144. [1,1-Bis(trimethylsilyl)-1*H*-cyclopropa[*b*]naphthalene]tricarbonylchromium: the First Arene-chromium Complex of a Cycloproparene

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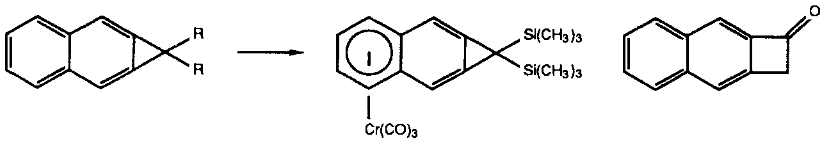
[1,1-Bis(trimethylsilyl)-1*H*-cyclopropa[*b*]naphthalene]tricarbonylchromium (**2**) was synthesized by reaction of 1,1-bis(trimethylsilyl)cyclopropa[*b*]naphthalene (**1b**) with tricarbonyltris(acetonitrile)chromium.

Cycloproparenes react with transition metals either by opening of one of the cyclopropane bonds, or *via* attack on the central double bond. For example, reaction of cyclopropabenzene with Ni(0) [1] or Pd(0) [2] complexes affords metalla-cyclobutabenzenes, while cyclopropa[*b*]naphthalene undergoes oxidative addition with $Fe_2(CO)_9$ followed by CO insertion to give a stable metalla-cyclopentenone [3]. 1,1-Difluorobenzocyclopropene, on the other hand, is attacked at the central bond and converted to a metalla-propellane [4]. We now report the synthesis and crystal structure of the first transition-metal complex of a cycloproparene in which the cyclopropene moiety remains intact.

[1,1-Bis(trimethylsilyl)-1*H*-cyclopropa[*b*]naphthalene]tricarbonylchromium (**2**) was synthesized by heating of 1,1-bis(trimethylsilyl)-1*H*-cyclopropa[*b*]naphthalene (**1b**) [5] with tricarbonyltris(acetonitrile)chromium [6] to 90° in Bu_2O under a slow current of N_2. The resulting solution was filtered through *Celite*, which was extracted repeatedly with Et_2O. After evaporation of the solvent, the product was recrystallized from hexane at 0°. The mother liquor was purified by column chromatography (SiO_2, elution with hexane, followed by CH_2Cl_2) to give **2** in 51 % combined yield as orange crystals, m.p. 179°.

Scheme



1a R = H
b R = $Si(CH_3)_3$

2

3

The ^1H-NMR of **2** consists of a *singlet* at 6.29 ppm (H–C(2), H–C(7)), and an *AA'BB'* system with *multiplets* at 5.26–5.22 ppm (H–C(3), H–C(6)) and 4.65–4.61 ppm (H–C(4), H–C(5)). The fact that the H-atoms adjacent to the cyclopropene ring (H–C(2), H–C(7)) resonate *ca.* 1 ppm below the H-atoms of the lateral cycle, indicates that the metal is attached to the latter, *i.e.* to C(2a), C(3), C(4), C(6), and C(6a). In tricarbonylnaphthalenechromium [7], the *AA'BB'* system of the uncomplexed ring is centered at 6.8 ppm, while that of the complexed part shows practically the same pattern as observed for **2** (*AA'BB'* system centered at 4.9 ppm). The Me_3Si groups of **2** are slightly 'non-equivalent' and resonate at 0.039 and −0.052 ppm.

The structural assignment is unequivocally confirmed by the X-ray structure of **2** (*Figure*) [8] [9]1). Details concerning the structure determination are summarized in the *Table*. The complexed part corresponds fairly well to the structure of tricarbonylnaphthalenechromium [10]. As in this latter, the Cr-atom is weakly decentered toward the C(4)–C(5) bond with the Cr–C distance varying between 2.21 (C(3,4)), 2.22 (C(4,5)), and

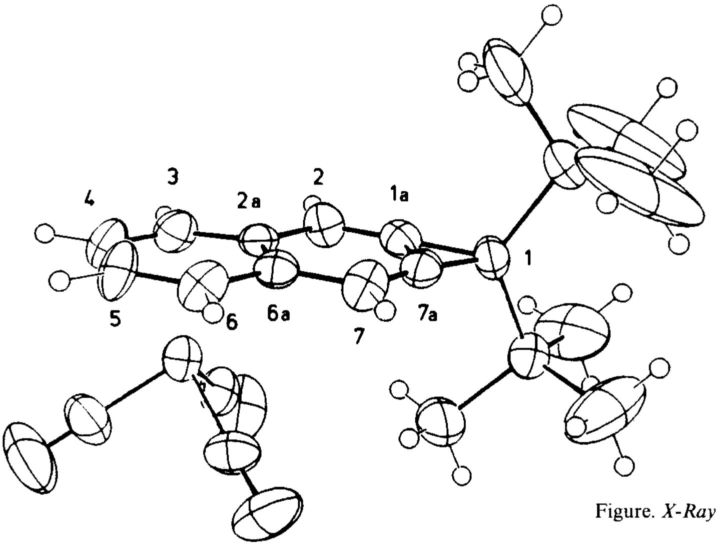


Figure. *X-Ray structure of* **2**

Table. *Crystal Data, Intensity Measurement, and Structure Refinement for* **2**

Formula	$C_{20}H_{24}O_3Si_2Cr$	μ [mm^{-1}]	0.614
Molecular weight	420.6	$(\sin\theta/\lambda)_{max}$ [Å^{-1}]	0.51
Crystal system	Monoclinic	No. of measured reflections	2645
Space group	$P2_1/n$	No. of observed reflections	1547
Crystal size [mm]	0.10 × 0.28 × 0.30	Criterion for observed	$\lvert F_o\rvert > 4\sigma(F_o)$
a [Å]	11.954(2)	No of parameters	235
b [Å]	15.652(3)	Refinement (on F)	full-matrix
c [Å]	13.080(2)	Weighting scheme	$\omega = 1/\sigma^2(F)$
β [°]	113.11(3)	H-atoms	calculated
V [Å^3]	2251.0(8)	Max. and average Δ/σ	0.118, 0.008
Z	4	Max. and min. $\Delta\rho$ [eÅ^{-3}]	0.82, −0.67
D_c [g·cm^3]	1.24	S	2.75
F_{000}	880	R, R_w [%]	6.8, 4.8

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1) Data were collected at room temperature on *Philips PW 1100* diffractometer (MoK_α). The structure was solved by direct methods (*Multan* 84) [8] and refined by full-matrix least-squares analysis (XTAL) [9]. Crystallographic data have been deposited with the *Cambridge Crystallographic Data Centre*, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, England.

2.30 Å (C(2a,6a)). The Cr–CO bonds are slightly distorted (6°) from the pseudo-symmetry plane bisecting the molecule. All the atoms of the cyclopropa[*b*]naphthalene moiety are distributed in a mean plane with a maximum deviation of 0.050(11) Å for C(1). The distance of the Cr-atom to this plane (1.742(5) Å) is comparable to that found in tricarbonylnaphthalenechromium (1.747 Å) [10]. Complexation of **1** brings about the same structural modifications as in the case of naphthalene. Thus the C(2a)–C(6a) bond length of **2** measures 1.441(14) Å. The corresponding distance in tricarbonylnaphthalenechromium is 1.439 Å [10]. In the uncomplexed part of the molecule, the characteristic features of the cycloproparene skeleton are retained. The C(1a)–C(7a) bond length is 1.384(14) Å in **2**, while 1.368 Å in the parent cyclopropa[*b*]naphthalene **1a** [11]. As evidenced from X-ray structures of other cycloproparenes [12] [13], the R_3Si substituents have no major effect on this bond, although the lateral cyclopropane bonds may be lengthened, when the substituents are extremely bulky.

The presence of the Me_3Si groups of **1** is essential for the success of the complexation. The unprotected cyclopropa[*b*]naphthalene (**1a**) subjected to identical reaction conditions afforded mainly decomposition products and a 6% yield of cyclobuta[*b*]naphthalen-1-one (**3**) [14]. When the reaction was carried out at room temperature, the yield of **3** increased to 40%.

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