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Regioselective complexation of 1,2 : 9,10-dibenzo[2.2]paracyclophane-1,9-dienes *

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Abstract

1,2 : 9,10-Dibenzo[2.2]paracyclophane-1,9-diene, **1**, and its 4′,5′,4″,5″-tetrakis(*p*-t-butylphenyl) derivative, **2b**, regioselectively form the tricarbonylchromium(0) complexes **3**, **5** and **4**, **6**, respectively, in which the $(CO)_3Cr$ units are attached to the phane arene units. This is manifestation of the increased π-basicities of their bent arene moieties; surprisingly even the second $(CO)_3Cr$ unit prefers the bent arene in spite of the electron withdrawing effect of the first one.

Introduction

Our interest in regiodirected substitutions of [2.2]paracyclophane derivatives [1,2] and the investigation of charge transfer phenomena in appropriate species [3,4] has led us to probe the complexation of doubly bridge-anellated [2.2]paracyclophanedienes such as **1** and **2**. This was designed as an intramolecular competition experiment for complexation of planar versus distorted benzene rings [5]. Our recently developed versatile synthesis [6] has made these compounds accessible in quantities large enough to facilitate the investigation of their interesting chemistry [7].

Results and discussion

1,2 : 9,10-Dibenzo[2.2]paracyclophane-1,9-diene (**1**) is made up from two orthogonally fixed biphenyl units, each consisting of two geometrically and thereby electronically different phenyl groups. Upon reaction of **1** with tricarbonyltrispropionitrilechromium(0) ($EtCN_3Cr(CO)_3$, 3 equiv.) [8] only a single complex was formed. It was isolated in 44% yield (along with 32% of recovered **1**) by column

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* Dedicated to Professor P.L. Pauson on the occasion of his retirement.

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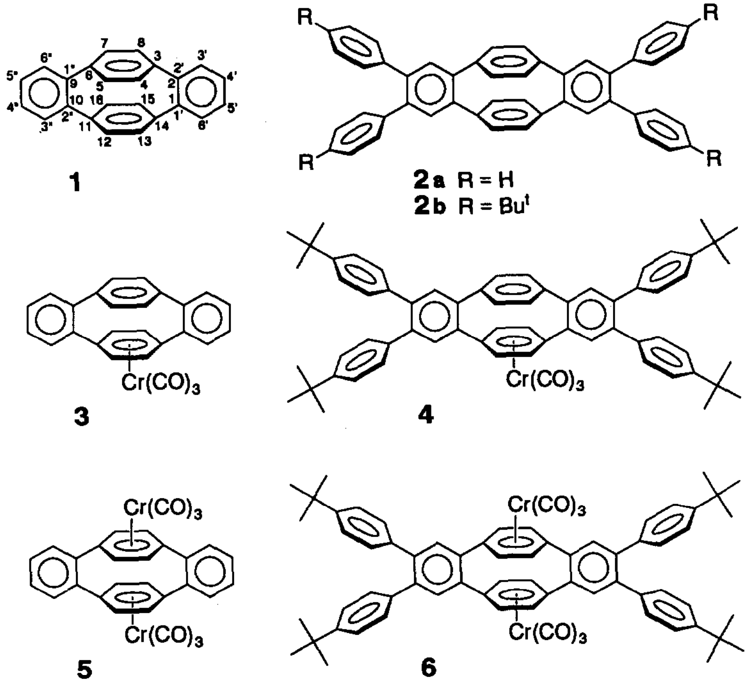

Scheme 1

chromatography and unequivocally characterized from its ^{1}H-NMR spectrum as **3** (see Table 1). With an excess of $(EtCN)_3Cr(CO)_3$ (3 equiv.) **3** reacted further to give the bis(tricarbonylchromium) complex **5** (36% yield) with both $(CO)_3Cr$ units attached to the phane-arene groups.

As Cram et al. had already deduced from the enhanced stability of the [2.2]paracyclophane-tetracyanoethylene complex [9], the bent arene groups in such systems are stronger π-bases than undistorted arenes, because the π-electron density is compressed between the rings and pushed outward accordingly [10]. Surprisingly, even in the 4′,5′,4″,5″-tetrakis(*p*-t-butylphenyl)-1,2 : 9,10-dibenzo[2.2]paracyclophane-1,9-diene (**2b**) [11*], with its four additional phenyl groups bearing electron-donating t-butyl groups, the bent arenes in the skeleton win when it comes to complexation. With 3 equiv. $(EtCN)_3Cr(CO)_3$, **2b** yields only **4** (38%) and 5% of the bis-complex **6** along with 48% of recovered starting material **2b**; the new complexes were identified from their spectral data (see Table 1). This outcome must be due solely to the relative π-basicity of the phane-arene moieties, since the t-butyl and phenyl groups on the outer rings would not prevent the attachment of a $(CO)_3Cr$ unit for steric or electronic reasons [12].

It is noteworthy that the proton NMR signals of the complexed arene units are shifted downfield upon going from the mono- to the bis-complex in both series (see Table 1). This must be a consequence of the less pronounced flattening of these rings in the bis-complexes [10].

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* Reference number with asterisk indicates a note in the list of references.

Table 1

^{1}H-NMR (270 MHz, $CDCl_3$), IR (CH_2Cl_2) and mass spectral data for tricarbonylchromium(0) complexes **3**–**6** derived from **1** and **2b** (chemical shifts in δ_{TMS}, coupling constants in Hz, υ(C=O) in cm^{-1})

Complex	Spectral data
3	^{1}H-NMR: 4.85 (s, 4H, compl. phane-Ar-H), 6.98 (s, 4H, uncompl. phane-Ar-H), 7.47-7.71 (m, 8H, bridge-Ar-H). IR (KBr): 1962 (C=O), 1878 (C=O). MS (70 eV): m/z (%) = 356 (20, $M-(CO)_3$), 304 (100, $M-Cr(CO)_3$). MS (field desorption): m/z (%) = 440 (100, M^+). MS (high resolution): m/z = 356.0611 ($M-(CO)_3$), calc. 356.0657
5	^{1}H-NMR: 5.11 (s, 8H, phane-Ar-H), 7.47 (bs, 8H, bridge-Ar-H). IR (KBr): 1964 (C=O), 1892 (C=O). MS (field desorption): m/z (%) = 576 (48, M^+), 440 (72, $M-Cr(CO)_3$), 376 (100, $M-2Cr(CO)_3$).
4	^{1}H-NMR: 1.29 (s, 18H, ^{t}Bu-H), 1.30 (s, 18H, ^{t}Bu-H), 4.96 (s, 4H, compl. phane-Ar-H), 7.08 (s, 4H, uncompl. phane-Ar-H), 7.20 (AB-system, $\delta_A = 7.27$, $\delta_B = 7.14$, $^3J = 8.4$, 8H, phenyl-H), 7.21 (AB-system, $\delta_A = 7.25$, $\delta_B = 7.18$, $^3J = 8.4$, 8H, phenyl-H ^{a}), 7.44 (s, 3′(6″)-H), 7.76 (s, 3″(6′)-H). IR (KBr): 1963 (C=O), 1888 (C=O).
6	^{1}H-NMR: 1.29 (s, 36H, ^{t}Bu-H), 5.22 (s, 8H, phane-Ar-H), 7.20 (AB-system, $\delta_A = 7.27$, $\delta_B = 7.13$, $^3J = 8.4$, 16H, phenyl-H), 7.50 (s, 3′(3″,6′,6″)-H). IR: 1962 (C=O), 1894 (C=O).
7	^{1}H-NMR: 2.72 (s, CH_3), 6.61–6.72 (m, 8H, phane-Ar-H), 7.55 (AB-system, $\delta_A = 7.65$, $\delta_B = 7.45$, $^3J = 8.2$, 3″(4″,5″,6″)-H), 8.02 (ABX-system, 8.07, 5′-H; 7.76, 6′-H; 8.23, 3′-H, $^3J = 8.2$; $^4J = 1.6$ Hz). IR (KBr): 1680 (C=O).

[a] Assignment by comparison with the spectrum of **6**.

It is most remarkable that even the second $Cr(CO)_3$ group is selectively attached to the phane arenes in **1** and **2b** in spite of the strong electron-withdrawing effect which the first such group exerts through the uniquely interacting π-systems of the [2.2]paracyclophane moiety [13].

Experimental

General

^{1}H-NMR: Bruker WH 270; δ (ppm) = 0 for tetramethylsilane, 7.24 for chloroform. ^{13}C-NMR: Bruker WH 270; δ (ppm) = 77.0 for deuterochloroform. IR: Perkin Elmer 297 and 399. MS: Varian MAT CH-7, MAT 311 A (high resolution) and Finnigan MAT 8002 (field desorption). All experiments were carried out in an inert atmosphere.

Tricarbonylchromium(0) complexes by reaction of ligands with tricarbonyltrispropionitrilechromium(0); general procedure

To a solution of the ligand in dioxane was added about 2/3 of the total amount of $(EtCN)_3Cr(CO)_3$ and the mixture was stirred at 40 °C for 30 min. All volatile species were evaporated, dioxane was added, and the mixture was again stirred for 30 min at 40 °C. This procedure was repeated four times, the last 1/3 of $(EtCN)_3Cr(CO)_3$ being added before the third procedure was carried out. Subsequently the mixture was concentrated and the residue purified by flash chromatography.

Tricarbonyl(3–8-η-1,2 : 9,10-dibenzo[2.2]paracyclophane-1,9-diene)chromium(0) (3)

The general procedure was applied to 68 mg (0.22 mmol) of **1**, and 120 mg (0.4 mmol) of $(EtCN)_3Cr(CO)_3$ in 10 ml of dioxane. Chromatography on 20 g silica gel (pentane/dichloromethane 3 : 1) yielded, as fraction I ($R_f = 0.60$), 22 mg (32%) of **1**, and as fraction II ($R_f = 0.35$), 43 mg (44%) of **3**. (See Table 1 for physical and spectroscopical data).

(μ-3–8-η : 11–16-η-1,2 : 9,10-Dibenzo[2.2]paracyclophane-1,9-diene)bis(tricarbonylchromium(0) (5)

Use of the general procedure with 25 mg (0.06 mmol) **3**, and 60 mg (0.2 mmol) of $(EtCN)_3Cr(CO)_3$ in 10 ml dioxane followed by chromatography on 10 g of silica gel (pentane/dichloromethane 3 : 1) yielded as fraction I ($R_f = 0.15$), 10 mg (36%) of **5**.

Tricarbonyl(3–8-η-4′,4″,5′,5″-tetrakis(t-butylphenyl)-1,2 : 9,10-dibenzo[2.2]paracyclophane-1,9-diene)chromium(0) (4)

The general procedure was applied to 100 mg (0.12 mmol) **2b** and 100 mg (0.33 mmol) of $(EtCN)_3Cr(CO)_3$ in 10 ml of dioxane. Chromatography on 20 g silica gel (pentane/dichloromethane 1 : 1) yielded as fraction I ($R_f = 0.82$) 48 mg (48%) of **2b**; as fraction II ($R_f = 0.58$), 44 mg (38%) of **4**; and as fraction III ($R_f = 0.47$); 7 mg (5%) of (μ-3–8-η : 11–16-η-(4′,4″,5′,5″-tetrakis(t-butyl-phenyl))-1,2 : 9,10-dibenzo[2.2]paracyclophane-1,9-diene)bis(tricarbonylchromium(0) (**6**).

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