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Preliminary communication

Conformationally rigid annelated arene complexes: Cyclobutabenzenetricarbonylchromium(0) derivatives

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Abstract

Several cyclobutabenzenetricarbonylchromium(0) complexes have been prepared by reaction of substituted cyclobutabenzenes with triammintricarbonylchromium(0) (**13**), and characterized by ^{1}H NMR, ^{13}C NMR, IR, and mass spectroscopy. Diastereomer ratios were determined by ^{1}H NMR, and signal assignments were verified by a NOE experiment. HPLC separation of diastereometric products was carried out in one representative case. A photochemical carbonyl ligand exchange took place in 70% yield with triphenylphosphane. Deprotonation of cyclobutabenzenetricarbonylchromium(0) (**2**) with n-BuLi/tmeda was observed only for the aromatic protons, not the benzylic ones.

Cyclobutabenzene (**1**) and its derivatives [1] have played a considerable role in mechanistic and preparative organic chemistry since 1958 [2], owing to the occurrence of electrocyclic ring opening and subsequent inter- or intra-molecular Diels–Alder addition of numerous dienophiles to reactive *ortho*-xylylene intermediates. Arenetricarbonylchromium(0) complexes, known since 1957 [3], have been recognized as useful in organic synthesis because of the facilitation of nucleophilic substitutions in the aromatic ligand and the enhancement of the acidity of the aromatic protons. In the light of the importance of these two types of compounds there has been surprisingly little study of combinations of them [4,5*]. Complexes of arenes with chiral substituents also offer stereochemical possibilities by differentiation of the two sides of the aromatic ligand. However, the systems with annelated five- or six-membered rings investigated so far [6] are conformationally non-rigid, and systems such as these may escape steric interactions by conformational changes. This could be avoided with conformationaly rigid ligands as cyclobutabenzene (**1**).

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

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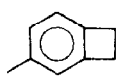

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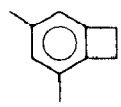

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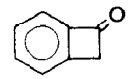

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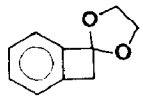

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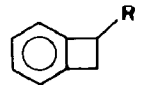


1-*d* : R = D
5 : R = Cl
6 : R = CH_3
7 : R = $(CH_2)_3CH_3$
8 : R = $(CH_2)_2CH{=}CH_2$
9 : R = $Si(CH_3)_3$
10 : R = $Sn(CH_3)_3$

We describe here the synthesis of some substituted cyclobutabenzenetricarbonylchromium(0) complexes, discuss their stereochemical characteristics, and present preliminary results on their reactions. Cyclobutabenzene (**1**) and its derivatives **3–12** were prepared by literature methods [7–11].

$Cr(CO)_3$ complexation was performed by reaction of these ligands with triammintricarbonylchromium(0) (**13**) [12,13]. Reactions of cyclobutabenzene (**1**) and derivatives **1-*d***, **3**, **4**, and **6–12** with **13** in dioxane at 101°C afforded known **2** [4] and new tricarbonylchromium(0) complexes **2-*d*** and **14–22** in satisfactory yields (Table 1) with one exception, complexation of cyclobutabenzene-1-one (**11**) giving only traces of **21** (along with starting material) under the conditions used for all the other complexes.

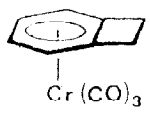
Ligands **1**, **3**, **4**, **11**, and **12** are achiral and give achiral (**2**) or chiral (**14**, **15**, and **22**) products. Complexation of the chiral ligands **1-*d***, **6–10** can take place on either side of the aromatic ring, thus generating another element of chirality, and allowing formation of *exo*- and *endo*-diastereomers of complexes **2-*d***, **16–20** (Table 1).

Table 1

Cyclobutabenzenetricarbonylchromium(0) derivatives

Ligand	Complex	Yield (%)	*endo*/*exo* ratio	M.p. (°C)
1	**2** [4]	51	–	88–89
1-*d*	**2-*d***	53	50/50 [a]	88–89
3	**14**	60	–	71.5
4	**15**	60	–	97–98
6	**16**	62	40/60 [a]	52.3 (*exo*-**16**) 66.3 (*endo*-**16**)
7	**17**	27	50/50 [a]	–
8	**18**	47	40/60 [b]	–
9	**19**	64	12/88 [a]	–
10	**20**	89	24/76 [a]	–
12	**22**	41	–	115

[a] By ^{1}H NMR. [b] By HPLC.



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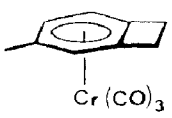

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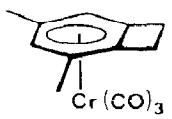

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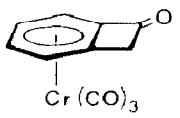

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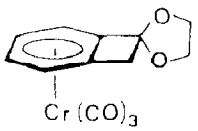

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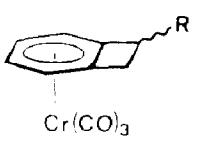


2-*d* : R = D
16 : R = CH_3
17 : R = $(CH_2)_3CH_3$
18 : R = $(CH_2)_2CH=CH_2$
19 : R = $Si(CH_3)_3$
20 : R = $Sn(CH_3)_3$

As **17** was isolated in only 27% yield, the significance of the observed *endo*/*exo*-ratio (50/50) should not be overestimated. As expected on steric grounds, in most cases the *exo*-isomers dominate, and the highest proportion of *exo*-complex was obtained for the trimethylsilyl compound **19** (88/12).

The identities of complexes **2-*d*, 14–20, 22** were verified by spectroscopic methods (IR, ^{1}H NMR, ^{13}C NMR), MS, HRMS and elemental analysis. A preparative HPLC separation [14] gave, 170 mg of *exo*-**16** and 200 mg of *endo*-**16** as diastereomerically pure fractions. (The effectiveness of HPLC separation of these diastereomers is important for investigations on ring-opening reactions of complexes **16–20** now under way in our group.) Some spectral data are listed in Table 2 for the representative compound **16**.

As *exo*- and *endo*-diastereomers were identified by ^{1}H and ^{13}C NMR spectroscopy, we felt it necessary to verify the signal assignments made, and so

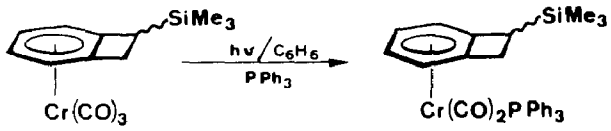
Table 2

Spectral data for *endo*/*exo*-1-methylcyclobutabenzenetricarbonylchromium(0) (*endo*/*exo*-**16**) (40/60)

IR (cyclohexane): ν 1975 cm^{-1} (m, C=O), 1906 (m, C=O). ^{1}H NMR (400 MHz, C_6D_6): 1) *exo*-**16** (60%): δ 0.83 (d, 3H, 7-H), 1.98 (dd, 1H, *exo*-2-H), 2.81 (dd, 1H, *endo*-2-H), 3.09 (m, 1H, 1-H), 4.3 (m, 2H, 4-H, 5-H), 4.75 (m, 2H, 3-H, 6-H), 2) *endo*-**16** (40%): δ 1.16 (d, 3H, 7-H), 2.31 (dd, 1H, *endo*-2-H), 2.54 (dd, 1H, *exo*-2-H), 2.75 (m, 1H, 1-H), 4.12 (dd, 1H, 5-H), 4.45 (d, 1H, 3-H), 4.57 (dd, 1H, 4-H), 4.87 (d, 1H, 6-H). ^{13}C NMR (50 MHz, C_6D_6) [a]: *exo*-**16**: δ 19.29 (q, C-7), 37.81 (t, C-2), 38.8 (d, C-1), 89.06 (d, C-3, C-4, C-5 or C-6), 89.9 (d, C-3, C-4, C-5 or C-6), 90.69 (d, C-3, C-4, C-5 or C-6), 91.09 (d, C-3, C-4, C-5 or C-6), 114.69 (s, C-2a), 120.97 (s, C-6a), 234.15 (s, C-8); 2) *endo*-**16**: δ. 1) 21.57 (q, C-7), 37.12 (t, C-2), 37.5 (d, C-1), 86.2 (d, C-3, C-4, C-5 or C-6), 87.08 (d, C-3, C-4, C-5 or C-6), 91.73 (d, C-3, C-4, C-5 or C-6), 94.53 (d, C-3, C-4, C-5 or C-6), 120.82 (s, C-6a), 116.02 (s, C-2a), 234.37 (s, C-8). MS (70 eV): m/z (%) = 254 (10, M^+), 226 (1, $M-CO$), 198 (5, $M-2CO$), 170 (33, $M-3CO$), 52 (100, $M-C_{12}H_{10}O_3$).

[a] Spectrum taken from that of the diastereometric mixture. Signal assignments by inspection of intensities taking account of the diastereomer ratio (40/60).

photochemical ligand exchange [15] was carried out with **19** to give *endo/exo*-dicarbonyl(1-trimethylsilylcyclobutabenzene)triphenylphosphanechromium(0) (**23**) in 70% yield.

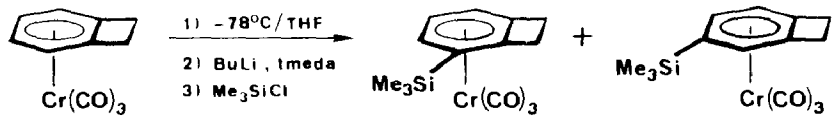


19 **23**

Since in **23** there is now another proton-containing ligand at chromium, it was possible to confirm the assigned stereochemistry by NOE measurements. A magnetization transfer difference spectrometry [16] investigation verified the signal assignments. This result is in accord with the data for related compounds reported by Ustynyuk [17].

Complexes **2**, **2-*d***, **14–20**, **22** are crystalline compounds, moderately air sensitive, **2**, **2-*d***, **14**, **15**, and **19** could be purified by sublimation (80 °C/10^{-3} mbar); **16**, **17**, and **20**, which were purified by crystallisation, decomposed at 90 °C. This indicates a stabilisation by aromatic methyl substitution.

The cyclobutabenzenetricarbonylchromium(0) complexes were found to be metallated by n-BuLi/tmeda in THF at −78 °C exclusively at the aromatic ring. The silylated derivatives **24** and **25** were obtained in almost quantitative yield from **2**, the 3-substituted complex **24** predominating over **25** (62/38).



2 **24** **25**

In contrast to observations on reactions with indanetricarbonylchromium(0) [18], no benzylic metallation took place in the case of cyclobutabenzenetricarbonylchromium(0) (**2**). This is consistent with the results of metallation of the uncomplexed ligand **1** by butylpotassium [19] (but not by n-BuLi/tmeda [11]) and with the expected order of acidity in the aromatic system [20] (but see ref. 21). Further studies of these observations are in progress.

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