Synthesis, molecular and crystal structure of a tricarbonylchromium complex of 7-(2-phenyl-*o*-carboran-1-yl)cyclohepta-1,3,5-triene

Valery N. Kalinin,*[a] Igor V. Shishkov,[a] Sergey K. Moiseev,[a] Pavel V. Petrovskii,[a] Zoya A. Starikova[a] and Dae Dong Sung[b]

[a] *A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 117813 Moscow, Russian Federation. Fax: +7 095 135 6549; e-mail: vkalin@ineos.ac.ru*

[b] *Department of Chemistry, Dong-A University, Saha-Gu, Pusan, 604-714, Korea. E-mail: ddsung@seunghak.donga.ac.kr*

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The reaction of substituted 1-lithio-*o*-carboranes with tropylium tetrafluoroborate produces 7-(*o*-carboran-1-yl)cyclohepta-1,3,5-trienes, which can also be obtained by decomplexation of the corresponding tricarbonylchromium complexes prepared from 1-lithio-*o*-carboranes and $[(C_7H_7)Cr(CO)_3]^+BF_4^-$.

Higher-order cycloaddition reactions are a promising approach to the preparation of otherwise hardly available carbocyclic compounds.[1] Cyclohepta-1,3,5-triene derivatives are very effective 6π-participants in [6π + 4π] and [6π +2π] cycloaddition reactions.[2,3] Tricarbonylchromium complexes of substituted cycloheptatrienes can also be involved in the reaction.[4,5] The complexes can be prepared by reactions of a tropylium tricarbonylchromium complex with the corresponding nucleophiles.[6] Their tricarbonylchromium complexes can also enter the reactions, and the cycloaddition products obtained differ in structure from those prepared from the uncomplexed starting cyclohepta-1,3,5-triene derivatives.[1,7]

The only cycloheptatriene derivative described to date is 7-(2-methyl-*o*-carboran-1-yl)cyclohepta-1,3,5-triene,[†] which was obtained from 1-lithio-2-methyl-*o*-carborane and 7-methoxycyclohepta-1,3,5-triene.[8] Here, we describe a common method for preparation of 7-(*o*- or *m*-carboran-1-yl)cyclohepta-1,3,5-triene derivatives along with their η⁶-tricarbonylchromium complexes.

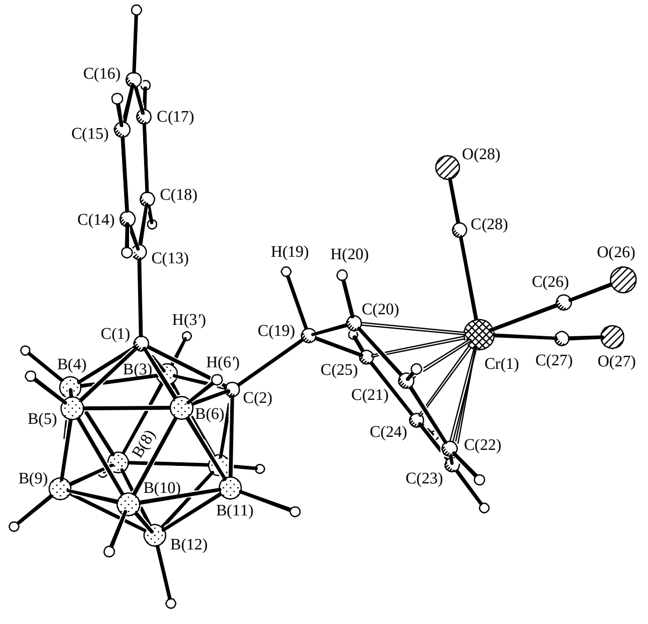
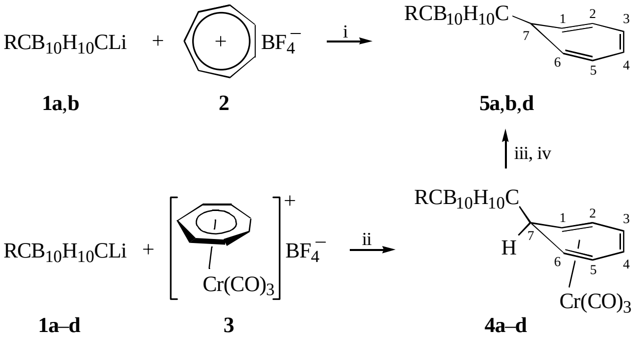


Figure 1 General view of a molecule of **4b**. Selected bond lengths (Å): Cr(1)–C(20) 2.323(8), Cr(1)–C(21) 2.215(7), Cr(1)–C(22) 2.198(8), Cr(1)–C(23) 2.212(7), Cr(1)–C(24) 2.218(7), Cr(1)–C(25) 2.295(6), C(2)–C(19) 1.550(9), C(1)–C(2) 1.700(9), C(1)–C(13) 1.522(9), C(1)–B(3) 1.680(11), C(1)–B(4) 1.679(9), C(1)–B(5) 1.695(11), C(1)–B(6) 1.737(8), C(2)–B(3) 1.723(9), C(2)–B(6) 1.711(11), C(2)–B(7) 1.741(10), C(2)–B(11) 1.708(10), Cr(1)···C(19) 2.825(8); selected bond angles (°): C(13)–C(1)–C(2) 118.8(5), C(1)–C(2)–C(19) 117.6(5), C(19)–C(20)–C(21) 127.3(7), C(19)–C(25)–C(24) 127.4(7), C(20)–C(19)–C(25) 108.8(6), Cr(1)–C(20)–C(19) 92.7(5), Cr(1)–C(25)–C19 93.9(4).



a R = *o*-Me
b R = *o*-Ph
c R = *o*-H
d R = *m*-Me

Scheme 1 *Reagents and conditions*: i, hexane–Et_2O, 20 °C, 3 h; ii, hexane–Et_2O, 20 °C, 10–20 min; iii, MeCN–THF (35:15); iv, $(NH_4)_2Ce(NO_3)_6$, H_2O–MeCN (35:20).

We found that 1-lithio-2-R-*o*-carboranes **1a**,**b** readily react with tropylium tetrafluoroborate **2** in a diethyl ether–hexane solution to form corresponding 7-(2-R-*o*-carboran-1-yl)cyclohepta-1,3,5-trienes **5a**,**b** in good yields (Scheme 1).[‡]

Only one regioisomer of product **5** was isolated in each case. The corresponding ¹H NMR spectra (in $CDCl_3$) show three signals attributed to three pairs of the alkenyl hydrogens and a peak of one nonalkenyl hydrogen of the cycloheptatrienyl ring. These data unambiguously indicate that the carboranyl moiety in pro-duct **5** is attached to the 7-position of cyclohepta-1,3,5-triene. That is, the carboranyl substituent occupies the allyl position regarding the carbon–carbon double bond system of the ring. This is important for cycloaddition reactions because a rather strong electron-accepting effect and the presence of a bulk carboranyl group lead to a decrease of the reactivity of the carborane-connected carbon–carbon double bonds in the cycloaddition processes.[9]

A reaction of lithiated carboranes **1a**–**d** with $[(C_7H_7)Cr(CO)_3]^+BF_4^-$ was used to prepare the tricarbonylchromium complexes of *o*- and *m*-carboranyl derivatives of cyclohepta-1,3,5-triene **4a**–**d**.[§] The chromium complexes obtained in 65–75% yields are red air-stable compounds slowly decomposing in solution.

[†] The terms ‘*o*-carborane’ and ‘*m*-carborane’ denote 1,2- and 1,7-dicarba-*closo*-dodecaborane(12), respectively.

[‡] *General procedure for preparation of* **5a**,**b**. To a solution of **1a** or **1b** (0.01 mmol) in dry diethyl ether (30 ml) a hexane solution of Bu^nLi (0.01 mmol) was added. The mixture was stirred at room temperature for 30 min. Next, compound **2** (0.01 mmol) was added. After additional vigorous stirring for 2.5–3 h, the reaction mixture was quenched with water (20 ml). The organic layer was separated and dried with anhydrous sodium sulfate. The solvent was removed under reduced pressure, and column chromatography (silica gel, diethyl ether–petroleum ether) of the residue followed by recrystallization from hexane gave **5a** (85%) or **5b** (80%).

[§] Complex **4c** was isolated in 2–3% yield.

An X-ray study of complex **4b**[¶] showed that the carboranyl moiety is attached to the cycloheptatrienyl ligand at the 7-position and has an *exo* orientation relative to the $Cr(CO)_3$ group (Figure 1).

^1H NMR spectra (in $CDCl_3$) of compounds **4a**–**d** unambiguously indicate that the carboranyl moiety is attached to the cyclohepta-1,3,5-triene ring at the 7-position.

The tricarbonylchromium group can be easily removed from complexes **4a**,**b**,**d** by the action of $(NH_4)_2Ce(NO_3)_6$ in a THF solution releasing free ligands **5a**,**b**,**d**.

Satisfactory analyses as well as IR and ^1H NMR[††] spectra were obtained for all 7-(carboran-1-yl)cyclohepta-1,3,5-triene derivatives and their η^6-tricarbonylchromium complexes.

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[¶] *Crystallographic data for* **4b**: $C_{18}H_{22}B_{10}CrO_3$, $M = 446.46$, orthorhombic crystals, spase group $P2_12_12_1$, $a = 8.292(2)$, $b = 8.674(2)$, $c = 30.658(11)$ Å, $V = 2205(1)$ Å^3, $z = 4$, $d_{calc} = 1.345$ g cm^{-3}, μ(MoKα) = 5.38 cm^{-1}, $F(000) = 912$. The intensities of 3426 reflections were measured on a Siemens P3/PC diffractometer at –120 °C (λMoKα radiation, $\theta/2\theta$ scan technique, $2\theta < 50°$), and 3048 independent reflections were used in further calculations and refinement. The absolute conformation for the molecule of **4b** was determined by calculation of the Flack parameter [$k = 0.05(5)$]. The structure was solved by a direct method and refined by a full-matrix least-squares technique against F^2 in an anisotropic–isotropic approximation. The positions of hydrogen atoms were located from the difference Fourier syntheses. The refinement was converged to $wR_2 = 0.1633$ and GOF = 0.974 for all 3023 independent reflections [$R_1 = 0.0565$ was calculated against F for the 2143 independent reflections with $I > 2\sigma(I)$]. The number of the refined parameters is 377. All the calculations were performed using SHELXTL PLUS 5.0 on an IBM computer. Atomic coordinates, bond lengths, bond anlges and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2000. Any request to the CCDC for data should quote the full literature citation and the reference number 1135/58.

[††] ^1H NMR spectra (400 MHz, $CDCl_3$, δ/ppm).

4a: 0.80–2.95 (m, 10H, $B_{10}H_{10}$), 2.05 (s, 3H, Me), 3.83 (m, 1H, 7-H), 3.64 (m, 2H, 1-H, 6-H), 5.04 (m, 2H, 2-H, 5-H), 6.03 (m, 2H, 3-H, 4-H).

4b: 0.9–3.30 (m, 10H, $B_{10}H_{10}$), 3.10–3.50 (m, 3H, 1-H, 6-H, 7-H), 4.94 (m, 2H, 2-H, 5-H), 5.96 (m, 2H, 3-H, 4-H), 7.23–7.95 (m, 5H, Ph).

4c: 0.90–2.85 (m, 10H, $B_{10}H_{10}$), 3.16 (br. s, 1H, HCCB$_{10}$H$_{10}$), 3.66 (m, 2H, 1-H, 6-H), 4.02 (t, 1H, 7-H, $^3J_{7,1} = {}^3J_{6,7} = 8.8$ Hz), 5.00 (m, 2H, 2-H, 5-H), 5.95–6.05 (m, 2H, 3-H, 4-H).

4d: 1.15–3.18 (m, 10H, $B_{10}H_{10}$), 1.59 (s, 3H, Me), 3.59–3.70 (m, 3H, 1-H, 6-H, 7-H), 4.91–5.00 (m, 2H, 2-H, 5-H), 5.95 (m, 2H, 3-H, 4-H).

5a: 1.00–3.75 (m, 10H, $B_{10}H_{10}$), 1.65 (t, 1H, 7-H, $^3J_{6,7} = {}^3J_{7,1} = 6.0$ Hz), 1.80 (s, 3H, Me), 5.38 (dd, 2H, 1-H, 6-H, $^3J_{1,7} = {}^3J_{6,7} = 6.0$ Hz, $^3J_{1,2} = {}^3J_{5,6} = 8.8$ Hz), 6.26 (m, 2H, 2-H, 5-H), 6.77 (m, 2H, 3-H, 4-H).

5b: 1.13 (t, 1H, 7-H, $^3J_{1,7} = {}^3J_{6,7} = 6.0$ Hz), 1.80–3.70 (m, 10H, $B_{10}H_{10}$), 5.32 (dd, 2H, 1-H, 6-H, $^3J_{1,2} = {}^3J_{5,6} = 8.8$ Hz, $^3J_{6,7} = {}^3J_{1,7} = 6.0$ Hz), 6.04 (m, 2H, 2-H, 5-H), 6.42 (m, 2H, 3-H, 4-H, $^3J_{3,2} = {}^3J_{4,5} = 3.2$ Hz), 7.23 (t, 2H, m-H$_{Ph}$, J 7.6 Hz), 7.34 (t, 1H, p-H$_{Ph}$, J 7.6 Hz), 7.44 (t, 2H, o-H$_{Ph}$, J 7.6 Hz).

5d: 1.05–3.65 (m, 10H, $B_{10}H_{10}$), 1.72 (s, 3H, Me), 1.68–1.78 (m, 1H, 7-H), 5.26 (dd, 2H, 1-H, 6-H, $^3J_{1,2} = {}^3J_{5,6} = 8.8$ Hz, $^3J_{1,7} = {}^3J_{6,7} = 6.0$ Hz), 6.16 (m, 2H, 2-H, 5-H), 6.70 (m, 2H, 3-H, 4-H).