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## Note

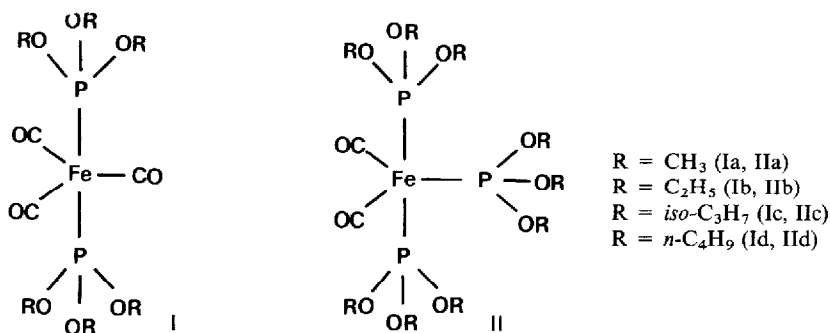
### High-performance liquid chromatography of alkyl phosphite-substituted derivatives of iron pentacarbonyl

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Because of the rôle of alkyl phosphite derivatives of iron pentacarbonyl in modelling important catalytic processes<sup>1,2</sup>, the simple, high-yield synthesis of these compounds is an important goal in organometallic chemistry. Most of the synthetic methods require  $[\text{Fe}(\text{CO})_5]$  as starting compound and give mono- and disubstituted products<sup>3</sup>. Higher degrees of substitution can be achieved by reacting either  $[\text{Fe}\{\text{P}(\text{OCH}_3)_3\}_5]$  with CO in an alcoholic medium<sup>4</sup>, or  $[\text{Fe}(\text{CO})_3(\text{C}_7\text{H}_8)]$  with a large excess of the ligand<sup>5</sup>. During the separation and purification procedures, carried out mostly by means of column chromatography, difficulties are frequently encountered especially in the separation of the mono- from the disubstituted products, as well as excess of ligand from the products<sup>3</sup>.

Recently we have found a new method for the synthesis of  $[\text{Fe}(\text{CO})_{5-n}\{\text{P}(\text{OR})_3\}_n]$  derivatives ( $n = 2, 3$ )<sup>6</sup>, starting from  $\text{FeCl}_2$ , and consequently we required a new, fast and reliable procedure for the separation and determination of these iron (0) derivatives in order to evaluate directly the efficiency and selectivity of the synthetic method.



Analytical high-performance liquid chromatography (HPLC), the potential of which in organometallic chemistry has recently been pointed out<sup>7</sup>, has been successfully used for this purpose and here we describe the behaviour of the compounds I and II in reversed-phase and adsorption chromatography, within the framework of a research program on the HPLC of metal complexes<sup>8-11</sup> and in particular of metal carbonyl derivatives<sup>1,2</sup>.

## EXPERIMENTAL

Synthetic operations were carried out under a dry nitrogen atmosphere in Schlenk-type flasks. Solvents were dried over appropriate drying agents, degassed on a vacuum line and distilled under nitrogen into storage flasks. The one-step synthesis of the iron (0) derivatives will be described elsewhere, together with the results of the X-ray structural analysis carried out on IIb<sup>6</sup>.

A Perkin-Elmer Series 3B liquid chromatograph, equipped with a Rheodyne 7105 injection valve and a LC-75 variable wavelength UV-visible detector, was used. Stainless-steel columns (25 × 0.4 cm I.D.) containing LiChrosorb RP-18 and Si 60, mean particle size 10 μm (E. Merck, Darmstadt, G.F.R.), were used. Solvents were HPLC grade (Carlo Erba, Milan, Italy).

Samples were injected as tetrahydrofuran (THF) solutions (5 μl). The presence of iron after the chromatographic run was verified in the fractions, corresponding to the peaks, by means of electrothermal atomic absorption spectroscopy (Perkin-Elmer Model 303 with HGA-72). Other aliquots of the eluted mobile phase were used as blank. The integrity of the phosphite-carbonyl iron derivatives after the chromatographic run was checked by means of IR spectroscopy (Perkin-Elmer Model 283B).

## RESULTS AND DISCUSSION

One of the goals of this work was to determine the optimum analytical conditions for the separation and determination of the pairs of bis- and tris(phosphite) derivatives, formed in the synthetic procedure. For this purpose both reversed-phase and adsorption chromatography were considered. The separation of the pairs (I-II)<sub>b</sub>, (I-II)<sub>c</sub> and (I-II)<sub>d</sub> was achieved on a RP-18 column, using methanol as mobile phase (Fig. 1), and in all cases the bis(phosphite) derivatives show lower retention volumes. The two trimethyl phosphite complexes Ia and IIa are only weakly retained; in fact, negligible resolution is obtained between them, and Ia is not retained at all. On the other hand, the use of water in the mobile phase causes a broadening of the peaks without improving the separation.

Although attempts to separate the four bis(phosphite) derivatives I on the same RP-18 column, were unsuccessful, Ia being not retained and the peaks of Ic and Id being overlapped, an effective separation was obtained among the tris(phosphite) compounds II on the same column using methanol as mobile phase (Fig. 2a; number of theoretical plates for IIc, 1860). The elution order, CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, *n*-C<sub>4</sub>H<sub>9</sub>, *iso*-C<sub>3</sub>H<sub>7</sub>, appears to be affected by the length as well as the branching of the alkyl chain.

The separation of the pair Ia-IIa was obtained using silica as stationary phase and *n*-hexane-THF (90:10) as mobile phase (Fig. 2b).

On this column the behaviour of compounds I was tested using different percentages of THF in the mobile phase; as an example, Fig. 3 shows the dependence of the corrected retention volumes of [Fe(CO)<sub>3</sub>{P(OC<sub>2</sub>H<sub>5</sub>)<sub>3</sub>}<sub>2</sub>] on the per cent of THF in the mixture *n*-hexane-THF.

The separation of the four complexes I, which was not obtained on the reversed-phase column, was achieved on the silica one even though a two-step gradient was necessary. These compounds differ greatly in their behaviour with the content

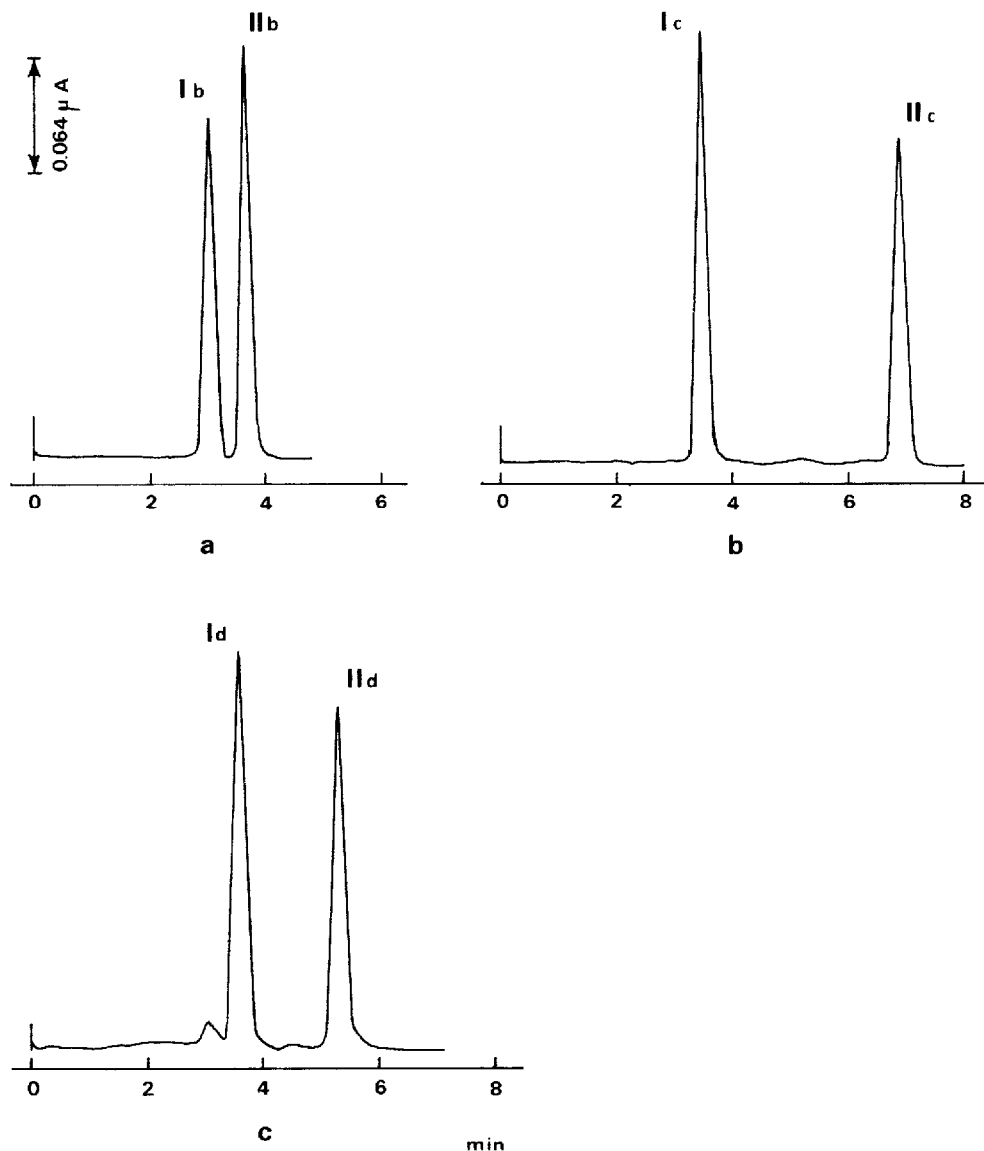


Fig. 1. Separation of pairs of bis- and tris(phosphite) derivatives: a,  $[\text{Fe}(\text{CO})_3\{\text{P}(\text{OC}_2\text{H}_5)_3\}_2]$  (Ib) and  $[\text{Fe}(\text{CO})_2\{\text{P}(\text{OC}_2\text{H}_5)_3\}_3]$  (IIb); b,  $[\text{Fe}(\text{CO})_3\{\text{P}(\text{OC}_3\text{H}_7)_3\}_2]$  (Ic) and  $[\text{Fe}(\text{CO})_2\{\text{P}(\text{OC}_3\text{H}_7)_3\}_3]$  (IIc); c,  $[\text{Fe}(\text{CO})_3\{\text{P}(\text{OC}_4\text{H}_9)_3\}_2]$  (Id) and  $[\text{Fe}(\text{CO})_2\{\text{P}(\text{OC}_4\text{H}_9)_3\}_3]$  (IIId). Column: LiChrosorb RP-18. Mobile phase: methanol, flow-rate  $1 \text{ cm}^3 \text{ min}^{-1}$ . Detector: UV,  $\lambda = 265 \text{ nm}$ .

of THF: *e.g.*, in THF-*n*-hexane (5:95) the retention volume of Ia is  $12 \text{ cm}^3$ , while the corresponding butyl derivative Id is unretained. Fig. 4 shows the separation of the bis(phosphite) complexes I, obtained with a linear two-step gradient of 0–6% THF (slope  $1\% \text{ min}^{-1}$ ) and 6–18% THF (slope  $2\% \text{ min}^{-1}$ ). The elution order follows the decreasing number of carbon atoms in the alkyl chains, with a small difference in the

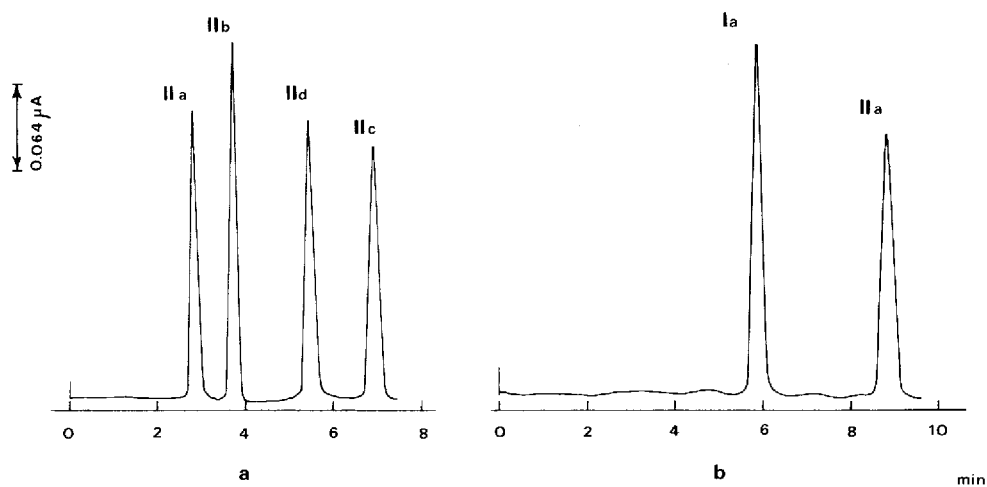


Fig. 2. a, Separation of the tris(phosphite) derivatives  $[\text{Fe}(\text{CO})_2\{\text{P}(\text{OR})_3\}_3]$  under the same conditions as in Fig. 1. b, Separation of  $[\text{Fe}(\text{CO})_3\{\text{P}(\text{OCH}_3)_3\}_2]$  (Ia) and  $[\text{Fe}(\text{CO})_2\{\text{P}(\text{OCH}_3)_3\}_3]$  (IIa). Column: LiChrosorb Si 60. Mobile phase: *n*-hexane-THF (90:10). Other conditions as in Fig. 1.

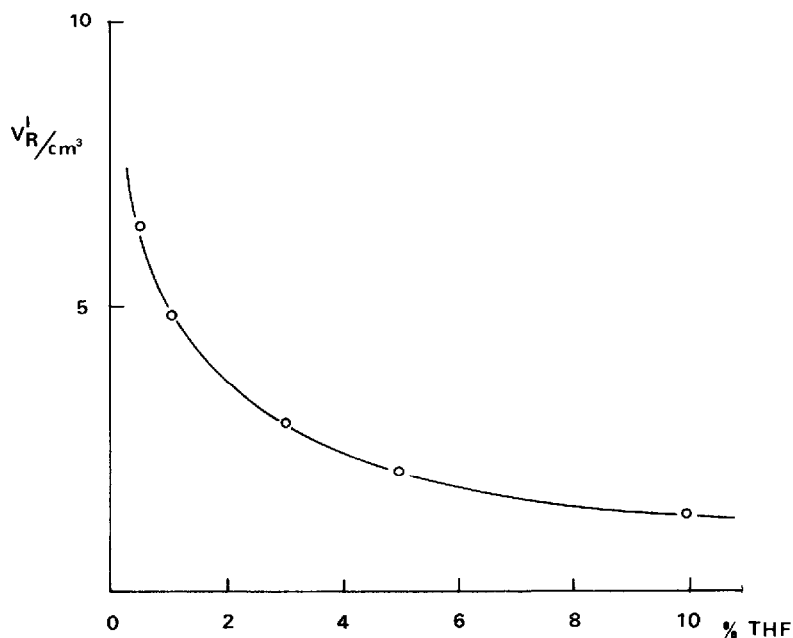


Fig. 3. Dependence of the corrected retention volumes ( $V_R^1$ ) for  $[\text{Fe}(\text{CO})_3\{\text{P}(\text{OC}_2\text{H}_5)_3\}_2]$  on the per cent of THF in the mixture hexane-THF, on the Si 60 column.

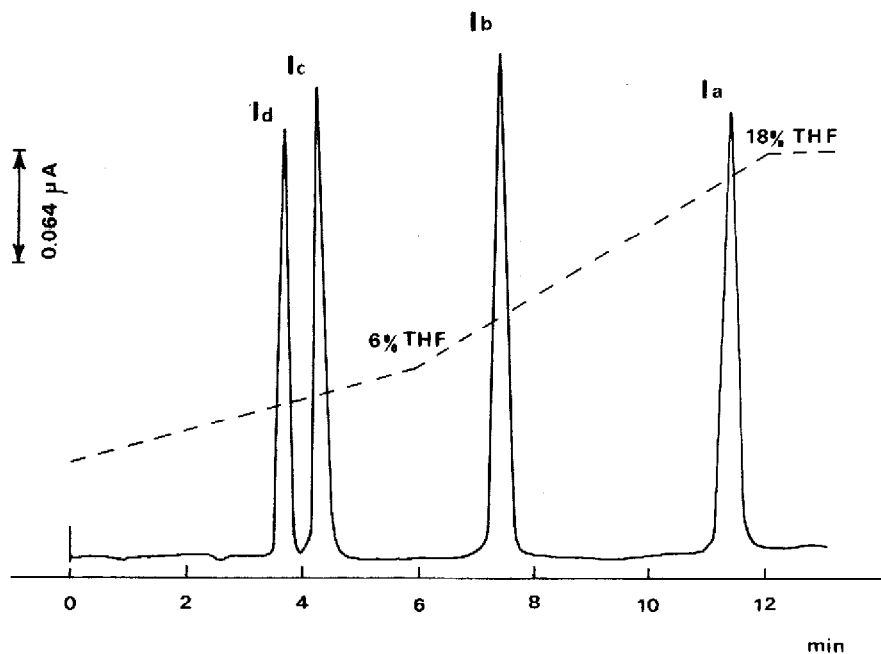


Fig. 4. Separation of bis(phosphite) complexes I on the silica column. Mobile phase: *n*-hexane-THF mixture, with two-step linear gradient. Flow-rate:  $1 \text{ cm}^3 \text{ min}^{-1}$ . Detector: UV,  $\lambda = 265 \text{ nm}$ .

retention volumes of the *iso*- $\text{C}_3\text{H}_7$  and *n*- $\text{C}_4\text{H}_9$  derivatives and a larger difference between those of the methyl and ethyl derivatives.

In order to investigate the possibility to determine these compounds and to find the concentration range in which HPLC could be applied, the dependence of the response of the UV detector on the amount of complex injected was tested at 265 nm. 5- $\mu\text{l}$  Volumes of acetonitrile solutions of  $[\text{Fe}(\text{CO})_2\{\text{P}(\text{OC}_2\text{H}_5)_3\}_3]$  (4–40 ppm) were injected, the amount of compound ranging between 20 and 200 ng. The dependence of the UV detector response on the amount of compound injected was found to fit the linear equation  $y = 0.256 - 0.032x$ , where  $y$  is the peak height in cm (recorder sensitivity:  $0.002 \text{ absorbance units} \cdot \text{cm}^{-1}$ ) and  $x$  is the amount in ng of compound injected. The relative standard deviation was 2% for  $n = 8$ . The detection limit is  $\approx 4 \text{ ng}$  of compound injected.

#### ACKNOWLEDGEMENTS

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