

70. Intramolecular Carbonyl Group Site Exchange in Symmetrically Substituted (η -1,3-Diene)tricarbonyliron Complexes

Short Communication

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Dedicated to Prof. Dr. Dr. Walter Boguth on the occasion of his 65th birthday

(19.II.82)

Summary

Activation parameters have been determined for the intramolecular site exchange of the carbonyl groups in tricarbonyliron complexes of 1,4- and 2,3-disubstituted 1,3-butadienes, of 1,3-cycloalkadienes and of 1,2-dimethylenecycloalkanes by temperature-dependent ¹³C-NMR. spectroscopy (see Table 1). The variations of the activation parameters are discussed in terms of a turnstile-type mechanism for the exchange process and of the differences in the ground state and transition state stability of the complexes. A VB-model of the complexes is used to explain the difference in the stabilities.

X-ray analyses of (1-4- η -1,3-diene)tricarbonyliron complexes show the diene moiety and two carbonyl groups to occupy the basal positions in a square-based pyramidal arrangement of the ligands (cf. e.g. [1] [2]). In solution, at room temperature, the ligands in these and related complexes undergo a rapid cyclic and concerted site exchange (ΔG_{298}^\ddagger about 38 to 53 kJmol⁻¹) as can be seen from several recent ¹³C-NMR. studies (cf. [3-5] and literature cited therein). The exchange process is strongly retarded with decreasing LUMO energy of the 1,3-diene while other factors such as steric effects and the non-planarity of the diene seem to exert only minor influences. The exchange process can proceed, mechanistically, by a type of *Berry* pseudorotation or a type of turnstile rotation of the ligands. The two processes are indistinguishable by means of dynamic ¹³C-NMR. spectroscopy. The turnstile type mechanism which consists in successive 120° rotations of the tricarbonyliron fragment relative to the diene moiety, is assumed to be favoured over the *Berry*-type mechanism since the latter one would involve a trigonal bipyramidal intermediate with the diene ligand in one of the apical and equatorial positions – an arrangement which seems to be unrealizable for steric reasons.

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Table 1. Activation parameters, spectral data and characteristic temperatures of the CO-exchange process in the complexes 1–15^{a)}

Complex	Solvent	T _c ^{b)}	E _a	lg A	ΔH [‡]	ΔS [‡]	ΔG ₂₉₈ [‡]	Remarks
1	c)	213	41.2	12.7	39.4	–7	41.5	d)
2	e)	215	37.9	11.9	36.1	–23	43.0	–
3	f)	170	28.5	11.4	26.9	–31	36.1 (39)	g)
4	h)	307	55.9	12.1	53.4	–21	59.6	–
5	e)	217	39.4	12.1	37.6	–19	43.3	i)
6	f)	216	36.5	11.4	34.7	–32	44.2	j)
7	f)	228	40.0	11.8	38.1	–25	45.7	j)
8	k)	231	42.5	12.3	40.6	–16	45.2	–
9	l)	160	28.2	11.9	26.8	–20	32.8	m)
10	e)	192	37.0	12.6	35.2	–9	37.9	n)
11	e)	219	42.9	12.9	41.0	–4	42.1	–
12	e)	215	40.7	12.6	38.9	–10	41.8	o)
13	e)	232	43.6	12.5	41.7	–13	45.4	–
14	e)	247	45.1	12.0	43.0	–22	49.7	–
15	e)	247	44.0	12.0	42.0	–23	48.9	p)

a) E_a, ΔH[‡], ΔG[‡] in kJmol^{–1}; ΔS[‡] in Jmol^{–1}deg^{–1}; temperatures in K; average error in E_a and ΔH[‡] ± 2, in ΔS[‡] ± 5, and in ΔG[‡] ± 3.

b) Coalescence temperature.

c) (2,2-Dimethylbutane/pentane 8:3)/CS₂/D₆-acetone 4:2:1.

d) The same values were obtained with CS₂/D₆-acetone as solvent; according to [3]: E_a = 39.7 ± 0.8; ΔH[‡] = 38.1 ± 2; ΔS[‡] = –19 ± 8; ΔG₂₉₈[‡] = 43.9 ± 2.0.

e) CD₂Cl₂.

f) Et₂O/Pr₂O/pentane/CH₂Cl₂/D₆-acetone/CS₂ 1:1:1:1:1:1.5.

g) Values are given for (1–4-η⁴-1,4-dimethoxy-1,3-cyclohexadiene)tricarbonyliron; in brackets ΔG[‡] estimated for 3.

h) Chlorobenzene/D₆-acetone 2:1.

i) The same values were obtained with CDCl₃/CS₂ and with pentane as solvents.

j) Complex 6 was prepared from 7 by methylation with diazomethane. Complex 7 was obtained by acid-catalyzed hydrolysis of the corresponding bis(trimethylsilyloxy) complex.

k) CD₂Cl₂/CHFC₂ 1:1.

l) CF₂Cl₂.

m) The same values were obtained with solvent mixture c).

n) According to [3]: ΔH[‡] = 42.4 ± 2.0; ΔS[‡] = +18 ± 8; ΔG₂₉₈[‡] = 36.8 ± 2.0 (in D₆-acetone/CS₂).

o) According to [3]: ΔH[‡] = 42.7 ± 2.0; ΔS[‡] = –3 ± 8; ΔG₂₉₈[‡] = 43.5 ± 2.0 (in D₈-toluene).

p) According to [6]: ΔH[‡] = 37.2 ± 1.3; ΔS[‡] = –37 ± 12; ΔG₂₉₈[‡] = 51.5 ± 2.0.

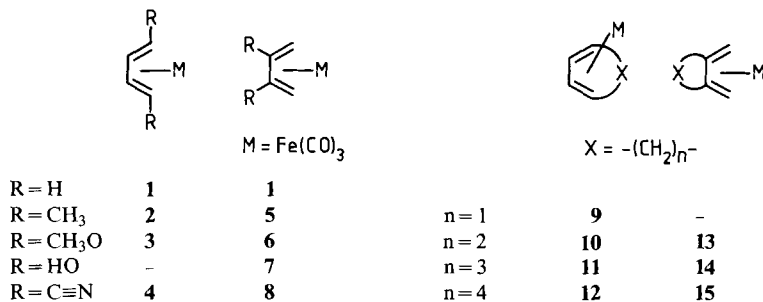
Table 2. Comparison of ΔG₂₉₈[‡] (13–15) and ΔG₂₉₈ (endo/exo) of comparable 1-methylcycloalkenes^{a)}

Ring size	Complex ΔG ₂₉₈ [‡]	1-Methylcycloalkene ⇌ Methylidenecycloalkane ΔG ₂₉₈	Reference
4	45.4 (13)	–4.3	[11]
5	49.7 (14)	–17.4	[11] [12]
6	48.9 (15)	–13.6	[11] [12]
7	(47) ^{b)}	–10.7	[12]
8	(49) ^{b)}	–15.9	[12]

a) ΔG in kJmol^{–1}.

b) Estimated values derived from ΔG₂₉₈ in the third column.

Scheme 1



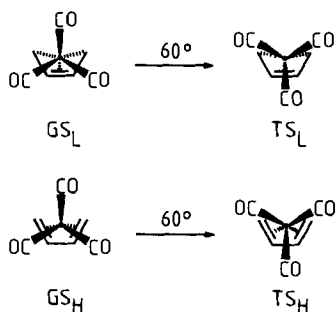
Since the hitherto existing investigations of the dynamic carbonyl group exchange were performed only on a few (1,3-diene)tricarbonyliron complexes with diene ligands of considerably varying structures (*cf.* [3] [5–7]), we have undertaken a study of the exchange process in function of systematically varied structural properties within the series of complexes **1–15** (Scheme 1).

The complexes were prepared by standard methods (see also the footnotes in Table 1). Activation parameters were determined from line-shape analysis of the temperature-dependent ¹³C-NMR signals (*cf.* [8]) of the carbonyl groups (Table 1).

The activation parameters for the complexes **1**, **10**, **12**, and **15** are in good agreement, within experimental error, with the values found in earlier studies (*cf.* [3] [6]). Within the series of 1,4-disubstituted butadiene complexes the observed data clearly show an increase of the energy barrier of the exchange process when electron attracting substituents such as the cyano group are linked to the diene ligand. This trend has already been observed in the earlier investigations (*cf.* [3] [7]). Our ΔG_{298}^\ddagger -values are in the range of 40 to 60 kJmol⁻¹. On the other hand, within the series of the 2,3-disubstituted complexes (**1**, **5–8**) almost no effect on the exchange process is exhibited by electron-attracting as well as electron-releasing substituents.

Within the series of cycloolefin complexes **9–15** three groups are clearly discernible: 1) the cyclopentadiene and cyclohexadiene complexes **9** and **10** which have ΔG_{298}^\ddagger -values significantly smaller than the related 2,4-hexadiene complex **2**; 2) the cycloheptadiene and cyclooctadiene complexes **11** and **12** the ΔG_{298}^\ddagger -values of which reach the value of the open-chain analogues **1** or **5**; 3) the *exo*-dimethylidene complexes **13–15** which have all fairly high ΔG_{298}^\ddagger -values compared to the open-chain pendants **1** or **5**. Within the series of the cycloolefin and the *exo*-dimethylidene complexes the lowest energy barriers are found for the complexes **9** and **13**, respectively. Since these complexes contain obviously the most rigid diene moiety, it is impossible that the exchange process occurs by a bipyramidal intermediate of the *Berry*-type mechanism with the involvement of a stretched and twisted diene moiety. It is more reasonable that the exchange occurs by 120°-rotations of the Fe(CO)₃ fragment relative to the diene group, *i.e.* by a turnstile-type mechanism. In this case, the transition state (TS) is reached from the ground state (GS) by a 60° rotation around the *pseudo*-C₃-axis of the tricarbonyliron group. If one understands the GS of the complex as a linear combination of the VB-structures GS_L and GS_H which resemble in the MO-model the LUMO_{diene}, HOMO_{Fe(CO)₃}

Scheme 2



(back-bonding) and the HOMO_{diene}, LUMO_{Fe(CO)₃} (bonding) interaction, respectively, two similar VB-structures (TS_L and TS_H) can be formulated for TS (Scheme 2).

Because of minimal closed shell electron repulsions the 'staggered' VB-structure GS_L should be energetically more favourable than the 'eclipsed' structure GS_H in the GS whereas the opposite should be valid for the TS (*cf.* Scheme 2). Hence the better the GS of a complex is described by GS_L the higher is the barrier of the exchange process ($\Delta G_{\text{TS}_L-\text{GS}_L} > \Delta G_{\text{TS}_H-\text{GS}_H}$)³). Thus, the considerable increase of the ΔG_{298}^\ddagger -values observed in the sequence of complexes **1** → **8** → **4** can be easily interpreted by an increasing importance of the GS_L VB-structure to the GS within this sequence. The order of the ΔG_{298}^\ddagger -values of the complexes **13**–**15** can be understood in the same way. Since it is known from equilibrium measurements that endocyclic 1-methylcycloalkenes are energetically favoured over their exocyclic methylenecycloalkene counterparts (*cf.* Table 2), the GS of the complexes **13**–**15** should resemble the GS_L VB-structure. Therefore higher ΔG_{298}^\ddagger -values are to be expected with respect to the energy barrier in complex **1** or **5** and this is evidently also observed. Furthermore, the ΔG_{298}^\ddagger -values of the complexes **13**–**15** correlate well with the ΔG_{298} -values of the *endo/exo*-isomerization equilibrium of comparable 1-methylcycloalkenes (Table 2). From the known ΔG_{298} (*endo/exo*)-values for 1-methylcycloheptene and -cyclooctene we would predict the unknown ΔG_{298}^\ddagger -values of the (1,2-dimethylenecycloheptane)- and (-cyclooctane)tricarbonyliron complexes to be smaller than that of complex **14**.

In the series of the 1,3-cycloalkadiene complexes **9**–**12** ΔG_{298}^\ddagger raises with the increasing ring size. As can be seen from Table 3 a good linear correlation exists between these data and the distance (d_{14}) of the terminal C-atoms of the 1,3-diene structure in the complexes. The correlation with d_{14} of the free ligands is not as good. A shortening of the distance d_{14} in the complexes means that the electronic structure of the complexes will develop into the direction of (cyclobutadiene)tricarbonyliron for which all four VB-structures (GS_L, GS_H, TS_L and TS_H) are identical. Therefore, the energy difference $\Delta G_{\text{TS}} - \Delta G_{\text{GS}}$ ($= \Delta G^\ddagger$) for complexes **9** and **10** should be smaller than that of the butadiene complex **1**.

³) This picture is supported by EH-calculations (*cf.* [9]) performed in our laboratory [10].

Table 3. Comparison of ΔG_{298}^\ddagger (9–12) and the distances of the terminal C-atoms of the diene structure in the free liquid (L) and the complex (LM)^{a)}

Ligand	ΔG_{298}^\ddagger	d_{14} (L)	d_{14} (LM) ^{b)}	References ^{c)}
Cyclopentadiene	32.8 (9)	235	228	[13] [14]
1,3-Cyclohexadiene	37.9 (10)	285	263	[15] [16]
1,3-Cycloheptadiene	42.1 (11)	315	287	[15] [17]
1,3-Cyclo-octadiene	41.8 (12)	324	283	[15] [18]
1,3-Butadiene	41.5 (1)	294	283	[13] [1]

a) ΔG^\ddagger in kJmol^{-1} ; d_{14} in pm.

b) Except for the butadiene complex d_{14} were taken from X-ray data of substituted ligands and complexes which contain the relevant diene structure.

c) First reference for d_{14} (L) and the second for d_{14} (LM).

Steric effects on the energy barrier ΔG_{298}^\ddagger have not been taken into account so far. In particular in the cyclopentadiene complex **9** one might assume a strong steric interference between the apical carbonyl group and the methylene moiety of the cyclopentadiene ligand. Such an interaction should rise the GS-energy relative to the TS-energy and thus, give raise to a lowering of the ΔG^\ddagger -value of the exchange process in the complex.

That steric interactions can play a significant role indeed is indicated by the unusually low ΔG_{298}^\ddagger -value of ca. 20 kJmol^{-1} which we have observed for the exchange process in (1–4- η -spiro [4.4]nona-1,3-diene)tricarbonyliron ($T_c \sim 150 \text{ K}$, $\delta\nu \sim 220 \text{ Hz}$ in CCl_2F_2).

We are grateful to the Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung for financial support of this work.

REFERENCES

- [1] O. S. Mills & G. Robinson, *Acta Cryst.* 16, 758 (1963).
- [2] F. H. Herbstein & M. G. Reisner, *Acta Cryst.* B33, 3304 (1977).
- [3] L. Kruczynski & J. Takats, *J. Am. Chem. Soc.* 96, 932 (1974); *idem*, *Inorg. Chem.* 15, 3140 (1976).
- [4] M. A. Busch & R. J. Clark, *Inorg. Chem.* 14, 226 (1975).
- [5] F. A. Cotton & B. E. Hanson, *Israel J. Chem.* 15, 165 (1977).
- [6] K. Bachmann, Thesis, University of Zurich, 1977.
- [7] C. G. Kreiter, S. Stüber & L. Wackerle, *J. Organometal. Chem.* 66, C49 (1974).
- [8] G. Binsch & H. Kessler, *Angew. Chem. Int. Ed.* 19, 411 (1980).
- [9] T. A. Albright, R. Hoffmann & P. Hofmann, *J. Am. Chem. Soc.* 99, 7546 (1977); T. A. Albright, P. Hofmann & R. Hoffmann, *Chem. Ber.* 111, 1591 (1978).
- [10] P. Bischofberger, Thesis, University of Fribourg, 1980.
- [11] J. Herling, J. Shabtai & E. Gil-Av, *J. Am. Chem. Soc.* 87, 4107 (1965).
- [12] A. C. Cope, D. Ambros, E. Ciganek, C. F. Howell & Z. Zacura, *J. Am. Chem. Soc.* 82, 1750 (1960).
- [13] Z. B. Maksić & A. Rubčić, *J. Am. Chem. Soc.* 99, 4233 (1977).
- [14] K. Hoffmann & E. Weiss, *J. Organometal. Chem.* 128, 237 and 389 (1977).
- [15] K. Hagen & M. Traetteberg, *Acta Chem. Scand.* 26, 3643 (1972).
- [16] F. A. Cotton, V. W. Day, B. A. Frenz, K. I. Hardcastle & J. M. Troup, *J. Am. Chem. Soc.* 95, 422 (1973).
- [17] R. P. Dodge, *J. Am. Chem. Soc.* 86, 5429 (1964).
- [18] B. Dickens & W. M. Lipscomb, *J. Chem. Phys.* 37, 2084 (1962).