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# THE USE OF HIGH PERFORMANCE LIQUID CHROMATOGRAPHY FOR THE ANALYSIS AND MONITORING OF IRON CARBONYL COMPLEXES IN A REACTION MIXTURE

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## Summary

The suitability of high performance liquid chromatography (HPLC) as an analytical and preparative tool for the analysis and isolation of the products resulting from a reaction of diironnonacarbonyl [$Fe_2(CO)_9$] with di-t-butylsulfurdiimine [DBSD] was investigated. Reversed phase chromatography with octyl-modified silica as stationary phase and methanol/water mixtures as mobile phase showed a high selectivity for the separation of the products, and by use of gradient elution the separation of 17 products was completed within 30 min, which meant that the progress of the reaction could be monitored, A semi-preparative column (dimensions 250 × 10 mm) was useful in isolating some of the products; with this column 7 mg of reaction products could be injected without loss in efficiency.

## Introduction

Since the revival of liquid chromatography in the late sixties the applicability of modern LC (HPLC) for the analysis of a wide range of organic substances has been extensively demonstrated [1]. However, until now little attention has been given to the use of HPLC for separating organometallic complexes. Other chromatographic techniques such as gas chromatography (GC) [2,3], thin layer chromatography (TLC) [4,5] and "classical" column chromatography [6,7] have been used for the separation of organometallic complexes. The disadvantages of these techniques, such as elevated temperature (GC), difficult quantitative measurements (TLC), low efficiency and long analysis times ("classical" column chromatography), are absent with HPLC. Furthermore, the appropriate choice of solvent systems and/or the use of degassed solvents means that HPLC can be used for organometallic complexes unstable in the presence of water or oxygen. The suitability of HPLC for the separation of

organometallic complexes has been shown in a number of papers [8—19], and it has recently been shown that reactions involving organometallic compounds can be monitored by HPLC [18,19].

We describe below the results of an investigation of the use of HPLC as an analytical and preparative technique for monitoring and isolating di- and trinuclear iron complexes formed in the reaction of diiron nonacarbonyl with di-t-butylsulfurdiimine.

## Experimental

### *Apparatus*

The liquid chromatographic systems were assembled from commercially available elements. The analytical instrumentation consisted of a reciprocating membrane pump (Orlita DMP 1515, Giessen, GFR), a manometer, a high pressure sampling valve (Valco CV-6-UHP$_{a\text{-}C}$ 20, Houston, USA) equipped with a calibrated microliter syringe (Glenco, Houston, USA) for injection of variable sample volumes (sample loop: 100 $\mu$l), a reversed phase column (Zorbax C-8, Dupont, Wilmington, USA; 250 mm length and 4.6 mm I.D.) and a variable wavelength detector (Cecil CE 212, Cambridge, Great Britain) set at 325 nm.

To obtain a stepwise gradient a three-way valve (Whitey SX-41 XS 2, Oakland, USA) was placed at the inlet side of the pump; switching was performed manually. For continuous gradient elution the reciprocating membrane pump was replaced by a microprocessor controlled pump module (Perkin—Elmer Series 3, Norwalk, USA). For semi-preparative HPLC a stainless steel 316 column (250 mm length and 10 mm I.D.), packed with LiChrosorb RP-8 (8 $\mu$m), (Merck, Darmstadt, GFR) was used. Peak areas were measured using a computing integrator. (Spectra Physics Autolab System I, Santa Clara, USA).

### *Chemicals and materials*

In all experiments doubly distilled water and analytical grade organic solvents were used. Pure iron carbonyl complexes and di-t-butylsulfurdiimine were a gift from Dr. Mey of the Laboratory for Inorganic Chemistry, University of Amsterdam.

### *Procedures*

The semi-preparative column was packed by a pressurized balanced slurry method [20]. The eluent was evacuated in order to remove dissolved air. The capacity ratios ($\kappa_i$) were determined from the retention times of the various reaction components ($t_{R_i}$) and that of an unretained compound [$K_2CrO_4$]-($t_{R_0}$) according to the following equation: $\kappa_i = (t_{R_i} - t_{R_0}/t_{R_0})$.

The reaction of diironnonacarbonyl [$Fe_2(CO)_9$] with di-t-butylsulfurdiimine [DBSD] was carried out in dry toluene under nitrogen. In order to monitor the reaction a mixture of 1.5 g $Fe_2(CO)_9$ and 0.7 g DBSD in 25 ml toluene was stirred at room temperature. Samples were taken from the reaction mixture under nitrogen with a 50 $\mu$l syringe and were analyzed directly or after dilution in methanol. For identification by IR and mass spectrometry samples of the various compounds were separated on the semi-preparative column and collected manually. The iron carbonyl complexes were then extracted from the water/

methanol mixture with n-hexane. After partial evaporation of n-hexane the concentrated solutions were stored at −23°C and later used as such for IR and mass-spectrometric analysis. The IR spectra were recorded on a Beckman IR 4250 and 70 eV E.I. mass spectra were taken on a Varian MAT 711. In the latter case the samples were introduced into the ion source (200°C) with a direct insertion probe at 0°C.

## Results and discussion

In order to investigate the potential of HPLC in organometalchemistry the reaction of $Fe_2(CO)_9$ with di-t-butylsulfurdiimine [DBSD] was selected. This reaction has the interesting features that the bonding of $Fe^0$ with ligands may be via the N atom, the S atom or via the $\pi$-N=S bond and that rearrangements between the various polynuclear species can occur, leading to novel iron clusters, as shown by Mey et al. [21]. These authors were able to isolate and to identify various di- and tri-nuclear iron complexes in the product mixtures; and the structures of these are shown in Fig. 1. However, the authors were not able to provide direct evidence for the formation sequences. More information about the reaction sequence might be obtained by monitoring the products during the reaction by a fast and selective chromatographic method such as HPLC.

In order to create optimal chromatographic conditions for the analysis of the reaction mixture by HPLC at fixed time intervals a number of experiments were carried out.

*Selection of phase system*

Initially two types of phase systems were investigated: normal phase adsorption chromatography using porous silica as the stationary and 2,2,4-trimethylpentane as the mobile phase, and reversed phase chromatography using octyl-modified silica as the stationary and water/methanol mixtures as the mobile phase.

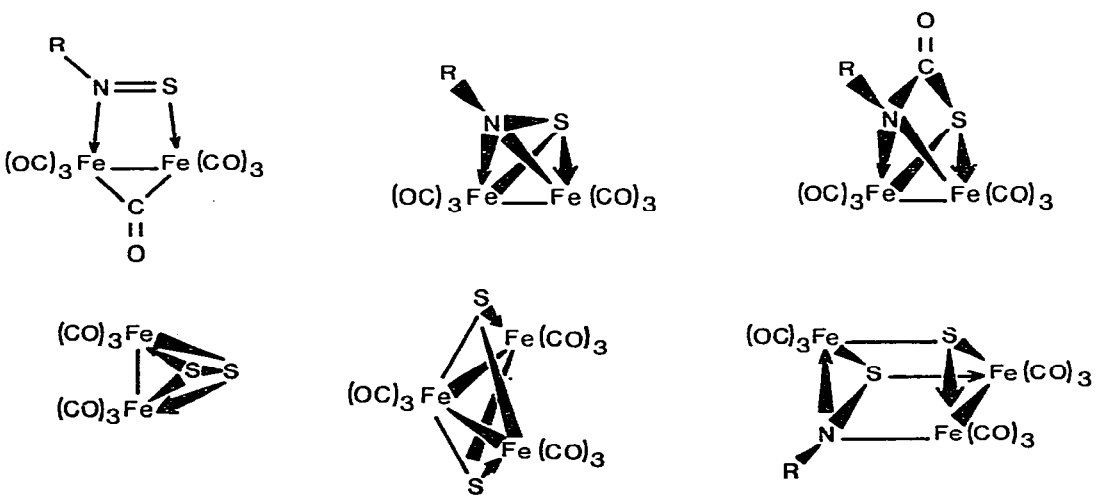


Fig. 1. Some products of the reaction of $Fe_2(CO)_9$ with RN=S=NR (R = t-$C_4H_9$) as described by Mey et al. [21].

On the normal phase adsorption system no significant retardation of the constituents of the reaction mixture was noticed, which indicates the hydrophobic nature of the solutes. Therefore normal phase adsorption is not suitable for this particular mixture.

In order to bring about retardation of hydrophobic compounds, phase systems with a hydrophobic stationary phase and a hydrophylic mobile phase must be used. Although liquid—liquid phase systems can be used for this purpose [8], phase systems using alkyl-modified silicas as the stationary phase [22] are far superior with respect to reproducibility, stability, performance and convenience. For that reason an octyl-modified silica (Zorbax C-8) was selected for further investigations.

Initially there was some doubt whether the iron carbonyl complexes would be stable in the water/methanol mixtures used as eluent. Injection of an aliquot of 5 μl reaction mixture in toluene directly into the column produced symmetrical peaks for all the components (see Fig. 2 and 3), indicating that no decomposition of the reaction components occurs in the column. (When decomposition occurs in the mobile phase distorted peak shapes are found unless complete decomposition occurs instantaneously in the injection system.) Even with elution times up to 2 h we did not observe distorted peak shapes for any of the reaction components.

The effect on the retention of varying the concentration of the organic modifier was investigated by measuring the retention of some iron carbonyl compounds, which were available in a pure state, with various water/methanol mixtures (60—90% (v/v) methanol). The retention time could be varied over a

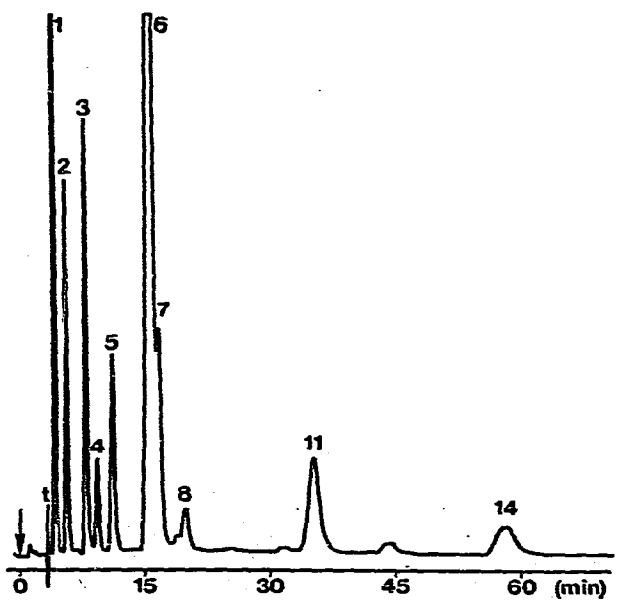


Fig. 2. Chromatogram of a sample from the product mixture obtained from $Fe_2(CO)_9$ with DBSD in toluene using reversed phase chromatography. Stationary phase: Zorbax C-8; mobile phase: 75% (v/v) methanol in water; sample: 5 μl reaction mixture in toluene; t = toluene. Peak numbers correspond to Fig. 4.

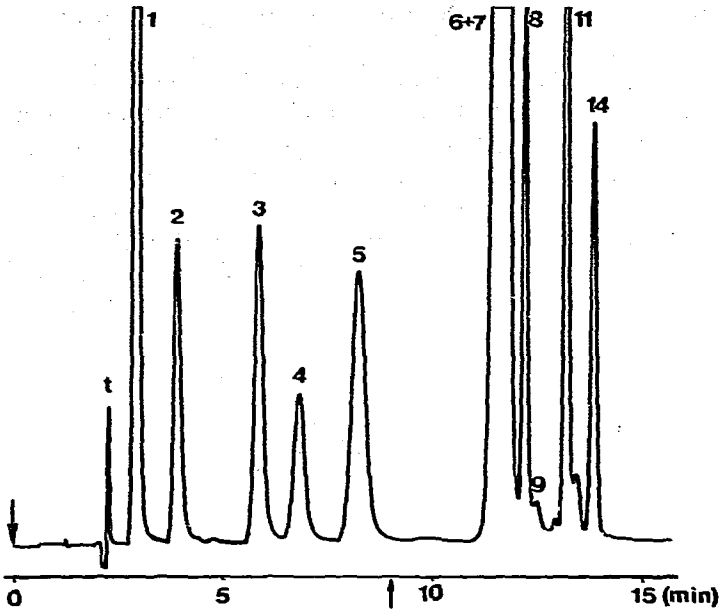


Fig. 3. Chromatogram of a sample from the reaction of $Fe_2(CO)_9$ with DBSD in toluene using a step gradient. Stationary phase: Zorbax C-8; mobile phase: 79% (v/v) methanol in water (0—9 min), 92% (v/v) methanol in water (9—15 min); sample: 5 µl reaction mixture in toluene; t = toluene, Peak numbers correspond to Fig. 4.

wide range by changing the methanol content of the mobile phase. The value of log $\kappa_i$ varies linearly with the methanol content, as is commonly found in reversed phase systems [23].

The reversed phase systems investigated show a high selectivity for the iron carbonyl complexes present in the mixture. The suitability of the reversed phase system for the analysis of the mixture, using water/methanol (25/75 (v/v)) as eluent is demonstrated in Fig. 2. It will be seen that at least ten compounds were found in the mixture in significant concentrations.

Figure 2 shows that reversed phase LC is suitable for the analysis of compounds in the mixture. However the total analysis time of 1 h is inconveniently long for monitoring this particular reaction by HPLC. In order to shorten the total analysis time, time optimization procedures involving column switching [24], step gradient or gradient elution [1] have to be applied. Thus step gradient and gradient elution were tested by varying the methanol content. Figure 3 shows an example of a step gradient by which the analysis time can be reduced from 1 h to about 13 min. In order to test gradient elution different shapes of gradients were tested. A concave/convex gradient of methanol was found to be optimal with respect to selectivity, number of separated peaks, and speed of analysis for this particular mixture.

*Monitoring the reaction with HPLC*

Use of gradient elution enabled the analysis of the reaction constituents to be completed within 25 min. As the time needed to equilibrate the column to

initial mobile phase composition was 5 min, a sample from the reaction mixture could be analyzed every 30 min.

At fixed time intervals samples (30 $\mu$l reaction mixture diluted ten times with methanol) were taken and analyzed directly. Peak areas were recorded and used as a measure of the relative concentration change for a reaction component. Figure 4 shows five chromatograms of the reaction mixture after various time intervals. As can be seen the number of reaction components increases with reaction time. The change in concentration of the reaction products during the reaction is graphically shown in Fig. 5. The occurrence of intermediate products (peak 15 and 16 in Fig. 4) can be observed from the chromatogram.

*Identification of reaction products*

In order to identify the various products the retention characteristics of pure substances can be used. However, in our study only four pure substances (peak numbers 1, 2, 6 and 7 in Fig. 4) were available. For the unknown substances identification methods such as IR or mass spectrometry have to be used. For the isolation of the reaction products a semi-preparative column (dimensions 250 X 10 mm), packed with octyl-modified silicagel (RP-8), was used. This column, when used with a step gradient (65—85% (v/v) methanol), permits injection of 80 $\mu$l of the reaction mixture, containing about 7 mg of the reaction products without loss in efficiency. After fractionation, extraction with n-hexane, and partial evaporation of the solvent the resulting concentrated iron carbonyl solutions in n-hexane were used for the recording of IR- and

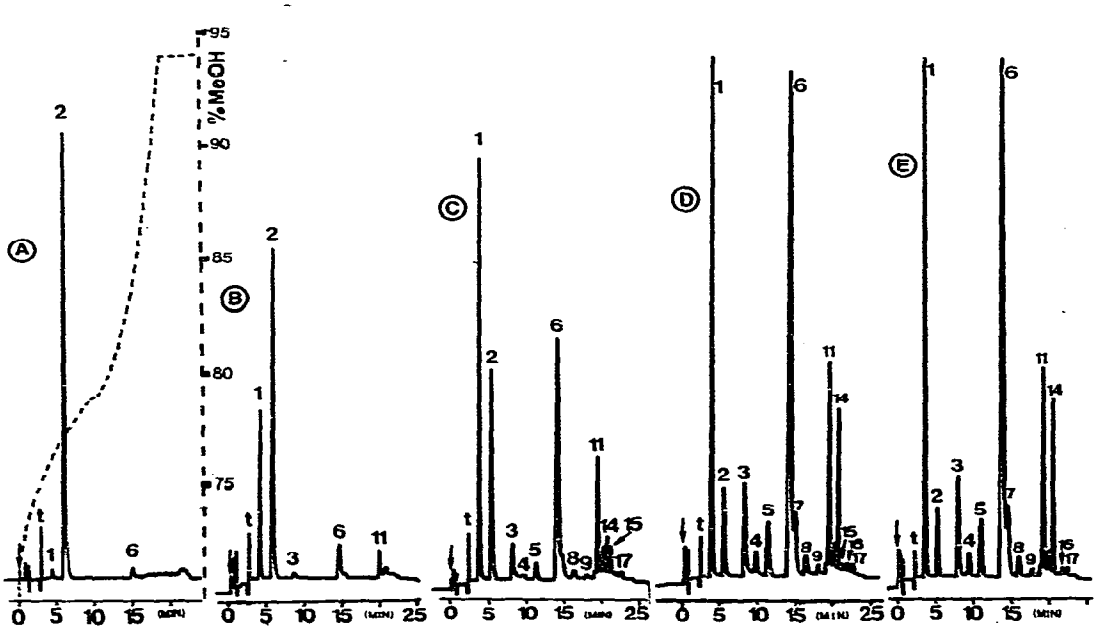


Fig. 4. Example of monitoring the reaction of $Fe_2(CO)_9$ with DNSD using gradient elution. Chromatograms of samples taken from the mixture at various times. A: after 5 min. B: after 1 h. C: after 2 h. D: after $3\frac{1}{2}$ h. E: after $4\frac{1}{2}$ h. Stationary phase: Zorbax C-8, Mobile phase: gradient from 70% (v/v) to 94% (v/v) methanol in water, gradient shape indicated in Fig. 4A; t = toluene.

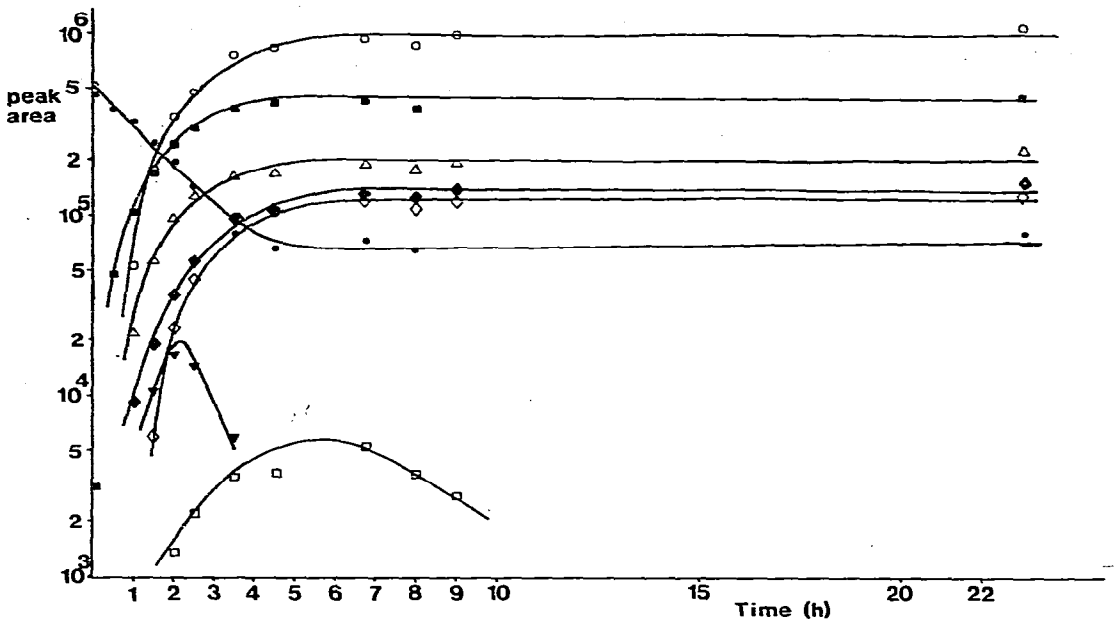


Fig. 5. The course of the reaction of $Fe_2(CO)_9$ with DNSD. The curves show the changes with time of the concentrations of some of the reaction components. Symbols correspond to peak numbers in Fig. 4: ■ = 1, ● = 2, ◆ = 3, ○ = 6, △ = 11, ◇ = 14, ▼ = 15, □ = 16.

mass spectra. The IR data are given in Table 1. Together with mass spectra, these enabled the identification of some reaction products (peak numbers 1, 6, 7 and 14 in Fig. 4). In the case of peak number 3 and 5 (Fig. 4) the data from IR and mass spectrometry did not match. IR measurements suggested the compounds

TABLE 1

INFRARED FREQUENCIES (in $cm^{-1}$) OF ISOLATED IRON CARBONYL COMPLEXES, IN n-HEXANE

| Peak numbers corresponding to ref. 4 | Ref. | IR frequencies ($cm^{-1}$) [a] | Compound |
|---|---|---|---|
| 1 | 25 | 2022s, 1999vs | $Fe(CO)_5$ |
| | | 2023, 2000 | |
| 3 | 21 | 2084m, 2044vs, 2007vs, 1733m(br) | |
| | | 2082s, 2043vs, 2007vs, 1720s | $Fe_2(CO)_6$ {t-BuN(CO)S} ? |
| 4 | | 2082w, 2047s, 2024w, 2008s, 2003m, 1942vs, 1733m(br) | |
| 5 | 21 | 2082w, 2046s, 2013m, 2007m, 1733w(br), 1700m | |
| | | 2084s, 2046vs, 2013vs, 2006vsm 1703m | $Fe_2(CO)_7$(t-BuNS) ? |
| 6 | | 2075s, 2033vs, 1998vs, 1988vs, 1978(sh), 1948w | |
| | | 2077s, 2032vs, 2000(sh), 2996vs, 1986(sh), 1979(sh), 1964w | $Fe_2(CO)_6$(t-BuNS) |
| 7 | 21 | 2062m, 2044s, 2024m, 2007w, 1996s, 1720w | |
| | | 2064vs, 2045sv, 2023vs, 1992w | $Fe_3(CO)_9S_2$ |
| 8 | | 2076m, 2042s, 1996vs, 1985w | |
| 14 | 21 | 2080w, 2039s, 2031vs, 2016s, 1988m, 1851w | |
| | | 2078m, 2061s, 2033vs, 2017s, 2005s, 1997s, 1974w, 1866w | $Fe_3(CO)_9$(t-BuNS)S |

[a] vs = very strong, s = strong, m = medium, w = weak, br = broad.

listed in Table 1, whereas mass spectra show parent peaks at *m/e* 341 and at *m/e* 443 (numbers 3 and 5 respectively). The fraction of peak number 14 shows a mass spectrum with an identical fragmentation as was reported by Mey et al. [21] for $Fe_3(CO)_9$(t-BuNS)S.

The mass spectrum of peak number 11 shows a parent peak at *m/e* 334 as well as fragments resulting from the successive loss of six carbonyl groups. This indicated that the compound $Fe_2(CO)_6S_2$ is present in the reaction mixture as found by Mey et al. [21]. The structures of the other components of the mixture, occurring at lower concentration levels, were not elucidated.

In order to establish the presence of iron in the observed reaction components an element-specific detector was coupled to the HPLC column. An Inductively Coupled Argon Plasma (ICAP) was applied for this purpose [26]. Chromatograms were recorded by observing an iron emission line (2599.40 Å); in these chromatograms only the peaks belonging to toluene (t in Fig. 4) and DBSD (2 in Fig. 4) were absent [26]. This revealed the presence of iron in all the other components.

There is an uncertainty about the main product of the reaction. Our results with the HPLC-ICAP combination indicate that $Fe(CO)_5$ is by far the major product. However, if there are assumed to be no large differences in the molar absorptivities of the iron carbonyl complexes at 325 nm the chromatograms obtained with the UV-detector at 325 nm suggest that $Fe_2(CO)_6$-t-BuNS is the main product, while Mey et al. [21] concluded that this was $Fe_2(CO)_7$-t-BuNS.

## Conclusion

The results presented in this paper indicate that HPLC is a powerful technique for monitoring reactions in organometallic chemistry and also for isolation of products for identification purposes. Because of its speed and separation efficiency, HPLC can provide valuable information about the kinetics and pathways of such reactions.

## Acknowledgement

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