APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. 2005; **19**: 102–103
Published online in Wiley InterScience (www.interscience.wiley.com). DOI:10.1002/aoc.762

Crystallographic report

The crystal structure of bis(η^5-cyclopentadienyl)-diazido-vanadium(IV)

Jan Honzíček[1], Milan Erben[1], Ivana Císařová[2] and Jaromír Vinklárek[1]*

[1]Department of General and Inorganic Chemistry, University of Pardubice, nám. Čs. legií 565, 532 10 Pardubice, Czech Republic
[2]Department of Inorganic Chemistry, Charles University, Hlavova 2030, 128 40 Prague 2, Czech Republic

Received 11 March 2004; Revised 13 July 2004; Accepted 16 July 2004

The crystal structure of the cyclopentadienyl vanadocene complex (η^5-$C_5H_5)_2V(N_3)_2$ was determined. The molecule has a typical bent metallocene structure in which two η^5-bonded cyclopentadienyl rings and two nitrogen atoms of azide ligands occupy the pseudotetrahedral coordination sites around the vanadium(IV) center. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: bent metallocene; vanadocene; pseudohalide; crystal structure; azide

COMMENT

Metallocene pseudohalide complexes of the η^5-Cp_2ML_2 (M = Ti, V; L = NCO, NCS, NCSe, N_3, CN) type have previously been the subject of several studies.[1–3] Despite the structures of some titanocene complexes having been determined by X-ray diffraction,[4–7] only one structure of a vanadocene pseudohalide complex, (η^5-$CH_3C_5H_4)_2V(NCO)_2$, is known.[8] The title compound, (η^5-$C_5H_5)_2V(N_3)_2$, has distorted tetrahedral geometry with V–ring centroid distances 1.976 and 1.970 Å and ring centroid–V–ring centroid angle 134.0°. The distance V–N (2.08 Å) is larger and N–V–N angle (86.1°) is less than in titanocene pseudohalide complexes (η^5-$C_5H_5)_2Ti(NCO)_2$ (2.01 Å; 94.7°),[4] (η^5-$C_5H_5)_2Ti(NCS)_2$ (2.02 Å; 93.9°),[5] (η^5-$C_5H_5)_2Ti(NNN)_2$ (2.03 Å; 94.1°).[7] The bond angle N–V–N is comparable to the structure of (η^5-$CH_3C_5H_4)_2V(NCO)_2$.[8] The coordinated azide groups were found to be almost linear: N(1)–N(2)–N(3) = 178.1°, N(4)–N(5)–N(6) = 178.0°. Similar to other metallocene azide complexes (Ti–N–N = 137.4°,[7] 129.6–129.8°,[9] Mo–N–N = 120.7–127.6°)[10] a significant deviation of the V–N–N angle from 180° (V–N–N = 118.9°, 121.4°) was observed. Unlike in halide complexes, the crystal packing of the pseudohalides is based on a network of weak van der Waals forces, either C–H···N (C(8)···N(3)^{i} 3.235(3) Å, C(8)–H(8)···N(3)^{i} 140°, symmetry code (i) $-x$, $-0.5+y$, $1.5-z$) in the structure presented or C–H···O in (η^5-$CH_3C_5H_4)_2V(NCO)_2$.[8]

*Correspondence to: Jaromír Vinklárek, Department of General and Inorganic Chemistry, University of Pardubice, nám. Čs. legií 565, 532 10 Pardubice, Czech Republic.
E-mail: jaromir.vinklarek@upce.cz
Contract/grant sponsor: Ministry of Education of the Czech Republic;
Contract/grant numbers: CZ 340003; 203/99/M037.

EXPERIMENTAL

Synthesis

The literature procedure was followed with some modifications.[2] To a solution of vanadocene dichloride (0.5 g; 2 mmol) in acetone (15 ml) was added NaN_3 (0.6 g; 10 mmol) and the mixture was heated to reflux for 2 h. Then, the solvent was evaporated *in vacuo* and the brown solid residue was extracted by boiling CH_2Cl_2. The *explosive* $Cp_2V(N_3)_2$ complex (CARE!) was obtained after evaporation of solvent to dryness. Yield 0.43 g (82%). The dark red crystals suitable for X-ray diffraction analysis were grown by cooling of saturated acetone solution at −15 °C. IR (KBr pellet, cm^{-1}): 3122sh (ν_a(C–H), Cp), 3112s (ν_s(C–H)), 3082m (ν_a(C–H)), 2083vs (ν_a(N–N)), 2056vs (ν_a(N=N)), 2028sh (ν_a(N=N)), 1479s (ν_a(C–C)), 1469s (ν_a(C–C)), 1403m, 1363s (ν_a(C–C)), 1311m, 1054s (δ(C–H)), 868s (γ(C–H)), 680m, 626m, 471m, 429m, 378m, 342m. Raman (quartz capillary, cm^{-1}): 3122(2) (ν_a(C–H), Cp), 3113(3.5) (ν_s(C–H), Cp), 3082(1.5) (ν_a(C–H), Cp), 2058(1) (ν(N=N)), 2035(<1) (ν(N=N)), 1441(1) (ν_a(C–C)), 1375(<1), 1330(1.5), 1281(<1), 1131(6) (ν_s(C–C), Cp), 1086(<1), 874(<1), 838(1), 590(<1), 430(4), 390(<1), 354(7), 306(1), 266(10) (κ Cp), 248(1.5), 221(1), 195(2.5). EPR (CH_2Cl_2): $A_{iso} = 66.6 \times 10^{-4}$ cm^{-1}, $g_{iso} = 1.983$.

Crystallography

Crystal data for: $C_{10}H_{10}N_6V$, $M_r = 265.18$, $0.4 \times 0.4 \times 0.25$ mm^3, monoclinic, $P2_1/c$, $a = 6.08900(10)$ Å, $b = 15.8840(3)$ Å, $c = 11.2340(2)$ Å, $\beta = 100.1510(15)°$, $V = 1069.52(3)$ Å^3,

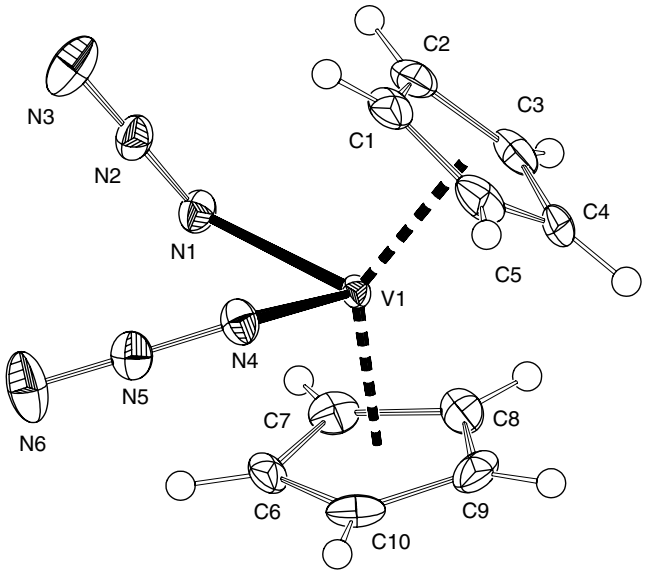

Figure 1. ORTEP drawing of molecular structure of $(\eta^5\text{-}C_5H_5)_2V(N_3)_2$ (ellipsoids: 50% probability). Important bond distances (Å) and angles (°): Cp(1)–V(1) 1.9762(10), Cp(2)–V 1.9700(10), Cp(1)–V(1)–Cp(2) 134.02(4), V(1)–N(1) 2.0800(16), V(1)–N(4) 2.0803(16), N(1)–V(1)–N(4) 86.11(6), N(1)–N(2) 1.204(2), N(4)–N(5) 1.203(2), N(2)–N(3) 1.152(2), N(5)–N(6) 1.156(2), V(1)–N(1)–N(2) 118.95(13), V(1)–N(4)–N(5) 121.39(13), N(1)–N(2)–N(3) 178.1(2), N(4)–N(5)–N(6) 178.0(2).

$Z = 4$, $D_x = 1.647\ \text{g cm}^{-3}$. Nonius KappaCCD diffractometer, $T = 150(2)$ K, $\theta_{max} = 27.48°$, $\mu(\text{Mo K}\alpha) = 0.912\ \text{mm}^{-1}$, $\lambda = 0.71073$ Å, 15 465 measured reflections, 2442 independent, $R_{int} = 0.027$, 2258 reflections with $I > 2\sigma(I)$, $R = 0.0292$ for observed diffractions, $wR(F^2) = 0.0729$ for all diffractions. Program used: DENZO-SMN,[11] Sir92,[12] SHELXL97,[13] PLATON.[14] CCDC number: 232819.

Acknowledgements

This work was supported by a grant from the Ministry of Education of the Czech Republic (no. CZ 340003) and GACR no. 203/99/M037.

REFERENCES

1. Burmeister JL, Deardorff EA, Jensen A, Christiansen VH. *Inorg. Chem.* 1970; **9**: 58.
2. Doyle G, Tobias S. *Inorg. Chem.* 1968; **7**: 2479.
3. Morán M, Fernández V. *J. Organometal. Chem.* 1979; **165**: 215.
4. Anderson SJ, Brown DS, Norbury AH. *J. Chem. Soc. Chem. Commun.* 1974; 996.
5. Villa AC, Manfredotti AG, Guastini C. *Acta Crystallogr. Sect. B* 1976; **32**: 909.
6. Raptopoulou CP, Tzavellas N, Klouras N. *Z. Anorg. Allg. Chem.* 1996; **622**: 1387.
7. De Gil ER, de Burguera M, Rivera AV. *Acta Crystallogr. Sect. B* 1977; **33**: 578.
8. Honzíček J, Erben M, Císařová I, Vinklárek J. *Appl. Organometal. Chem.* 2004; **18**: in press.
9. Honzíček J, Vinklárek J, Erben M, Císařová I. *Acta Crystallogr. Sect. E* 2004; **60**: m1090.
10. Shin JH, Bridgewater BM, Churchill DG, Baik MH, Friesner RA, Parkin G. *J. Am. Chem. Soc.* 2001; **123**: 10 111.
11. Otwinowski Z, Minor W. *Methods Enzymol. Part A* 1997; **276**: 307.
12. Altomare A, Cascarano G, Giacovazzo C, Guagliardi A, Burla MC, Polidori G, Camalli M. *J. Appl. Crystallogr.* 1994; **27**: 435.
13. Sheldrick GM. SHELXL97; University of Göttingen, Germany, 1997.
14. Spek AL. *J. Appl. Crystallogr.* 2003; **36**: 7.