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(η^6-Cyclophane)(η^6-benzene)ruthenium(II) bis(tetrafluoroborate) complexes and their geometry-dependent ^{13}C NMR behavior

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Abstract

Transition-metal complexation effects which can be observed in ^{13}C NMR spectra have been investigated for the (η^6-cyclophane)(η^6-benzene)ruthenium(II) bis(tetrafluoroborate) complexes, where the cyclophane moiety is [8]–[15]paracyclophane, [2.2]paracyclophane, [2.2]metacyclophane or 5,13-dimethyl[2.2]metacyclophane. The complexation shifts for the complexed cyclophane-ring carbons are dependent on the degree and direction of 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.

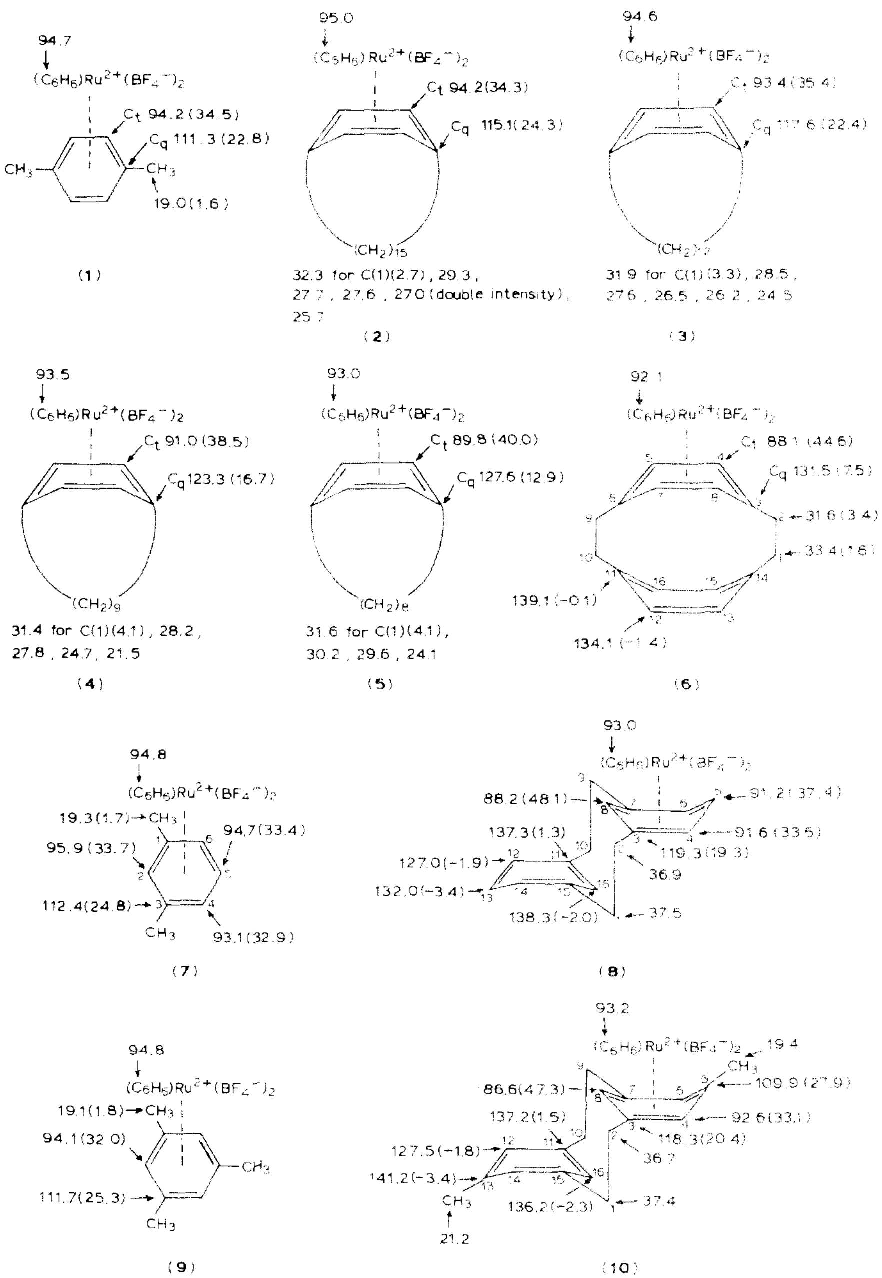
Introduction

Complexations of arenes with transition metals cause large upfield shifts of ^{13}C NMR peaks for the aryl carbons. Recently, we found that the complexation shift in Cr, Fe and Mo complexes of cyclophanes [1–4] is dependent on the metal–carbon distance.

In order to accumulate further data for complexes of other metals, our study was extended to a series of ruthenium cation complexes of the types [Ru(η^6-[*n*]pc)(η^6-C_6H_6)][BF_4]$_2$ (**2–5**), [Ru(η^6-[2.2]pc)(η^6-C_6H_6)][BF_4]$_2$ (**6**), [Ru(η^6-[2.2]mc)(η^6-C_6H_6)][BF_4]$_2$ (**8**) and [Ru(η^6-5,13-dimethyl[2.2]mc)(η^6-C_6H_6)][BF_4]$_2$ (**10**), where *n* is 15, 12, 9 or 8, and pc and mc denote para- and metacyclophane. Similar complexes of *p*-xylene (**1**), *m*-xylene (**7**) and mesitylene (**9**) were used as reference complexes. All complexes, new substances except for **6** and **9**, were prepared in the usual manner [5] and their identities were confirmed by ^{1}H NMR and by elemental analysis (see Experimental).

Results and discussion

The ^{13}C chemical shifts (δ in ppm from internal TMS, recorded in $(CD_3)_2SO$) for **1–10** are given in Scheme 1. The values in parentheses are the shift differences



Scheme 1. ^{13}C NMR chemical shifts (in ppm from internal TMS) for complexes **1–10** in $(CD_3)_2SO$. Complexation shifts are given in parentheses.

from the parent hydrocarbons, i.e., the complexation shifts: $\Delta\delta = \delta$(hydrocarbon) − δ(complex). Table 1 gives the $\Delta\delta$ values for the aromatic tertiary (C_t) and quaternary carbons (C_q) of **1–10** together with the one-bond aromatic C–H coupling data. The δ values used for the parent hydrocarbons **2–5** (in $CDCl_3$ solution) are data taken from the literature [4].

Table 1

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-ray
1	C_q	22.8						
	C_t	34.5		180	24			
2	C_q	24.3	1.5			< 5 [i]		
	C_t	34.3	−0.2	182	27			
3	C_q	22.4	−0.4			5 [j]		
	C_t	35.4	0.9	182	28			
4	C_q	16.7	−6.1			5 [i]		
	C_t	38.5	4.0	183	26			
5	C_q	12.9	−9.9			20 [j]	12.5 [k]	9.1 [l]
	C_t	40.0	5.5	184	28			
6	C_q(3)	7.5	−15.3					12.6 [m]
	C_t(4)	44.6	10.1	186	30			
	C_q(11)	−0.1						
	C_t(12)	−1.4		158	2			
7	C_q(3)	24.8						
	C_t(4)	32.9		185	28			
	C_t(5)	33.4		186	27			
	C_t(2)	33.7		183	29			
8	C_q(3)	19.3	−5.5 [f]					
	C_t(4)	33.5	0.6 [f]	182	25			
	C_t(5)	37.4	4.0 [f]	186	27			4.1 [n]
	C_t(8)	48.1	14.4 [f]	– [h]				9.5 [n]
	C_q(11)	1.3						
	C_t(12)	−3.4		157	0			
	C_t(13)	−1.9		161	2			
	C_t(16)	−2.0		157	−1			
9	C_q	25.3						
	C_t	32.0		182	22			
10	C_q(3)	20.4	−4.9 [g]					
	C_t(4)	33.1	1.1 [g]	– [h]				
	C_q(5)	27.9	2.6 [g]					3.6 [o]
	C_t(8)	47.3	15.3 [g]	– [h]				10.2 [o]
	C_q(11)	1.5						
	C_t(12)	−1.8		– [h]				
	C_q(13)	−3.4						
	C_t(16)	−2.3		– [h]				

[a] $\Delta\delta = \delta$(hydrocarbon) − δ(complex). [b] $\Delta\Delta\delta = \Delta\delta$(cyclophane complex) − $\Delta\delta$ (referred to **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 cyclophane, predicted by UV spectroscopy (UV) or molecular force field calculation (FF) or based on crystal X-ray diffraction. [f] $\Delta\Delta\delta$ referred to **7**. [g] $\Delta\Delta\delta$ referred to **9**. [h] Not measured. [i] Ref. [6]. [j] Ref. [7]. [k] Ref. [8]. [l] Ref. [9]; [m] Ref. [10]. [n] Ref. [11]. [o] Ref. [12].

The chemical shift assignments for C_t, C_q, C(1) (benzylic methylene carbon) and the ligand benzene carbons were based on their characteristic chemical shifts and signal intensities. C(5) and C(8) of **8**, and also C(2) and C(5) of **7** were distinguished by off-resonance decoupling.

Basic geometry

The molecular structures of **1**–**10** 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 [6–12], see Table 1. In the [*n*]pc hydrocarbons, the predicted ring-bending angle (θ) increases with a decrease in *n*. In [8]pc, the predicted angles are both larger than the measured angle of 9.1° [9], which is small compared with the measured 12.6° in [2.2]pc [10]. On the other hand, Cr(η^6-[2.2]pc)(CO)$_3$ shows a θ value of 12.2° [13], indicating that there is no substantial change in θ upon complexation. These results taken together suggest that θ in each complex increases on going from **1** to **6**.

In 5,13-dimethyl[2.2]mc, C(5) and C(8) are displaced out of the mean plane by 3.6 and 10.2°, respectively, away from the other ring [12]. Similar ring-bending is seen in [2.2]mc [11]. Interestingly, [Fe^{II}(η^6-5,13-dimethyl[2.2]mc)(η^5-C$_5$H$_5$)][PF$_6$] shows 1.0° for C(5) and 10.7° for C(8) [12], indicating that complexation causes a substantial decrease in θ for C(5).

Complexation shifts

In Scheme 1, inspection of the C(1) resonance of **2**–**5** shows that $\Delta\delta$ increases, on going from **2**–**5**, from 2.7 to 4.1 ppm. The methyl carbons of **1** has a smaller $\Delta\delta$ of 1.6 ppm. The same trend was observed in Cr, Fe and Mo complexes of [*n*]pc's [3,4].

In Table 1, the reference complex, **1**, (and also **7** and **9**) shows a 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 [14]. It was seen that in the [*n*] and [2.2]pc complexes **2**–**6** the difference in $\Delta\delta$ between C$_t$ and C$_q$ increases with an increase in θ. That is, on going from **2** to **5**, the complexation-shift difference ($\Delta\Delta\delta$) for C$_t$ from **1** increases from −0.2 to 5.5 ppm, whereas $\Delta\Delta\delta$ for C$_q$ decreases from 1.5 to −9.9 ppm. In **6**, with a larger θ, where there is neither a significant transannular nor a through-bond electronic effect on $\Delta\delta$ of the uncomplexed ring [1,2], C$_t$ shows a larger positive $\Delta\Delta\delta$ (10.1 ppm) and C$_q$ shows a larger negative $\Delta\Delta\delta$ (−15.3 ppm). Moreover, in the [2.2]mc complex **8**, C$_t$(5) and C$_q$(8), which are both displaced from planarity toward Ru, show large positive $\Delta\Delta\delta$'s from **7** (4.0 and 14.4 ppm) compared with −5.5 ppm for C$_q$(3) and 0.6 ppm for C$_t$(4). Comparison of the results of the dimethyl[2.2]mc complex **10** with those of **9** showed no significant differences.

These results reflect just how diverse the ring bending is among the parent cyclophanes. That is, the magnitude of $\Delta\Delta\delta$ or $\Delta\delta$ is dependent on both the degree and the direction of the ring bending and is probably related to the interatomic distance between the Ru and the ligand carbon [1–4].

One-bond aromatic ^{13}C–^{1}H coupling constants. Transition metal complexation of arenes generally increase one-bond aromatic C–H coupling constants in the arene and the origin of this complexation effect has been ascribed to several factors [15]. In complex **8**, the magnitude of the complexation effect (Δ^1J) is much larger in the complexed ring than in the uncomplexed ring and correlates with the magnitude of $\Delta\delta$, as Table 1 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 **6** [16] and **9** [15] are known and were prepared by the Bennett method using di-μ-chloro-bis[(η^6-benzene)chlororuthenium(II)] [18]. The other complexes, which are new, were prepared in a similar manner. Of these, **6** and **9** are pale yellow crystals, and the others white. The parent cyclophanes used were already available in our laboratory as a consequence of previous work [1–4].

*(η^6-Benzene)(η^6-p-xylene)ruthenium(II) bis(tetrafluoroborate) (**1**).* M.p. 225 °C (dec.); ^{1}H NMR, δ 2.40(6H, s, CH_3), 6.89(6H, s, C_6H_6), 6.92(4H, s, C_6H_4). Anal. Found: C, 36.52; H, 3.43. $C_{14}H_{16}RuB_2F_8$ calc: C, 36.63; H, 3.51%.

*(η^6-Benzene)(η^6-[15]paracyclophane)ruthenium(II) bis(tetrafluoroborate) (**2**).* M.p. 207 °C (dec.); ^{1}H NMR, δ 0.76–1.40(22H, m, CH_2), 1.42–1.90(4H, m, CH_2), 2.50–2.88(4H, m, CH_2), 6.91(6H, s, C_6H_6), 7.01(4H, s, CH_2). Anal. Found: C, 50.52; H, 6.20. $C_{27}H_{40}RuB_2F_8$ calc: C, 50.72; H, 6.30%.

*(η^6-Benzene)(η^6-[12]paracyclophane)ruthenium(II) bis(tetrafluoroborate) (**3**).* M.p. 170 °C (dec.); ^{1}H NMR, δ 0.55–1.40(16H, m, CH_2), 1.40–1.95(4H, m, CH_2), 2.50–2.92(4H, m, CH_2), 6.95(6H, S, C_6H_6), 7.08(4H, s, C_6H_4). Anal. Found: C, 48.13; H, 5.60. $C_{24}H_{34}RuB_2F_8$ calc: C, 48.26; H, 5.73%.

*(η^6-Benzene)(η^6-[9]paracyclophane)ruthenium(II) bis(tetrafluoroborate) (**4**).* M.p. 175 °C (dec.); ^{1}H NMR, δ 0.24–0.81(6H, m, CH_2), 0.81–1.28(4H, m, CH_2), 1.38–1.84(4H, m, CH_2), 2.50–2.86(4H, m, CH_2), 6.88(6H, s, C_6H_6), 6.99(4H, m, C_6H_4). Anal. Found: C, 45.50; H, 4.95. $C_{21}H_{28}RuB_2F_8$ calc: C, 45.43; H, 5.08%.

*(η^6-Benzene)(η^6-[8]paracyclophane)ruthenium(II) bis(tetrafluoroborate) (**5**).* M.p. 230 °C (dec.); ^{1}H NMR, δ 0.32–0.68(4H, m, CH_2), 0.72–1.20(4H, m, CH_2), 1.52–1.87(4H, m, CH_2), 2.52–2.84(4H, m, CH_2), 6.87(6H, s, C_6H_6), 7.00(4H, s, C_6H_4). Anal. Found: C, 44.45; H, 4.53. $C_{20}H_{26}RuB_2F_8$ calc: C, 44.39; H, 4.84%.

*(η^6-Benzene)(η^6-m-xylene)ruthenium(II) bis(tetrafluoroborate) (**7**).* M.p. 182 °C (dec.); ^{1}H NMR, δ 2.10(6H, s, CH_3), 6.91(6H, s, C_6H_6), 6.89–7.49(4H, m, C_6H_4). Anal. Found: C, 36.52; H, 3.51. $C_{14}H_{16}RuB_2F_8$ calc: C, 36.63; H, 3.51%.

*(η^6-Benzene)(η^6-[2.2]metacyclophane)ruthenium(II) bis(tetrafluoroborate) (**8**).* M.p. 173 °C (dec.); ^{1}H NMR, δ 2.03–2.22(4H, m, CH_2), 3.00–3.70(4H, m, CH_2), 5.20–5.32(2H, m, complexed C_6H_4), 6.69–7.00(2H, m, complexed C_6H_4), 6.70(6H, s, C_6H_6), 7.12–7.49(4H, m, uncomplexed C_6H_4). Anal. Found: C, 46.93; H, 3.89. $C_{22}H_{22}RuB_2F_8$ calc: C, 47.09; H, 3.95%.

*(η^6-Benzene)(η^6-5,13-dimethyl[2.2]metacyclophane)ruthenium(II) bis(tetrafluoroborate) (**10**).* M.p. 220 °C (dec.); ^{1}H NMR, δ 2.15–2.62(4H, m, CH_2), 2.30(6H, s, CH_3), 3.00–3.51(4H, m, CH_2), 5.09–5.15(2H, m, complexed C_6H_3), 6.70(6H, s, C_6H_6), 6.70–7.13(4H, m, uncomplexed and complexed C_6H_3). Anal. Found: C, 48.58; H, 4.17. $C_{24}H_{26}RuB_2F_8$ calc: C, 48.92; H, 4.45%.

Spectra

The ^{13}C and ^{1}H NMR spectra were recorded on JEOL JNM-FX100 (25.15 MHz) and JEOL JNM4H-100 (100 MHz) spectrometers, respectively, at ambient temperature as described previously [17], for ca. $\leqslant 5$ w/v % solutions in $(CD_3)_2SO$; tetramethylsilane was used as the internal reference. The C–H coupling constants were measured with gated decoupling.

References

1 N. Mori, M. Takamori and T. Takemura, J. Chem. Soc., Dalton Trans., (1985) 1065.
2 N. Mori and M. Takamori, J. Chem. Soc., Dalton Trans., (1985) 1661.
3 N. Mori and M. Takamori, Magn. Reson. Chem., 24 (1986) 151.
4 M. Takamori and N. Mori, J. Organomet. Chem., 301 (1986) 321.
5 M.A. Bennett and T.W. Matheson, J. Organomet. Chem., 175 (1979) 87. See also, M.A. Bennett, T.W. Matheson, G.B. Robertson, A.K. Smith and P.A. Tucker, Inorg. Chem., 19 (1980) 1014.
6 N. Mori, T. Takemura and T. Ohkuma, Bull. Chem. Soc. Jpn., 50 (1977) 179.
7 N.L. Allinger, L.A. Freiberg, R.B. Hermann and M.A. Miller, J. Amer. Chem. Soc., 85 (1963) 1171.
8 N.L. Allinger, J.T. Sprague and T. Liljefors, J. Amer. Chem. Soc., 96 (1974) 5100.
9 M.G. Newton, T.J. Walter and N.L. Allinger, J. Amer. Chem. Soc., 95 (1973) 5652.
10 H. Hope, J. Bernstein and K.N. Trueblood, Acta Cryst., B28 (1972) 1733.
11 Y. Kai, N. Yasuoka and N. Kasai, Acta Cryst., B33 (1977) 754.
12 A.R. Koray, T. Zahn and M.L. Ziegler, J. Organomet. Chem., 291 (1985) 53.
13 Y. Kai, N. Yasuoka and N. Kasai, Acta Cryst., B34 (1978) 2840.
14 B.R. Steele, R.G. Sutherland and C.C. Lee, J. Chem. Soc., Dalton Trans., (1981) 529.
15 B.E. Mann, J. Chem. Soc., Dalton Trans., (1973) 2012; R.V. Emanuel 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.
16 E.D. Laganis, R.G. Finke and V. Boekelheide, Tetrahedron Lett., (1980) 4405.
17 N. Mori and T. Takemura, J. Chem. Soc., Perkin Trans. II, (1978) 1259.
18 M.A. Bennett and A.K. Smith, J. Chem. Soc., Dalton Trans., (1974) 233.