Journal of Organometallic Chemistry, 301 (1986) 321–327
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

TRICARBONYL(η^6-CYCLOPHANE)MOLYBDENUM COMPLEXES AND THEIR GEOMETRY-DEPENDENT ^{13}C NMR BEHAVIOR

MICHIKO TAKAMORI and NOBUO MORI*
Department of Chemistry, Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo 162 (Japan)

(Received August 24th, 1985)

Summary

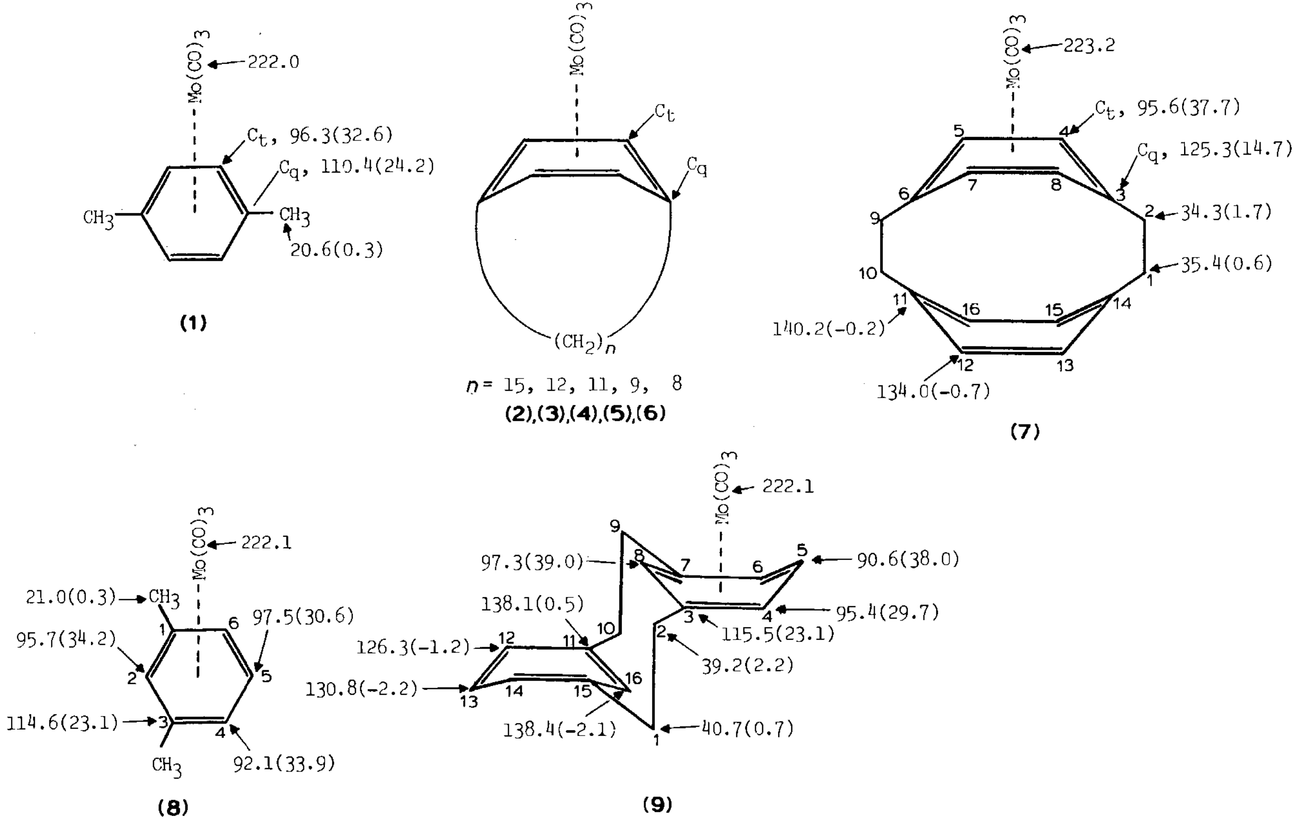
In the ^{13}C NMR spectra of tricarbonyl(η^6-cyclophane)molybdenum complexes, where the cyclophane moiety is [8]–[15]paracyclophanes, [2.2]paracyclophane, or [2.2]metacyclophane, the complexation shifts for the complexed-ring carbons are dependent on both the degree and the direction of the ring bending. The magnitude of the complexation effect on the one-bond aromatic ^{13}C–^{1}H coupling correlates with the magnitude of the complexation shift.

Introduction

As is well known, complexation of arenes with transition metals causes large upfield shifts of ^{13}C NMR peaks for the aryl carbons. Many attempts have been made to explain the origin of the complexation shift in terms of a variety of causes associated with the π-bonding [1,2], but they are all hampered by the approximations involved in any theoretical approach. It should be noted that no attention has been paid to geometrical factors, such as changes in molecular geometry on complexation [3]. Quite recently, we found in Cr and Fe complexes of [2.2]cyclophanes [4,5] and [*n*]paracyclophanes [6] that the complexation shift is dependent on the interatomic metal–carbon distance.

In order to accumulate further data for complexes of other metals, our study has been extended to a series of molybdenum complexes of the types ([*n*]pc)$(CO)_3$Mo (**2–6**), ([2.2]pc)$(CO)_3$Mo (**7**), and ([2.2]mc)$(CO)_3$Mo (**9**), where *n* is 15, 12, 11, 9 or 8, and pc and mc denote para- and meta-cyclophane. These new cyclophane complexes were prepared in the usual manner [7] and were confirmed by ^{1}H NMR and elemental analysis (see Experimental). Similar complexes of *p*- and *m*-xylene (**1** and **8**) were used as reference complexes.

0022-328X/86/$03.50



SCHEME 1. ^{13}C NMR chemical shifts (in ppm from internal TMS) for complexes **1**, **7**, **8**, and **9** in $CDCl_3$ (data for **2**–**6** are given in Table 1). Complexation shifts ($\Delta\delta$) are given in parentheses.

Results and discussion

The ^{13}C NMR chemical shifts (δ in ppm from internal TMS, recorded in $CDCl_3$) for **1**–**9** and their parent hydrocarbons are summarized in Scheme 1 and Table 1. In Scheme 1 the values in parentheses are the shift differences from the parent hydrocarbons, i.e., the complexation shifts: $\Delta\delta = \delta(\text{hydrocarbon}) - \delta(\text{complex})$. Table 2 gives the $\Delta\delta$ values for the aromatic tertiary (C_t) and quaternary carbons (C_q) of **1**–**9** together with the one-bond aromatic C–H coupling data. The chemical shifts for the parent hydrocarbons of **1**–**9** are the same as those reported in the literature [8,9].

The chemical shift assignments for C_t, C_q, C(1) (benzylic methylene carbon), and CO of **1**–**9** are based on their characteristic chemical shifts and signal intensities. In **9**, C(5) and C(8) were discriminated with off-resonance decoupling. In Table 1, the methylene carbons, except for C(1), of **3**–**6** were assigned mainly by comparison with the data for their parent cyclophanes [9] by taking account of the fact that the complexation effects on side-chain carbons of arenes are generally very small [10]. Signal intensity consideration was also paid to C(8) of **2**, C(6) of **4**, and C(5) of **5**. The C(2)–C(7) assignments for **2** and its parent hydrocarbon are all uncertain.

Basic geometry. The molecular structures of **1**–**9** are not known, but the benzene rings of the parent cyclophanes are known or were predicted to be bent into shallow boats to different degrees [11–16], as summarized in Table 2. In the [*n*]pc hydrocarbons, the predicted ring-bending angle (θ) increases with a decreasing *n*. In the parent [8]pc hydrocarbon of **6**, the predicted angles are larger than the measured value of 9.1° [14], which is small compared with the measured angle of 12.6° in [2.2]pc [15]. On the other hand, ([2.2]pc)$(CO)_3$Cr shows a value of 12.2° for θ, in the solid state [17], indicating that there is no substantial change in θ upon complexation. These results taken together suggest that θ in each complex increases in going from **1** to **7**. In [2.2]mc, the benzene rings are bent into unsymmetrical boats, where C(5) is displaced out of the mean plane by 4.1° away from the other ring and C(8) is displaced by 9.5° in the same direction [16].

In Table 1, the complexation shifts for the methylene carbons in each [*n*]pc complex are very small. In accordance with the results of a molecular-model examination, this suggests that the Mo atom is coordinated onto the outside face of the benzene ring, as shown in Scheme 1. Moreover, the CO carbon resonance shows a sharp singlet in all cases indicating rapid intramolecular motion.

Complexation shifts. In Table 1, inspection of the methylene carbon resonances shows that $\Delta\delta$ of C(1) increases, in going from **2** to **6**, from 0.1 to 1.7 ppm. Such a distinct trend is not found for any of the other methylene complexes. The CO carbon resonance is not sensitive to the change in θ.

In Table 2, the reference complex **1** shows smaller $\Delta\delta$ for C_q than for C_t, perhaps because of a lower electron density on C_q resulting from the electronic effects of the attached methyl groups [2]. It is of interest that the difference in $\Delta\delta$ between C_t and C_q increases with an increase in θ. In going from **2** to **6**, the complexation-shift difference ($\Delta\Delta\delta$) for C_t from **1** increases from 0.1 to 3.5 ppm, whereas $\Delta\Delta\delta$ for C_q decreases from 0.2 to -6.1 ppm. In **7** with a larger θ value, where there is neither a significant transannular nor a through-bond electronic effect on $\Delta\delta$ of the uncomplexed ring [4,5], C_t shows a larger positive $\Delta\Delta\delta$ (5.1 ppm) and C_q shows a larger negative $\Delta\Delta\delta$ (-9.5 ppm). Moreover, in **9**, C_t(5) and C_t(8), both displaced from

TABLE 1

^{13}C CHEMICAL SHIFTS (δ) FOR THE ([*n*]pc)$(CO)_3Mo$ COMPLEXES **2–6** AND THEIR PARENT HYDROCARBONS IN $CDCl_3$

Compound	δ [a] (ppm)										
	C_q	C_t	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	CO
2	115.0	95.8	34.9	(31.2	26.7	27.6	27.6	28.1	28.3) [b]	28.9	221.9
[15]pc	139.4	128.5	35.0	(30.4	26.8	27.7	27.7	28.1	28.5) [b]	29.2	
3	116.6	95.3	34.6	30.3	25.1	27.8 [d]	27.3 [d]	26.7			222.0
[12]pc [c]	140.0	128.8	35.2	29.8	25.4	27.5	27.5	26.7			
4	116.8	95.3	35.1	29.1 [e]	25.4	28.5 [e]	26.8	27.6			221.9
[11]pb [c]	140.2	129.0	35.8	29.0	25.6	28.2	26.8	27.4			
5	119.6	94.3	34.0	29.7	22.8	28.5	25.9				222.4
[9]pc [c]	140.0	129.5	35.5	29.4	23.3	28.0	26.1				
6	122.4	93.7	34.0	31.5 [f]	25.6	31.2 [f]					222.6
[8]pc [c]	140.5	129.8	35.7	31.5	26.0	30.1					

[a] From internal TMS. The methylene carbons are numbered from one of the benzylic methylene complexes toward the other. [b] Assignments in parentheses are uncertain. [c] Ref. 9. [d–f] Assignments may be reversed.

TABLE 2

COMPLEXATION SHIFTS ($\Delta\delta$), ONE-BOND C_t–H COUPLING CONSTANTS (^1J(CH)) AND RING-BENDING ANGLES (θ)

Complex	Carbon	$\Delta\delta$ [a] (ppm)	$\Delta\Delta\delta$ [b] (ppm)	^1J(CH) [c] (Hz)	Δ^1J [d] (Hz)	θ [e] (°)		
						UV	FF	X-rat
1	C_q	24.2						
	C_t	32.6		171	15			
2	C_q	24.4	0.2			< 5 [h]		
	C_t	32.7	0.1	171	16			
3	C_q	23.4	−0.8			5 [i]		
	C_t	33.5	0.9	171	16			
4	C_q	23.4	−0.8			5 [h]		
	C_t	33.7	1.1	171	16			
5	C_q	20.4	−3.8			15 [i]	8.5 [j]	
	C_t	35.2	2.6	171	14			
6	C_q	18.1	−6.1			20 [i]	12.5 [j]	9.1 [k]
	C_t	36.1	3.5	– [g]				
7	$C_q(3)$	14.7	−9.5					12.6 [l]
	$C_t(4)$	37.7	5.1	– [g]				
	$C_q(11)$	−0.2						
	$C_t(12)$	−0.7		– [g]				
8	$C_q(3)$	23.1						
	$C_t(4)$	33.9		174	17			
	$C_t(5)$	30.6		171	12			
	$C_t(2)$	34.2		171	17			
9	$C_q(3)$	23.1	0.0 [f]					
	$C_t(4)$	29.7	−4.2 [f]	171	14			
	$C_t(5)$	38.0	7.4 [f]	174	15			4.1 [m]
	$C_t(8)$	39.0	4.8 [f]	174	16			9.5 [m]
	$C_q(11)$	0.5						
	$C_t(12)$	−1.2		161	4			
	$C_t(13)$	−2.2		161	2			
	$C_t(16)$	−2.1		159	1			

[a] $\Delta\delta = \delta$(hydrocarbon)$-\,\delta$(complex). [b] $\Delta\Delta\delta = \Delta\delta$(cyclophane complex)$-\,\Delta\delta$(reference 1). [c] ^1J(CH) for the indicated C_t atom. [d] $\Delta^1J = {}^1J$(CH)(complex)$-\,{}^1J$(CH)(hydrocarbon). [e] The bending angle of the benzene ring in the parent hydrocarbon, predicted by UV spectroscopy (UV) or molecular force field calculation (FF) or based on crystal X-ray diffraction. [f] $\Delta\Delta\delta$ from reference **8**. [g] Not measured. [h] Ref. 11. [i] Ref. 12. [j] Ref. 13. [k] Ref. 14. [l] Ref. 15. [m] Ref. 16.

planarity towards Mo, show large positive $\Delta\Delta\delta$'s from those of **8** (7.4 and 4.8 ppm) compared with −4.2 ppm for $C_q(3)$ and 0.0 ppm for $C_t(4)$. Therefore the magnitude of $\Delta\Delta\delta$ or $\Delta\delta$ is dependent on both the degree and the direction of the ring bending. This geometry dependence of $\Delta\delta$ is probably related to the interatomic distance between the Mo and the ligand carbon, because the Mo–C_q distances in [1,3,5-$(CH_3)_3C_6H_3$] and [$(CH_3)_6C_6$]$(CO)_3$Mo, in the solid state, [18] correlate with the $\Delta\delta$ values for the C_q atoms [19] (Table 3). Similar correlations are known in (π-arene)Cr and Fe complexes [4–6].

One-bond aromatic ^{13}C–^1H coupling constants. Transition metal complexations of arenes generally increase one-bond aromatic C–H coupling constants in the arenes and the origin of this complexation effect has been ascribed to several causes [19,20]. In complex **9**, the magnitude of the complexation effect (Δ^1J) is much larger

TABLE 3

COMPLEXATION SHIFTS ($\Delta\delta$) AND INTERATOMIC Mo–C DISTANCES (d)

Complex	Carbon	d [a] (Å)	$\Delta\delta$ [b] (ppm)
$[1,3,5\text{-}(CH_3)_3C_6H_3](CO)_3Mo$	C_t	2.372	32.9
	C_q		26.9
$[(CH_3)_6C_6](CO)_3Mo$	C_q	2.392	20.8

[a] Mean distance between Mo and the indicated carbon in the solid state [18]. [b] Data in CH_2Cl_2 [19].

in the complexed ring than in the uncomplexed ring and correlates with the magnitude of $\Delta\delta$, as Table 2 shows. In all complexes, Δ^1J tends to increase with an increase in $\Delta\delta$ but does not always reflect small differences in $\Delta\delta$. It thus appears that the factors which influence $\Delta\delta$ have some direct influence on Δ^1J.

Experimental

Materials. The complexes **1** and **8** [7] were prepared by literature methods and the new substances, were prepared in a similar manner. The parent cyclophanes used were already available in our laboratory as a consequence of previous work [4–6].

Tricarbonyl(η^6-[15]paracyclophane)molybdenum (2). M.p. 95–96°C (from pentane); ^{1}H NMR, δ 0.78–1.80 (26 H, m, CH_2), 2.20–2.50 (4H, m, CH_2), 5.61 (4 H, s, C_6H_4). Anal. Found: C, 61.78; H, 7.35. $C_{24}H_{34}MoO_3$ calcd.: C, 61.80; H, 7.35%.

Tricarbonyl(η^6-[12]paracyclophane)molybdenum (3). M.p. dec. 126°C (from hexane); ^{1}H NMR, δ 0.84–1.80 (20 H, m, CH_2), 2.20–2.48 (4 H, m, CH_2), 5.61 (4H, s, C_6H_4). Anal. Found: C, 59.42; H, 6.68. $C_{21}H_{28}MoO_3$ calcd.: C, 59.43; H, 6.65%.

Triarbonyl(η^6-[11]paracyclophane)molybdenum (4). M.p. dec. 132°C (from hexane); ^{1}H NMR, δ 0.76–1.80 (18 H, m, CH_2), 2.20–2.44 (4H, m, CH_2), 5.63 (4 H, s, C_6H_4). Anal. Found: C, 58.43; H, 6.39. $C_{20}H_{26}MoO_3$ calcd.: C, 58.54; H, 6.39%.

Tricarbonyl(η^6-[9]paracyclophane)molybdenum (5). M.p. dec. 148°C (from hexane); ^{1}H NMR, δ 0.70–1.00 (6 H, m, CH_2), 1.10–1.39 (4 H, m, CH_2), 1.46–1.77 (4 H, m, CH_2), 2.28–2.49 (4 H, m, CH_2), 5.61 (4 H, s, C_6H_4). Anal. Found: C, 56.46; H, 5.81. $C_{18}H_{22}MoO_3$ calcd.: C, 56.55; H, 5.80%.

Tricarbonyl(η^6-[8]paracyclophane)molybdenum (6). M.p. dec. 137°C (from hexane); ^{1}H NMR, δ 0.75–0.94 (4 H, m, CH_2), 1.08–1.36 (4 H, m, CH_2), 1.56–1.85 (4 H, m, CH_2), 1.33–1.58 (4 H, m, CH_2), 5.65 (4 H, s, C_6H_4). Anal. Found: C, 55.15; H, 5.45. $C_{17}H_{20}MoO_3$ calcd.: C, 55.44; H, 5.47%.

Tricarbonyl(3–8-η-[2.2]paracyclophane)molybdenum (7). M.p. dec. 172°C (from benzene); ^{1}H NMR, δ 2.76–3.03 (4 H, m, CH_2), 3.12–3.37 (4 H, m, CH_2), 4.99 (4 H, s, complexed C_6H_4), 6.90 (4 H, s, uncomplexed C_6H_4). Anal. Found: C, 58.84; H, 4.18. $C_{19}H_{16}MoO_3$ calcd.: C, 58.78; H, 4.15%.

Tricarbonyl(3–8-η-[2.2]metacyclophane)molybdenum (9). M.p. dec. 158°C (from hexane); ^{1}H NMR, δ 1.89 (2 H, m, CH_2), 2.42 (2 H, m, CH_2), 2.72 (1 H, broad s, C(8)H), 2.85 (2 H, m, CH_2), 3.29 (2 H, m, CH_2), 5.52 (1 H, broad s, C(16)H), 5.63 (3 H, m, C(4), C(5) and C(6) H's), 7.07 (2 H, m, C(12) and C(15) H's), 7.34–7.48 (1 H, m, C(13)H). Anal. Found: C, 58.44; H, 4.15. $C_{19}H_{16}MoO_3$ calcd.: C, 58.78; H, 4.15%.

Spectra. The ^{13}C and ^{1}H NMR spectra were measured on a JEOL JNM-FX-100 (25.15 MHz) and a JEOL JNM4H-100 spectrometer (100 MHz), respectively, at ambient temperature, as described previously [21], for ca. 5 w/v% or less solutions in $CDCl_3$; tetramethylsilane was used as the internal reference. The C–H coupling constants were measured with gated decoupling.

References

1 M.M. Maric, J.S. Waugh, J.L. Fletcher and M.J. McGlinchey, J. Am. Chem. Soc., 100 (1978) 6902.
2 B.R. Steele, R.G. Sutherland and C.C. Lee, J. Chem. Soc., Dalton Trans., (1981) 529 and ref. therein.
3 A.D. Redhouse in F.R. Hartley and S. Patai (Eds.), The Chemistry of the Metal–Carbon Bond, John Wiley, New York, Vol. 1, 1982, p. 1.
4 N. Mori, M. Takamori and T. Takemura, J. Chem. Soc., Dalton Trans., (1985) 1065.
5 N. Mori and M. Takamori, J. Chem. Soc., Dalton Trans., (1985) 1661.
6 N. Mori and M. Takamori, Magn. Reson. Chem., in press.
7 A. Pidcock, J.D. Smith and B.W. Taylor, J. Chem. Soc. A, (1967) 872.
8 K. Tokita, T. Takemura, S. Kondo and N. Mori, Bull. Chem. Soc. Jpn., 53 (1980) 450.
9 T. Kanda, T. Otsubo, H. Horita and S. Misumi, Bull. Chem. Soc. Jpn., 53 (1980) 1015.
10 D.A. Brown, N.J. Fitzpatrick, I.J. King and N.J. Mathews, J. Organomet. Chem., 104 (1976) C9; L.A. Fedorov, P.V. Petrovskii, E.I. Fedin, G.A. Panosyan, A.A. Tsoi, N.K. Baranetskaya and V.N. Setokina, ibid., 182 (1979) 499.
11 N. Mori, T. Takemura and T. Ohkuma, Bull. Chem. Soc. Jpn., 50 (1977) 179.
12 N.L. Allinger, L.A. Freiberg, R.B. Hermann and M.A. Miller, J. Am. Chem. Soc., 85 (1963) 1171.
13 N.L. Allinger, J.T. Sprague and T. Liljefors, J. Am. Chem. Soc., 96 (1974) 5100.
14 M.G. Newton, T.J. Walter and N.L. Allinger, J. Am. Chem. Soc., 95 (1973) 6562.
15 H. Hope, H. Bernstein and K.N. Trueblood, Acta Cryst. B, 28 (1972) 1733.
16 Y. Kai, N. Yasuoka and N. Kasai, Acta Cryst. B, 33 (1977) 754.
17 Y. Kai, N. Yasuoka and N. Kasai, Acta Cryst. B, 34 (1978) 2840.
18 D.E. Koshland, S.E. Myers and J.P. Chesick, Acta Cryst. B, 33 (1977) 2013.
19 B.E. Mann, J. Chem. Soc., Dalton Trans., (1973) 2012.
20 R.V. Emanual and E.W. Randall, J. Chem. Soc. A, (1969) 3002; G.M. Godner and L.J. Todd, Inorg. Chem., 13 (1974) 360; R. Aydin, H. Günther, J. Runsink, H. Schmickler and H. Seel, Org. Magn. Reson., 13 (1980) 210.
21 N. Mori and T. Takemura, J. Chem. Soc., Perkin Trans. II, (1978) 1259.