.23 mmol) of 2,6-xylylisocyanide was added at −80°C. Upon warming to room temperature the red solution slowly turned dark. After another 2 h stirring the solvent was removed in vacuo. The product was washed twice with 25 ml of pentane to remove **5a** completely (no ν(CN) band at 1965 cm^{-1} in IR). The resulting black solid was recrystallized from 25 ml of toluene by slowly condensing 50 ml of pentane on to it. Black **6a** was isolated in 30% yield. Elemental analysis found (calcd. for $C_{22}H_{24}NV$) in %: V, 14.41 (14.42); C, 74.26 (74.78); H, 6.87 (6.85); N, 4.02 (3.96); DTA dec. 148°C.

The complexes **6b** and **6c** were prepared from **1b** and **1c** respectively in essentially the same way as **6a**.

Yield of **6b** 56%; Elemental analysis found (calcd. for $C_{20}H_{22}NV$) in %: V, 15.31 (15.56); C, 73.60 (73.38); H, 4.32 (4.28); DTA m.p. 137°C, dec. > 180°C; ^{1}H-NMR (C_6D_6, 19°C) H_0(ppm) −134.5 (Cp), −41.6 (α-CH_3), −9.30 (m-H), −4.70 (p-H), −4.35 (xyl-CH_3).

Yield of **6c** 44%; Elemental analysis found (calcd. for $C_{25}H_{24}NV$) in %: V, 13.28 (13.08); C, 77.26 (77.11); H, 6.28 (6.21); DTA m.p. 160°C, dec. 171°C; μ_{eff} 2.86 (calcd. for two unpaired electrons 2.83).

$Cp_2V[\eta^1\text{-}OC(O)C_3H_5]$ (7)

A solution of 0.257 g (1.15 mmol) of **1a** in 6 ml of toluene was stirred at room temperature under carbon dioxide. For measurement of CO_2 uptake the solvent in the gas burette was previously saturated with CO_2. After 24 h an uptake of 0.948 mmol (82%) of CO_2 had occurred. The solvent was then removed in vacuo, and the resulting blue solid extracted with 20 ml of pentane. Slow cooling to −80°C gave 0.116 g (38%) of the purple-blue **7**.

Elemental analysis found (calcd. for $C_{14}H_{15}O_2V$) in %: V, 19.45 (19.14); C, 62.98 (63.16); H, 5.79 (5.68); DTA m.p. 48°C, dec. 95°C; IR ν(OCO) at 1605 and 1330 cm^{-1}; ^{1}H-NMR (C_6D_6, 18°C) H_0 (ppm) −121 (Cp), −8.60, −7.35, −5.10 and −4.10 (C_3H_5).

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