Journal of Organometallic Chemistry, 231 (1982) 137—142
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

INDENYL AND FLUORENYL TRANSITION METAL COMPLEXES

IX *. A STUDY OF THE REVERSIBLE ISOMERISATION OF η^6- AND η^5-FLUORENYLCHROMIUM TRICARBONYL ANIONS BY ^{13}C NMR SPECTROSCOPY

Yu.F. OPRUNENKO, Yu.N. LUZIKOV, Yu.A. USTYNYUK *
Department of Chemistry, Moscow State University, Moscow 117234 (U.S.S.R.)

and N.A. USTYNYUK
A.N. Nesmeyanov Institute of Organoelement Compounds, U.S.S.R. Academy of Sciences, Vavilov st. 28, Moscow 117813 (U.S.S.R.)

(Received November 17th, 1981)

Summary

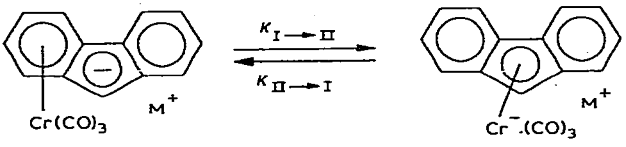
^{13}C NMR spectroscopy was used to study the reversible isomerisation of η^6- and η^5-fluorenylchromium tricarbonyl anions. The influence of the electron withdrawing effect of the $Cr(CO)_3$ moiety on the π-electron distribution has been examined in the uncoordinated rings of η^6-(I), η^5-(II) fluorenylchromium tricarbonyl anions and fluorenylchromium tricarbonyl (III). IR spectra of I-M^+ (M = Li, Na, K, Rb, Cs, Ph_3PCH_3) is discussed in connection with the structure of ion pairs in these salts.

Introduction

We have recently reported on the reversible isomerisation of η^6- and η^5-fluorenylchromium tricarbonyl anions [1]. This new type of metallotropic tautomerism was studied by IR (in the region of CO stretching vibrations) and PMR spectroscopy. In the course of the investigations we determined the structures of the isomeric anions I and II and examined the dependence of rate constants $K_{I\to II}$ and $K_{II\to I}$ of the $Cr(CO)_3$ moiety migration and of the equilibrium constant $K_{eq} = K_{I\to II}/K_{II\to I}$ of the isomerisation of the M^+ counterion, the solvent and temperature.

---

* For part VIII see J. Organometal. Chem., 231 (1982) 5.



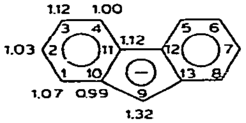
(I) (II)

M = Li, Na, K, Rb, Cs, Ph_3PCH_3

However, proton resonance signals and IR ν(CO) bands tend to overlap, which complicates considerably the quantitative and qualitative analysis of these systems. Moreover, the above-mentioned methods do not provide reliable information on the π-electron distribution in aromatic ligands. The large range of shielding and the good correlation of ^{13}C chemical shifts with the electronic structure of indenyl and fluorenyl anions [2] undoubtedly make ^{13}C NMR a very promising tool to obtain a clear understanding of the structural and electronic disturbances that take place in the course of the deprotonation of fluorenechromium tricarbonyl (III), i.e., of the driving force of the rearrangement in question.

Results and discussion

The ^{13}C NMR spectrum with total proton decoupling at −40°C confirms the structural formulation as that of a η^6-anion for the product formed via the deprotonation of III with t-BuOK. Due to the low rate of I → II isomerization at this temperature carbon signals of anion II are absent. The signals in this spectrum have been assigned, based on off-resonance decoupling, analysis of ^{13}C NMR spectra of III [3] and fluorenyllithium [2] and the π-electron density distribution in fluorenyl anion calculated by the INDO method:



At 28°C the spectrum shows a gradual increase in the resonances of the η^5-anion and a simultaneous decrease in the resonances of the η^6-anion. Equilibrium is reached in about 1 h, and the equilibrium constant equals 7.3. Resonance signals in the spectrum of II were assigned by means of the "fingerprint" method [4] and the above-mentioned INDO calculations. The data obtained are listed in Table 1. It is of interest to note an appreciable difference between the changes of carbon chemical shifts in the fluorene—fluorenyl anion pair ($\Delta\delta_i = \delta_i$(fluorene) − δ_i(fluorenyl)) and the III—I pair ($\Delta\delta_i = \delta_i$(III) − δ_i(I)), which is in line with ^{13}C NMR data obtained in the course of studying π-complexes of fluorene and fluorenyl anions with iron and manganese [5], and serves as a direct indication of a significant change in the π-electron density distribution in the aromatic ligand due to its bonding with the transition metal. Accounting for π-electron density changes in the coordinated part of the fluorenyl anion presents certain difficulties because, in this case, the high-field shift of the carbon resonances should be treated both in terms of electron density increase and the change in hybridization of carbons from sp^2 to the type intermediate between sp^2 and sp^3 [6]. At the same time, the changes in carbon chemical shifts in the uncoordinated ring can be assumed to reflect principally the electron withdrawing effect of the $Cr(CO)_3$ moiety. If one introduces the sum of carbon chemical shifts ($\Sigma = \Sigma_i \delta_i$) for the uncoordinated ring as a new parameter for the substances under consideration it turns out that for I this parameter has a considerably higher value than for the fluorenyl anion (752.3 and 723.0 ppm, respectively). This effect can be explained by π-electron density being "withdrawn" by the $Cr(CO)_3$ moiety, and it is indicative of the existence of a closed π-electron system in I, in contrast to the practically noninteracting π-systems in the neutral complex III ($\Sigma_{III} - \Sigma_{fluorene} = 786.6 - 783.1 = 3.5$ ppm). As could be expected, transition from I to II is followed by an increase in the electron withdrawing effect of the $Cr(CO)_3$ moiety on the uncoordinated ring of the fluorenyl anion ($\Sigma_I = 491.6$ ppm and $\Sigma_{II} = 472.3$ ppm) * due to the closer proximity of $Cr(CO)_3$ to the uncoordinated ring in II as compared with I. It has already been noted [7] that for cyclopentadienyl and arene complexes of transition metals there exists a correlation between the ^{13}C carbonyl chemical shifts and the carbonyl stretching force constants. In accordance with this correlation, $\nu(CO)$ and ^{13}C chemical shifts of the carbonyls follow the sequence III, I, II (Table 1), which can be accounted for by a successive increase in the negative charge on chromium atom.

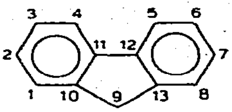
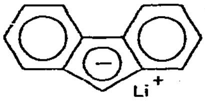
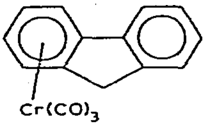
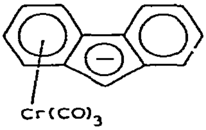
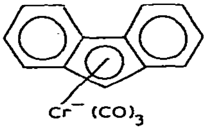
Of special interest is the determination of the detailed molecular structure of ion pairs in the investigated systems. The data obtained by means of ^7Li, ^1H [8] and ^{13}C [2,9] NMR spectroscopy clearly show that in the case of a contact ion pair the alkali cation is situated above the five-membered ring and shifted toward C(9). INDO calculations of the potential energy minima [10] and X-ray diffraction analysis of the fluorenyllithium quinuclidine complex [11] are in line with such a geometry. It is reasonable to assume that contact ion pairs (CIP) of fluorenylpotassium [10] and fluorenylsodium [12] have a similar structure in solution. Because of this one can expect the chemical shift at C(9) to be the most sensitive to the interionic distance in the ion pair. For fluorenyllithium the transition from CIP to solvent-separated ion pair (SSIP) is, indeed, accompanied by a low-field shift of the C(9) signal ($\Delta\delta = 4.87$ ppm) [9]. Alkali cations of much greater radii (K^+, Cs^+, Rb^+) exert only a minor influence on the C(9) chemical shift on transition from CIP to SSIP, which makes it impossible to differentiate between CIP and SSIP by means of ^{13}C NMR spectroscopy. A decrease in π-electron density on the five-membered ring, caused by charge delocalisation, for indenyl, fluorenyl and fluoradenyl anions is known to decrease the cation—anion interaction and increase the SSIP fraction in this series [13]. One notes a considerable decrease in π-electron density on the five-membered ring in I caused by the influence of the $Cr(CO)_3$ moiety, as compared with fluorenyllithium in THF [2] ($\delta C(9)$ and $\delta C(12) + \delta C(13) = 353.3$ and 342.4 ppm, respectively). Such a decrease in π-electron density supports the assumption of the prevalence of the SSIP fraction for the K salt of I. This assumption is in line with IR spectra of I in the $\nu(CO)$ region (Table 2). IR

---

[*] Chemical shifts of quaternary carbons in the fluorenyl anion which coordinated to chromium in II are, therefore, excluded from the sum.

TABLE 1

^{13}C NMR CHEMICAL SHIFTS FOR I, II AND III (in ppm)

	Solvent	CO	C(1)	C(2)	C(3)	C(4)	C(5)
	$CDCl_3$		125.0	126.7	126.7	119.8	119.8
	THF-d_8		116.3 (−8.7) [a]	119.1 (−7.6)	108.1 (−18.6)	118.7 (−1.1)	118.7 (−1.1)
	$CDCl_3$	233	90.13	91.44	90.61	86.23	119.9
	THF-d_8	240.43 (+7.43)	84.76 (−5.37)	94.53 (+3.09)	76.81 (−13.80)	93.60 (+7.37)	119.51 (−0.39)
	THF-d_8	245.87	125.13	122.79	118.11	125.60	125.60

[a] ^{13}C NMR chemical shifts differences $\Delta\delta = \delta_{anion} - \delta_{neutral}$ in ppm (given in parentheses).

TABLE 2

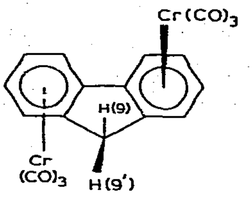
IR FREQUENCIES IN THE ν(CO) REGION OF THE SALTS OF I IN THF

Counter ion	ν(CO)(E)	ν(CO)(A)	Ion pair type
Li^+	1820, 1839	1927	SSIP
Na^+	1812, 1835	1925	SSIP
K^+	1817, 1841	1927	SSIP
Rb^+	1839	1930	CIP
Cs^+	1839	1929	CIP
$Ph_3PCH_3^+$	1832	1927	CIP
Rb^+ [a]	1819, 1841	1927	SSIP
Cs^+ [a]	1821, 1841	1927	SSIP
$Ph_3PCH_3^+$ [a,b]	1820, 1841	1927	SSIP

[a] In the presence of solvating additives (HMPA, cryptand-[2.2.2]). [b] Effective solvation of $Ph_3PCH_3^+$ in the presence of cryptand requires additional study.

C(6)	C(7)	C(8)	C(9)	C(10)	C(11)	C(12)	C(13)
126.7	126.7	125.0	36.9	143.2	141.7	141.7	143.2
108.1 (−18.6)	119.1 (−7.6)	116.3 (−8.7)	81.6 (44.7)	137.6 (−5.6)	123.2 (−18.5)	123.2 (−18.5)	137.6 (−5.6)
127.23	128.35	124.91	36.66	112.70	110.75	138.45	141.88
112.70 (−14.53)	122.38 (−5.97)	117.70 (−7.21)	83.24 (+46.58)	122.38 (+9.68)	92.48 (−18.27)	126.65 (−11.80)	143.38 (+1.5)
118.11	122.79	125.13	69.65	111.03	98.98	98.98	111.03

spectra reveal that SSIP are favoured for K^+, Na^+ and Li^+ cations. In this case the low frequency band of class E, which is degenerate in neutral complex (III), is split into two components due to lowering of the local symmetry C_{3v} of the $Cr(CO)_3$ moiety to C_s under the effect of the negative charge on the five-membered ring. For Rb^+, Cs^+ and $Ph_3PCH_3^+$, the less solvated by THF salts of I exist as CIP, where the cation is situated above the five-membered ring on the opposite side to the $Cr(CO)_3$ moiety. This leads to a decrease in the disturbing effect of the negative charge on the $Cr(CO)_3$ moiety and this preserves the C_{3v} symmetry of the latter (the E band is degenerate). The position of the $Cr(CO)_3$ moiety and M^+ on the opposite sides of the fluorenyl plane is dictated by steric reasons. Solvating additives (HMPA, cryptand-[2.2.2.]) lead to destruction of the CIP. IR spectra in this case correspond to SSIP (the E band is split). Noteworthy is that for Rb^+, Cs^+ and $Ph_3PCH_3^+$ salts of η^6,η^6-fluorenyl-bis-(chromium tricarbonyl)anion prepared via deprotonation of neutral η^6,η^6-fluorene-bis(chromium tricarbonyl) (IV) [3], steric hindrance leads to SSIP for these salts (the E band is split).



(IV)

A very interesting paper by Ceccon et al. [15] appeared in the course of preparing this paper for publication. Among other studies, K salts of I, II and also the neutral complex III were investigated by means of ^{13}C NMR spectroscopy in THF-d_8. Generally, chemical shifts for I and II are practically equal to that of ours. Peak assignments for I are absolutely consistent with our assignments. However, for II and III the assignments are not in accordance with our ones, based on signal multiplicities in non-decoupled spectra ("fingerprint" method [4]). Our assignments also agree with the fact that the low-field shift of the "β-resonances" (C(2) and C(3)) for the coordinated ring in III is similar to the shift for indane- [16] and indene- [17] chromium tricarbonyl complexes.

Experimental

All the reactions and operations were performed under an atmosphere of dry argon. Only purified solvents were used. η^6-Fluorenechromium tricarbonyl was synthesized by the previously described method [14]. The η^6-anion was generated by treating III with a threefold excess of t-BuOK at −78°C. The solution of I was rapidly filtered into an NMR tube containing 0.5 ml THF-d_8 (internal ^{2}D lock) and TMS. The NMR tube was sealed and thermostatted at −78°C. The concentration of I was 50 mg/ml. ^{13}C NMR spectra were recorded on a JEOL FX-100 spectrometer equipped with Fourier transform facilities. All chemical shifts are expressed in ppm downfield from TMS. The sample temperature was controlled within ±3°C using standard variable-temperature equipment. IR experiments were performed as described in ref. 1.

References

1 N.A. Ustynyuk, B.V. Lokshin, Yu.F. Oprunenko, V.A. Rosnyatovsky, Yu.N. Luzikov and Yu.A. Ustynyuk, J. Organometal. Chem., 202 (1980) 279.
2 U. Edlund, Org. Magn. Reson., 12 (1979) 661.
3 Yu.N. Luzikov, Yu.F. Oprunenko and Yu.A. Ustynyuk, J. Organometal. Chem., 202 (1980) 289.
4 H. Gunter, H. Schmicker and G. Jekeli, J. Magn. Reson., 11 (1973) 344.
5 J.W. Johnson and P.M. Treichel, J. Amer. Chem. Soc., 99 (1977) 1427; Inorg. Chem., 16 (1977) 749.
6 B.E. Mann, Adv. Organometal. Chem., 12 (1974) 135.
7 B.E. Mann, J. Chem. Soc., Dalton, (1973) 2012.
8 V.A. Dixon, P.A. Gwinner and D.C. Lini, J. Amer. Chem. Soc., 87 (1965) 1379.
9 D.H. O'Brien, C.R. Russel and A.J. Hart, J. Amer. Chem. Soc., 101 (1979) 633.
10 R. Zerger, W. Rhine and G.D. Stucky, J. Amer. Chem. Soc., 96 (1974) 5441.
11 J.J. Brooks, W.E. Rhine and G.D. Stucky, J. Amer. Chem. Soc., 94 (1972) 7339.
12 R.H. Wong, G. Konizer and J. Smid, J. Amer. Chem. Soc., 92 (1970) 666.
13 T.E. Hogen Esch, Adv. Phys. Org. Chem., 15 (1977) 153.
14 A.N. Nesmeyanov, N.A. Ustynyuk, L.G. Makarova, S. Andrae, Yu.A. Ustynyuk, L.N. Novikova and Yu.N. Luzikov, J. Organometal. Chem., 154 (1978) 45.
15 A. Ceccon, A. Gambaro, G. Agostini and A. Venzo, J. Organometal. Chem., 217 (1981) 79.
16 F. Coletta, A. Gambaro, G. Rigatti and A. Venzo, Spectroscopy Letters, 10 (1977) 971.
17 F.M. Kohler, Chem. Ber., 107 (1975) 570.