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Reactions of naphthaleneytterbium with bis(cyclopentadienyl)complexes of cobalt, nickel, chromium and vanadium. X-Ray crystal structure of the triple-decker $CpVC_{10}H_8VCp$

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Abstract

Naphthaleneytterbium, $C_{10}H_8Yb(THF)_3$, reacts with Cp_2Cr, Cp_2Co, Cp_2Ni, and Cp_2V in THF to give Cp_2Yb. In the case of the reaction of $C_{10}H_8Yb(THF)_3$ with Cp_2V, vanadium-containing intermediates could be isolated. One of them, $CpVC_{10}H_8VCp$, has been characterized by X-ray diffraction. The crystals are monoclinic, space group $P2_1/n$, with a 907.0(5), b 798.8(3), c 1080.8(5) pm, β 105.21(4)°; $Z = 2$. The structure was refined to $R = 0.0288$ for 1131 observed reflections ($F_o > 4\sigma(F_o)$).

Introduction

One of the most interesting and still unresolved problems in organolanthanoid chemistry is the synthesis and characterization of complexes with direct lanthanoid–transition metal bonds. The first experiments in this field were the reactions between carbonyl complexes of several transition metals and lanthanide metals, their salts or cyclopentadienyl derivatives. However, only compounds with isocarbonyl bridges Ln–O–C–M could be isolated [1–4]. We attempted the synthesis of a complex with an Yb–V bond by the reaction of Cp_2VCl_2 with metallic ytterbium, but were unsuccessful. The only products were Cp_2V and $YbCl_2$ [5].

Here, we present the results of the reactions of naphthaleneytterbium [6] with metallocenes of Co, Ni, Cr and V. Again, we could not isolate compounds with Yb–M bonds, but a new divanadium triple-decker sandwich-complex could be isolated and characterized by X-ray structural analysis.

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Results and discussion

Bis(cyclopentadienyl)chromium reacts with naphthaleneytterbium in THF below 0 °C to give bis(cyclopentadienyl)ytterbium, bis(naphthalene)chromium and naphthalene in yields of 65%, 14%, and 65%, respectively, along with small amounts of unidentified insoluble products.

Cp_2Ni, Cp_2Co and Cp_2V react with $C_{10}H_8Yb(THF)_3$ in a quite similar manner affording Cp_2Yb in yields up to 95%. During the normal work-up of the mixture obtained from reaction of Cp_2V and $C_{10}H_8Yb(THF)_3$ some black rhombic crystals were isolated, which X-ray structure analysis revealed to be $CpVC_{10}H_8VCp$, apparently an intermediate in the reaction process:

$$C_{10}H_8Yb(THF)_3 + 2\ Cp_2V \xrightarrow{THF} Cp_2Yb + CpVC_{10}H_8VCp$$

It should be noted that the reaction of Cp_2V with an excess of $C_{10}H_8Yb(THF)_3$ under the same conditions yields another paramagnetic complex containing vanadium, ytterbium, naphthalene and cyclopentadienylgroups, whose characterization is still in progress.

Molecular structure of $(C_5H_5)VC_{10}H_8V(C_5H_5)$

The X-ray structure of the black crystals shows them to be (μ,η^6,η^6-naphthalene)bis(η^5-cyclopentadienyl)divanadate, a slipped triple-decker sandwich compound consisting of two cyclopentadienyl-vanadium units bridged by a naphthalene (Fig. 1). The vanadium atoms lie above and below the two aromatic rings of the naphthalene system, resulting in a 30-electron complex, analogous to the

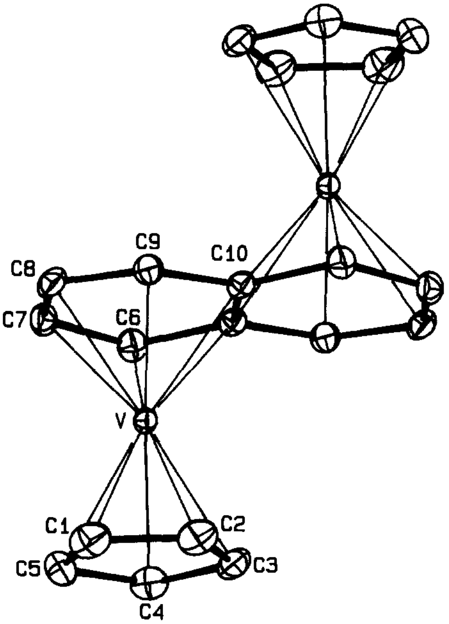

Fig. 1. ORTEP drawing [14] of $(C_5H_5)VC_{10}H_8V(C_5H_5)$, with the numbering scheme. Thermal ellipsoids scaled at 50% probability level.

structure of (μ,η^6,η^6-naphthalene)bis(η^6-benzene)dichromium [7] which is a 34-electron triple-decker complex. The Cp–V distance (191.8(1) pm) is the same as in other compounds of this type, for example $(C_5H_5)V(C_6H_6)V(C_5H_5)$ [8] (192.2 pm) and $(tmed)Li(C_6H_6)VCp$ [9] (192.0 pm). The V–C distances to the naphthalene rings range from 213.7(3) to 221.9(3) pm and average 218.7 pm, which is significantly shorter than in $(C_5H_5)V(C_6H_6)V(C_5H_5)$ (223.3(2) pm). In $CpVC_{10}H_8VCp$ the two ends of the naphthalene moiety carry more electron density than the central portion, which is manifested as a reduced bonding character between the naphthalene bridgehead carbons (C(10)–C(10′) 146.8(5) pm) with shortening of the C(7)–C(8) bond (139.7(4) pm). This agrees well with the observations reported by Bush et al. [7] with the similar triple-decker (μ,η^6,η^6-naphthalene)bis(η^6-benzene)dichromium, where the chromium atoms are also not located directly above the benzene rings of the naphthalene system.

Experimental

All reactions and preparations were performed *in vacuo* by standard Schlenk techniques. Solvents were dried and freed of oxygen by refluxing and were kept over sodium ketyl. IR spectra were recorded on a Perkin–Elmer 577 spectrophotometer.

Reaction of $C_{10}H_8Yb(THF)_3$ with Cp_2Cr

A solution of 0.49 g (2.7 mmol) of Cp_2Cr in 8 ml of THF was added to a suspension of 1.25 g (2.43 mmol) of $C_{10}H_8Yb(THF)_3$ in 10 ml of THF. After a few minutes the naphthaleneytterbium dissolved almost completely and the reaction mixture became red-brown. The solution was filtered off, the solvent removed *in vacuo* and the remaining solid was washed two times with 20 ml of pentane. The pentane solution was concentrated to yield a solid product, which gave 0.1 g (13.9%) of $(C_{10}H_8)_2Cr$ and 0.20 g (67%) of $C_{10}H_8$ after fractional sublimation. 1,2-Dimethoxyethane (1 ml) was added to the residue, which was insoluble in pentane, and green crystals of Cp_2Yb were formed. These crystals were washed in a small amount of cold DME and dried *in vacuo*. Yield 0.65 g (65%). The reactions of Cp_2Ni and Cp_2Co with $C_{10}H_8Yb(THF)_3$ were carried out in a similar way.

Reaction of $C_{10}H_8Yb(THF)_3$ with Cp_2V

A solution of 1.45 g (8 mmol) of Cp_2V in 30 ml of THF was added to 2.6 g (5.0 mmol) of $C_{10}H_8Yb(THF)_3$ suspended in 20 ml of THF. The mixture was shaken for 4 h at room temperature. During this time the $C_{10}H_8Yb(THF)_3$ dissolved almost completely and the solution became dark reddish-brown. It was decanted and the solvent was removed. The residue was washed twice with pentane and dried *in vacuo*. From this pentane solution 0.4 g (27%) of Cp_2V and 0.16 g (23%) of $C_{10}H_8$ were isolated. The remaining black powder, 2.4 g, was insoluble in pentane. A few black rhombic crystals of $CpVC_{10}H_8VCp$ crystallized from benzene. Yield: 0.48 g (27%); m.p.: 213–216 °C (with decomp.). IR (Nujol): 1170, 1100, 1005, 980, 810, 780, 735, 475, 440, 420 cm^{-1}.

X-Ray crystal structure determination

A crystal of dimensions $0.300 \times 0.288 \times 0.045$ mm^3 was selected, attached with grease to a glass fibre, and placed in the nitrogen beam of the diffractometer.

Lattice parameters were obtained by least-squares refinement of 25 reflections with $30° < 2\theta < 36°$. The intensities $0 \leqslant h \leqslant 10$, $0 \leqslant k \leqslant 9$, $-12 \leqslant l \leqslant 12$ in the 2θ range $2° \leqslant 2\theta \leqslant 50°$ were measured at 138(5) K by applying ω–2θ scans and Mo-K_α radiation (λ 71.069 pm). Three intensity check reflections were measured every 2 h of X-ray exposure. The maximum fluctuation of these reflections was 11.7%. Three orientation reflections were measured every 200 data points and a new orientation matrix was calculated from a list of 25 new centered reflections if the angular change of the control reflections was more than 0.1°. The raw data were corrected for Lorentz and polarization effects and decay (minimum correction factor 1.00052, maximum 1.06400). From intensity statistics and refinement the space group was determined to be $P2_1/n$.

The structure was solved by Patterson methods with successive difference Fourier syntheses. The compound lies on a center of symmetry that is located halfway between the bridgehead carbon atoms of the naphthalene moiety. After isotropic refinement of all atoms an empirical absorption correction was applied (DIFABS [10], minimum and maximum correction factors: 0.893, 1.133). All nonhydrogen atoms were then refined anisotropically, and the hydrogen atoms were located and refined isotropically. Maximum ratio of shift to error in the final cycle of refinement was 0.000. Maximum electron density in final difference Fourier map was 0.42 e/(10^6 pm^3).

Scattering factors for vanadium and carbon atoms and anomalous dispersion terms for the former were taken from International Tables of X-Ray Crystallography [11], and scattering factors for hydrogene from Stewart, Davidson and Simpson [12]. All calculations were made by SHELX76 [13] and all plots with ORTEP [14].

Table 1

Crystal and data collection parameters for $(C_5H_5)V(C_{10}H_8)V(C_5H_5)$

Formula	$C_{20}H_{18}V_2$
fw, g/mol	360.25
Space group	$P2_1/n$ (nonstandard of Nr. 14)
a, pm	907.0(5)
b, pm	798.8(3)
c, pm	1080.8(5)
β, deg	105.21(4)
V, 10^{-30} m^3	755.6(6)
Z	2
D_{calc}, g/cm^3	1.583
μ, cm^{-1}	11.9
$F(000)$	368
Diffractometer	Enraf–Nonius CAD-4
Radiation; λ, pm	71.069
Monochromator	graphite crystal
Temp., K	138(5)
2θ Limits, deg	$2 \leqslant 2\theta \leqslant 50$
Scan technique	$\omega-2\theta$
No. of unique data	1247
No. of obs. data, $F_o > 4\sigma(F_o)$	1131
Corrections	Lorentz, polarization, absorption, anomalous dispersion
No. of refined parameters	136
$R = \Sigma \|\|F_o\| - \|F_c\|\| / \Sigma\|F_o\|$	0.0288 (unit weights)

Table 2

Positional parameters and equivalent isotropic thermal parameters (10^4 pm^2) of $(C_5H_5)V(C_{10}H_8)V(C_5H_5)$

Atom	x	y	z	B_{eq}
V	0.82733(5)	−0.16575(6)	0.50955(4)	0.86
C(1)	0.7217(4)	−0.4212(4)	0.5237(3)	1.92
C(2)	0.8713(4)	−0.4202(4)	0.6049(3)	1.71
C(3)	0.8769(4)	−0.2980(4)	0.6994(3)	1.57
C(4)	0.7309(4)	−0.2222(4)	0.6767(3)	1.67
C(5)	0.6359(3)	−0.3002(4)	0.5678(3)	1.81
C(6)	0.8059(3)	0.1003(4)	0.4930(3)	1.25
C(7)	0.7168(3)	0.0330(4)	0.3757(3)	1.31
C(8)	0.7782(3)	−0.0837(4)	0.3067(3)	1.35
C(9)	0.9316(3)	−0.1394(4)	0.3521(3)	1.19
C(10)	1.0319(3)	−0.0622(3)	0.4642(3)	1.00

Table 3

Bond distances (pm) in $(C_5H_5)V(C_{10}H_8)V(C_5H_5)$

Atoms	Distance	Atoms	Distance
V–C(1)	227.7(3)	C(1)–C(2)	141.0(5)
V–C(2)	226.6(3)	C(1)–C(5)	140.1(5)
V–C(3)	224.6(3)	C(2)–C(3)	140.4(4)
V–C(4)	225.0(3)	C(3)–C(4)	141.9(4)
V–C(5)	226.7(3)	C(4)–C(5)	140.9(4)
V–C(6)	213.7(3)	C(6)–C(7)	141.8(4)
V–C(7)	220.4(3)	C(7)–C(8)	139.7(4)
V–C(8)	221.9(3)	C(8)–C(9)	142.0(4)
V–C(9)	216.2(3)	C(9)–C(10)	144.8(4)
V–C(10)	220.1(3)	C(10)–C(10′)	146.8(5)
V–C(10′)	219.9(3)	C(6)–C(10′)	145.4(4)
V–Ph	165.2(1)	V–Cp	191.8(1)

Table 4

Bond angles (°) in $(C_5H_5)V(C_{10}H_8)V(C_5H_5)$

Atoms	Angle	Atoms	Angle
C(2)–C(1)–C(5)	108.3(3)	C(6)–C(7)–C(8)	121.1(3)
C(1)–C(2)–C(3)	107.6(3)	C(7)–C(8)–C(9)	121.1(3)
C(2)–C(3)–C(4)	108.5(3)	C(8)–C(9)–C(10)	120.0(3)
C(3)–C(4)–C(5)	107.1(3)	C(7)–C(6)–C(10)	119.8(3)
C(1)–C(5)–C(4)	108.5(3)	C(9)–C(10)–C(10′)	118.8(3)
Cp–V–Ph	176.79(6)	C(6)–C(10′)–C(10)	118.6(3)

Additional information on the crystal structure determination are summarized in Table 1. Final positional parameters are listed in Table 2. Interatomic distances and angles are listed in Tables 3 and 4, respectively. The atomic numbering scheme followed in these listings is shown in Fig. 1. Further details of the structure determination are available on request from Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, W-7514 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD-55351, the names of the authors, and the journal citation.

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