

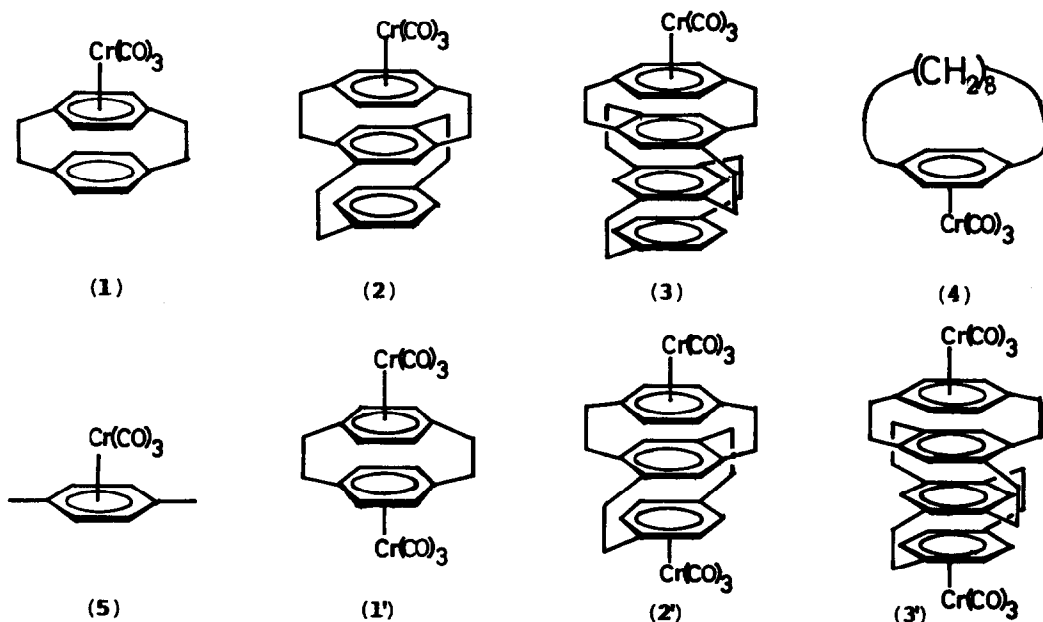
LAYERED COMPOUNDS. XLI.<sup>1)</sup> TRICARBONYLCHROMIUM COMPLEXES  
OF MULTILAYERED [2.2]PARACYCLOPHANES

H. Ohno, H. Horita, T. Otsubo, Y. Sakata, and S. Misumi

The Institute of Scientific and Industrial Research, Osaka University  
Suita, Osaka 565, Japan

(Received in Japan 15 November 1976; received in UK for publication 7 December 1976)

Tricarbonylchromium complexes of cyclophanes have been studied to demonstrate transannular electronic interaction between the aromatic rings in the ligand cyclophanes.<sup>2)</sup> In a series of tricarbonylchromium complexes of [m.n]-paracyclophanes, it was reported that the electronic interaction between the two benzene rings in the cyclophanes was increased with shortening of methylene bridge lengths m and n, and that bis-tricarbonylchromium complex was formed only in the case of [4.5]- or [6.6]-homolog where the two benzene rings are far apart from each other.<sup>2a)</sup> We now wish to report the syntheses and properties of mono- and bis-tricarbonylchromium complexes of multilayered [2.2]paracyclophanes, with a view to pursue further the electronic interaction among their benzene rings<sup>3)</sup>



and the physical properties of organochromium complexes.<sup>4)</sup>

Mono-complexes 1~4 and bis-complexes 1'~3' were prepared by treatment of the corresponding cyclophanes with hexacarbonylchromium in purified diglyme at 140 - 150°C for 2 - 3 hrs in a nitrogen atmosphere. Mono-complexes were separated from bis-complexes and inorganic chromium by extraction with dichloromethane, and purified by chromatography on a short column of silica gel with dichloromethane-hexane (1:1) and recrystallization from the same solvent; 1: yellow prisms, dec.p. 188°C; 2: yellow columns, dec.p. 180°C; 3: yellow leaflets, dec.p. 185°C; 4: yellow leaflets, dec.p. 149°C.<sup>5)</sup> Bis-complexes insoluble in dichloromethane were extracted continuously with tetrahydrofuran using a Soxhlet type of extractor in a nitrogen atmosphere and crystallized out of the extract; 1': yellow fine crystals, dec.p. 183°C; 2': yellow fine crystals, dec.p. 181°C; 3': yellow fine crystals, dec.p. 182°C.<sup>5)</sup> Complex 5 was prepared as a reference according to the literature.<sup>6)</sup> All the yields are summarized in Table 1.

Table 1. Yields of paracyclophane complexes

| cyclophane                               | molar ratio<br>Cr(CO) <sub>6</sub> /cyclophane | yield (%) |             |
|--|--|-----------|-------------|
|  |  | mono-     | bis-complex |
| [2.2]paracyclophane                      | 1.1  | (1) 50    | (1') 0      |
|  | 2.2  | 52        | 8           |
| triple-layered<br>[2.2]paracyclophane    | 1.3  | (2) 27    | (2') 0      |
|  | 2.1  | 30        | 29          |
| quadruple-layered<br>[2.2]paracyclophane | 1.2  | (3) 17    | (3') 6      |
| [8]paracyclophane                        | 1.2  | (4) 4     |             |

Cram et al. pointed out that bis-complex of [2.2]paracyclophane was not formed from the same reaction since the non-complexed benzene ring of complex 1 was deactivated by electron-withdrawing character of the attached tricarbonylchromium group.<sup>2a)</sup> In the present case, bis-complex 1' was obtained in 8% yield by use of two molar ratio of hexacarbonylchromium to [2.2]paracyclophane. Similarly bis-complex 2' of triple-layered one was prepared in a better yield than 1'. Bis-complex 3' of quadruple-layered one was formed even in the case of one molar ratio. These results indicate that the first attached tricarbonylchromium group exerts less transspacial electronic interaction on the other outside benzene ring as the layer number increases.

The PMR data of these complexes are shown in Table 2. For a series of

Table 2. PMR data ( $\delta$ , ppm) of the complexes 1~5 (in  $\text{CDCl}_3$ ) and 1'~3' (in  $\text{DMSO-d}_6$ ) (values in parentheses:  $\Delta\delta = \delta_{\text{complex}} - \delta_{\text{free ligand}}$ )

| complex<br>Ar-H | (4)             | (5)             | (1)             | (2)             | (3)             | average<br>of $\Delta\delta$ | (1') | (2') | (3') |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|------------------------------|------|------|------|
| 1st ring        | 5.32<br>(-1.73) | 5.25<br>(-1.83) | 4.64<br>(-1.83) | 4.37<br>(-1.82) | 4.29<br>(-1.82) | (-1.81)                      | 5.33 | 4.83 | 4.66 |
| 2nd ring        |                 |                 | 6.77<br>(0.30)  | 5.77<br>(0.37)  | 5.51<br>(0.36)  | (0.34)                       |      | 6.16 | 5.60 |
| 3rd ring        |                 |                 |                 | 6.28<br>(0.09)  | 5.27<br>(0.12)  | (0.11)                       |      |      |      |
| 4th ring        |                 |                 |                 |                 | 6.15<br>(0.06)  | (0.06)                       |      |      |      |

Methylene protons appear as multiplets in the range of  $\delta$  2.0-3.5 except 4 ( $\delta$  0.7-2.5).

mono-complexes, the aromatic protons of the ring to which tricarbonylchromium group is attached to higher field by an average 1.81 ppm than the corresponding protons of free ligand cyclophanes. This is considered to be due to both a principal effect of decreasing ring current of the complexed benzene ring and a minor effect of additional magnetic anisotropy of chromium metal.<sup>7)</sup> The former effect is also responsible for the apparent downfield shifts of the aromatic protons of the other benzene rings as indicated in Table 2. The  $^1\text{H}$ -chemical shifts of the bis-complexes can be explained by an additivity of the both shielding effects.

The IR spectra of both series of mono- and bis-complexes show two strong bands at 1951-1962 and 1872-1884  $\text{cm}^{-1}$ , associated with carbonyl stretching vibrations, and the bands are successively shifted to lower wavenumber as the layer increases (Table 3). Such decreases of the carbonyl bond strength are

Table 3. IR ( $\nu_{\text{C=O}}$ ) and UV spectra of all the complexes

| complex | $\nu_{\text{C=O}}$ in THF ( $\text{cm}^{-1}$ ) |      | UV in THF                   |                              |
|---------|--|------|-----------------------------|------------------------------|
|         | $A_1$  | E    | $\lambda_{\text{max}}$ (nm) | $\epsilon$ ( $\times 10^3$ ) |
| 4       | 1962   | 1883 | 324                         | 10.3                         |
| 5       | 1962   | 1884 | 318                         | 9.72                         |
| 1       | 1959   | 1878 | 341                         | 10.9                         |
| 2       | 1954   | 1873 | 342                         | 9.95                         |
| 3       | 1952   | 1872 | 341                         | 9.86                         |
| 1'      | 1952   | 1884 | 358                         | 22.8                         |
| 2'      | 1951   | 1874 | 346                         | 19.4                         |
| 3'      | 1951   | 1873 | 342                         | 18.4                         |

probably caused by a strong electron donation from the cyclophane to the metal, indicating the increase of  $\pi$ -basicity in the series of multilayered [2.2]paracyclophanes.

The electronic absorption maxima in long wavelength region, associated with charge-transfer transition from chromium to aromatic ring,<sup>8)</sup> for all the complexes are presented in Table 3. The three mono-complexes 1~3 show significant bathochromic shifts compared with the complex 5 or 4 in which appreciable distortion of the benzene ring comparable to that of [2.2]paracyclophane was observed by X-ray crystallography.<sup>9)</sup> Such bathochromic shifts may therefore arise from the transannular delocalization in the ligand cyclophanes. A stronger bathochromic shift of bis-complex 1' than mono-complex 1 indicates that the excited state of the former is more stabilized by electron withdrawing of another tricarbonylchromium group. The effect decreases with increasing distance between the two metacarbonyl groups, that is, the increase of layer number, as seen in the case of 3 vs. 3'.

#### References

- 1) Part XL, T. Otsubo, H. Horita, and S. Misumi, *Synth. Commun.*, in press.
- 2) a) D. J. Cram and D. I. Wilkinson, *J. Am. Chem. Soc.*, **82**, 5721 (1960).  
b) E. Langer and H. Lehner, *Tetrahedron*, **29**, 375 (1973).
- 3) T. Otsubo, S. Mizogami, I. Otsubo, Z. Tozuka, A. Sakagami, Y. Sakata, and S. Misumi, *Bull. Chem. Soc. Jpn.*, **46**, 3519 (1973); D. T. Longone and H. S. Chow, *J. Am. Chem. Soc.*, **92**, 994 (1970).
- 4) W. E. Silverthorn, *Advances in Organometallic Chemistry* Vol. 13, ed. by F. G. A. Stone and R. West, Academic Press (1975), p. 47, references cited therein.
- 5) All the new complexes gave satisfactory elemental analyses.
- 6) B. Nicholls and M. C. Whiting, *J. Chem. Soc.*, 551 (1959).
- 7) W. McFarlane and S. O. Grin, *J. Organomet. Chem.*, **5**, 1476 (1966); J. T. Price and T. S. Sorensen, *Can. J. Chem.*, **46**, 515 (1968).
- 8) D. G. Carrol and S. P. McGlynn, *Inorg. Chem.*, **7**, 1285 (1968).
- 9) M. G. Newton, T. J. Walter, and N. L. Allinger, *J. Am. Chem. Soc.*, **95**, 5652 (1973).