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MONITORING OF THE FORMATION OF BINUCLEAR RUTHENIUM CARBONYL COMPLEXES DURING REACTIONS BY MEANS OF HIGH PERFORMANCE LIQUID CHROMATOGRAPHY

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Summary

Reversed-phase high performance liquid chromatography has been used to monitor the reactions of $Ru_3(CO)_{12}$ with 1,4-diazabutadiene (DAB) and of $Ru_2(CO)_6$ (DAB) with DAB. The kinetic data show that the formation of an intermediate in the former reaction is the rate determining step, which is first order in $Ru_3(CO)_{12}$ as well as in DAB. The reactivity depends strongly on the type of substituent on DAB. Exchange of free and coordinated ligands (isopropyl DAB and tert-butyl DAB) is demonstrated in the reaction of $Ru_2(CO)_6$ (DAB) with DAB. A reversible reaction is proposed to account for this exchange.

Introduction

The use of high performance liquid chromatography (HPLC) for the isolation and determination of organometallic complexes has been described in a number of papers (see ref. 1 and references given therein). Especially for reaction monitoring, HPLC offers several important advantages. The sample volumes needed can be very small (5—50 μl), so that a large number of samples can be taken without markedly affecting the total volume of the reaction mixture. Usually analysis times of about 5 to 10 min can be achieved permitting frequent sampling. For simple separations an analysis time of 1 min is possible. Further-

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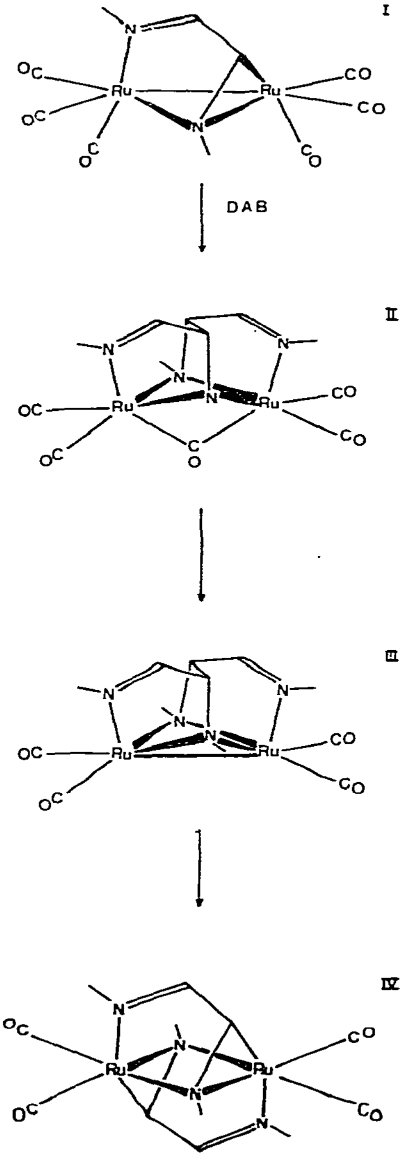

Fig. 1. Reaction sequence for the reaction between $Ru_3(CO)_{12}$ and DAB showing the isolated products: I = $Ru_2(CO)_6(DAB)$; II = $Ru_2(CO)_5(IAE)$; III = $Ru_2(CO)_4(IAE)$; IV = $Ru_2(CO)_4(DAB)_2$.

more the use of a UV-detector or of other sensitive detection devices [2,3] permits the analysis of compounds at low concentration levels with good accuracy. In spite of these advantages this analytical technique has seldom been used for reaction monitoring [1,4,5].

The reaction of $Ru_3(CO)_{12}$ with 1,4-diazabutadiene (DAB) (R—N=CH—CH=N—R) results in the formation of several binuclear ruthenium complexes [6,7] (Fig. 1). It is known that the reaction proceeds via a complicated pathway and that unstable intermediates are formed [6,7]. Up to four products can be obtained for one DAB ligand by varying the $Ru_3(CO)_{12}$/DAB ligand ratio and by carefully controlling the reaction conditions. They can all be isolated in a pure state and used as standard compounds for the development of suitable HPLC separation systems and for the identification of peaks in the chromatogram of a sample from a reaction mixture.

A study of the kinetics of this reaction by means of HPLC was undertaken in order to obtain more information about the reaction pathway and evidence for the existence of intermediates.

Experimental

Procedures

All reactions were carried out under nitrogen. The toluene used as solvent was carefully dried and distilled before use. The conditions used for the various reactions are summarized in Table 1.

A reaction was started by the addition of the required amount of DAB dissolved in a small volume ($\simeq$ 200 μl) of toluene. In order to take samples from the reaction mixture under nitrogen a piece of Teflon tubing (1.63 mm O.D. and 0.3 mm I.D.) was inserted through a septum into the reaction vessel. The outside of the Teflon tubing was connected, by means of a Swagelock® low-dead volume union, with a calibrated microliter syringe (maximal volume 100 μl). The total volume of the Teflon tubing was kept small relative to the sample

TABLE 1

REACTION CONDITIONS

Amounts (mmol) of reacting species		Amount (g) of toluene	Temp. (°C)
$Ru_3(CO)_{12}$	0.052	25.58	110
i-propyl DAB	0.076		
$Ru_3(CO)_{12}$	0.100	23.25	110
t-butyl DAB	0.152		
$Ru_2(CO)_6$(i-propyl DAB)	0.150	20.36	110
i-propyl DAB	0.153		
$Ru_3(CO)_{12}$	0.048	66.34	70
i-propyl DAB	1.550		
$Ru_3(CO)_{12}$	0.054	63.01	110
t-butyl DAB	1.628		
$Ru_2(CO)_6$(i-propyl DAB)	0.049	65.79	90
i-propyl DAB	1.689		
$Ru_2(CO)_6$(i-propyl DAB)	0.150	24.04	110
t-butyl DAB	0.152		
$Ru_2(CO)_6$(t-butyl DAB)	0.155	22.25	110
i=propyl DAB	0.160		

volume (50 µl) in order to give samples of the actual composition of the mixture at the moment of sampling. The sample was immediately evaporated to dryness and the residue was dissolved in 50 µl of tetrahydrofuran (THF). Of this solution 5 µl was analyzed directly by HPLC. Concentrations were calculated from the peak are of the compound of interest in the chromatogram by comparing this area to that obtained from a similar injection of a standard solution of the pure compound dissolved in THF.

Determination of reaction order and rate constant

The over-all order of a reaction was measured for mixtures in which the reacting species were present in stoichiometric ratio [8]. The order with respect to each compound was obtained by the method of isolation, all the other reactants being present in considerable excess so that the observed order of the reaction is that for the compound of interest.

The order of the reaction and the rate constant were determined by means of the differential method (Van 't Hoff method) and fitting the experimental data into an integrated rate equation [8]. The least squares method was used to calculate the reaction constants.

Chromatographic equipment

The liquid chromatographic system was assembled from commercially available elements. It consisted of a microprocessor controlled pump module (Perkin-Elmer Series 3, Norwalk, Conn., U.S.A.), a precolumn (25 mm length and 3 mm I.D.) filled with Zorbax ODS, a high pressure sampling valve (HPV-4; Chromatronix, Berkeley, Calif., U.S.A.), a stainless steel column (150 mm length and 4.6 mm I.D.) packed by the slurry method [9] with Zorbax ODS (7 µm) (Dupont, Wilmington, Del., U.S.A.) and a variable wavelength UV-detector (837 spectrophotometer; Dupont, Wilmington, Del., U.S.A.) set at 290 nm. A linear potentiometric recorder (Servogor RE 511; Goerz, Vienna, Austria) was applied for signal readout of the detector. Peak area measurements were performed with an electronic integrator (Autolab System I; Spectra Physics, Santa Clara, Calif., U.S.A.).

Chemicals

1,4-Diazabutadiene (R—N=CH—CH=N—R) (R = iso-propyl or tert-butyl) was prepared by standard procedures [10]. The preparation of $Ru_2(CO)_6$ (DAB) [DAB is glyoxal-bis-(iso-propylimine) or glyoxal-bis-(tert-butylimine)] involved reaction of $Ru_3(CO)_{12}$ and $Ru_2(CO)_6$ (DAB) in a stoichiometric ratio in toluene at 110°C. After the reaction had come to completion this solution of $Ru_2(CO)_6$ (DAB) was used for further measurements. $Ru_3(CO)_{12}$ was purchased from Strem Chemicals and used without purification. Triethylamine (TEA) (for synthesis, Merck-Schuchardt, Hohenbrunn, GFR), tetrahydrofuran (Analyzed reagent, Baker, Phillipsburg, N.J., U.S.A.) (stabilized with 0.025% butylated hydroxytoluene) and doubly-distilled water were used to prepare the mobile phase.

Results and discussion

Selection of the phase system for chromatographic analysis

In order to investigate the concentration changes of the components ocurring in the reaction, one must be able to separate all the components within a short time. The adsorption of most ruthenium-DAB complexes on porous silica appeared to be very strong, and in many cases irreversible. Therefore normal phase adsorption chromatography using porous silica as stationary phase could not be used to monitor the reaction. Also the adsorption with chemically modified silica matrices (octyl-, octadecyl- or diolmodified) was found to be irreversible, especially for $Ru_2(CO)_n$ (IAE) complexes ($n = 4$ or 5) (IAE = bis[dialkylimino-μ-dialkylamino]ethane-*N,N'*) [6,7]. A detailed report of the behaviour of these ruthenium-carbonyl-diazabutadiene complexes in several chromatographic phase systems that are normally used in HPLC, will be published elsewhere [11].

In reversed phase systems the addition of amines, especially triethylamine (TEA), to a mobile phase consisting of water/THF significantly lowers the strong interaction of these complexes with the remaining polar sites of the alkyl-modified silica and enables the separation and quantitative determination of most of the compounds under consideration. Unfortunately, in the case of $Ru_2(CO)_n$ (IAE) ($n = 4$ or 5) the results were not quantitatively reliable [11], and could only be used as a qualitative indication of the presence of such complexes. In order to prevent a rapid degradation of the stationary phase due to the addition of TEA [12], a short precolumn filled with the same stationary phase was placed in front of the injection valve. The reactions were carried out in toluene to ensure the solubility of all compounds present during the reaction. However, direct injection of a toluene sample in a water/THF mobile phase gives rise to a major disturbance in the chromatogram and so evaporation of the toluene prior to injection is necessary. The residue is dissolved in THF and from this solution an aliquot is analysed by HPLC. The difference in solvent composition between the mobile phase and the injected solution gives rise to a minor disturbance of the chromatogram. A negative peak is observed between $Ru_2(CO)_6$(iso-propyl DAB) and $Ru_2(CO)_6$(tert-butyl DAB) (Fig. 5D, 6 and 7). During the evaporation the free DAB is partly removed, and cannot be determined in this way. The chemical kinetics are determined with a mobile phase consisting of 70% (v/v) THF in water, with the addition of TEA (5 mMol/l). Under these conditions chromatographic analysis is performed within 5 min, as is shown in Fig. 5.

Kinetic results

Reaction of $Ru_3(CO)_{12}$ with DAB (iso-propyl DAB or tert-butyl DAB)

When $Ru_3(CO)_{12}$ is mixed in a 2 : 3 molar ratio with DAB, $Ru_2(CO)_6$ (DAB) is formed, according to the following equation [6,7]:

$$2\ Ru_3(CO)_{12} + 3\ DAB \rightarrow 3\ Ru_2(CO)_6\ (DAB) + 6\ CO \qquad (1)$$

Under these conditions the overall order of the reaction was determined from the decrease in concentration of $Ru_3(CO)_{12}$ with time, as shown for iso-propyl

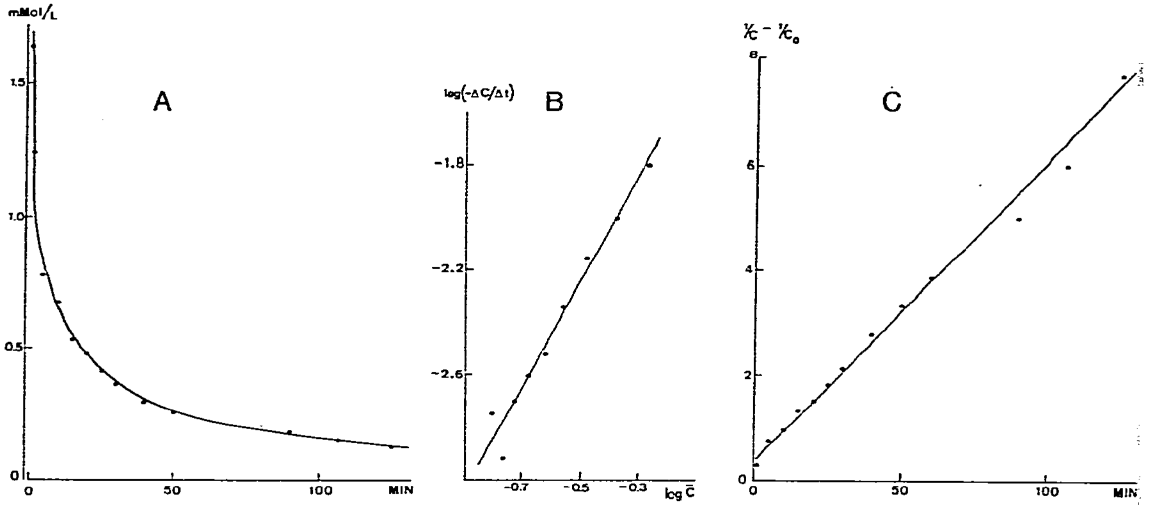

Fig. 2. Reaction of $Ru_3(CO)_{12}$ with iso-propyl DAB in stoichiometric ratio; 2a: decrease of $Ru_3(CO)_{12}$ concentration with time; 2b: Van 't Hoff plot; 2c: experimental data plotted according to the integrated rate equation for second order kinetics.

DAB in Fig. 2a. In order to determine the reaction order by means of the Van 't Hoff method, $\log(-\Delta C/\Delta t)$ is plotted against $\log \bar{C}$ ($\bar{C}$ is the mid-point concentration over the interval ΔC). The scattering in the experimental data strongly influences the value of $\log(-\Delta C/\Delta t)$, so a smooth curve was fitted manually through the experimental data, and data from this curve were used to construct a Van 't Hoff plot. This is shown in Fig. 2b. From the slope of this plot it can be concluded that the reaction is second order. Assuming second order kinetics, the experimental data were plotted according to the integrated rate equation: $(1/C - 1/C_0) = kt$ (C_0 = concentration at $t = 0$). As can be seen from Fig. 2c a straight line is obtained, indicating also second order kinetics.

The reactions between a) $Ru_3(CO)_{12}$ and tert-butyl DAB present in a stoichiometric ratio, b) $Ru_3(CO)_{12}$ and an excess of iso-propyl DAB and c) $Ru_3(CO)_{12}$ and an excess of tert-butyl DAB were also studied by measuring the concentration of $Ru_3(CO)_{12}$. The data were treated in the way described above. The results of these experiments are summarized in Table 2. The reaction of $Ru_3(CO)_{12}$ with an excess of iso-propyl DAB is complete within 5 min at 110°C, which is too fast to enable reaction monitoring with HPLC. Lowering the concentrations in order to slow down the reaction, was rejected because the concentrations then become too small for accurate measurements, and so the temperature was lowered to 70°C. From the results in Table 2 it can be concluded that in the case of iso-propyl DAB the overall order of the reaction is two and that the orders with respect to $Ru_3(CO)_{12}$ and iso-propyl DAB are both one. However, from the results for tert-butyl DAB no firm conclusion can be drawn. The overall order of the reaction also seems to be two, but the order with respect to $Ru_3(CO)_{12}$ cannot be determined from the experimental results.

The outstanding feature is the large difference in the reactivities of tert-

TABLE 2

KINETIC DATA FROM THE REACTION OF $Ru_3(CO)_{12}$ WITH DAB [a]

Reacting species	Temp. (°C)	Van 't Hoff method	Integrated rate equation
$Ru_3(CO)_{12}$ i-Pr DAB (stoich. conc.)	110	slope: 2.05 → 2nd order intercept: —1.22 → k = 0.060 r^2 = 0.967 n = 9	2nd order: k = 0.055 r^2 = 0.991 n = 14
$Ru_3(CO)_{12}$ t-Bu DAB (stoich. conc.)	110	slope: 1.97 → 2nd order intercept: —2.86 → k = 0.0014 r^2 = 0.999 n = 10	2nd order: k = 0.0014 r^2 = 0.999 n = 15
$Ru_3(CO)_{12}$ i-Pr DAB (excess conc.)	70	slope: 1.09 → 1st order intercept: —1.41 → k = 0.039 r^2 = 0.979 n = 11	1st order: k = 0.057 r^2 = 0.978 n = 14
$Ru_3(CO)_{12}$ t-Bu DAB (excess conc.)	110	slope: 2.35 intercept: —5.96 r^2 = 0.884 n = 13	1st order: k = 0.002 r^2 = 0.972 n = 14 2nd order: k = 0.014 r^2 = 0.950 n = 14

[a] For 1st order k is expressed in min^{-1}, for 2nd order k is expressed in $1'$ $(mmol)^{-1}$, r^2 = coefficient of determination, n = number of points.

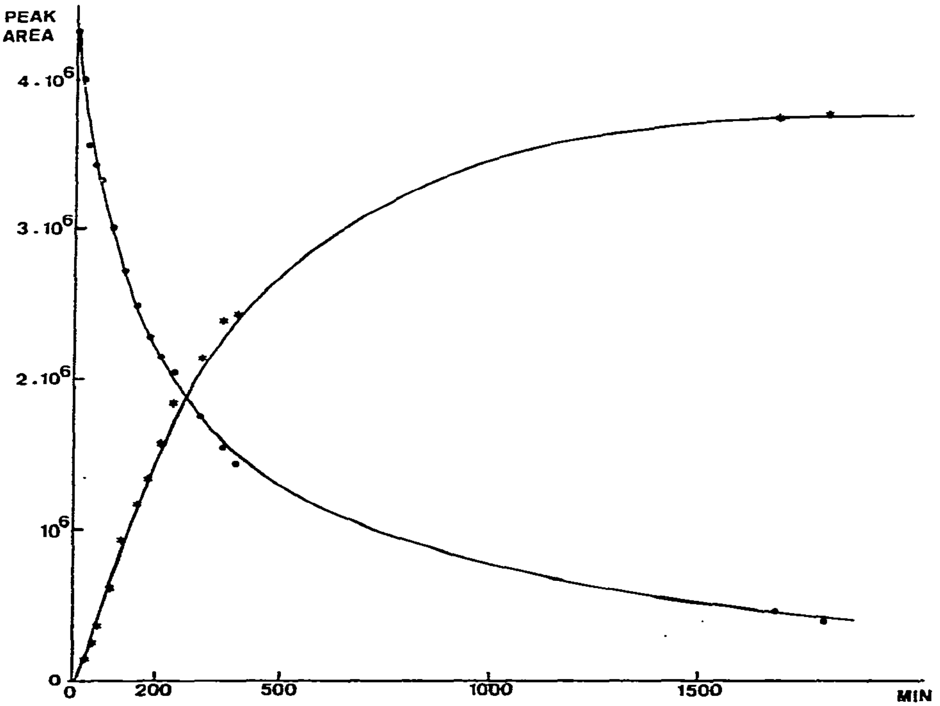

Fig. 3. Material balance of the reaction of $Ru_3(CO)_{12}$ with tert-butyl DAB in stoichiometric ratio. ● = $Ru_3(CO)_{12}$; ★ = $Ru_2(CO)_6$(tert-butyl DAB).

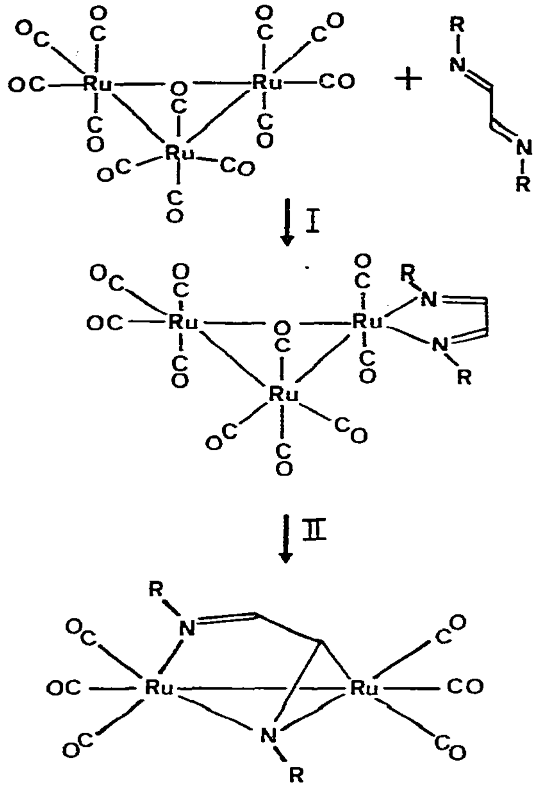

Fig. 4. Proposed reaction mechanism for the formation of $Ru_2(CO)_6(DAB)$ via $Ru_3(CO)_{10}(DAB)$ as an intermediate.

butyl DAB and iso-propyl DAB, which is reflected in a factor 40 between the respective rate constants, under similar reaction conditions. The kinetic data for the reaction between $Ru_3(CO)_{12}$ and tert-butyl DAB are probably less reliable due to the long reaction time, which allows thermal decomposition of the starting materials.

The material balances show a simultaneous decrease of $Ru_3(CO)_{12}$ and an increase of $Ru_2(CO)_6$ (DAB) concentrations (Fig. 3). The absence of any delay in the formation of $Ru_2(CO)_6$ (DAB) indicates that reaction intermediates (the existence of which is obvious from the colour changes during the reactions) have short lifetimes. Consequently the rate-determining step is the formation of an unstable intermediate.

The reaction orders with respect to $Ru_3(CO)_{12}$ and with respect to DAB are both one. On the basis of these results a mechanism is proposed which involves the formation of a (postulated) $Ru_3(CO)_{10}$ (DAB) species which has the DAB ligand coordinated via the nitrogen lone pairs as is shown in Fig. 4. Additional evidence for the existence of $Ru_3(CO)_{10}$ (DAB) as an intermediate can be found in the synthesis of $Ru_3(CO)_8$ (DAB). These stable trinuclear complexes have been isolated with iso-butyl DAB and neopentyl DAB [10] and the formation of such complexes starting from $Ru_3(CO)_{12}$ also requires $Ru_3(CO)_{10}$ (DAB) as

TABLE 3

KINETIC DATA FROM THE REACTION OF $Ru_2(CO)_6$(i-propyl DAB) WITH i-propyl DAB [a]

Reaction conditions	Van 't Hoff method	Integrated rate equation
stoichiometric concentrations 110°C	slope: 0.95 → 1st order intercept: —1.36 → k = 0.044 r^2 = 0.987 n = 7	1st order: k = 0.044 r^2 = 0.985 n = 14
excess of i-propyl DAB 90°C	slope: 0.91 → 1st order intercept: —1.59 → k = 0.026 r^2 = 0.960 n = 10	1st order: k = 0.016 r^2 = 0.984 n = 12

[a] k is expressed in min^{-1}, r^2 = coefficient of determination, n = number of points.

an intermediate. Step I in the proposed mechanism is a simple substitution of carbon monoxide with retention of the triangular backbone of the molecule. Step II is a very complicated internal rearrangement of the molecule followed by a breakdown of the cluster, about which no further information could be obtained from the kinetic results.

Reaction of $Ru_2(CO)_6$ (DAB) with DAB (iso-propyl DAB or tert-butyl DAB)

The reaction of $Ru_2(CO)_6$ (DAB) with DAB was carried out both with the same ligand already present in the $Ru_2(CO)_6$ (DAB) complex and with a different DAB ligand. The products resulting from the reaction of $Ru_2(CO)_6$ (DAB) with the corresponding DAB have been described [7] and the complete reaction sequence is shown in Fig. 1.

With iso-propyl DAB the reaction was found to proceed to completion, but with tert-butyl DAB the reaction stops at the formation of $Ru_2(CO)_5$ (tert-butyl IAE) except for extremely long reaction times [7]. The first step of this reaction sequence is given in equation 2.

$$Ru_2(CO)_6\,(DAB) + DAB \rightarrow Ru_2(CO)_5\,IAE + CO \quad (2)$$

Kinetic data for this reaction were obtained for iso-propyl DAB only. The reaction with tert-butyl DAB proceeded too slowly for study.

The experimental data were handled in the way described above. The results are given in Table 3. Again the experiment with an excess of iso-propyl DAB was carried out at a lower temperature (90° C) in order to slow down the reaction, as it was expected otherwise to be too fast for reaction monitoring. However, this was later realized to be unnecessary, as the kinetic data showed that the reaction rate is independent of the DAB concentration. The over-all order of the reaction as well as the order with respect to $Ru_2(CO)_6$ (iso-propyl DAB) are both equal to one, and consequently the order with respect to DAB is zero.

The reaction of $Ru_2(CO)_6$ (DAB) with a different DAB molecule was investigated for the two combinations that exist for iso-propyl DAB and tert-butyl DAB. The kinetic data obtained from these reactions could not be related to simple reaction orders, indicating a complicated reaction. Again a marked difference in reactivity is observed. The reaction of $Ru_2(CO)_6$ (tert-butyl DAB) with iso-propyl DAB is much slower ($t_{1/2} \approx$ 2600 min) than the reaction of $Ru_2(CO)_6$·(iso-propyl DAB) with tert-butyl DAB ($t_{1/2} \approx$ 160 min). Furthermore

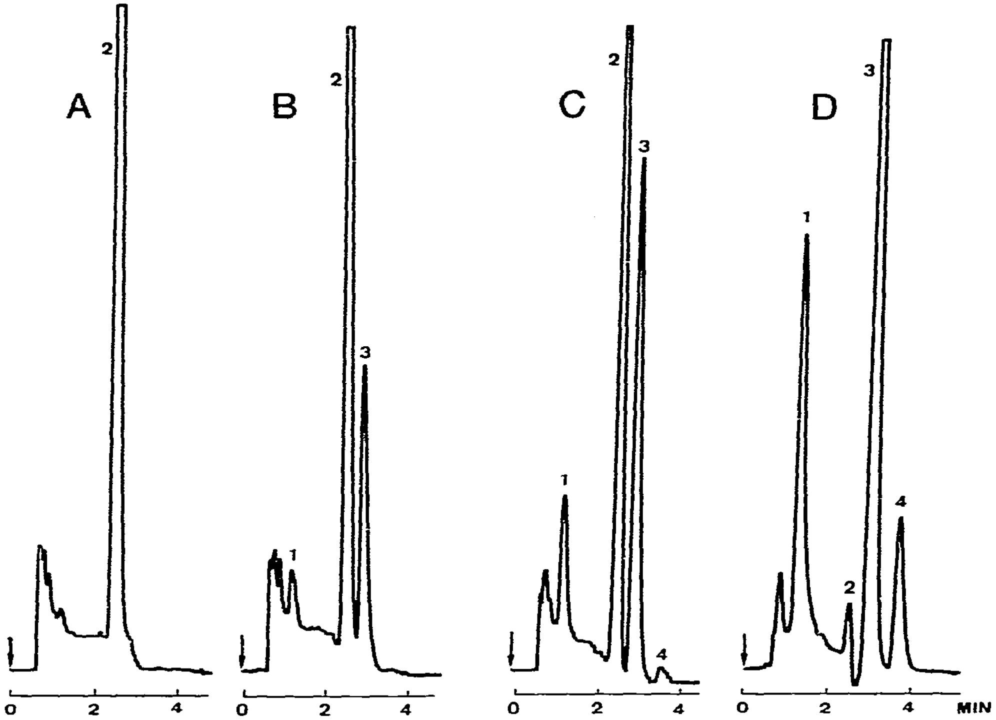

Fig. 5. Monitoring of the reaction of $Ru_2(CO)_6$(iso-propyl DAB) with tert-butyl DAB. Chromatograms of samples taken from the reaction at various times. A: after 20 sec; B: after 2 h; C: after 5 h; D: after 22 h. Peaks: 1 = $Ru_2(CO)_n$(iso-propyl IAE) ($n = 4$ or 5); 2 = $Ru_2(CO)_6$(iso-propyl IAE); 3 = $Ru_2(CO)_6$(tert-butyl IAE); 4 = $Ru_2(CO)_4$(iso-propyl $DAB)_2$. Stationary phase: Zorbax-ODS; mobile phase: 70% (v/v) THF in water + TEA (5 m*M*).

different products are obtained from these two reactions.

In Fig. 5 the progress of the reaction of $Ru_2(CO)_6$ (iso-propyl DAB) with tert-butyl DAB is shown by four chromatograms, given by samples taken from the reaction mixture at various times after starting the reaction. First of all the production of $Ru_2(CO)_6$ (tert-butyl DAB) (peak 3) is clearly demonstrated, as well as the production of $Ru_2(CO)_n$ (iso-propyl IAE) ($n = 4$ or 5) (peak 1) and $Ru_2(CO)_4$ (iso-propyl $DAB)_2$ (peak 4) (see also Fig. 1). The identification was based on the retention times of the pure substances. In the reaction of $Ru_2(CO)_6$-(tert-butyl DAB) with iso-propyl DAB no $Ru_2(CO)_6$ (iso-propyl DAB) showed up in the chromatograms, but $Ru_2(CO)_n$ (iso-propyl IAE) ($n = 4$ or 5) and $Ru_2(CO)_4$ (iso-propyl $DAB)_2$ were present. These results reveal that in both reactions an exchange of free and coordinated DAB has occurred. The fact that $Ru_2(CO)_6$ (tert-butyl DAB) but not $Ru_2(CO)_6$ (iso-propyl DAB) is found is caused by the large difference in reactivity between these compounds. $Ru_2(CO)_6$-(iso-propyl DAB) rapidly produces $Ru_2(CO)_n$ (iso-propyl IAE) ($n = 4$ or 5) and $Ru_2(CO)_4$ (iso-propyl $DAB)_2$, while the reaction of $Ru_2(CO)_6$ (tert-butyl DAB) with tert-butyl DAB hardly proceeds under these conditions.

The presence of other compounds was suspected from the chromatograms. Therefore samples were analysed by means of a chromatographic system with

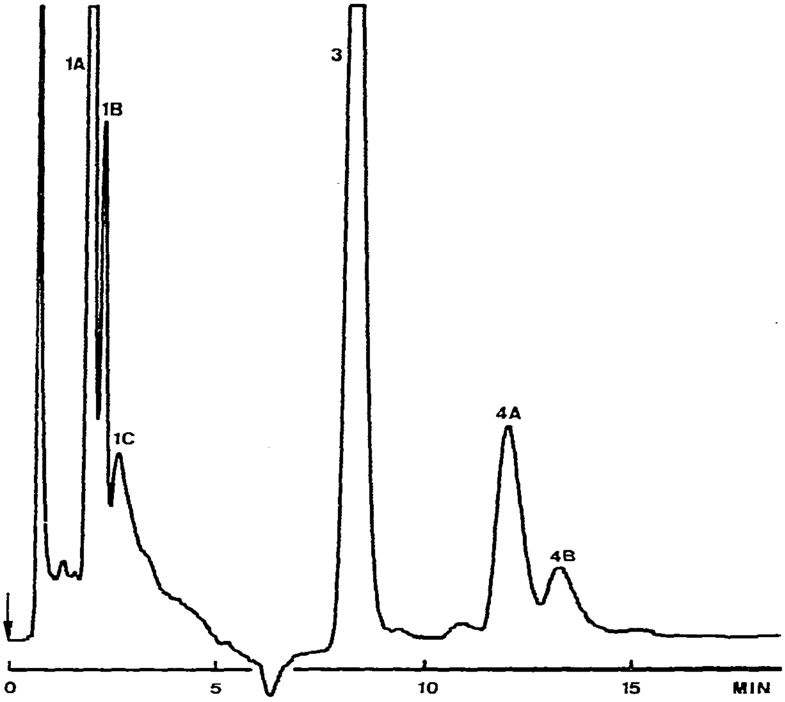

Fig. 6. Chromatogram of a sample from the reaction of $Ru_2(CO)_6$(tert-butyl DAB) with iso-propyl DAB taken after 47 h. Peaks: 3 = $Ru_3(CO)_6$(tert-butyl DAB); others are explained in the text. Stationary phase: Zorbax ODS; mobile phase: 55% (v/v) THF in water + TEA (5 m*M*).

a mobile phase consisting of 55% (v/v) THF in water. The THF concentration in the mobile phase was decreased in order to increase the retention and the resolution of the compounds present in the reaction mixture. Figs. 6 and 7 clearly demonstrate the improved resolution with this mobile phase composition. Peak 1 from Fig. 5 appears to consist of three substances, while peak 4 from Fig. 5 consists, in one case, of two substances. By comparison with the retention times of pure compounds it was concluded that peak 1a represents $Ru_2(CO)_4$-(iso-propyl IAE), that peak 1b represents $Ru_2(CO)_5$ (iso-propyl IAE) and that no $Ru_2(CO)_5$ (tert-butyl IAE) is present in these samples. The latter compound has a slightly, but significantly, larger retention time than peak 1c. From the fact that the retention time of peak 1c is between $Ru_2(CO)_n$ (iso-propyl IAE) ($n = 4$ or 5) and $Ru_2(CO)_5$ (tert-butyl IAE) it might be concluded that it represents a mixed IAE compound, containing iso-propyl DAB as well as tert-butyl DAB. Peak 4a was identified on the basis of its retention time as $Ru_2(CO)_4$ (iso-propyl $DAB)_2$. In the reaction of $Ru_2(CO)_6$ (tert-butyl DAB) with iso-propyl DAB another compound is formed (peak 4b in Fig. 6). The retention time of this compound is comparable to that of $Ru_2(CO)_4$ (iso-propyl $DAB)_2$, suggesting that it is also a $Ru_2(CO)_4(DAB)_2$ complex. From the fact that the retention time is larger than that of $Ru_2(CO)_4$ (iso-propyl $DAB)_2$ one can tentatively conclude that this compound is a mixed $Ru_2(CO)_4(DAB)_2$ complex,

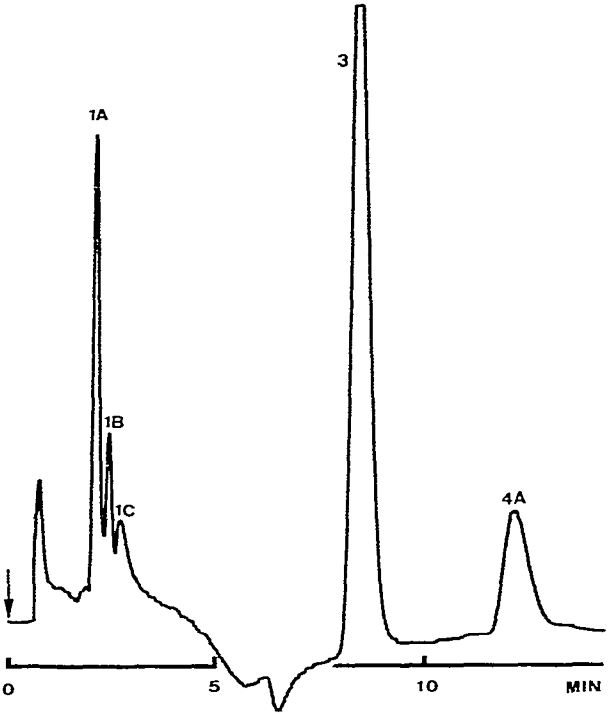

Fig. 7. Chromatogram of a sample from the reaction of $Ru_2(CO)_6$(iso-propyl DAB) with tert-butyl DAB taken after 25 h. Peak numbers and conditions as in Fig. 6.

containing iso-propyl DAB as well as tert-butyl DAB.

Although equation 2 points to a direct reaction of a DAB molecule with $Ru_2(CO)_6$(DAB), it appears, especially from the observed exchange of free and coordinated DAB, that the reaction is in fact very complicated. The kinetic data for the reaction of $Ru_2(CO)_6$(iso-propyl DAB) with iso-propyl DAB, which show that this reaction is first order in $Ru_2(CO)_6$(iso-propyl DAB) and zero order in free DAB, do not allow a firm proposal for the reaction mechanism, but they are not inconsistent with a proposed mechanism based upon series of analogous reactions [7]. However, comparison with analogous reactions can give a better insight into the observed exchange. $Fe_2(CO)_6$(cyclo-hexyl DAB) reacts with cyclo-hexyl DAB to form the mononuclear complex $Fe(CO)_3$(cyclohexyl DAB). Recently, mononuclear $Ru(CO)_3$(DAB) complexes have been obtained with bulky substituents attached to the imine nitrogen atoms (R = 2,6-xylyl; 2,4,6-mesityl; 2,4-dimethyl-pentyl-3) [13]. On the basis of these results an equilibrium is proposed between $M_2(CO)_6DAB$ and $M(CO)_3DAB$ according to equation 3.

$$M_2(CO)_6DAB \underset{-DAB}{\overset{+DAB}{\rightleftharpoons}} 2\,M(CO)_3DAB \qquad (3)$$

In the case of iron or when DAB with bulky substituents is used as the ligand, $M(CO)_3DAB$ is the thermodynamically favoured product, whereas with other

DAB molecules $Ru_2(CO)_6(DAB)$ is the stable product. This (proposed) reaction can also account for the exchange of coordinated and free DAB ligand according to equation 4.

$$Ru_2(CO)_6DAB + DAB' \rightleftharpoons Ru(CO)_3DAB + Ru(CO)_3DAB' \rightleftharpoons Ru_2(CO)_6DAB' + DAB \quad (4)$$

At present there is no explanation for the large differences in the reactivity of ligands which at first sight seem to be closely analogous.

Conclusion

A better insight into the reaction mechanism of the formation of binuclear ruthenium carbonyl complexes resulting from the reaction of $Ru_3(CO)_{12}$ with 1,4-diazabutadiene has been obtained by means of kinetic analysis with HPLC. The existence of intermediates in these reactions was not demonstrated directly by chromatographic analysis, but was indirectly derived from kinetic data, visual observations and formation of reaction products. Development of a chromatographic phase system, capable of analysing such intermediates and the use of oxygen-free mobile phases and oxygen-free sample pretreatment seem to be necessary if more information about the reaction mechanisms is to be obtained by HPLC.

A large difference in reactivity between iso-propyl DAB and tert-butyl DAB has been observed. This explains why the reaction shown in Fig. 1, stops after the formation of $Ru_2(CO)_5(IAE)$ when tert-butyl DAB is the ligand, while with iso-propyl DAB the reaction goes on to the formation of $Ru_2(CO)_4(DAB)_2$.

The exchange of free and coordinated ligands observed in the reaction of $Ru_2(CO)_6(DAB)$ with DAB′ explains the formation of $Ru_2(CO)_n$ (IAE) (n = 4 or 5) and $Ru_2(CO)_4(DAB)_2$ complexes containing two corresponding DAB units in this reaction [7]. In the experiments described in this paper, the complexes containing two corresponding DAB units are present in great excess over the mixed complexes containing two different DAB units, but this might not be so for other types of DAB molecules.

The formation of $Ru_2(CO)_6(DAB)$ in the reaction of $Ru_3(CO)_{12}$ with DAB proceeds via an intermediate. The rate-determining step in this reaction is the formation of this intermediate, this step being first order in $Ru_3(CO)_{12}$ and first order in DAB.

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