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HPLC studies of $Fe_2(CO)_6$(ligand) complexes

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Abstract

We present a systematic study of the reverse-phase high performance liquid chromatography (HPLC) of complexes containing an $Fe_2(CO)_6$ unit bonded to a variety of organic chains, namely the butatriene moiety $R_2C{=}C{=}C{=}CR_2$, the butadienyl fragment, –RC=CR–RC=CR– (the ferroles), and the ring-opened cyclopentadienone diradical, –RC=CR–C(O)–RC=CR– (the flyover bridges). Since the $Fe_2(CO)_6$ unit shows an almost identical conformation in all the complexes, this enables us to evaluate the effect of the geometrical arrangement of the organic chains and of their substituents on chromatographic behaviour. Reverse-phase HPLC allows the separation of the positional isomers of ferroles and flyover bridges (R = Me or Ph), but not the *cis/trans* isomers of butatrienes (R = H or Me).

Introduction

High performance liquid chromatography (HPLC) has been successfully employed in organometallic chemistry to monitor reaction sequences and to separate complex mixtures [1,2]. Indeed, the speed of analysis, the high efficiency, and the accuracy of the measures on small samples make the HPLC technique a very useful tool in organometallic chemistry. The use of a steel column and the possibility of sub-ambient temperature conditioning provide a convenient separation method for light- and thermal-sensitive compounds [1]. Carbonyl complexes have strong UV absorption owing to their metal to ligand charge transfer (MLCT) transition [$d(M) \rightarrow \pi^*(CO)$], so they can be revealed by the usual UV detector [3]. Higher sensibility can be achieved by using the electrochemical detector (ED), since most of the polymetallic complexes easily undergo redox process, owing to the metal–metal character of their frontier orbitals [4].

In order to understand the role played by the organic chain, we have investigated three series of complexes having the $Fe_2(CO)_6$ fragment in a very similar structural rearrangement [5]. In the butatriene complexes $Fe_2(CO)_6$ assumes a

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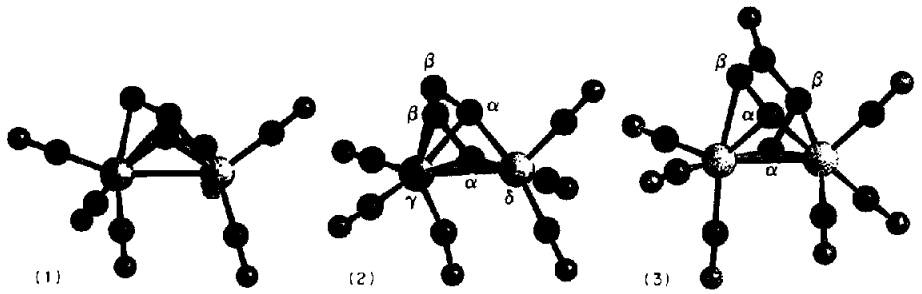

Fig. 1. Sketch of the structures of butatriene (**1**), ferrole (**2**) and flyover (**3**) complexes obtained by means of SCHAKAL software using the crystallographic data of $[Fe_2(CO)_5(PPh_3)(H_2C{=}C{=}C{=}CH_2)]$ [6], $[Fe_2(CO)_6(HOC_\alpha{=}C_\beta Me{-}C_\beta Me{=}C_\alpha OH)]$ [7], and $[Fe_2(CO)_6(PhC_\alpha{=}C_\beta PhC(O)PhC_\beta{=}C_\alpha Ph)]$ [8], respectively. We employ the usual convention to label as α the carbon atoms adjacent to the metallic frame and relative substituents and as β the others.

perfect "sawhorse" geometry, in flyover bridges and in ferroles one $Fe(CO)_3$ group is somewhat tilted, in the latter complexes mainly because of the presence of a semibridging CO. However, slight energy differences have been calculated for these rearrangements [5].

The structures of the three series of complexes are represented in Fig. 1.

Results and discussion

Syntheses and characterization of compounds

The butatriene complexes were synthesized by reaction of $[Fe_3(CO)_{12}]$ with the appropriate alkyne diols according to reaction 1 [9].

$$[Fe_3(CO)_{12}] + RR'(OH)C{-}C{\equiv}C{-}C(OH)RR' \rightarrow$$
$$[Fe_2(CO)_6(RR'C{=}C{=}C{=}CRR')]\ (\mathbf{1}) + Fe(OH)_2 + 6\ CO \qquad (1)$$

(R = R′ = H, **1a**; R = H, R′ = Me, **1b**; R = R′ = Me, **1c**; R = R′ = Ph, **1d**)

As in a previous study [10], complex **1b**, $[Fe_2(CO)_6(MeHC{=}C{=}C{=}CMeH)]$ was obtained as an isomeric mixture unresolved by column or thin layer chromatography, in which the isomer having the two methyl groups *trans* to carbon atoms is by far the most abundant.

Ferroles and flyover bridges have been synthesized by reaction of $[Fe_2(CO)_9]$ with the appropriate alkyne in 1:2 molecular ratio at room temperature according to reaction 2 [11]:

$$2[Fe_2(CO)_9] + 4\ RC{\equiv}CR' \rightarrow [Fe_2(CO)_6(RC_\alpha{=}C_\beta R'{-}RC_\beta{=}C_\alpha R')]\ (\mathbf{2})$$
$$+ [Fe_2(CO)_6(RC_\alpha{=}C_\beta R'{-}C(O){-}RC_\beta{=}C_\alpha R')]\ (\mathbf{3}) + 5\ CO \qquad (2)$$

(Symmetrical alkynes: R = R′ = Me, **2a** and **3a**; R = R′ = Et, **2b** and **3b**; R = R′ = ^{n}Pr, **2c** and **3c**; R = R′ = ^{i}Pr, **2d** and **3d**; R = R′ = Ph, **2e** and **3e**)

(Asymmetrical alkyne: $R_\alpha = R_\alpha' =$ Me, $R_\beta' = R_\beta =$ Ph, **2f** and **3f**; $R_\alpha = R_\beta =$ Me, $R_\beta' = R_\alpha' =$ Ph, **2g** and **3g**; $R_\alpha = R_\alpha' =$ Ph, $R_\beta' = R_\beta =$ Me, **2h** and **3h**)

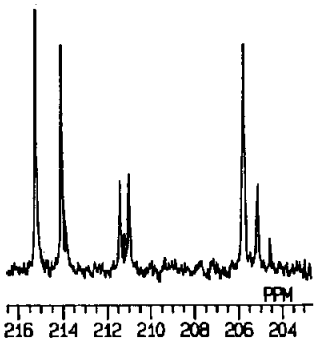

Fig. 2. ^{13}C NMR spectrum of $[Fe_2(CO)_6(MeC_2Ph)_2]$ isomeric mixture in the CO region, recorded in $CDCl_3$ at 100.6 MHz (25°C).

The identification of the flyover isomers **3f–3h** (separable by using extra-long TLC plates) has been achieved by a reported method [11]. The ferrole isomers **2f–2h** could not be separated by column or thin-layer chromatography. Their assignments (in the mixture) have been achieved by means of ^1H- and ^{13}C-NMR spectroscopy, on the basis of the generally accepted downfield shift of the σ/π bonded carbon atoms (C_α) and the relative substituents (R_α) [12,13]. In particular, the ^1H NMR spectrum exhibits a complex pattern in the phenyl region (7.6–6.9 ppm), and four resonances at 2.24, 2.18, 2.00 and 1.72 ppm with relative integration of: 3.3 : 5.0 : 1.0 : 3.3. The assignment of the two resonances at 2.24 and 1.72 (of equal intensity) to the asymmetrical isomer **2g** leaves the resonance at 2.18 to isomer **2f** and the resonance at 2.00 to isomer **2h**. On this assumption, the molecular ratio among **2g**, **2f** and **2h** is 52 : 40 : 8.

The ^{13}C NMR spectrum in the methyl region confirms the existence of three isomers. There are, in fact, four resonances, at 31.6, 30.7, 22.1, 17.3 ppm, assigned to **2g** (the first and the last resonances), **2f** and **2h**, respectively. Moreover, in the carbonyl region (Fig. 2), the usual pattern of ferrole resonances, assigned to $Fe(\gamma)(CO)_3$ (integration 3) (rapidly scrambling) (216–214), to the CO axially bonded to $Fe(\delta)$ (integration 1) (212–210), and to the two CO moieties equatorially bonded to $Fe(\delta)$ (integration 2) (206–204 ppm), is split, confirming the presence of three isomers [12].

Chromatographic behaviour

Effect of the coordination mode of the organic chains. As a first approach, we have evaluated the polarity introduced by the different organic chains in selected complexes of the three series ($R_\alpha = R_\beta$ = Me or $R_\alpha = R_\beta$ = Ph), assuming that the isostructural $Fe_2(CO)_6$ fragment plays an identical role in each compound (see Table 1). The TLC retention indices, R_f (silica as stationary phase and n-hexane/diethyl ether mixture as mobile phase) and the reverse phase HPLC capacity factors, k' [14*] (RP-18 as the stationary phase and acetonitrile as the mobile

* Reference number with asterisk indicates a note in the list of references.

Table 1

RP-18 HPLC capacity factors and silica TLC R_f values of selected butatriene (**1**), ferrole (**2**), and flyover bridge (**3**) complexes

Compounds	k'	R_f
$[Fe_2(CO)_6(Me_2C{=}C{=}C{=}CMe_2)]$ (**1c**)	1.96	0.91
$[Fe_2(CO)_6(Ph_2C{=}C{=}C{=}CPh_2)]$ (**1d**)	2.21	0.80
$[Fe_2(CO)_6(MeC{=}CMe{-}MeC{=}CMe)]$ (**2a**)	1.71	0.84
$[Fe_2(CO)_6(PhC{=}CPh{-}PhC{=}CPh)]$ (**2e**)	1.77	0.79
$[Fe_2(CO)_6(MeC{=}CMeC(O)MeC{=}CMe)]$ (**3a**)	1.11	0.71
$[Fe_2(CO)_6(PhC{=}CPhC(O)PhC{=}CPh)]$ (**3e**)	1.19	0.54

phase) have obviously opposite trends, both indicating the overall polarity of the molecules to be as follows:

flyover bridges (**3**) ≫ ferroles (**2**) > butatrienes (**1**)

Among the $[Fe_2(CO)_6(\text{ligand})]$ complexes, the flyover bridges (which are the slowest moving in TLC and the fastest moving in the RP-18 HPLC technique) exhibit the highest polarity because of the ketone functionality. The lower symmetry in the organic chain and the inherent polarity of the Fe–Fe bond, as shown by the presence of the semibridging CO [16], make ferroles slightly more polar than their butatriene counterparts.

Table 2

RP-18 HPLC capacity factors of butatrienes (**1**), ferroles (**2**), and flyover bridges (**3**) along with the sum of the Total Surface Area (TSA) values of the substituents

Compounds	k'	TSA (Å^2)
$[Fe_2(CO)_6(H_2C{=}C{=}C{=}CH_2)]$ (**1a**)	1.29	0
$[Fe_2(CO)_6(HMeC{=}C{=}C{=}CHMe)]$ (**1b**)	1.63	65.4
$[Fe_2(CO)_6(MeC{=}C{=}C{=}CMe_2)]$ (**1c**)	1.96	130.8
$[Fe_2(CO)_6(Ph_2C{=}C{=}C{=}CPh_2)]$ (**1d**)	2.21	369.2
$[Fe_2(CO)_6(MeC_2Me{-}MeC_2Me)]$ (**2a**)	1.71	130.8
$[Fe_2(CO)_6(PhC_2Ph{-}PhC_2Ph)]$ (**2e**)	1.77	369.2
$[Fe_2(CO)_6(PhC_2Me{-}MeC_2Ph)]$ (**2h**)	1.85	250
$[Fe_2(CO)_6(MeC_2Ph{-}MeC_2Ph)]$ (**2g**)	2.15	250
$[Fe_2(CO)_6(MeC_2Ph{-}PhC_2Me)]$ (**2f**)	2.29	250
$[Fe_2(CO)_6(EtC_2Et{-}EtC_2Et)]$ (**2b**)	3.32	221.6
$[Fe_2(CO)_6(PrC_2Pr{-}PrC_2Pr)]$ (**2c**)	5.92	297.6
$[Fe_2(CO)_6({}^iPrC_2{}^iPr{-}{}^iPrC_2{}^iPr)]$ (**2d**)	6.17	302.4
$[Fe_2(CO)_6(MeC_2MeC(O)MeC_2Me)]$ (**3a**)	1.11	130.8
$[Fe_2(CO)_6(PhC_2PhC(O)PhC_2Ph)]$ (**3e**)	1.19	369.2
$[Fe_2(CO)_6(MeC_2PhC(O)PhC_2Me)]$ (**3f**)	1.32	250
$[Fe_2(CO)_6(MeC_2PhC(O)MeC_2Ph)]$ (**3g**)	1.39	250
$[Fe_2(CO)_6(PhC_2MeC(O)MeC_2Ph)]$ (**3h**)	1.47	250
$[Fe_2(CO)_6(EtC_2EtC(O)EtC_2Et)]$ (**3b**)	2.24	221.6
$[Fe_2(CO)_6(PrC_2PrC(O)PrC_2Pr)]$ (**3c**)	4.06	297.6
$[Fe_2(CO)_6({}^iPrC_2{}^iPrC(O){}^iPrC_2{}^iPr)]$ (**3d**)	4.18	302.4

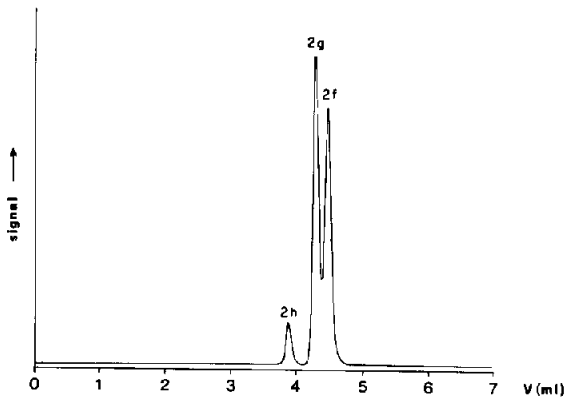

Fig. 3. Reversed phase HPLC chromatogram of the $[Fe_2(CO)_6(MeC_2Ph)_2]$ isomeric mixture. The integrated intensity ratio evaluated at UV detector (254 nm) is 7:49:44 for **2h**, **2g**, and **2f** respectively. Mobile phase: acetonitrile; column: LiChrospher 100 RP-18; flow rate: 1 ml/min.

Effect of the substituents within each series. We now try to rationalize the reverse phase chromatographic behaviour within each series of complexes with reference to the nature of the substituents (Table 2). First there is no apparent link between the capacity factor of the complexes and the electronic effect of the substituents, evaluated using Taft σ^* values [17]. In fact, a plot of ln k' against the sum of σ^* values of the substituents does not reveal any correlation. This holds at least for these non-functionalized alkyl and aryl groups. The electronic effects of substituents have been proven previously to modulate the electronic transitions [18] and the electrochemical potentials [19] of flyover bridges, but here they play a minor role.

In previous work on some ferroles [2f], reverse phase HPLC retention times were rationalized solely in terms of the polarity of the molecules. In particular, the (internal-internal, *ii*) isomer of $[Fe_2(CO)_6(HC_\alpha{=}C_\beta{}^tBu{-}{}^tBuC_\beta{=}C_\alpha H)]$ exhibited a shorter elution time than the (internal-external, *ie*) isomer of $[Fe_2(CO)_6(HC_\alpha{=}C_\beta{}^tBu{-}HC_\beta{=}C_\alpha{}^tBu)]$ [2f]. It was reasoned that in the *ie* isomer the effects of the substituents in non-adjacent positions of the ring compensate for each other, whereas in the *ii* isomer a dipole is formed [2f]. We have obtained a full separation of the three positional isomers of $[Fe_2(CO)_6(PhC_2Me)_2]$ (Fig. 3). The assignment of HPLC peaks is straightforward, since the integrated intensity ratio is in good agreement with NMR data (see above). The *ie* isomer, **2g**, exhibits an intermediate capacity factor and therefore any effect of the reduced polarity is not evident. The same holds for the *ie* flyover bridge isomer, **3g** (Table 2).

Assuming that the actual retention mechanism is a simple association process of low-polarity organometallic molecules in polar solvents (acetonitrile) with surface hydrocarbon ligands (C-18), the solvophobic theory proposed by Sinanoglu *et al.* [20] and developed by Horváth *et al.* [21] can be employed. The capacity factor must relate to the contact surface area of the species (δA) according to the following equation:

$$\ln k' = B + \frac{N}{RT}\delta A \cdot y$$

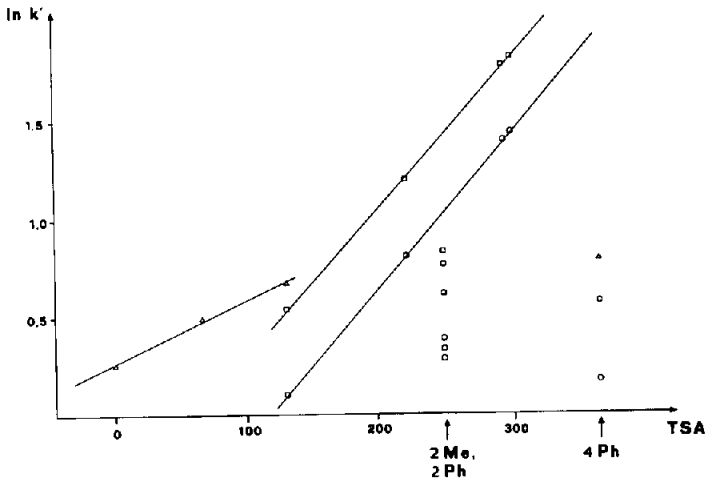

Fig. 4. Plot of ln k' against the sum of the TSA values of the substituents of the butatrienes (△), ferroles (□) and flyover bridges (○).

In this equation, B is constant for a strictly homologous series, N is the Avogadro number, and y is the surface tension in solution.

In a further extension, Brinckman *et al.* [22] used the well-known total surface area (TSA) values of the substituents in place of δA values and obtained good correlations for several organotin complexes.

The frequently-used correlation between ln k' and the carbon atom number of the substituents can be viewed as an oversimplification of these approaches [21]. The plots of ln k' against the sum of the Brinckman's TSA values of the substituents of each complex are reported in Fig. 4. Linear correlations are obtained, except for complexes bearing phenyl substituents (**2e–2h**, **3e–3h**). This phenyl anomaly has several precedents [23]. The solvophobic activity is larger for a flexible alkyl group than for a rigid (planar) aromatic substituent. Thus, the phenyl TSA value overestimates its actual chromatographic behaviour.

For the other compounds, dependence of the capacity factor on the substituent effect is higher for ferroles and flyover bridges than for butatrienes, where the organic chain is more crumpled.

Conclusions

Firstly, the main effect on the chromatographic behaviour is induced by the coordination mode of the organic chain. Secondly, within each series of complex, the chromatographic behaviour is modulated by the steric effect of the substituents and this can be rationalized, at least for alkyl groups, by using the solvophobic approach.

Experimental

Acetonitrile was Aldrich HPLC-grade. A Kontron model 420 HPLC pump and model 720 UV variable wavelength detector (set at 254 nm) connected to an IBM

PC equipped with Integration Pack software was used. The column was Merck LiChrospher 100 RP-18 5 μm, 250 × 4 mm diameter with removable guard column.

All the cluster complexes were synthesized starting from iron carbonyls, as reported in the literature [9,11], purified by TLC and identified by IR and NMR spectroscopy.

Acknowledgements

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$$k'_i = \frac{t_i - t_0}{t_0}$$

where, t_0 is the retention time of the non-retained species (K_2CrO_4), equivalent to the column void volume, and t_i is the retention time for the i^{th} analyte peak [15].
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