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Synthesis of Tricarbonyl(η^6-[6]paracyclophane)chromium. Smallest-Bridged Paracyclophane-Metal Complex

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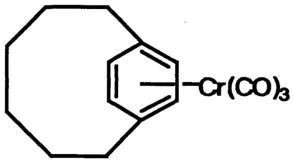
Tricarbonyl(η^6-[6]paracyclophane)chromium has been synthesized and its spectral properties have been investigated.

Considerable interest has been shown on the transition metal complexes of small-bridged paracyclophanes,1) because of anticipated strain in the pi bonding between metal and nonplanar η^6-ligand deformed in a boat shape. For example, recent calculations revealed linear correlations between the out-of-plane bending angle of the aromatic ring and the charge density of the aryl carbons.1d,e) In this connection, we wish to report the synthesis and spectral properties of tricarbonyl(η^6-[6]paracyclophane)chromium (1), the smallest-bridged paracyclophane-metal complex yet known.



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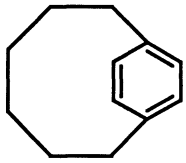

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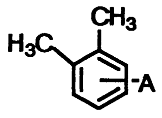

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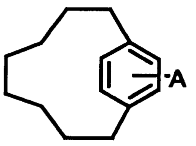

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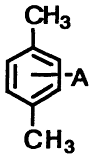

5

A=Cr(CO)$_3$

Reaction of [6]paracyclophane (2)2) with 3 equiv. of hexacarbonyl chromium in dibutyl ether under usual conditions3) gave unexpectedly the *o*-xylene complex 3 as the single product in 58% yield. When an excess of 2 was used instead, the desired cyclophane complex 1 was obtained in 3% yield as air-sensitive reddish orange plates, decomp. at 115 °C.4)

In the ^{1}H NMR spectrum, the aromatic protons of 1 (δ 5.45, 5.70 (dd, J=2, 8 Hz)) show complexation shift ($\Delta\delta$) of -1.68 and -1.52 ppm which is considerably smaller than those of [8]paracyclophane complex 4$^{1a-c,f)}$ ($\Delta\delta$=-1.79) and *p*-xylene complex 5$^{1a-c)}$ ($\Delta\delta$=-1.81). This indicates weaker arene-chromium bonding or larger arene-chromium distance in 1 than in 4 and 5. Similarly, in the ^{13}C NMR spectrum, the aromatic carbons of 1 exhibit marked difference in complexation shift compared with those of 4 and 5; $\Delta\delta$ of the quaternary carbons is 10.5 (4 22.0, 5 27.9) and $\Delta\delta$ of the tertiary carbons is 40.3 (4 37.9, 5 34.4) ppm. Remarkably small complexation shift of the quaternary bridgehead carbons of 1 is in accord with the larger arene-chromium distance at this position than those of 4 and 5. It is worth noting that $\Delta\delta$ of the aromatic carbons of **1**, **4**, and **5** shows linear correlation with the out-of-plane bending angle of the para carbons observed for derivatives of parent hydrocarbon by X-ray crystallography (**1** 20°,2) **4** 9°5)) as predicted from the calculations.1d,e) On the contrary, $\Delta\delta$ of the bridge carbons is small (0.1-0.6) and the chemical shift of the carbonyl carbons of **1** (235.9) is not much different from those of **4** (234.5) and **5** (233.7).

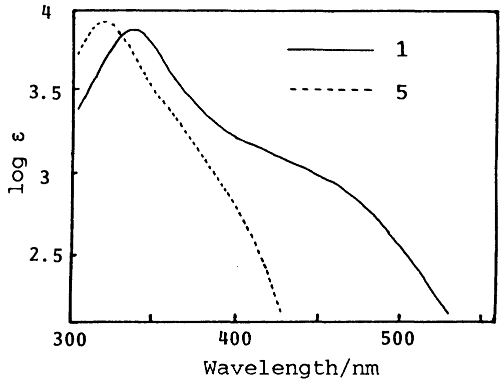

Fig. 1. Electronic spectra of **1** and **5** in benzene.

As for the conformational behavior of the bridge of **1**, temperature dependence in the ^{1}H NMR spectrum (100 MHz, $CDCl_3$) was observed. The aromatic protons of **1** appear as a sharp singlet at 80 °C, which broadens at 25 °C, coalesces at 12.5 °C, and splits into two doublet of doublets at -50 °C. The barrier of the flipping of the bridge at the coalescence temperature was estimated to be 14.4 kcal/mol, which is essentially very similar to that of the parent hydrocarbon **2**.2,6)

The electronic spectrum of **1** is shown in Fig. 1. The longest-wavelength absorption of **1** (460 nm) exhibits remarkable bathochromic shift relative to that of **5** (380 nm). Since this band has been assigned to the charge-transfer band from chromium to arene polarized in the *xy* plane,7) the above bathochromic shift is probably due to low lying a_2 (LUMO) level of the cyclophane ligand.8,9)

References
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3) C. A. L. Mahaffy and P. L. Paulson, Inorg. Synth., 19, 154 (1979).
4) IR (C_6H_6) 1955, 1881 cm^{-1}; ^{1}H NMR ($CDCl_3$, -50 °C) δ 5.70 (dd, J=2, 8 Hz, 2H), 5.45 (dd, J=2, 8 Hz, 2H), 3.2-2.8 (m, 2H), 2.4-0.8 (m, 8H), 0.4--0.1(m, 2H); ^{13}C NMR ($CDCl_3$, -30 °C) δ 236.26 (s), 133.15 (s), 93.54 (d, J=175.8 Hz), 89.34 (d, J=175.8 Hz), 36.31 (t, J=128.5 Hz), 35.26 (t, J=134.9 Hz), 26.82 (t, J=126.0 Hz). Anal. Calcd for $C_{15}H_{16}O_3Cr$: C, 60.81; H, 5.44. Found: C, 60.62; H, 5.61.
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9) We are grateful to Professor N. Mori for invaluable suggestions and to Professor F. Bickelhaupt for informing us with unpublished results.1f,6)

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