# Geometry-dependent Complexation Effects in Carbon-13 Nuclear Magnetic Resonance Spectra of Tricarbonyl(3—8-η-[2.2]paracyclophane)chromium and Related Complexes

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A comparison of the aryl $^{13}C$ chemical shifts and one-bond aryl $^{13}C$–$^{1}H$ coupling constants for tricarbonyl(3—8-η-[2.2]paracyclophane)chromium and some related complexes with their molecular geometry indicates that the magnitudes of the complexation effects on the chemical shifts and coupling constants correlate with the interatomic distances between the Cr and the ligand carbons.

Carbon-13 n.m.r. parameters in arenes complexed to transition metals have long been studied, but attempts to correlate the parameters with descriptions of the bonding are hampered owing to the approximations involved in any theoretical approach.[1] We think that this situation is due, at least in part, to no special regard being paid to geometrical factors, such as differences in interatomic distance between the metal and the ligand carbon atoms, which result from changes in molecular geometry upon complexation.[2] For this reason, we have studied the relationships between the complexation effects on $^{13}C$ n.m.r. spectra and the geometrical parameters in tricarbonyl(3—8-η-[2.2]paracyclophane)chromium (**2**) and the related complexes (**3**)—(**10**).

## Results and Discussion

Chemical shifts [δ/p.p.m. downfield from internal $SiMe_4$; spectra run in $(CD_3)_2SO$], given in the Scheme, were assigned by off-resonance continuous-wave decoupling, intensity considerations, and comparison with analogues.[3] For the complexes (**2**)—(**10**), the shift differences from the corresponding free hydrocarbons, $\Delta\delta = \delta(\text{complex}) - \delta(\text{hydrocarbon})$, are given in parentheses.

*Basic Geometry in Crystals.*—As is well known,[4] [2.2]paracyclophane (**1**) has a peculiar structure with two 1,4-bridged benzene rings close together, within their van der Waals distance, and bent into shallow boat forms by virtue of the short bridging chains owing to severe transannular electronic repulsion.[5] In the $^{13}C$ spectrum of (**1**),[6,7] the facing ring carbons, which are close together along almost the same $2p_z$-orbital axis, are subject to a large paramagnetic effect of 5 p.p.m. caused by their close proximity. A similar $^{13}C$ spectral anomaly is known for the close carbons, $C^8$ and $C^{16}$, in [2.2]metacyclophanes.[6,7]

Among the complexes (**2**) and (**8**)—(**10**), the molecular structure is known for (**2**) only.[8] In crystals, the structure of the [2.2]paracyclophane ligand is different in bond length and inter-bond angle from that of (**1**). In the complexed benzene ring, $C^3$ and $C^6$ are each displaced out of the mean plane by 12.2° [by 12.6° in (**1**)], bending away from the Cr atom. The mean interatomic distances between the Cr and the complexed ring carbons are 2.342 Å to $C^3$ and $C^6$ and 2.211 Å to the others, compared to 2.232 Å in ($\eta^6$-benzene)tricarbonylchromium (**3**),[9] where the complexed benzene ring is accurately planar.[9,10]

The structures of the free hydrocarbons of (**8**) and (**9**) are known. In 10-carboxy[8]paracyclophane,[11] $C^9$ and $C^{12}$ are again displaced out of the mean plane of the benzene ring inside the whole ring system by 9.1°. In [2.2]metacyclophane, having two stepwise-stacked benzene rings,[12] $C^5$ and $C^8$ are displaced in a direction away from the other ring by 0.042 and 0.143 Å, respectively, and $C^8$ is in extremely close proximity to $C^{16}$ of the other ring. In view of the small difference in bending angle in (**1**) and (**2**), it is expected that the bending angles of the benzene rings in the free hydrocarbons are left substantially unchanged upon complexation.

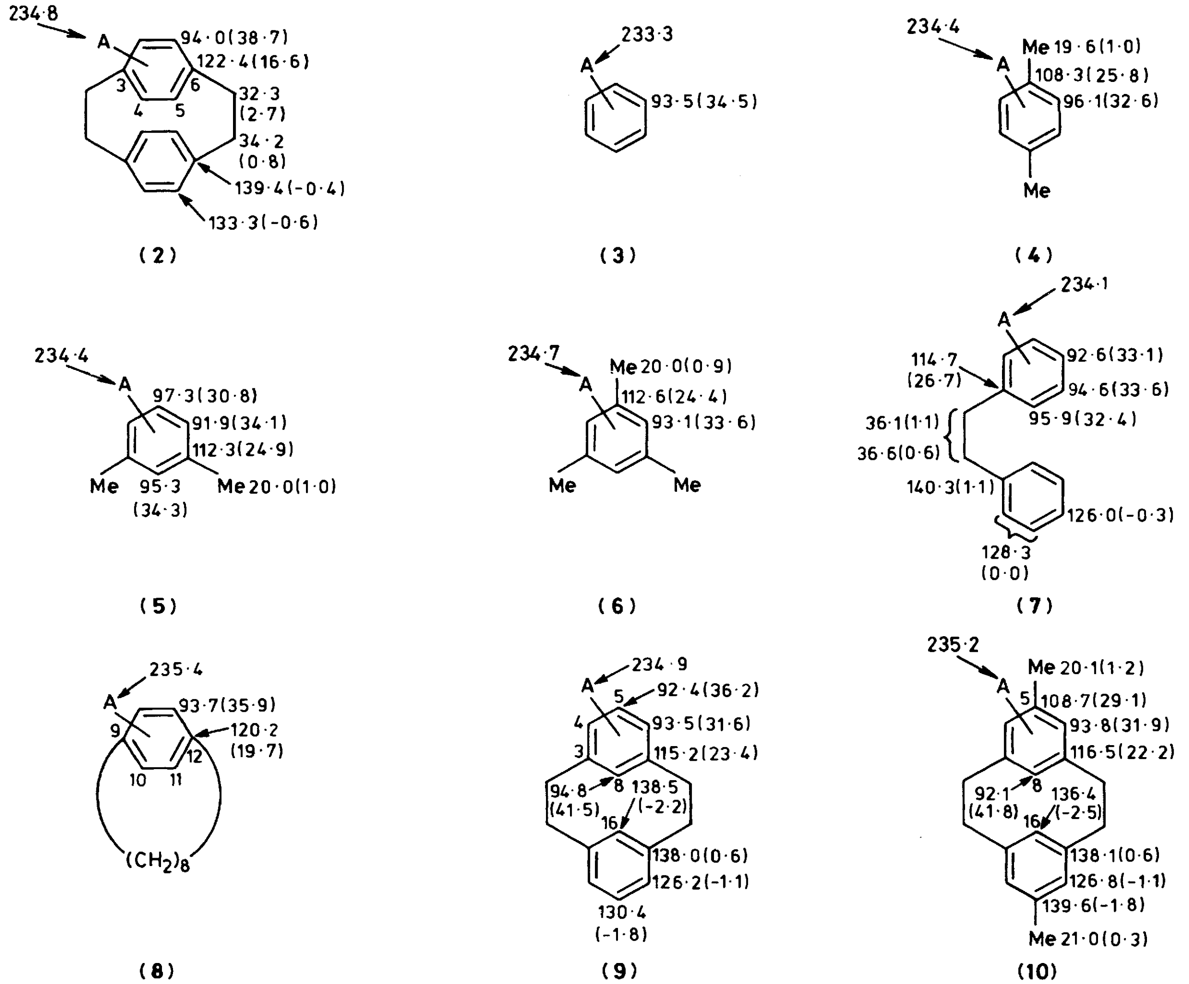
Under the conditions of n.m.r. measurements in solutions at ambient temperature, the above geometries in crystals are assumed to remain unchanged but the alternating C–C bond lengths are averaged by intramolecular motion.[10]

*Complexation Shifts.*—Complexations of arenes cause generally large upfield shifts for the aryl carbons and the origin of the effect has been ascribed to a variety of causes.[1] In the mono- and di-cyclic models (**3**)—(**7**), Δδ values for the tertiary carbons are almost constant, ranging from 30.8 to 34.5 p.p.m. (average 33 p.p.m.) and those for the quaternary ones are 24.4—26.7 p.p.m. (average 25 p.p.m.). Among the tertiary carbons, $C^5$ of (**5**) shows the lowest Δδ value (30.8 p.p.m.). On the other hand, among the quaternary ones, $C^1$ of (**7**), to which a phenylethyl group is attached, shows the largest Δδ (26.7 p.p.m.).[3]

In the complexed ring of (**2**), the tertiary carbons show a Δδ value of 38.7 p.p.m., larger by 6.1 p.p.m. than that for (**4**), whereas for the quaternary carbons it is 16.6 p.p.m., smaller by 9.2 p.p.m. than in (**4**). Similar anomaly is found for the aryl carbons of the less bent model (**8**), in which $C^9$ and $C^{12}$ are both displaced away from Cr. In the complexed ring of (**9**) and (**10**), $C^5$ and $C^8$ which are displaced towards Cr show large Δδ compared to the other carbons of the same ring.

Table 1 gives the geometrical parameters for (**2**), (**3**), (**8**), and (**9**) together with their complexation shift data. In (**2**) and (**3**), the correlation between the interatomic Cr ••• C distance (*d*) and complexation shift difference (ΔΔδ) is quite satisfactory. The same is probably true in (**8**) and (**9**).

In this connection it should be noted that ΔΔδ can be related to neither magnetic anisotropy and field effects of the $Cr(CO)_3$ group nor changes in transannular effect, such as electronic repulsion[5] or charge transfer,[7] upon complexation, because of the following reasons. The former effects should be small compared to the observed magnitude of ΔΔδ.[13] The latter complexation effect is also insignificant, if there is any, because similar magnitudes of ΔΔδ are found for the bent model (**8**) and for $C^5$ of (**9**) and (**10**) which is remote from the uncomplexed ring. Moreover, the fact that the uncomplexed ring carbons of (**2**) show only a slight downfield trend compared to the dicyclic model (**7**) suggests that there is no significant change in transannular effect upon complexation.



**Scheme.** Carbon-13 chemical shifts for some (arene)tricarbonylchromium complexes. Δδ Values are given in parentheses. A = $Cr(CO)_3$. Data for complex (3) (in $CD_2Cl_2$) are from ref. 16

**Table 1.** Geometrical parameters and complexation shift data

| Complex | Complexed ring carbons | $\theta^a$/° | $d^b$/Å | $\Delta\delta^c$/p.p.m. | $\Delta\Delta\delta^d$/p.p.m. |
|---|---|---|---|---|---|
| (2) | $C^3, C^6$ | −12.2 | 2.342 | 16.6 | $-9.2^e$ |
| | $C^4, C^5, C^7, C^8$ | 0 | 2.211 | 38.7 | $6.1^e$ |
| (3) | $C^1$—$C^6$ | 0 | 2.232 | 34.5 | |
| (8) | $C^9, C^{12}$ | (−9.1) | | 19.7 | $-6.1^e$ |
| | $C^{10}, C^{11}, C^{13}, C^{14}$ | (0) | | 35.9 | $3.3^e$ |
| (9) | $C^3, C^7$ | (0) | | 23.4 | $-1.5^f$ |
| | $C^4, C^6$ | (0) | | 31.6 | $-2.5^f$ |
| | $C^5$ | (0.042 Å) | | 36.2 | $5.4^f$ |
| | $C^8$ | (0.143 Å) | | 41.5 | $7.2^f$ |

[a] Angles of the indicated carbons bent out of the mean plane of the complexed benzene ring; angles, or distances, in the free hydrocarbons are given in parentheses. θ = 0 means the mean plane made with the indicated carbons and a minus sign denotes the bending away from Cr. [b] Mean interatomic distance between Cr and the indicated carbons. [c] Δδ = δ(complex) − δ(hydrocarbon). [d] Difference in Δδ from the indicated reference: ΔΔδ = Δδ(complex) − Δδ(reference). [e] From (4). [f] From (5).

It seems likely that ΔΔδ is directly related to orbital interaction between the Cr and the ligand carbon atom. This interaction, such as back-bonding of the metal to the ligand,[14] would be dependent on the interatomic distance ($d$) between the Cr and the ligand carbon and orientation of the $2p_z$ orbital of the carbon with respect to the Cr atom. A smaller ΔΔδ is expected when $d$ is larger and the $2p_z$-orbital axis is oriented away from Cr. This is the case for $C^3$ and $C^6$ of (**2**) and for $C^9$ and $C^{12}$ of (**8**). The reverse conditions predict a larger ΔΔδ, as has been observed for $C^5$ and $C^8$ of (**9**) and (**10**).

*One-bond* C–H *Coupling Constants.*—Complexations of arenes generally increase one-bond aryl C–H coupling constants for those arenes[1b,15] and the origin of the effect has

**Table 2.** One-bond $^{13}C-^{1}H$ coupling constants ($^{1}J_{CH}$) in $CDCl_3$

| Complex | $^{1}J_{CH}$/Hz | $\Delta^{1}J_{CH}{}^{a}$/Hz | $\Delta\delta$/p.p.m. | Ref. |
|---|---|---|---|---|
| **(2)** | 171 ($C^4$–H) | 15 | 38.7 | *b* |
| | 158 ($C^{12}$–H) | 2 | −0.6 | |
| **(3)**$^c$ | 173 | 14 | 34.5 | 15 |
| **(4)**$^c$ | 172 | 18 | 32.6 | 15 |
| **(6)**$^c$ | 172 | 12 | 33.6 | 15 |
| **(8)** | 172 | 16 | 35.9 | *b* |
| **(9)** | 170 ($C^4$–H) | 13 | 31.6 | *b* |
| | 174 ($C^5$–H) | 15 | 36.2 | |
| | 177 ($C^8$–H) | 19 | 41.5 | |
| | 158 ($C^{12}$–H) | 1 | −1.1 | |
| | 160 ($C^{13}$–H) | 1 | −1.8 | |
| | 158 ($C^{16}$–H) | 0 | −2.2 | |

$^a$ $\Delta^{1}J_{CH} = {}^{1}J_{CH}$(complex) − $^{1}J_{CH}$(hydrocarbon). $^b$ This work. $^c$ Values for melted samples.

been ascribed to several causes.[15–18] In **(2)** and **(9)**, complexation effects on $^{1}J_{CH}$ ($\Delta^{1}J_{CH}$) for the complexed ring are much larger than those for the uncomplexed ring (Table 2). In all complexes, there is a fairly good correlation between $\Delta^{1}J_{CH}$ and $\Delta\delta$, although the data for **(3)**, **(4)**, and **(6)** are those for their melted samples.[15] It thus appears that the factors which influence $\Delta\delta$ have some direct influence on $\Delta^{1}J_{CH}$.

Finally, we note briefly that there is no significant influence of the stacked, deformed benzene rings on the chromium–carbonyl resonance.

## Experimental

The samples **(2)**,[19] **(4)**,[20] **(5)**,[20] **(6)**,[20] **(7)**,[12] **(8)**,[19] **(9)**,[21] and **(10)**[22] were prepared by literature methods. Carbon-13 n.m.r. spectra were recorded on a JEOL JNM-FX-100 spectrometer (25 MHz) at ambient temperature, as described previously,[7] for *ca.* 5% (w/v) or less solutions in $(CD_3)_2SO$, unless otherwise noted; $SiMe_4$ was used as internal reference. One-bond C–H coupling constants were measured in $CDCl_3$.

## References

1(*a*) M. M. Maricq, J. S. Waugh, J. L. Fletcher, and M. J. McGlinchey, *J. Am. Chem. Soc.*, 1978, **100**, 6902; (*b*) B. R. Steele, R. G. Sutherland, and C. C. Lee, *J. Chem. Soc., Dalton Trans.*, 1981, 529 and refs. therein.
2 A. D. Redhouse, 'The Chemistry of the Metal–Carbon Bond,' eds. F. R. Hartley and S. Patai, John Wiley, New York, 1982, vol. 1, p. 1.
3 D. A. Brown, N. J. Fitzpatrick, I. J. King, and N. J. Mathews, *J. Organomet. Chem.*, 1976, **104**, C9; L. A. Fedorov, P. V. Petrovskii, E. I. Fedin, G. A. Panosyan, A. A. Tsoi, N. K. Baranetskaya, and V. N. Setkina, *ibid.*, 1979, **182**, 499.
4 H. Hope, J. Bernstein, and K. N. Trueblood, *Acta Crystallogr., Sect. B*, 1972, **28**, 1733; C. J. Brown, *J. Chem. Soc.*, 1953, 3265.
5 J. D. Cram and J. M. Cram, *Acc. Chem. Res.*, 1971, **4**, 204.
6 T. Takemura and T. Sato, *Can. J. Chem.*, 1976, **54**, 3412.
7 T. Takemura, K. Tokita, S. Kondo, and N. Mori, *J. Chem. Res.* (*S*), 1978, 452; K. Tokita, T. Takemura, S. Kondo, and N. Mori, *Bull. Chem. Soc. Jpn.*, 1980, **53**, 450.
8 Y. Kai, N. Yasuoka, and N. Kasai, *Acta Crystallogr., Sect. B*, 1978, **34**, 2840.
9 B. Rees and P. Coppens, *Acta Crystallogr., Sect. B*, 1973, **29**, 2516.
10 N.-S. Chiu and L. Schäfer, *J. Organomet. Chem.*, 1975, **101**, 331.
11 N. G. Newton, T. J. Walter, and N. L. Allinger, *J. Am. Chem. Soc.*, 1973, **95**, 5652.
12 C. J. Brown, *J. Chem. Soc.*, 1953, 3278.
13 W. McFarlane and S. O. Grin, *J. Organomet. Chem.*, 1966, **5**, 1476; J. T. Price and T. S. Sorenson, *Can. J. Chem.*, 1968, **46**, 515.
14 M. F. Guest, I. H. Hiller, B. R. Higginson, and D. R. Lloyd, *Mol. Phys.*, 1975, **29**, 113.
15 R. V. Emanuel and E. W. Randall, *J. Chem. Soc. A*, 1969, 3002.
16 B. E. Mann, *J. Chem. Soc., Dalton Trans.*, 1973, 2012; *Adv. Organomet. Chem.*, 1974, **12**, 135.
17 G. M. Bodner and L. J. Todd, *Inorg. Chem.*, 1974, **13**, 360.
18 R. Aydin, H. Günther, J. Runsink, H. Schmickler, and H. Seel, *Org. Magn. Reson.*, 1980, **13**, 210.
19 H. Ohno, H. Horita, T. Otsubo, Y. Sakata, and S. Misumi, *Tetrahedron Lett.*, 1977, 265.
20 B. Nicholls and M. C. Whiteng, *J. Chem. Soc.*, 1959, 551.
21 E. Langer and H. Lehner, *Tetrahedron*, 1973, **29**, 375.
22 R. Eberhardt, H. Lehner, and K. Schlögl, *Monatsh. Chem.*, 1973, **104**, 1409.

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