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Note

High-performance liquid chromatographic separations of some palladium(II) complexes with substituted hydrazones

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Several applications of high-performance liquid chromatography (HPLC) to organic compounds have been reported recently¹, but only a few examples of separations of organometallic compounds have been described²⁻¹¹.

HPLC is an effective method for the separation of compounds that either are thermally unstable or do not exhibit the appropriate vapour pressure to permit direct analysis by gas-liquid chromatography. Hence this technique may be applicable to most organometallic compounds.

The strong interactions between metal complexes and the polar centres of siliceous matrices (silanol groups, $\equiv\text{Si}-\text{OH}$) have been reduced by using bonded phases with substituted silanol groups.

In connection with our studies on the behaviour of palladium(II)-labile complexes with substituted hydrazones¹²⁻¹⁵, several methods have been investigated in order to separate these complexes. A siliceous matrix modified by the introduction of alcoholic groups (LiChrosorb DIOL 10 μm) has been found to provide a solution to this problem.

We have separated complexes of the type *trans*- $[\text{PdL}_2\text{Cl}_2]$ (I-VI) ($\text{L}^1 = \text{N-methyl-N-phenylhydrazone of methyl isopropyl ketone}$, I; $\text{L}^2 = \text{N-methyl-N-phenylhydrazone of diethyl ketone}$, II; $\text{L}^3 = \text{N-methyl-N-phenylhydrazone of methyl } n\text{-propyl ketone}$, III; $\text{L}^4 = \text{N,N-dimethylhydrazone of acetone}$, IV; $\text{L}^5 = \text{N-methyl-N-phenylhydrazone of acetone}$, V; $\text{L}^6 = \text{N-methyl-N-phenylhydrazone of acetaldehyde}$, VI) and also mixed ligand complexes of the type *trans*- $[\text{PdL}'\text{L}''\text{Cl}_2]$.

The method can be employed to monitor the progress of the synthesis of these complexes, and also provides information about their purity and the rate of exchange between different ligands.

The separation of small amounts of pure compounds for elemental analysis and IR and NMR spectroscopy is an additional aspect of interest.

EXPERIMENTAL

Reagents

The complexes were prepared according to the methods described previously^{16,17}; solvents (*n*-hexane and dichloromethane) were LiChrosolv (Merck, Darmstadt, G.F.R.) reagents and the stationary phase was LiChrosorb DIOL 10 μm (Merck).

Analytical system

The chromatograph used was a Waters Model ALC/GPC-202 (Waters Assoc., Milford, Mass., U.S.A.) equipped with a U6-K universal injector, a Model M6000 solvent delivery system, a Model 660 solvent programmer, a differential UV detector (254 nm) and a Model 401 refractive index detector.

The column was a high-efficiency microparticulate column (25 cm \times 4.2 mm I.D.), packed with LiChrosorb DIOL, 10 μm .

RESULTS AND DISCUSSION

On the basis of preliminary studies carried out in order to select the optimal conditions, it was possible to exclude columns of unmodified silica as the complexes were strongly adsorbed on silica and generally unstable. It was considered that the separation might be more effective on bonded-phase LiChrosorb RP-8 or LiChrosorb DIOL, and we found that by using the latter phase, which permits the use of solvents such as *n*-hexane and dichloromethane in which the complexes are readily soluble and stable, we could achieve the quantitative separation of the complexes. Even semi-preparative separations could be carried out on this phase.

Separation of the complexes I–VI under isocratic conditions is illustrated in Fig. 1. The chromatographic parameters are summarized in Table I.

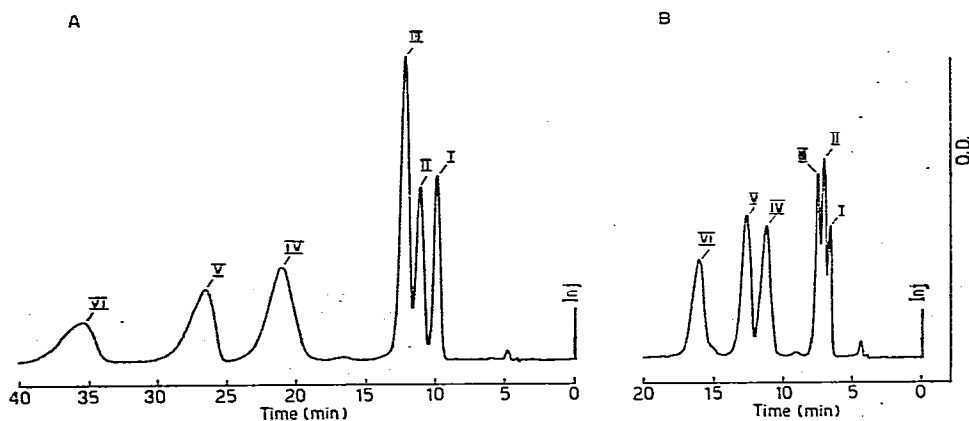


Fig. 1. (A) Separation of a mixture of *trans*-[PdL₂Cl₂] complexes under isocratic conditions. Two columns of 25 cm \times 4.2 mm I.D. packed with LiChrosorb DIOL, 10 μm . Mobile phase: *n*-hexane-dichloromethane (88:12). Flow-rate: 1.5 ml/min. Pressure: 50 bar. Temperature: 25°. Detector: UV (254 nm). Attenuation: a.u.f.s. \times 0.64. Amount injected: 6 μl . (B) Separation of a mixture of *trans*-[PdL₂Cl₂] complexes under isocratic conditions. Mobile phase: *n*-hexane-dichloromethane (80:20). Other conditions as in (A).

TABLE I

PARAMETERS FOR THE SEPARATION OF A MIXTURE OF *trans*-[PdL₂Cl₂] COMPLEXES

Two columns of 25 cm × 4.2 mm I.D. packed with LiChrosorb DIOL, 10 μm. Mobile phase: *n*-hexane-dichloromethane (88:12). Flow-rate: 1.5 ml/min. *V_r* = Elution volume; α = separation factor. (See Fig. 1A.)

<i>trans</i> -[PdL ₂ Cl ₂]	No.	<i>V_r</i> (ml)	<i>k₁</i>	α
<i>trans</i> -[PdL ¹ Cl ₂]	I	14.7	1.45	1.24
<i>trans</i> -[PdL ² Cl ₂]	II	16.8	1.80	1.16
<i>trans</i> -[PdL ³ Cl ₂]	III	18.6	2.10	2.07
<i>trans</i> -[PdL ⁴ Cl ₂]	IV	32.1	4.35	1.26
<i>trans</i> -[PdL ⁵ Cl ₂]	V	39.0	5.50	1.44
<i>trans</i> -[PdL ⁶ Cl ₂]	VI	53.7	7.95	

The separation of all of the complexes in one run could be achieved by using a solvent gradient, and such a separation is shown in Fig. 2.

The chromatograms in Figs. 1 and 2 indicate that the capacity factor, *k₁*, decreases as the chain-length of the ketone increases (*R₁* and/or *R₂*), and that it also depends on substituent *R₃* on the sp³-nitrogen atom.

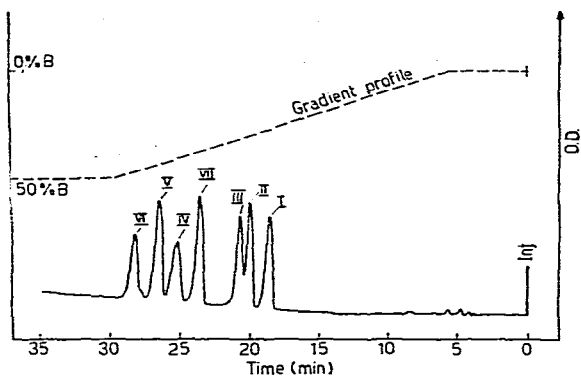


Fig. 2. Separation of a mixture of *trans*-[PdL₂Cl₂] complexes with a solvent gradient. Two columns of 25 cm. × 4.2 mm I.D. packed with LiChrosorb DIOL, 10 μm. Mobile phase: A, *n*-hexane; B, dichloromethane. Flow-rate: 1.5 ml/min. Temperature: 25°. Detector: UV (254 nm). Attenuation: a.u.f.s. × 1.28. Amount injected: 10 μl. Compound VII is *trans*-[PdL²L⁵Cl₂].

Further evidence of the dependence of *k₁* on *R₁* and *R₂* is derived from the HPLC analysis of the mixture obtained by refluxing compounds II and V for 5 h.

Fig. 3 shows an additional peak (VII) among those corresponding to II and V. This peak is due to the complex *trans*-[PdL²L⁵Cl₂], which results from ligand exchange in solution. By measurement of the area of this peak it is possible to follow

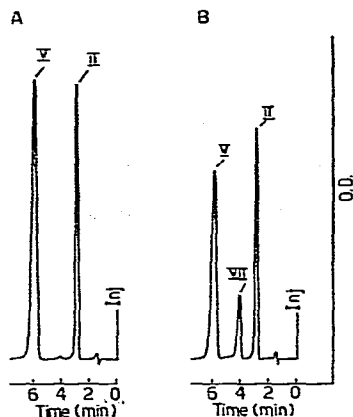


Fig. 3. Analysis of a mixture obtained by refluxing $trans$ -[PdL²₂Cl₂] and $trans$ -[PdL⁵₂Cl₂] for 5 h. A, Initial conditions; B, final conditions. Column: LiChrosorb DIOL, 10 μ m, 25 cm \times 4.2 mm I.D. Mobile phase: *n*-hexane-dichloromethane (78:22). Flow-rate: 2.0 ml/min. Pressure: 28 bar. Temperature: 25°. Detector: UV (254 nm). Attenuation: a.u.f.s. \times 0.64. Amount injected: 6 μ l.

the progress of the reaction and to determine the corresponding kinetic parameters. The high sensitivity of this technique enables one to determine even trace amounts of exchanged product that are hardly detectable with other analytical methods.

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