Journal of Organometallic Chemistry, 265 (1984) 249–255
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

SYNTHESIS AND CRYSTALLOGRAPHIC CHARACTERIZATION OF A DICYCLOPENTADIENYLVANADIUM ALKYNIDE COMPLEX: $(C_5H_5)_2VC{\equiv}CC(CH_3)_3$

WILLIAM J. EVANS* *, IRA BLOOM and ROBERT J. DOEDENS*

Department of Chemistry, University of California, Irvine, California 92717 and University of Chicago, Chicago, Illinois 60637 (U.S.A.)

(Received September 19th, 1983)

Summary

$(C_5H_5)_2VCl$ reacts with $LiC{\equiv}CC(CH_3)_3$ to form $(C_5H_5)_2VC{\equiv}CC(CH_3)_3$ which was characterized by spectroscopic, analytical, and crystallographic methods. The complex crystallizes from pentane at 0°C as a monomer in the orthorhombic space group *Pnma* with four molecules in a unit cell of dimensions a 9.075(3), b 9.807(3), c 16.444(5) Å. Full-matrix least-squares refinement based upon 1300 nonzero intensity data converged to a final conventional R factor of 0.060. The molecule has a mean $V{-}C_5H_5$-ring centroid distance of 1.941 Å with 146.6° ring centroid-V-ring centroid angle. The vanadium alkynide carbon distance is 2.075(5) Å.

Introduction

As part of our general investigation of the chemistry of the lanthanide carbon bond [1], we have found that alkynide ligands, particularly 3,3-dimethylbutynide, $C{\equiv}CC(CH_3)_3$, give complexes with interesting chemical and structural features [2–4]. The alkynide moiety in the complexes $[(C_5H_4R)_2LnC{\equiv}CC(CH_3)_3]_2$ ($R = H$, $Ln = Er$; $R = CH_3$, $Ln = Yb$) constitutes a strong bridging ligand which stabilizes these molecules as dimers [3]. For example, these alkynide complexes remain dimeric even in the presence of oxygen donor atom solvents (e.g. THF) which usually convert organometallic dimers of the oxophilic lanthanides to monomeric solvated species [5]. However, the alkynide ligand in $[(CH_3C_5H_4)_2SmC{\equiv}CC(CH_3)_3]_2$ is reactive enough to participate in metallation reactions (eq. 1) [4].

$$[(CH_3C_5H_4)_2SmC{\equiv}CC(CH_3)_3]_2 + 2HP(C_6H_5)_2 \rightarrow 2(CH_3C_5H_4)_2SmP(C_6H_5)_2 + 2HC{\equiv}CC(CH_3)_3 \qquad (1)$$

---

* Camille and Henry Dreyfus Teacher-Scholar; Alfred P. Sloan Research Fellow; to whom correspondence should be addressed at the University of California, Irvine, California 92717.

Structurally, the bridging alkynide ligands in $[(C_5H_4R)_2LnC{\equiv}CC(CH_3)_3]_2$ display unusual asymmetry in the Ln–C≡C and Ln′–C≡C angles [3,4].

We were interested in comparing these lanthanide alkynides with analogous bis(cyclopentadienyl) transition metal alkynides both to more fully define the special properties of the lanthanides and to explore further the potential of the $C{\equiv}CC(CH_3)_3$ ligand in organometallic chemistry. Relatively few $(C_5H_5)_2MC{\equiv}CR$ complexes (M = transition metal) are available for comparison and even fewer have been structurally characterized. The titanium example of this class, $[(C_5H_5)_2TiC{\equiv}CC_6H_5]_2$ [6], has a structure [7] substantially different from a simple alkynide complex: the alkynide groups undergo oxidative coupling to form a 1,4-diphenylbutadiene ligand. A vanadium example, $(C_5Me_4Et)_2VC{\equiv}CC_6H_2Me_3$, (II) has been structurally characterized, but how this peralkylated derivative compared with simple cyclopentadienyl analogs was uncertain [8,9]. In that study [8], the C_5H_5 analog was reported to decompose at 25°C and peralkylation of the ring was deemed necessary to stabilize the thermolabile vanadium carbon single bond [9]. The synthesis of $(C_5H_5)_2VC{\equiv}CC_6H_5$ (III) has been reported [6], but decomposition of III in solution made it difficult to fully purify the crystalline product. Subsequent attempts to synthesize III as well as the dimer $(C_5H_5)_2VC{\equiv}CC_6H_4C{\equiv}CV(C_5H_5)_2$ in pure form were unsuccessful due to the thermal lability of the V–C bond [10,11]. In the latter studies, the importance of alkylating the cyclopentadienyl ring to obtain stable $(ring)_2V{-}C$ complexes was reiterated as both peralkylated derivatives $(C_5Me_4Et)_2VC{\equiv}CC_6H_5$ (IV) and $(C_5Me_4Et)_2VC{\equiv}CC_6H_4C{\equiv}CV(C_5Me_4Et)_2$ (V) were synthesized and found to be stable.

We report here the synthesis and X-ray crystal structure of $(C_5H_5)_2VC{\equiv}CC(CH_3)_3$ (I) a prototypical nonbridged $(C_5H_5)_2MC{\equiv}CR$ complex with simple cyclopentadienyl ligands. This study provides structural information on this class of transition metal alkynides and on the vanadium carbon single bond, for which very little structural data exist [9,10,12,13].

Experimental

The complex described below is extremely air- and moisture-sensitive. Therefore, both the synthesis and subsequent manipulations of this compound were conducted with rigorous exclusion of air and water using Schlenk, vacuum line, and glove box (Vacuum/Atmospheres HE-43 Dri-Lab) techniques. THF was distilled from potassium benzophenone ketyl. Pentane was washed with sulfuric acid, dried over $MgSO_4$, refluxed over finely-divided $LiAlH_4$ and vacuum transferred. $LiC{\equiv}CC(CH_3)_3$ was made from $t\text{-}C_4H_9Li$ and 3,3-dimethylbut-1-yne (Chemical Samples) which was dried over Linde 4A molecular sieves which had been heated under vacuum. VCl_3 (Aldrich) was used as received and converted to $(C_5H_5)_2VCl$ by the method of Manzer [14] using sublimed TlC_5H_5 (Aldrich). Infrared spectra were obtained as Nujol mulls on NaCl plates contained in an O-ring sealed Barnes Presslok holder. The IR measurements were obtained on a Perkin–Elmer 283 spectrometer. The mass spectrum was obtained on a Finnegan 105 mass spectrometer. Elemental analysis was obtained from Analytische Laboratorien, Engelskirchen, West Germany. Magnetic moment data were obtained by the Evans method on a Bruker HX-270 NMR spectrometer [15].

$(C_5H_5)_2VC\equiv CC(CH_3)_3$

A solution of $LiC\equiv CC(CH_3)_3$ (0.125 g, 1.42 mmol) in THF (3 ml) was added dropwise from a Schlenk addition funnel to freshly-sublimed $(C_5H_5)_2VCl$ (0.292 g, 1.42 mmol) suspended in pentane (50 ml) in a 100 ml Schlenk flask cooled to 0°C. Upon addition of the lithium reagent, the magnetically-stirred solution immediately turned green and more of the $(C_5H_5)_2VCl$ dissolved. The reaction mixture was stirred for 2 h and the solvent removed in vacuo. In the glove box, the solids were extracted with pentane and the extract was filtered through a fine frit. Removal of solvent from the green filtrate gave the crude product as brown needles (0.281 g). Recrystallization from pentane at 0°C over a 2 day period gave black needles of I (0.100 g, 0.4 mmol, 28%). Anal. Found for I: V, 19.40; C, 73.30; H, 7.30. $VC_{16}H_{19}$ calcd.: V, 19.30; C, 73.25; H, 7.30%. IR (Nujol, cm^{-1}): 3075w, 2250w, 1830w, 1810w, 1750br, 1700w, 1600w, 1365sh, 1350s, 1200m, 1120m, 1070m, 1020m, 1005m, 870m, 850m, 840m, 800s, 770m. Magnetic susceptibility (299 K): χ_g 13.2×10^{-6} ($\mu_{eff} = 2.89$ μ_B). Mass spectrum: M^+ at 262 m/e.

Collection and reduction of X-ray data

The general procedures followed in data collection and processing have been described [16]. Data were collected from a crystal of approximate dimensions $0.3 \times 0.3 \times 0.7$ mm mounted under an inert atmosphere in a glass capillary. Refined cell parameters were obtained from the settings of 15 reflections with $30° \leq 2\theta \leq 35°$. Orthorhombic symmetry was suggested by interaxial angles and confirmed by axial rotation photography. Systematic absences ($0kl$, $k + l \neq 2n$; $hk0$, $h \neq 2n$) corresponded to space groups $Pnma$ and $Pn2_1a$ (nonstandard setting of $Pna2_1$). Crystal data are summarized in part A of Table 1. Data were collected by the θ-2θ scan technique in bisecting geometry. Experimental parameters are listed in part B of Table 1. Four reflections which exceeded the valid range of the coincidence correc-

TABLE 1

CRYSTAL DATA AND EXPERIMENTAL PARAMETERS

A. Crystal data			
Formula	$(C_5H_5)_2VC\equiv CC(CH_3)_3$	Vol	1463.4(8) Å^3
Fw.	262.27	Z	4
a	9.075(3) Å	d(calcd),	1.19 g cm^{-3}
b	9.807(3) Å	Space group	$Pnma$
c	16.444(3) Å	μ(Mo-K_α)	6.9 cm^{-1}

B. Experimental parameters	
Radiation	Mo-K_α; $\lambda(K_\alpha) = 0.71073$ Å graphite-monochromator
Temp.	22°C
Receiving aperture	circular, 4-mm diam, 20 cm from crystal
Scan rate, deg min^{-1}	variable, 2-19.5
Scan range	$-1.1°$ from K_{α_1} to $+1.2°$ from K_{α_2}
Bkgd counting	estimated from 96-step peak profile
2θ (max)	55°
Data collected	1796
Data with $F_o^2 > 3\sigma(F_o^2)$	1300
Decay of standards	< 3%
Final R	0.060
Final R_w	0.085

tion were remeasured at a lower filament current. Four standard reflections were monitored after every 50 data. The p factor in the expression [17] for the standard deviation of the observed intensities was given a value of 0.05. No absorption correction was made. All computations were carried out with a local version of the UCLA Crystallographic Computing Package [18].

Structure solution and refinement

Intensity statistics did not provide a conclusive discrimination between the centrosymmetric and noncentrosymmetric space group alternatives. The successful solution and refinement of the structure in the centrosymmetric group *Pnma* indicates that, within experimental error, this is the appropriate space group choice. The space group requires the molecule to possess crystallographic symmetry, a requirement which is realized by the presence of a molecular mirror plane. Solution of the structure was achieved by Patterson and difference Fourier methods. Refinement was carried out by full-matrix least squares methods with anisotropic temperature factors for all nonhydrogen atoms and with cyclopentadienyl hydrogen atoms included at fixed positions (idealized trigonal geometry; C–H 0.95 Å). A final difference Fourier map showed no anomalous features and a maximum peak height of 0.8 e $Å^{-3}$. In the final refinement cycle, all parameter shifts were less than the corresponding estimated standard deviations. In all structure factor calculations, atomic scattering factors were taken from ref. 19.

Discussion

The reaction of $(C_5H_5)_2VCl$ with $LiC{\equiv}CC(CH_3)_3$ in THF/pentane at 0°C forms a green solution. Removal of solvent after 2 h, extraction of the brown solid with pentane, and removal of the pentane generates the crude product as brown needles. Recrystallization of this material from pentane at 0°C gives analytically pure, lustrous black crystals of I. $(C_5H_5)_2V$ is also formed as a by-product, but since it is more soluble it remains in the mother liquor. The mass spectrum and complete elemental analysis of I indicated the composition $(C_5H_5)_2VC{\equiv}CC(CH_3)_3$. A weak absorption at 2075 cm^{-1} in the infrared spectrum was consistent with an alkynide $\nu(C{\equiv}C)$ stretch, although this band was much weaker than the 2025 cm^{-1} absorption of $LiC{\equiv}CC(CH_3)_3$ and the 2040–2050 cm^{-1} absorptions of $[(C_5H_5)_2LnC{\equiv}CC(CH_3)_3]_2$ (Ln = Er, Y) and $[(CH_3C_5H_4)_2LnC{\equiv}CC(CH_3)_3]_2$ (Ln = Sm, Y, Yb) [2–4]. III and IV have IR absorptions at 2060 and 2040 cm^{-1}, respectively.

I crystallizes in the orthorhombic space group *Pnma* as a monomer (Fig. 1). Important structural parameters are given in Tables 2–4. The vanadium atom and carbon atoms 1,2,3,5,8, and 9 all lie in the crystallographic mirror plane. The mean vanadium cyclopentadienyl–ring-centroid distance, 1.941 Å, is similar to the analogous distances in $(C_5H_5)_2VCl$, (VI), [20], 1.946(7) Å. Distances of 1.965 Å average and 1.975(15) Å were found in $[(CH_3C_5H_4)_2V]_2C_6H_4$, (VII) [10], and in II [9], respectively. The ring centroid–V–ring centroid angles are: I, 146.6°; II, 149.7°; VII, 146.2°; VI, 139.5(3)°.

The only vanadium carbon single bond lengths available for comparison of the vanadium(III) carbon bond length in I, 2.075(5) Å, are the vanadium(III) alkynide bond in II, 2.03(1) Å, the vanadium(III) aryl bonds in VII, 2.125(11) and 2.154(10) Å [10], and the vanadium(IV) aryl bonds in $V(mesityl)_4$, (VIII) [16], 2.071(8)–2.095(7)

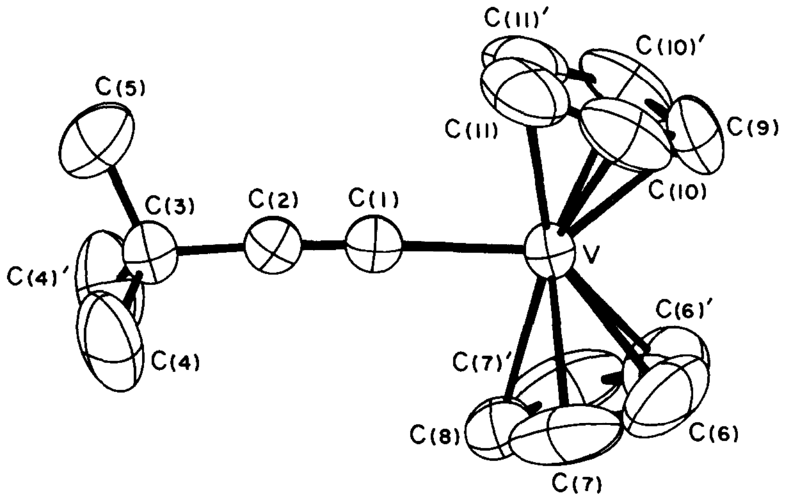

Fig. 1. A view of the molecular structure of $(C_5H_5)_2VC{\equiv}CC(CH_3)_3$. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity.

Å. The V–C distances in I and VII follow the trend that metal alkynide bonds are generally shorter than metal aryl bonds. This trend and the fact that V^{III}–R bonds would be expected to be longer than V^{IV}–R bonds for a given R rationalize the similarity of V–C distances in I and VIII. The fact that the V–C distance in I is greater than that in II is not consistent with simple electrostatic arguments. However, since the two crystal structures were not done at the same temperature, this difference may not be significant [21].

TABLE 2

ATOMIC POSITIONAL PARAMETERS FOR $(C_5H_5)_2VC{\equiv}CC(CH_3)_3$

Atom	*x*	*y*	*z*
V	0.0343(.9)	0.25	0.0755(.5)
C(1)	0.1857(5)	0.25	−0.0190(3)
C(2)	0.2766(6)	0.25	−0.0707(3)
C(3)	0.3958(6)	0.25	−0.1322(3)
C(4)	0.4914(6)	0.3800(7)	−0.1207(3)
C(5)	0.3321(10)	0.25	−0.2171(4)
C(6)	0.0599(7)	0.1835(8)	0.2049(3)
C(7)	0.1771(9)	0.1393(6)	0.1676(3)
C(8)	0.2544(9)	0.25	0.1414(5)
C(9)	−0.2117(8)	0.25	0.0923(5)
C(10)	−0.1732(5)	0.1354(5)	0.0432(4)
C(11)	−0.1145(5)	0.1837(6)	−0.0265(3)
H(6)	−0.0150	0.1252	0.2280
H(7)	0.2094	0.0471	0.1592
H(8)	0.3433	0.25	0.1080
H(9)	−0.2524	0.25	0.1467
H(10)	−0.1859	0.0401	0.0567
H(11)	−0.0775	0.1283	−0.0710

TABLE 3

ANISOTROPIC THERMAL PARAMETERS[a] ($\times 10^3$)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
V	43(0.5)	41(0.4)	46(0.5)	0	4(0.4)	0
C(1)	45(3)	52(3)	46(2)	0	−1(2)	0
C(2)	46(3)	57(3)	50(3)	0	−1(2)	0
C(3)	48(3)	62(3)	56(3)	0	8(2)	0
C(4)	93(4)	94(4)	143(5)	−35(3)	50(4)	−22(4)
C(5)	107(7)	225(12)	49(4)	0	−4(4)	0
C(6)	141(6)	157(7)	66(3)	−41(5)	−9(3)	44(3)
C(7)	168(7)	100(4)	94(5)	62(5)	−66(5)	−22(4)
C(8)	63(5)	284(17)	47(4)	0	−11(3)	0
C(9)	48(4)	159(9)	89(5)	0	22(3)	0
C(10)	51(2)	55(2)	161(5)	−15(2)	−17(3)	17(3)
C(11)	58(3)	119(4)	108(4)	−4(3)	−25(2)	−30(3)

[a] The form of the anisotropic temperature factor is $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}h\,k\,a^*b^* + 2U_{13}h\,l\,a^*c^* + 2U_{23}k\,l\,b^*c^*)]$.

TABLE 4

BOND DISTANCES AND ANGLES

(a) Distances (Å)			
V–C(1)	2.075(5)	C(1)–C(2)	1.191(7)
V–C(6)	2.237(5)	C(2)–C(3)	1.474(7)
V–C(7)	2.269(5)	C(3)–C(4)	1.554(6)
V–C(8)	2.272(5)	C(3)–C(5)	1.510(9)
V–C(9)	2.249(7)	C(6)–C(6)′ [b]	1.305(15)
V–C(10)	2.257(4)	C(6)–C(7)	1.302(10)
V–C(11)	2.249(4)	C(7)–C(8)	1.363(9)
V–RC(1) [a]	1.927	C(9)–C(10)	1.428(7)
V–RC(2)	1.955	C(10)–C(11)	1.349(8)
		C(11)–C(11)′	1.300(12)
(b) Angles (deg.)			
C(1)–V–RC(1)	107.4	C(4)–C(3)–C(5)	109.0(4)
C(1)–V–RC(2)	106.0	C(6)′–C(6)–C(7)	109.4(5)
RC(1)–V–RC(2)	146.6	C(6)–C(7)–C(8)	107.8(6)
V–C(1)–C(2)	177.0(4)	C(7)–C(8)–C(7)′	105.6(8)
C(1)–C(2)–C(3)	177.8(6)	C(10)′–C(9)–C(10)	103.9(6)
C(2)–C(3)–C(4)	108.8(3)	C(9)–C(10)–C(11)	107.4(5)
C(2)–C(3)–C(5)	110.8(5)	C(10)–C(11)–C(11)′	110.6(3)
C(4)–C(3)–C(4)′	110.3(6)		

[a] The designations RC(1) and RC(2) refer to the centroids of the two cyclopentadienyl rings. [b] Primes denote atoms related to those in the asymmetric unit by the mirror plane at $y = 1/4$.

Conclusion

The fact that $(C_5H_5)_2VC{\equiv}CR$ could be easily isolated in crystallographically pure form in this study when $R = C(CH_3)_3$ compared to the difficulties encountered with $R = C_6H_5$ [6,10,11] is consistent with the relative stabilities of complexes of these alkynide ligands with lanthanide metals [2]. With lanthanide complexes, generally the sterically bulkier ligand generates the more stable complex and the importance of steric factors in organovanadium chemistry has been discussed [10]. The successful use of the $C{\equiv}CC(CH_3)_3$ ligand in providing a crystallographically characterizable vanadium alkynide complex with simple cyclopentadienyl ligands suggests this ligand may be special in other areas of organometallic alkynide chemistry.

Acknowledgment

We thank the Division of Basic Energy Sciences of the Department of Energy for support of this research, the Camille and Henry Dreyfus Foundation for a Teacher-Scholar Grant (to W.J.E.), and the Alfred P. Sloan Foundation for a Research Fellowship (to W.J.E.).

References

1 W.J. Evans, J. Organomet. Chem., 250 (1983) 217.
2 W.J. Evans and A.L. Wayda, J. Organomet. Chem., 202 (1980) C6.
3 J.L. Atwood, W.E. Hunter, A.L. Wayda and W.J. Evans, Inorg. Chem., 20 (1981) 4115.
4 W.J. Evans, I. Bloom, W.E. Hunter and J.L. Atwood, Organometallics, 2 (1983) 709.
5 W.J. Evans, A.L. Wayda, W.E. Hunter, and J.L. Atwood, J. Chem. Soc., Chem. Commun., (1981) 292.
6 J.H. Teuben and H.J. DeLiefde Meijer, J. Organomet. Chem., 17 (1969) 87.
7 D.G. Sekutowski and G.D. Stucky, J. Am. Chem. Soc., 98 (1976) 1376.
8 F.H. Köhler, W. Prössdorf, U. Schubert and D. Neugebauer, Angew. Chem. Int. Ed. Engl., 17 (1978) 850.
9 U. Schubert, F.H. Köhler and W. Prössdorf, Cryst. Struct. Comm., 10 (1981) 245.
10 F.H. Köhler, W. Prössdorf, U. Schubert, Inorg. Chem., 20 (1981) 4096.
11 F.H. Köhler, P. Hofmann, and W. Prössdorf, J. Am. Chem. Soc., 103 (1981) 6359.
12 T. Glowiak, R. Grobelny, B. Jezowska-Trzebiatowska, G. Kreisel, W. Seidel, E. Uhlig, J. Organomet. Chem., 155 (1978) 39.
13 G. Wilkinson, F.G.A. Stone, E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, Vol. 9, Pergamon Press, Oxford, 1982, p. 1492–1494.
14 L.E. Manzer, J. Organomet. Chem., 110 (1976) 291.
15 D.F. Evans, J. Chem. Soc., (1959) 2003; J.K. Becconsall, Mol. Phys., 15 (1968) 129.
16 D.B. Sams and R.J. Doedens, Inorg. Chem., 18 (1979) 153.
17 P.W.R. Corfield, R.J. Doedens, and J.A. Ibers, Inorg. Chem., 6 (1967) 197.
18 C.E. Strouse, personal communication.
19 International Tables for X-ray Crystallography, Vol. 4, Kynoch Press, Birmingham, England, 1974.
20 B.F. Fieselmann and G.D. Stucky, J. Organomet. Chem., 137 (1977) 43.
21 R.G. Teller and J.M. Williams, Inorg. Chem., 19 (1980) 2770.