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Synthesis and characterization of diboradiazaronaphthalenetricarbonylchromium complexes

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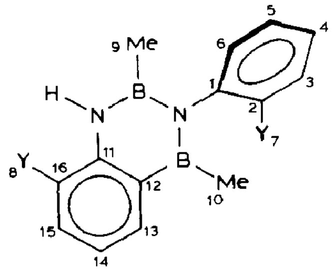
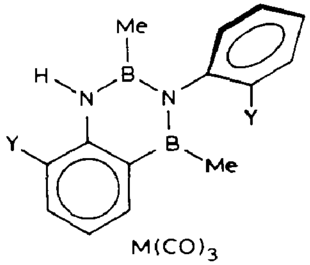
Abstract

Reaction of $Cr(CO)_6$ with the boron-nitrogen heterocycle **1a** gives exclusively complex **2a** in which the $Cr(CO)_3$ moiety is attached to the benzo ring, although three coordination sites are possible. The product is formed as a 1/1 mixture of



(**1a**, Y = Me ;
1b, Y = Br)



(**2a** : Y = Me, M = Cr ;
2b : Y = Br, M = Cr ;
2c : Y = Me, M = Mo ;
2d : Y = Me, M = W)

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* For further correspondence.

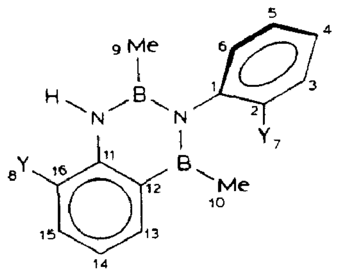
isomers differing in the position of the $Cr(CO)_3$ group with respect to the extracyclic methyl substituent. When the ligand **1b** was treated with $Cr(CO)_6$, a similar compound **2b** was obtained, but, surprisingly, no isomers could be detected. The reaction of **1a** and $W(CO)_6$ gives the expected complex **2d** (mixed with **1a**), whereas the related complex **2c** formed from **1a** and $Mo(CO)_6$ decomposes before it can be spectroscopically characterized.

Introduction

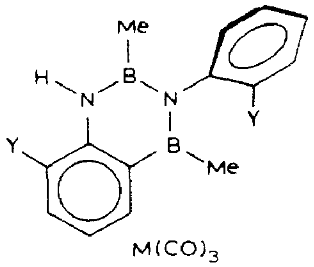
In recent years the preparations and studies of $LM(CO)_3$ complexes (M = Cr, Mn), where L represents a polycyclic aromatic ligand, have attracted considerable attention. Their importance stems on the one hand from the considerable synthetic potential of such complexes [1] and on the other hand from the growing interest, from both an experimental [2] and a theoretical [3] point of view, in the haptotropic rearrangement, that is in the aptitude of the $M(CO)_3$ moiety to migrate from one cycle to the other. Such rearrangements are especially important with charged species and with neutral systems containing a naphthalene ring. Here we describe the synthesis and characterization of such compounds $LCr(CO)_3$ (**2a** and **2b**) (Fig. 1) starting from the naphthalene-isoelectronic ligands **1a** and **1b**, the preparations of which [4] and their study by means of 2D NMR spectroscopy [5], have been reported previously.

Results and discussion

From the reaction of **1a** with $Cr(CO)_6$ by an established procedure [6], **2a** was obtained in moderate yield as a yellow air stable solid, which was soluble in common solvents. However, the solutions became cloudy within hours, especially in the case of chlorinated solvents, and gave greenish materials from which the ligand **1a** could be recovered. The structure of **2a** could be deduced from NMR data. The ^1H NMR spectrum of **2a** in $CDCl_3$ shows four aromatic proton signals in the usual range and four others (three aromatic protons and the nitrogen bonded one)



(**1a**, Y = Me ;
1b, Y = Br)



(**2a** : Y = Me , M = Cr ;
2b : Y = Br , M = Cr ,
2c : Y = Me , M = Mo ;
2d : Y = Me , M = W)

Table 1

^1H chemical shifts for **1a** and **2a**

Proton	**1a** [a]	**2a**	Δ [d]
3	7.25		
4	7.14	7.19–7.26 (m)	
5	7.19		
6	6.90	6.95 (t)	
7	2.02	2.08	
8	2.39	2.31	
9	0.25 [b]	0.22	
10	0.52 [b]	0.45	
13	7.84	5.90 (d)	1.94
14	6.99	4.93 (t)	2.06
15	7.34	5.84 (d)	1.50
N*H*	6.45	5.90 [c]	

[a] Data from ref. 5. [b] These assignements were based on unpublished NOE experiments on a related molecule. [c] This proton overlaps with the signals from protons 13 and 15. [d] $\Delta = \delta$**1a** $- \delta$**2a** in ppm.

strongly shielded (Table 1), the typical pattern for an arene-bonded $Cr(CO)_3$ moiety [7]; the ^1H NMR spectrum of **2a** in DMSO-d_6 displays three singlets upfield corresponding to the three shielded aromatic protons and a complex multiplet arising from five protons, the four aromatic ones and the NH proton. More accurate conclusions can be drawn from the ^{13}C NMR spectra of **2a** (Table 2). Thus, from the observed upfield shifts of carbon atoms 11, 13, 14, 15 and 16, it may safely be concluded that the $Cr(CO)_3$ ligand is attached to the benzo-ring rather than to the phenyl ring (boron-bonded carbon 12 could not be detected in the complex **2a**). Additional features were to be expected in these spectra; for instance, two isomers are present, differing in whether the $Cr(CO)_3$ moiety is on one side or the other side of the benzo-ring plane. Thus, each carbon of the phenyl ring gives rise to a doublet except for carbons 1 and 4 which lie in the plane of the molecule, and carbon 5 which is probably too remote. From this point of view, the signals from carbons 7 and 8 are quite significant: the carbon atom 8, in the plane of the molecule, displays a sharp singlet about twice as high as each peak of the doublet corresponding to carbon 7. For the same reason, two signals of the same intensity are observed for the carbonyl groups. The small splitting (less than 0.1 ppm) for the primary aromatic carbons 13, 14 and 15 is a further consequence of the slightly different positions of the $Cr(CO)_3$ moiety in the isomers. Indeed, the observation of different conformers arising from hindered rotation of the $Cr(CO)_3$ group is unlikely, and has never been reported, even at −60 ° C, for arenes containing a large number of bulky substituents [8]. Furthermore, the presence of such conformers would result in several signals in the CO range, rather than the two signals observed in the ^{13}C NMR spectra of **2a**. The ^{11}B NMR spectra of both compounds are of limited interest (Table 3), the small downfield shift observed for both boron atoms of **2a** indicating that the $Cr(CO)_3$ is not bonded to the heterocyclic ring. Such a result is by no means unexpected, and is in accord with earlier reports [9,10]: the $Cr(CO)_3$ moiety prefers the $6\pi e$ homocyclic ring to the $6\pi e$ $C_2N_2B_2$ one when the choice is available.

When heated in dibutyl ether (containing THF), compound **2a** displays thermochromic effects: the solution initially yellow turns orange below the boiling point,

Table 2

^{13}C chemical shifts for **1a** and **2a**

Carbon atom	**1a**	**2a**	Δ [a]
1	147.00	145.51	
2	133.34	133.89, 132.89	
3	130.33	130.85, 130.47	
4	125.30	125.92	
5	126.55	126.64	
6	127.52	127.86, 127.04	
7	18.32	18.27, 18.15	
8	17.10	16.97	
9	0.8 (broad)	0.3 (broad)	
10	0.8 (broad)	0.3 (broad)	
11	144.95	118.2	26.8
12	123.75	[b]	
13	133.83	100.17, 100.07	33.7
14	119.56	86.10, 86.03	33.5
15	132.91	99.45, 99.37	33.4
16	122.14	91.93	30.2
CO		233.87, 233.77	

[a] $\Delta = \delta$**1a**$- \delta$**2a** in ppm. [b] Not observed; detection of corresponding signal with ligand **1a** requires a very high concentration.

becoming yellow upon cooling. Similar phenomena were observed in the solid state and are not uncommon with boron–nitrogen complexes [9,10]. As such changes in colour have in some cases been associated with haptotropic rearrangement, careful variable temperature NMR studies were carried out with compound **2a**. When a sample of **2a** is heated in DMSO-d_6, large changes are observed in its ^{1}H NMR spectrum above 120 °C, the three upfield signals having almost disappeared with the 7 protons appearing in the usual range for aromatic protons. If the temperature is then raised to 130° there is no further noticeable change in the ^{1}H NMR spectrum. After cooling, only a small amount of the starting complex **2a** was recovered, together with the free ligand **1a** which was the main product. Thus, with compound **2a**, no migration of the Cr(CO)$_3$ from the benzo-ring to the phenyl was observed in DMSO-d_6; instead, in this solvent, the main reaction involved oxidation and subsequent destruction of the complex with liberation of the free ligand. This conclusion is supported by consideration of the methyl chemical shifts in the ^{1}H NMR spectrum. In order to check the possibility of a migration of the Cr(CO)$_3$ ligand to the heterocyclic ring, the ^{11}B NMR spectra of **2a** were recorded in dibutyl ether/THF; the temperature of the solution being raised slowly to the boiling point

Table 3

^{11}B chemical shifts for **1a** and **2a**

Boron atom	**1a**	**2a**	Δ [a]
9 [b]	32.5	34.0	−1.5
10	44.6	45.0	−0.4

[a] $\Delta = \delta$**1a**$- \delta$**2a** in ppm. [b] The boron atom bonded to carbon 9.

Table 4

^1H chemical shifts for **1b** and **2b**

Proton	**1b**[a]	**2b**[b]	Δ[c]
3	7.42	7.70	
4	6.66	7.15–7.19(m)[d]	
5	6.92	7.39	
6	6.72	7.15–7.19(m)	
9	0.32	0.27	
10	0.55	0.45	
13	7.80	6.25	1.65
14	6.68	4.96	1.72
15	7.54	5.93	1.61
N*H*	7.10	6.48	0.62

[a] From ref. 5, 400 MHz, C_6D_6. [b] 400 MHz, CD_2Cl_2. [c] $\Delta = \delta$**1b**$-\delta$**2b** in ppm. [d] Every proton of **2b** appeared as broad singlet (with overlap of signals from protons 4 and 6), probably because of paramagnetic impurities.

(about 117 °C). Again the studies were inconclusive, but at 80 °C and above one of the boron atom, the carbon 9 bonded one, appeared as an asymmetric doublet. The magnitude of the splitting (about 160 Hz at 100 °C) and its variation with temperature preclude a coupling with the hydrogen atom of the NH neighbouring group and it is more likely that such a doublet is in fact present for the starting complex **2a**, and the increase in temperature allows its observation because of the narrowing of the signals. This is supported by the fact that cooling the sample results in the disappearance of the fine structure. Thus splitting possibly arises from two positions of the nitrogen lone pairs, one near to and one remote from the $Cr(CO)_3$: similar results have been reported with $LCr(CO)_3$ (L = aniline, 4-aminobiphenyl) [11]. The

Table 5

^{13}C chemical shifts of **1b** and **2b**

Carbon atom	**1b**[a]	**2b**[b]	Δ[c]
1	146.53	145.52	
2	122.51	122.49	
3	132.89	133.27	
4	126.93	127.92	
5	128.16	128.97	
6	128.69	129.45	
9	0.9 (broad)	0.3 (broad)	
10	0.9 (broad)	0.3 (broad)	
11	143.58	127.60	16.0
12	125.48[d]	80.8(?)[e]	44.7
13	135.26	100.42	34.7
14	120.91	86.49	34.4
15	134.98	100.37	34.6
16	111.77	83.05	28.7
CO	–	232.87	

[a] 300 MHz, $CDCl_3$. [b] 400 MHz, CD_2Cl_2. [c] $\Delta = \delta$**1b**$-\delta$**2b** in ppm. [d] A very high concentration (about 0.6 *M*) of **1b** is required for observation of this carbon atom. [e] Very broad, and difficult to detect.

very small splitting sometimes observed in the ^1H NMR spectrum of one of the BCH_3 of **2a** may have this origin. We should emphasize that in spite of our unsuccessfull attempts to detect it, it is quite possible that an haptotropic rearrangement does take place with **2a** and it will be of interest to find a suitable deuterated high boiling solvent to continue studies.

When the same reaction was carried out with $Mo(CO)_6$ instead of $Cr(CO)_6$, the complex **2c** was found to decompose before it could be detected by NMR spectroscopy, whereas with $W(CO)_6$, the relevant complex **2d** was obtained mixed with the starting ligand, and was partially characterized. The reaction of the ligand **1b** with $Cr(CO)_6$ gave similar results, leading to the same complex **2b**, as deduced from the ^1H and ^{13}C NMR data (Table 4 and 5). However, quite unexpectedly, no isomers could be observed for **2b** in spite of the higher resolution used for the spectra (400 MHz instead of 300 MHz). The reason for such difference is a matter of speculation: despite the similar steric requirements of a methyl group and a bromine atom [12], the carbon–bromine bond (1.85 Å) is significantly longer than the carbon–carbon one (1.50 Å), thus precluding the formation of the more crowded isomer (with the bromine atom and the $Cr(CO)_3$ moiety on the same side of the plane); alternatively, an explanation might be found in a slight puckering of the benzo-ring of **2b**, which permits free rotation of the extracyclic aryl group.

Experimental

General

All reactions were carried out under dry argon by Schlenck techniques. NMR spectra were recorded on a Bruker AM 300 spectrometer at 300.13 MHz for ^1H, 75.47 MHz for ^{13}C and 96.28 for ^{11}B, and on a Bruker AM 400 at 400.13 MHz for ^1H and 100.61 MHz for ^{13}C. The following abbreviations are used: d, doublet; t, triplet and m, multiplet. TMS was the reference for ^{13}C and ^1H, and BF_3Et_2O for ^{11}B.

*Preparation of **2a**.* A solution of **1a** (1 g, 3.82 mmol) and $Cr(CO)_6$ (0.9 g, 4.08 mmol) in 50 ml dibutyl ether and 5 ml THF was refluxed 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 silica column to yield 0.39 g of a yellow solid (yield 26%, calculated for **1a**, recrystallization $CHCl_3$/hexane) (*F* 100–110 °C, dec.). Analysis: Found: C, 56.98; H, 5.19; Cr, 12.47; N, 6.31; $C_{19}H_{20}B_2Cr_2N_2O_3$ calcd.: C, 57.34; H, 5.03; Cr, 13.08; N, 7.04%. IR data as Nujol mulls: $\nu(NH)$ 3420 cm^{-1}, $\nu(CO)$ 1945, 1880, 1845 cm^{-1}.

*Preparation of **2b**.* A solution of **1b** (0.50 g, 1.28 mmol) and $Cr(CO)_6$ (0.56 g, 2.54 mmol) was refluxed for 18 h in a 30/5 Bu_2O/THF mixture. The solution was filtered hot and then evaporated to dryness. The residue was chromatographed on silica (benzene/hexane 1/1); the yellow fraction yielding 0.10 g of **2b** (yield 15%).

*Preparation of **2c** and **2d**.* The procedure used for the reaction of **1a** and $Mo(CO)_6$ gave a yield of about 9% of a yellow solid that readily decomposed. The yield was ca. 10% from **1a** and $W(CO)_6$, a mixture of **1a** and **2d** (84/16) being obtained as according to NMR data. ^1H NMR: 5.90 ppm (2H, 13 and 15), 5.07 (1H, 14). ^{13}C NMR: 130.9, 127.0 and 126.0 (carbon atoms 3,4 and 5), 97.1, 96.2 and 85.5 (carbon atoms 13, 15 and 14).

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