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^{1}H and ^{13}C NMR studies of η^6-benzo-bonded (boron–nitrogen heteroarene)tricarbonylchromium complexes and related η^6-phenyl-bonded (*B*,*B*′,*B*″-trimethyl-*N*,*N*′,*N*″-triarylborazine)-tricarbonylchromium complexes: crystallographic structure of a boron–nitrogen heteroarene

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Abstract

2,4-Dimethyl-3-phenyl-[2′-methyl-3′chloro]-7-chloro-8-methyl-2,4-dibora-1,3-diazaronaphthalene ($C_{16}H_{18}B_2N_2Cl_2$) crystallizes in the monoclinic system: $P_{2/a}$; $a = 8.149(3)$ Å, $b = 13.379(3)$ Å and $c = 15.193(3)$ Å; $\beta = 91.03(2)°$; $Z = 4$; $R = 0.043$; $R_w = 0.041$. Reaction with $[Cr(CO)_6]$ gives exclusively the compounds with $Cr(CO)_3$ η^6-bonded to the benzo part of the molecule. This derivative is a 1:1 mixture of atropisomers which were partially separated and whose configurations could be deduced by means of solvent effects in nuclear magnetic resonance (NMR) spectroscopy. Similar results were obtained with 2,4-dimethyl-3-phenyl-[2′-methyl-4′-chloro]-6-chloro-8-methyl-2,4-dibora-1,3-diazaronaphthalene and $[Cr(CO)_6]$ although the separation of isomers failed. Additionally, two closely related η^6-bonded isomers originating from the above ligands were identified in which the chlorine atom was replaced by a hydrogen atom. All these compounds were thoroughly characterized by high resolution ^{1}H and ^{13}C one-dimensional and ^{1}H–^{1}H nuclear Overhauser spectroscopy (NOESY) and correlated two-dimensional NMR spectroscopy (COSY). Further, the reaction of $[Cr(CO)_6]$ with *B*,*B*′,*B*″-trimethyl-*N*,*N*′,*N*″-triarylborazine, the phenyl bearing a *para* substituent (H, F or Me), was shown by ^{1}H and ^{13}C NMR spectroscopy to yield a compound with one phenyl group η^6 bonded to $Cr(CO)_3$.

Key words: Chromium; Boron; Nuclear magnetic resonance

1. Introduction

In recent years complexes $[LCr(CO)_3]$ where L represents a polycyclic ligand have attracted considerable attention. Their importance stems from the considerable synthetic potential of such complexes [1] as a result of the major modification in their chemistry caused by coordination to $Cr(CO)_3$ moieties. Furthermore, the existence of several 6π-electron coordination sites in these ligands is of additional theoretical interest since the position of attachment of the $Cr(CO)_3$ group is quite sensitive to the nature of the rings, *i.e.* fused or non-fused, and aromatic or heteroaromatic [2]. In a previous report [3], we described the synthesis and characterization of two such complexes $[LCr(CO)_3]$ where L is **1** or **2** isoelectronic with naphthalene (Fig. 1). This paper describes the reactions of the two closely

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related ligands **3** and **4** as well as that of the related B,B',B''-trimethyl-N,N',N''-triarylborazines **5** with $[Cr(CO)_6]$.

2. Experimental section

2.1. General comments

All reactions were carried out under dry argon using Schlenk techniques. The solvents used were thoroughly dried with naphthalene–sodium (tetrahydrofuran (THF) and $^nBu_2O$) or P_2O_5 (C_6H_6 and hexane), deoxygenated and kept under argon. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AM 300 spectrometer at 300.13 MHz for ^1H and 75.47 MHz for ^{13}C, and on a Varian HT 80A spectrometer at 20.0 MHz for ^{13}C and 80 MHz for ^1H. Chemical shifts are with respect to tetramethylsilane in both cases, and coupling constants in hertz. Unless otherwise stated, all NMR spectra were run in $CDCl_3$. Filtration of complex solutions, through Millipore frits (0.5 μm diameter) prior to examination resulted in considerable improvement in the ^1H NMR spectra. It was observed during NMR experiments that the complexes ($LCr(CO)_3$) slowly degrade, especially with chlorinated solvents, leading to the appearance in the spectrum of signals from the ligand.

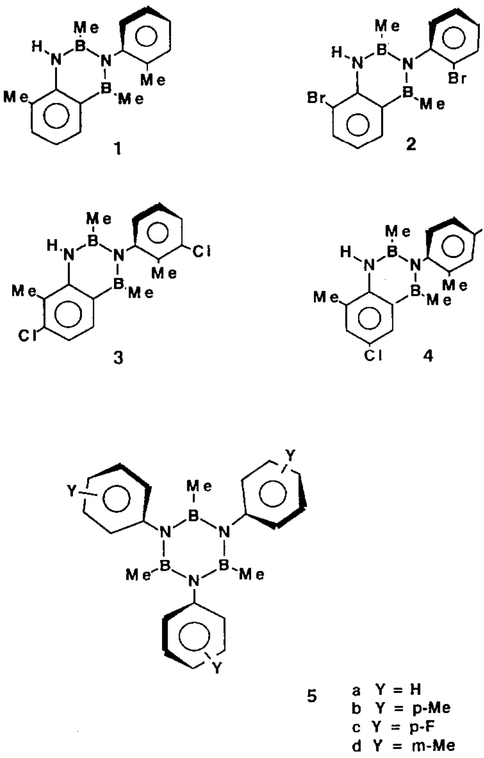


Fig. 1. Representation of 1–5.

TABLE 1. Crystal data for 3

Formula	$C_{16}H_{18}B_2Cl_2N_2$
Formula weight	330.86
Crystal system	Monoclinic
Space group	$P2_1/a$
a (Å)	8.149(3)
b (Å)	13.379(3)
c(Å)	15.193(3)
β (°)	91.03(2)
V (Å^3)	1656(1)
Z	4
ρ_{calc} (g cm^{-3})	1.33
Systematic absences	$h0l$ ($h = 2n+1$), $0k0$ ($k = 2n+1$)
Diffractometer	Enraf–Nonius CAD-4
Radiation	Mo Kα (λ = 0.71069 Å) (graphite monochromator)
Linear absorption coefficient (cm^{-1})	3.87
Scan type	$\omega-2\theta$
Scan range (°)	$0.8+0.345\tan\theta$
θ limits (°)	1–25
Octants collected	−9,9; 0.15; 0.18
Number of data collected	4568
Number of unique data collected	2902
Number of unique data used	1514 $F_0^2 > 3\sigma(F_0^2)$
Decay (%)	< 1
$R = \Sigma(\|\|F_o\| - \|F_c\|\|)/\Sigma\|F_o\|$	0.043
$R_w = [\Sigma_w(\|F_o\| - \|F_c\|)^2/\Sigma_w F_o^2]^{1/2}$	0.041

2.2. Crystal data

Crystals of the boron–nitrogen heterocycle **3** were mounted on a Nonius CAD 4 automatic four-circle diffractometer and data collected via a θ–2θ scan type and a scan range of $0.8 + \tan\theta$ at 20°C. Accurate unit-cell dimensions and crystal orientation matrix together with their estimated standard deviations were obtained from least-squares refinements of the setting angles of 25 reflections. Three standard reflections were monitored periodically; they showed no change during data collection. Crystallographic data and other pertinent information are summarized in Table 1. Corrections were made for Lorentz and polarization effects. No absorption correction was applied. Computations were performed using CRYSTALS [4]. Atomic form factors for neutral B, C, N, Cl and H were taken from ref. 5. The structure was solved by direct methods using the SHELX 86 program [6] and subsequent Fourier syntheses. Anisotropic temperature factors were introduced for all non-hydrogen atoms. Hydrogen atoms were located on difference electron density maps. They were given a fixed isotropic thermal parameter $U = 0.0964$ Å^2. Least-squares refinements with approximation to the normal matrix were carried out by minimizing the function $\Sigma w(|F_o| - |F_c|)^2$, where F_o and F_c are the observed and calculated structure factors. The weighting scheme used is $w = w'[1(\Delta F/6\sigma(F)^2]^2$ with

TABLE 2. Fractional atomic coordinates with their estimated standard deviations for **3**

Atom	x	y	z	U_{eq} (Å^2)	U_{iso} (Å^2)
Cl(1)	0.1214(2)	0.6908(1)	0.01337(9)	0.0714	
Cl(2)	1.2261(1)	0.4292(1)	−0.37719(9)	0.0728	
B(1)	0.5652(6)	0.3949(4)	−0.2163(3)	0.0432	
B(2)	0.5656(6)	0.5656(4)	−0.2832(3)	0.0442	
N(1)	0.4571(4)	0.4299(2)	−0.1528(2)	0.0452	
N(2)	0.6253(4)	0.4651(2)	−0.2802(2)	0.0407	
C(1)	0.2452(5)	0.6508(3)	−0.0722(3)	0.0501	
C(2)	0.2964(5)	0.5528(3)	−0.0753(3)	0.0444	
C(3)	0.3984(5)	0.5269(3)	−0.1458(3)	0.0411	
C(4)	0.4478(5)	0.5966(3)	−0.2099(3)	0.0428	
C(5)	0.3876(5)	0.6946(3)	−0.2013(3)	0.0530	
C(6)	0.2882(6)	0.7221(3)	−0.1344(3)	0.0584	
C(7)	0.7432(5)	0.4319(3)	−0.3435(2)	0.0402	
C(8)	0.6862(5)	0.3832(3)	−0.4193(3)	0.0546	
C(9)	0.7977(6)	0.3509(4)	−0.4808(3)	0.0628	
C(10)	0.9625(6)	0.3654(3)	−0.4672(3)	0.0559	
C(11)	1.0165(5)	0.4139(3)	−0.3918(3)	0.0461	
C(12)	0.9094(5)	0.4473(3)	−0.3281(2)	0.0419	
C(13)	0.9706(6)	0.4989(4)	−0.2464(3)	0.0596	
C(14)	0.6182(6)	0.2819(3)	−0.2159(3)	0.0604	
C(15)	0.6193(6)	0.6398(4)	−0.3569(3)	0.0658	
C(16)	0.2496(6)	0.4764(4)	−0.0092(3)	0.0588	
H(1)	0.4093	0.3973	−0.1097		0.0964
H(5)	0.4187	0.7449	−0.2499		0.0964
H(6)	0.2440	0.7861	−0.1311		0.0964
H(8)	0.5652	0.3802	−0.4270		0.0964
H(9)	0.7626	0.3213	−0.5349		0.0964
H(10)	1.0358	0.3516	−0.5103		0.0964
H(131)	0.8849	0.5163	−0.2081		0.0964
H(132)	1.0413	0.4636	−0.2169		0.0964
H(133)	1.0482	0.5526	−0.2597		0.0964
H(141)	0.5630	0.2526	−0.2589		0.0964
H(142)	0.5843	0.2442	−0.1625		0.0964
H(143)	0.7321	0.2648	−0.2249		0.0964
H(151)	0.7060	0.6659	−0.3539		0.0964
H(152)	0.5229	0.6520	−0.3841		0.0964
H(153)	0.6526	0.6141	−0.4129		0.0964
H(161)	0.1839	0.4947	0.0340		0.0964
H(162)	0.1697	0.4272	−0.0343		0.0964
H(163)	0.3511	0.4467	0.0171		0.0964

$w' = 1/\Sigma_1^n A_r T_r(X)$ where n ($n = 3$) is the number of coefficients A_r for a Chebyshev series, for which X is F_c/F_c(max) [7]. The model reached convergence with $R = \Sigma(\|F_o| - |F_c\|)/\Sigma|F_o|$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]^{1/2}$ having values of $R = 0.043$ and $R_w = 0.041$. Criteria for a satisfactory complete analysis were the ratio of rms shift to standard deviation being less than 0.1 and no significant features in the final difference map. Atomic coordinates are given in Table 2.

2.3. Preparation of [Cr(CO)$_3$ · 3]

This was obtained by a classical method [8]. A solution of **3** (0.50 g, 1.51 mmol) and [Cr(CO)$_6$] (0.48 g, 2.18 mmol) in 50 ml of dibutyl ether and 5 ml of THF was heated under reflux for 24 h with vigorous stirring. After cooling and filtration through silica, the solution was evaporated to dryness. The residue was taken up in ethyl acetate and chromatographed on a Florisil column (SiO_2 : MgO = 85 : 15) with a benzoene–hexane mixture (benzene : hexane = 1 : 1); the yellow fractions give 0.19 g of [Cr(CO)$_3$ · **3**] (yield, 29%), including 0.03 g of pure isomer **1** and 0.16 g of a

TABLE 3. ^{1}H nuclear magnetic resonance data for **3** and [Cr(CO)$_3$·**3**] isomers in CDCl$_3$

Atom	Isomer **1** [a]		Isomer **2** [a]		**3** [b]
	δ (ppm)	J (Hz)	δ (ppm)	J (Hz)	δ (ppm)
4	7.31	d,[c] $^3J = 8.0$	7.31	d, $^3J = 8.0$	7.28
5	7.14	t, $^3J = 7.8$	7.15	t, $^3J = 7.8$	7.12
6	6.85	d, $^3J = 7.8$	6.85	d, $^3J = 7.8$	6.84
7	2.12	s	2.14	s	2.09
8	2.49	s	2.48	s	2.46
9	0.24	s	0.24	s	0.26 [d]
10	0.43	s	0.41	s	0.49 [d]
13	5.87	d, $^3J = 6.4$	5.88	d, $^3J = 6.3$	7.71
14	5.26	d, $^3J = 6.5$	5.26	d, $^3J = 6.5$	7.09
17	5.98	b	5.92	b	6.51

[a] Throughout the text, where both isomers are involved, isomer **1** denotes the one with the most deshielded nitrogen-bonded proton. [b] From ref. 9. [c] Abbreviations used are as follows: d, doublet; t, triplet; s, singlet; b, broad. [d] The correct assignment for the two methyl groups of **3** was readily deduced from ^{1}H–^{1}H nuclear Overhauser spectroscopy (see text).

TABLE 4. ^{13}C nuclear magnetic resonance chemical shifts for **3** and [Cr(CO)$_3$·**3**] isomers in CDCl$_3$

Atom	δ (ppm)		d [c] (ppm)	δ, **3** [b] (ppm)	D [e] (ppm)
	Isomer **1** [a,b]	Isomer **2** [a,b]			
1	146.61	146.54	+0.07	148.1	1.5
2	132.56	131.74	+0.82	132.1	0
3	135.53	135.22	+0.31	135.2	−0.2
4	126.81	126.81	+0.00	126.5	−0.3
5	127.10	127.17	−0.07	126.7	−0.4
6	125.75	126.44	−0.69	126.1	0
7	14.93	15.24	−0.31	15.2	0.1
8	14.08	14.08		13.3	−0.8
9	0.40 (b)	0.40 (b)		0.9 (b)	
10	1.02 (b)	1.02 (b)		0.9 (b)	
11	127.13	127.10	−0.03	145.9	18.8
12	79.5 (vb)	79.5(vb)		125.1 [f] (vb)	45.6
13	97.90	97.98	−0.08	134.1	36.2
14	87.45	87.33	+0.12	121.0	33.7
15	118.64	118.82	−0.18	137.9	19.2
16	91.16	90.92	−0.24	120.2	29.2
CO	232.72	232.64			

[a] See Table 3 for the convention used for isomers **1** and **2**. [b] The abbreviations used are as follows: b, broad; vb, very broad. [c] $d = \delta$(^{13}C, isomer **1**) − δ(^{13}C, isomer **2**). [d] From reference 9. [e] $D = \delta$(^{13}C, **3**) − δ(^{13}C, [Cr(CO)$_3$·**3**]) (mean value). [f] Unpublished results.

TABLE 5. T_1 relaxation time for protons of **3** and [Cr(CO)$_3$·**3**] isomers in CDCl$_3$ at 22°C

Atom	T_1 (s)		
	Isomer 1 [a]	Isomer 2 [a]	3
7	1.45	1.45	1.70
8	1.20	1.15	[b]
9	1.20	1.20	1.45
10	1.25	1.20	1.50

[a] See Table 3. [b] Could not be measured because of overlapping signals.

mixture of both isomers (see text). (Melting point (m.p.), 200–202°C). Anal. Found: C, 49.5; H, 4.3; N, 5.2; Cr, 10.5. $C_{19}H_{18}B_2Cl_2CrN_2O_3$. calc.: C, 48.9; H, 3.9; N, 6.0; Cr, 11.1%. NMR data are summarized in Tables 3–6.

2.4. Preparation of [Cr(CO)$_3$·4]

The same reaction was applied to **4** (0.50 g, 1.51 mmol) and [Cr(CO)$_6$] (0.52 g, 2.36 mmol). After the same chromatographic work-up, three yellow fractions were collected. The first two (0.12 g) were different mixtures of both isomers of [Cr(CO)$_3$·**4**]. The third fraction (0.04 g) contained the same isomeric mixture (75% according to NMR integration; about 0.03 g) and (25%; about 0.01 g) of a mixture of both isomers of [Cr(CO)$_3$·**6**] (see text) (yield, 23% for [Cr(CO)$_3$·**4**] and 2% for [Cr(CO)$_3$·**6**]. NMR data are summarized in Tables 7 and 8.

TABLE 6. ^{1}H nuclear magnetic resonance chemical shifts for **3** and [Cr(CO)$_3$·**3**] in C_6D_6 and CDCl$_3$

Atom	δ (ppm)					
	C_6D_6			CDCl$_3$		
	Isomer 1	Isomer 2	3	Isomer 1 [a]	Isomer 2 [a]	3
4	7.15 [b]	7.12 [b]	7.16 [b]	7.31	7.31	7.28
5	6.78	6.68	6.78	7.14	7.15	7.12
6	6.51	6.58	6.57	6.85	6.85	6.84
7	2.20	2.07	2.08	2.12	2.14	2.09
8	1.79	1.77	2.05	2.49	2.48	2.46
9	0.03	0.01	0.14	0.24	0.24	0.26
10	0.29	0.31	0.52	0.43	0.41	0.49
13	5.25	5.27	7.63	5.87	5.88	7.71
14	4.66	4.66	7.14	5.26	5.26	7.09
17	5.37	5.30	6.10	5.98	5.92	6.51

[a] See Table 3. [b] Despite considerable overlap of these three signals with that of free C_6H_6 and of hydrogen atom 14 of **3**, the correct assignment was deduced from the ^{1}H–^{1}H COSY spectrum of the mixture. Thus cross-peaks were observed between methyl protons 7 and aromatic protons 4, 5 and 6 involving scalar interactions through five and/or six bonds.

TABLE 7. ^{1}H nuclear magnetic resonance data for **4** and [Cr(CO)$_3$·**4**] isomers in CDCl$_3$

Atom	Isomer 1 [a]		Isomer 2 [a]		4 [b]
	δ (ppm)	J [c] (Hz)	δ (ppm)	J [c] (Hz)	δ (ppm)
3	7.28 [d]	d	7.27_5	d	7.26
5	7.20	dd, $^3J = 8.3$ $^4J = 2.7$	7.21	dd, $^3J = 8.3$ $^4J = 2.7$	7.18
6	6.85	d, $^3J = 8.3$	6.86	d, $^3J = 8.3$	6.83
7	2.03	s	2.04	s	1.99
8	2.35	s	2.34	s	2.38
9	0.20	s	0.19	s	0.25
10	0.50	s	0.49	s	0.49
13	6.00 [e]	d, $^4J = 1.8$	6.00 [e]	d, $^4J = 1.7$	7.74
15	6.02	d, $^4J = 1.8$	5.98	d, $^4J = 1.7$	7.34
17	5.87	s	5.80	s	6.44

[a] See Table 3. [b] From ref. 9. [c] The abbreviations used are as follows: d, doublet; dd, doublet of doublet; s, singlet. [d] Two overlapping doublets appearing as a poorly resolved triplet. [e] Each isomer gives an AB system, the correct assignment for υ_A and υ_B being derived from ^{1}H–^{1}H nuclear Overhauser spectroscopy.

2.5. Preparation of B,B′,B″-trichloro-N,N′,N″-triphenylborazine ((C$_6$H$_5$NBCl)$_3$)

This was obtained by the slow addition of aniline (8 ml, 85 mmol) in 40 ml of toluene to an ice-cooled solution of boron trichloride (10 g, 85 mmol) in 80 ml of toluene according to a standard procedure [10]. After 4 h of reflux, then cooling and concentrating the solution, 10.8 g of crystals were recovered (yield, 92.5%). The same reaction was applied to *m*-toluidine, *p*-toluidine and *p*-fluoroaniline.

TABLE 8. ^{13}C nuclear magnetic resonance chemical shifts for **4** and [Cr(CO)$_3$·**4**] isomers in CDCl$_3$

Atom	δ (ppm)		d [c] (ppm)	δ, 4 [d] (ppm)	D [e] (ppm)
	Isomer 1 [a,b]	Isomer 2 [a,b]			
1	143.90	143.90	0	145.4	1.5
2	135.70	134.81	+0.89	135.3	0
3	130.71	130.42	+0.29	130.4	−0.2
4	131.18	131.24	−0.06	130.8	−0.4
5	126.84	127.15	−0.31	126.8	−0.2
6	128.23	128.94	−0.71	128.7	+0.1
7	18.04	18.22	−0.18	18.2	+0.1
8	16.87	16.87	0	16.9	0
9	1.0 (b)	1.0 (b)		0.9	
10	0.9 (b)	0.9 (b)		0.9	
11	125.66	125.11	+0.55	143.4	18.1
12	81.2 (vb)	81.0 (vb)	+0.2	125.1 [f]	44.0
13	98.76	98.87	−0.11	132.9	34.1
14	92.03	91.90	+0.13	124.8	32.9
15	98.59	98.68	−0.09	132.7	34.1
16	102.91	103.34	−0.43	124.5	21.4
CO	232.48	232.62	−0.14		

[a] See Table 3. [b] The abbreviations used are as follows: b,broad; vb, very broad. [c] $d = \delta(^{13}C$, isomer **1**$) - \delta(^{13}C$, isomer **2**). [d] From ref. 9. [e] $D = \delta(^{13}C, \mathbf{4}) - \delta(^{13}C$, [Cr(CO)$_3$·**4**]) (mean value). [f] Unpublished results.

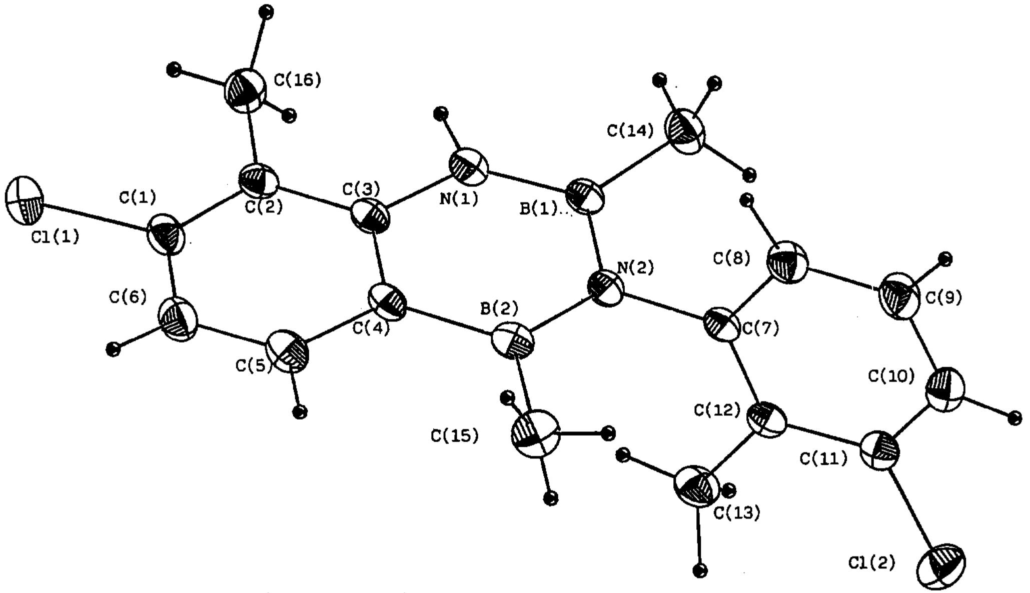


Fig. 2. ORTEP drawing of 3 (50% ellipsoids).

TABLE 9. Selected interatomic distances and angles for 3

	Interatomic distance (Å)		Interatomic distance (Å)
Cl(1)–C(1)	1.744(4)	Cl(2)–C(11)	1.731(4)
B(1)–N(1)	1.399(5)	B(1)–N(2)	1.443(5)
B(1)–C(14)	1.572(6)	B(2)–N(2)	1.431(6)
B(2)–C(4)	1.540(6)	B(2)–C(15)	1.564(6)
N(1)–C(3)	1.388(5)	N(2)–C(7)	1.441(5)
C(1)–C(2)	1.376(6)	C(1)–C(6)	1.393(6)
C(2)–C(3)	1.410(5)	C(2)–C(16)	1.488(6)
C(3)–C(4)	1.412(5)	C(4)–C(5)	1.407(6)
C(5)–C(6)	1.362(6)	C(7)–C(8)	1.395(5)
C(7)–C(12)	1.386(5)	C(8)–C(9)	1.384(6)
C(9)–C(10)	1.369(6)	C(10)–C(11)	1.381(6)
C(11)–C(12)	1.390(5)	C(12)–C913)	1.498(6)

	Interatomic angle (°)		Interatomic angle (°)
N(2)–B(1)–N(1)	118.1(4)	C(14)–B(1)–N(1)	119.7(4)
C(14)–B(1)–N(2)	122.1(4)	C(4)–B(2)–N(2)	116.5(4)
C(15)–B(2)–N(2)	121.3(4)	C(15)–B(2)–C(4)	122.2(4)
C(3)–N(1)–B(1)	126.0(4)	B(2)–N(2)–B(1)	120.9(4)
C(7)–N(2)–B(1)	119.1(3)	C(7)–N(2)–B(2)	119.9(3)
C(2)–C(1)–Cl(1)	119.9(4)	C(6)–C(1)–Cl(1)	116.8(3)
C(6)–C(1)–C(2)	123.3(4)	C(3)–C(2)–C(1)	116.3(4)
C(16)–C(2)–C(1)	123.3(4)	C(16)–C(2)–C(3)	120.4(4)
C(2)–C(3)–N(1)	119.8(4)	C(4)–C(3)–N(1)	117.5(3)
C(4)–C(3)–C(2)	122.7(4)	C(3)–C(4)–B(2)	120.7(4)
C(5)–C(4)–B(2)	122.7(4)	C(5)–C(4)–C(3)	116.5(4)
C(6)–C(5)–C(4)	122.3(4)	C(5)–C(6)–C(1)	118.8(4)
C(8)–C(7)–N(2)	118.6(3)	C(12)–C(7)–N(2)	120.2(3)
C(12)–C(7)–C(8)	121.2(4)	C(9)–C(8)–C(7)	119.4(4)
C(10)–C(9)–C(8)	120.6(4)	C(11)–C(10)–C(9)	119.2(4)
C(10)–C(11)–Cl(2)	117.5(3)	C(12)–C(11)–Cl(2)	120.2(3)
C(12)–C(11)–C(10)	122.3(4)	C(11)–C(12)–C(7)	117.3(4)
C(13)–C(12)–C(7)	121.3(4)	C(13)–C(12)–C(11)	121.4(4)

2.6. Preparation of B,B′,B″-trimethyl-N,N′,N″-triphenylborazine ($C_6H_5NBMe)_3$) (5a)

To 10.8 g of $(C_6H_5NBCl)_3$ (26.2 mmol) in diethyl ether was added a suspension of CH_3MgI prepared from 11.35 g (80 mmol) of methyl iodide and 1.95 g (80 mmol) of Mg under an atmosphere of dry nitrogen. After 1 h of reflux, the slurry was cooled and quenched with an aqueous solution of ammonium chloride. After filtration and washing with diethyl ether, the organic layers were dried with calcium chloride and evaporated to dryness under reduced pressure to give 5.96 g (17 mmol (65%)) of pure **5a** (m.p., 264–266°C; m.p. [11] (Et_2O–MeOH), 264–269°C). ^{13}C NMR: 148.7 (1); 128.7 (3,5); 128.2 (2,6), 124.7(4); 0.8 (B–Me) ppm. ^1H NMR: 7 (m); −0.2 (B–Me) ppm ^{11}B NMR: 35.8 ppm.

A similar reaction led to the following.

***B,B′,B″*-trimethyl-*N,N′,N′*-tri-*p*-tolylborazine (5b):** yield, 92%; m.p., 266–268°C; m.p. [12] 269–271°C. ^{13}C NMR: 146.1 (1); 133.9 (4); 129.3 (2,6); 127.9 (3,5); 20.4 (7, C–Me); 1.1 (8, B–Me) ppm.

***B,B′,B″*-trimethyl-*N,N′,N″*-tri-*p*-fluoroborazine (5c):** yield, 15%; m.p., 194–196°C.

***B,B′,B″*-trimethyl-*N,N′,N″*-tri-*m*-tolylborazine (5d):** yield, 82%; m.p., 240–242°C; m.p. [12], 240°C.

2.7. Preparation of [Cr(CO)$_3$ · 5a]

1.5 g of **5a** (4.28 mmol) was heated with 2 g of $[Cr(CO)_6]$ (9.09 mmol) in 50 ml of Bu_2O–THF = 10:1 for 24 h. After work-up as for $[Cr(CO)_3 \cdot$ **3**] and elution with benzene–hexane (benzene : hexane = 1 : 1) 0.58 g (1.29 mmol) (yield, 30%) of a yellow solid was recovered (m.p., 266–268°C). ^1H NMR: 7.2 (10 p); 4.1 and 5.3 (5 p) ppm. ^{11}B NMR: 36.1 ppm. IR (Nujol): ν(CO) 1870, 1900, 1970 cm^{-1}.

2.8. Preparation of [Cr(CO)$_3$ · 5b]

1.5 g of **5b** (4.28 mmol) and 2 g of $[Cr(CO)_6]$ (9.09 mmol) heated for 24 h in Bu_2O–THF led, after the same work-up, to 0.62 g (1.26 mmol) (yield, 33%) of a yellow solid (m.p., 198–200°C). ^{13}C NMR: 233.7 (CO); 146.1 (1); 133.9 (4); 129.3 (2,6); 127.9 (3,5); 124.1 (1′); 106.4 (4′); 95.7 (2′,6′); 92.4 (3′,5′); 20.9 (7); 20.0 (7′); 3.1 (8′); 1.1 (8) ppm.

A similar reaction was applied to **5c** to yield 5% of $Cr(CO)_3 \cdot$ **5c** and to **5d** to yield 18% of $Cr(CO)_3 \cdot$ **5d**.

3. Results and discussion

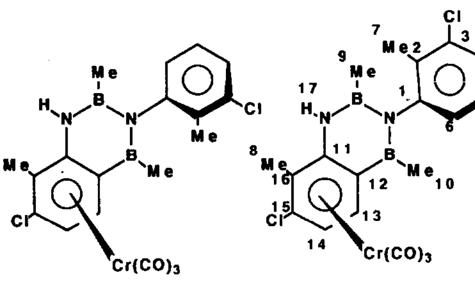
3.1. Molecular structure of 3

The molecular structure of **3** is shown in Fig. 2 and selected intramolecular distances and angles are given in Table 9. The molecular structure of **3** consists of an aromatic ring, C(7)–C(12), and a diboradiazaronaphthalene-like ring, numbered clockwise from N(2) to B(1). The aromatic ring is quite regular with C–C distances ranging from 1.362(6) to 1.412(5) Å and angles from 117.3(4) to 122.3(4)°, within the values generally observed in related borazines [13]. The B–N distances vary from 1.399(5) to 1.443(5) Å and are in good agreement with the related distances reported for the unchlorinated parent $C_{16}H_{20}N_2B_2$ [13], 1.405(4) to 1.454(4) Å. The central borazine ring is strictly planar with a mean angle of 120°, confirming the aromaticity of the ring. This aromatic ring is fused through the C(3)–C(4) bond with the C(3)–C(2)–C(1)–C(6)–C(5)–C(4) phenyl ring in a planar overall arrangement, the angle between these two planes being 2.9°. The angle between the diboradiazaronaphthalene mean plane and the extra phenyl ring is 95.8°, significantly higher than observed for the unchlorinated homologue. The Cl(1) and Cl(2) atoms are located respectively in the planes of the phenyl rings within a mean deviation of 0.11 Å.

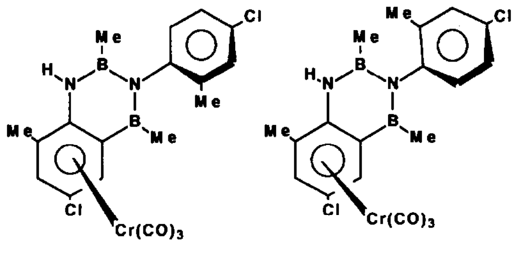
3.2. Isomers of Cr(CO)$_3$ · 3

Reaction of $[Cr(CO)_6]$ with the boron nitrogen heterocycle **3** gave $[Cr(CO)_3 \cdot$ **3**] exclusively in which the $Cr(CO)_3$ is attached to the benzo ring, although three 6π-electron coordination sites are available. This was shown by the ^1H NMR spectra of these complexes; a shielding of 1.8 ppm for two aromatic protons and 0.6 ppm for the nitrogen-bonded proton was observed. Further support was from the ^{13}C NMR spectra where six carbon atoms experience a shielding of about 19–45 ppm. Furthermore, two isomers are present in the mixture in a 1 : 1 ratio, depending on the position of the $Cr(CO)_3$ moiety with respect to the methyl substituent of the phenyl group which is nearly perpendicular to the plane of the diboradiazaronaphthalene system [13]. The lack of isomer preference indicates little interaction of the NH, Me and Cl benzo substituents of **3** with the incoming $Cr(CO)_3$ while the two B–Me and the phenyl-bonded Me groups are probably too remote to exert any significant interaction with $Cr(CO)_3$. These results are consistent with our previous report [3].

The evidence of a single isomer with **2** resulted from the complete separation by chromatographic methods. Similarly, one isomer could be obtained pure from $[Cr(CO)_3 \cdot$ **3**], whereas the other isomer was always mixed with the first (Fig. 3). Thus the ^1H and ^{13}C chemical shifts of both isomers of 3 were readily deduced and are summarized in Tables 3 and 4. Furthermore, when samples of the pure isomer of $[Cr(CO)_3 \cdot$ **3**] were kept at room temperature or near 60°C in the solid state for long periods, no changes were detected in the ^1H NMR spectra, suggesting a kinetically rather than a thermodynamically controlled ratio.



[Cr(CO)$_3$·3]



[Cr(CO)$_3$·4]

Fig. 3. Representation of complexes [Cr(CO)$_3$·3] and [Cr(CO)$_3$·4].

The difference observed between the ^1H chemical shifts of the two isomers are very small as a result of two opposing factors: a deshielding from the electron-withdrawing properties of the Cr(CO)$_3$ group and a shielding due to the magnetic anisotropy of the chromium–CO bond [14]. The chromium–carbonyl group attached to the benzo ring influences the closer hydrogen atoms 17, 7, 8, and 10 and unexpectedly the aromatic protons 13 and 5 (one would expect a larger influence on proton 6 than on 5). With ^{13}C NMR spectroscopy, if one considers the chemical shifts of the carbon atoms of the extra phenyl group for both isomers, these are observed at either upper or lower field depending on the position of the carbon atoms above (2,3) or below (5,6) the plane of the molecule. This influence does not affect carbon atoms 1 and 4, located in that plane. A similar trend was obtained with [Cr(CO)$_3$·**4**] isomers. This effect could originate from a weakening of the ring current associated with the C_2NBNB aromatic system. Similar effects were observed with the 4π-electron cycle of bis-(η^6-biphenylene)chromium complexes [15].

Various NMR experiments were performed in order to obtain accurate information on the configuration of each isomer. Relaxation times T_1 were measured for the methyl protons 7, 8, 9 and 10 of **3** and both isomers. The values are reported in Table 4. The small differences observed between the two isomers are not significant, whereas the larger value obtained for **3** alone simply denotes a smaller correlation time for the latter because of its smaller steric requirement.

A heteronuclear ^1H–^{13}C nuclear Overhauser effect (NOE) experiment was also performed by pre-irradiation of the satellite ^{13}C band of the hydrogen atom 7 of each isomer in order to observe, by means of ^{13}C NMR spectroscopy an eventual enhancement of the CO signal. However, because of the remoteness of these atoms, no effect was noticeable.

Finally, it was possible to take advantage of solvent effects on the ^1H NMR spectra of **3** and [Cr(CO)$_3$·**3**] in $CDCl_3$ and C_6D_6. In C_6D_6, a ^1H–^1H COSY doubly quantum filtered spectrum and a ^1H–^1H NOE spectrum were used to obtain the correct assignments. Additionally, the NOE spectrum gave straightforward attribution for methyl groups 9 and 10. The chemical shifts are summarized in Table 6. Dissolution in C_6D_6 results in a general deshielding compared with $CDCl_3$. Further, a comparison of the chemical shifts of both isomers in C_6D_6 is very informative. Thus methyl protons 8, 9 and 10 lying in the same plane have nearly identical chemical shifts in both isomers, the stacking of the benzene molecules being identical in each case. The methyl proton 7 is quite deshielded in isomer **1** (2.20 ppm) whereas the relevant chemical shifts for isomer **2** and **3** are quite similar (2.07 ppm and 2.08 ppm respectively). Conversely, proton 6 is the most deshielded for isomer **2** at 6.58 ppm instead of 6.51 ppm for isomer **1**. Thus we can tentatively conclude that Cr(CO)$_3$ lies on the opposite side of the methyl group 7 in isomer **2**. Similar results were reported from the ^1H NMR spectra of other molecules in which the incorporation of a chromium tripod yields diastereomeric products, rendering the faces non-equivalent. In every case, the *exo*-methyl, *i.e.* the methyl group opposite the Cr(CO)$_3$ moiety, is shielded relative to the *endo*-methyl group [16–19]. These observations were recently extended to ^{13}C NMR spectroscopy, the methyl groups of [(C_6Et_5COMe)Cr(CO)$_3$] resonating at lower field when proximal rather than distal, *i.e.* near to or remote from the Cr(CO)$_3$ [20].

In order to study the barrier to rotation of the phenyl substituent, mixtures of [Cr(CO)$_3$·**3**] isomers were heated in C_6D_6 at about 70°C but no coalescence could be observed for the two methyl signals at 2.07 and 2.20 ppm in the ^1H NMR spectra. Further, an exchange reaction between Cr(CO)$_3$·**3** and C_6D_6 was suspected since the presence of [(C_6H_6)Cr(CO)$_3$] was readily detected by a very sharp signal near 93.0 ppm in the ^{13}C NMR spectra of some samples of [Cr(CO)$_3$·**3**] that had been recrystallized from benzene (92.9 ppm [21]). With higher boiling solvents such as dimethylsulphoxide-d_6, extensive degradation of the complexes resulted. Complexes [$Cr(CO)_3 \cdot$ **3**] decompose slowly in solution especially with chlorinated solvents to **3** and solid green materials.

3.3. Isomers of [$Cr(CO)_3 \cdot 4$]

No pure isomer could be obtained in this case. However, fractions with varying amounts of both isomers enabled the NMR spectra to be assigned (Tables 7 and 8). In the ^1H NMR spectra, shieldings of 1.3–1.7 ppm for two aromatic protons and of 0.6 ppm for the NH hydrogen were observed, together with a shielding of about 18–44 ppm in the ^{13}C NMR spectra. The other carbon atoms are not affected except for carbon 1 whose shielding, about 1.5 ppm, reflects some subtle changes in anisotropy, probably caused by variation in the interplanar angle θ as observed in biphenyl derivatives [22].

Some samples of the isomers were contaminated by another compound. This was indicated by the presence in the ^1H NMR spectrum of the mixture by two very close 1:2:1 triplets at about 4.93 ppm and a poorly resolved multiplet overlapping with the NH signals at about 5.8–5.9 ppm. Additional signals were also observed in the methyl region at 2.31, 2.30, 2.07, 2.06, 0.45, 0.44, 0.22 and 0.21 ppm different from those belonging to the reported isomers and/or the ligand **4**. The presence of a second isomer with $Cr(CO)_3$ bonded to the phenyl group is at variance with the appearance of the triplet-structured aromatic proton that requires three adjacent protons on a benzene nucleus. On the contrary, the presence of a chain-like derivative, after breaking of the boron–carbon bond, would result in an averaging of the methyl resonances, which was not observed in the NMR spectra. A ^1H–^1H NOE spectrum was therefore undertaken to provide additional information. Thus, in the NH–methyl 8 region, four different cross-peaks are observed. Two of them can be attributed to isomers **1** and **2** of **4** (Table 7). The other two belong to the signals at 2.31, 2.30, 0.22 and 0.21 ppm noted above. These data, together with the other signals at 2.07, 2.06, 0.45 and 0.44 ppm, support the existence of a second pair of isomers having structures quite similar to those of isomers **1** and **2**.

An attempted exchange of this fraction with D_2O in order to shift the overlapping NH resonances failed and resulted in the complete hydrolysis of the complexes. This problem was resolved by a ^1H–^1H COSY experiment (Fig. 4). In the one-dimensional spectrum, three peaks of growing intensity appeared at 7.83 (d), 7.36 (d) and 7.01 (t) ppm, corresponding to three adjacent hydrogen atoms in a benzene nucleus. These three signals are related to a product resulting from the decomposition of the second pair of isomers. Surprisingly, the chemical shifts are very close to those of aromatic protons 13, 14 and 15 of ligand **1**: 7.84 (d), 6.99 (t) and 7.34 (d) ppm, respectively [9]. Furthermore, the unexplained triplet observed at 4.93 ppm as well as the complex pattern at about 5.8–5.9 ppm closely fit the values reported for the ^1H NMR spectrum of [$Cr(CO)_3 \cdot$ **1**]: 5.90 (d), 4.93 (t) and 5.84 (d) ppm [3]. Thus the ligand of the second pair of isomers can be identified as **6** and the two isomers as of [$Cr(CO)_3 \cdot$ **6**] (Fig. 5). This ligand **6** differs from **4** by replacement of a Cl atom by a hydrogen atom. Although $Cr(CO)_3$ is known to favour nucleophilic substitution in aromatic compounds, by MeO or NR_2 for instance, the replacement of Cl by H when no conventional reducing agent is present is surprising unless this occurs during chromatography.

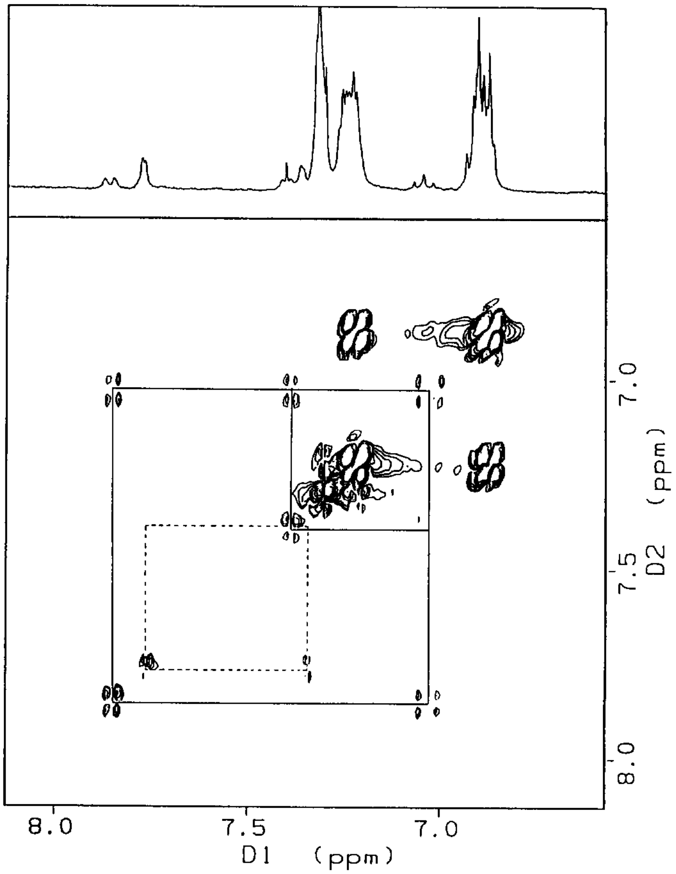
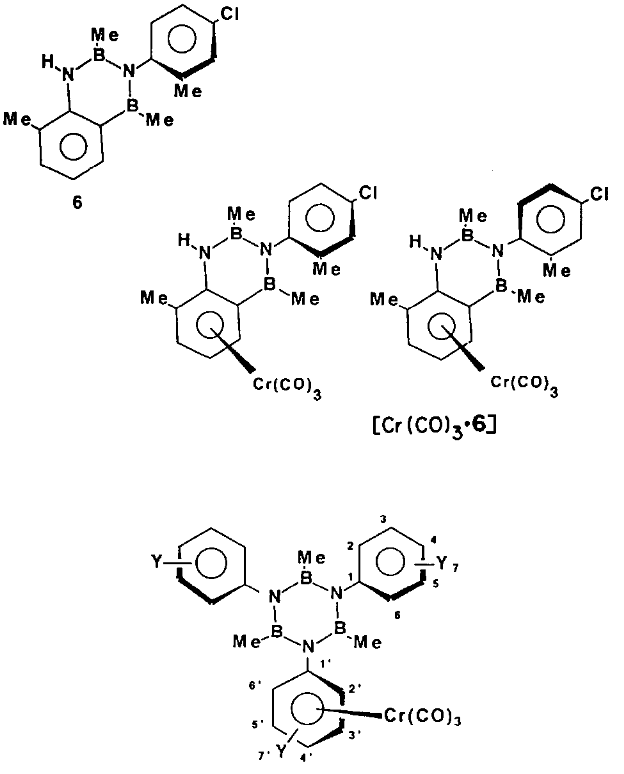


Fig. 4. ^1H–^1H partial COSY doubly quantum filtered spectrum of the mixture of isomers of [$Cr(CO)_3 \cdot 4$], [$Cr(CO)_3 \cdot 6$] and **4** or **6** in $CDCl_3$. The cross-peaks joined by a bold line at 7.83, 7.36 and 7.01 ppm belong to **6** (protons 13, 15 and 14 respectively). **4** gives the cross-peaks with the broken line at 7.74 and 7.34 ppm (protons 13 and 15) whereas the main cross-peaks at about 7.25, 7.20 and 6.85 ppm pertain to protons 3, 5 and 6 of isomers of [$Cr(CO)_3 \cdot 4$], [$Cr(CO)_3 \cdot 6$], **4** and **6**. Acquisition parameters are as follows: spectral width = 3000 Hz; acquisition time = 0.341 s; size = 2048; number of experiments = 512. The final matrix size is 1024 × 1024 real. Prior to Fourier transform, a $\sin^2$ bell was applied in two dimensions.



6

[Cr(CO)$_3$·6]

[Cr(CO)$_3$·5]

Fig. 5. Representation of 6 and complexes [Cr(CO)$_3$·6] and [Cr(CO)$_3$·5].

3.4. system: [Cr(CO)$_3$·5]

In an attempt to prepare compounds where Cr(CO)$_3$ is bonded to the phenyl group of 3, the same reaction was carried out using an excess of [Cr(CO)$_6$] or a higher boiling solvent such as diglyme but always unsuccessfully, and the ^{1}H NMR spectrum revealed the benzo-bonded monosubstituted isomer [Cr(CO)$_3$·3] only. However, when [Cr(CO)$_6$] reacted with the *B,B′,B″*-trimethyl-*N,N′,N″*-triarylborazines (**5a** and **5b**), the expected [Cr(CO)$_3$·5] compound was readily obtained and characterized by its ^{1}H and ^{13}C NMR spectra as a phenyl-bonded monosubstituted compound. These results contrast with the reported existence of [2Cr(CO)$_3$·L] and [3Cr(CO)$_3$·L] with $(C_6H_5NBH)_3$ as the ligand [23]. Although derivatives where Cr(CO)$_3$ is η^6 bonded to the borazine ring [24] or related boron–nitrogen heterocycles [25] are well documented, in all cases where a choice of coordination site is available [23,26], ^{1}H and ^{11}B NMR spectra indicated exclusive attachment of Cr(CO)$_3$ to the benzo or phenyl ring. The only exception is the recently synthesized 3-methyl-3-benzoborepin in which the Cr(CO)$_3$ prefers the η^7-boron-containing cycle to the η^6-benzo-fused ring [27]. When the *meta*-substituted *B,B′,B″*-trimethyl-*N,N′,N″*-triarylborazine (**5d**) reacted with [Cr(CO)$_6$], a complex mixture of atropisomers was obtained [28]. In this case, careful ^{1}H NMR integration again indicated compounds with only one Cr(CO)$_3$ bonded to borazine.

4. Supplementary material available

^{1}H NMR spectra (5 pages) and listings of observed and calculated structure factors (9 pages) are available from the authors. Tables of anisotropic temperature factors, important least-squares planes, complete distances and angles (4 pages) are available from the Cambridge Crystallographic Data Centre.

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