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HYDROGENOLYSIS OF HYDROCARBONS OVER SUPPORTED CATALYSTS DERIVED FROM METAL CARBONYL CLUSTERS *

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Summary

A comparison between the activities of silica-supported ruthenium, rhodium and platinum catalysts prepared from metal cluster compounds and their conventional analogues towards the activation of saturated hydrocarbons has been made. Ruthenium cluster-derived catalysts display greatly enhanced activity for the complete hydrogenolysis of straight chain aliphatic hydrocarbons to methane and provide a temperature advantage of 150° C relative to conventionally prepared ruthenium catalysts where only moderate hydrocarbon conversions are noted. The increased activity superficially correlates with the smaller metal crystallite sizes (15—20 Å) reproducibly obtainable using metal cluster compounds as catalyst precursors. The highly specific activity for the hydrogenolysis of C—C bonds in saturated hydrocarbons has been applied to the selective cleavage of the alkyl group in ethylbenzene, giving toluene and methane. Conversions of up to 30% ethylbenzene have been observed at 225° C and 1 atm using a $Ru_3(CO)_{12}/SiO_2$-based catalyst. The xylenes, particularly *o*-xylene, are much less susceptible to hydrogenolysis and, at 225° C, relative hydrocarbon destruction rates of 30 : 1 and 7 : 1 have been observed using mixed feeds of ethylbenzene/*o*-xylene and ethylbenzene/*p*-xylene, respectively. Such a catalyst system can, in principle, therefore provide a means of separating ethylbenzene from its mixtures with xylenes.

Introduction

The contributions of the late Paolo Chini to cluster chemistry have provided a great stimulus to scientists from widely differing disciplines — inorganic, organometallic and physical chemists, surface scientists, physicists and theo-

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* Dedicated to the memory of Professor Paolo Chini.

reticians (see for example the authors referred to in ref. 1). Many of the contributions to this Memorial Issue will contain details of the preparation, structural characterisation and properties of organometallic cluster compounds. To the industrial chemist, however, the ultimate value of this elegant scientific work is most likely to be realised in improving the understanding of catalytic reactions which, in turn, may lead to the development of new or more effective catalysts. It is hoped that the results described in this paper represent a small step towards such goals.

Developments are likely to arise either from the use of cluster compounds themselves as homogeneous catalysts or from their use as precursors to heterogeneous catalysts, by supporting on "inert" oxide supports followed by activation with either partial or complete removal of ligands. The extensive current interest in both these approaches, together with the inherent difficulties and likely future potential, have recently been reviewed [2,3]. It is clear from the more recent work of Paolo Chini that the relationship between the large metal carbonyl clusters and small metal crystallites is an area which was under active consideration by him [1,4].

As far as the development of heterogeneous catalysts derived from metal cluster compounds is concerned, such catalysts will be valuable only if they exhibit activities and selectivities which differ from those afforded by conventionally prepared materials. Unfortunately, it is a deficiency of much of the work so far reported that such comparisons have not been made. In order to rectify this situation we initiated a programme of work to compare the catalytic activity of supported metal clusters of known particle size (prepared by the impregnation and decomposition of metal cluster compounds on supports) with that displayed by catalysts containing the typical crystallite sizes available from conventional methods of heterogeneous catalyst preparation, namely halide impregnation or ion-exchange, followed by hydrogen reduction. Based on our previous conclusions [2] that significant differences in catalytic activities/selectivities are most likely to be observed in reactions which exhibit structure-sensitivity, for example the activation of C—C and C—H bonds in saturated hydrocarbons and the hydrogenation of carbon monoxide and nitrogen, we selected the reactions of hydrocarbons as the initial test reaction. This paper describes the results obtained from the reactions of n-heptane and hydrogen over various supported ruthenium, rhodium and platinum catalysts and the application of these results to provide a catalyst for the selective hydrogenolysis of ethylbenzene (in the presence of various xylene isomers) to toluene and methane.

Results and discussion

Catalyst preparation and characterisation

In order to avoid an unacceptably large synthetic effort we decided to use only those cluster compounds which are well-characterised and relatively easily synthesised. At the start of this work complexes of ruthenium, rhodium and platinum fulfilled these requirements most closely. The cluster compounds used and the precursor complexes to the "conventional" catalysts are listed in Table 1.

TABLE 1

HYDROCARBON TRANSFORMATION REACTIONS OVER SILICA-SUPPORTED CATALYSTS. CATALYST PRECURSOR COMPLEXES

Type	Ru	Rh	Pt
Cluster	$Ru_3(CO)_{12}$ $Ru_6C(CO)_{17}$	$Rh_4(CO)_{12}$ $Rh_6(CO)_{16}$	$[Et_4N]_2[Pt_3(CO)_6]_3$
Ion-exchange	$[Ru(NH_3)_5N_2]Cl_2$	$[Rh(NH_3)_5Cl]Cl_2$	
Impregnation	$RuCl_3 \cdot xH_2O$	$RhCl_3 \cdot xH_2O$	H_2PtCl_6

The cluster compounds were supported on silica (and γ-alumina) by impregnation from organic solvents using the method outlined in the Experimental section. The "conventional" catalysts, produced by ion-exchange and halide-impregnation were usually supported from aqueous solutions. After drying, all materials were activated/reduced by treatment with a nitrogen/hydrogen mixture at elevated temperatures for several hours.

Catalyst precursors and activated catalysts were characterised by various combinations of physical techniques including infrared and Raman spectroscopy, hydrogen and carbon monoxide chemisorption, and electron microscopy. Vibrational spectroscopy was applied primarily to the characterisation of the initial interaction between the cluster compound and the support. For example, using Raman spectroscopy it was shown that $Ru_3(CO)_{12}$, $Ru_6C(CO)_{17}$ and $Rh_6(CO)_{16}$ were physically adsorbed unchanged onto the surface of silica. In contrast, both $Rh_4(CO)_{12}$ and $(Et_4N)_2[Pt_3(CO)_6]_3$ appeared to react on contact with silica. Infrared spectroscopic evidence suggested that $Rh_4(CO)_{12}$ interacts with the surface hydroxyl groups of silica, fragments and produces dimeric species chemically bonded through rhodium—oxygen bonds to the silica surface [2]. In the case of the platinum compound, red-violet solutions of $[Pt_3(CO)_6]_3^{2-}$ in tetrahydrofuran change colour immediately on addition of silica, irrespective of the pretreatment of the silica (e.g., degassing at room temperature, 350 or 550°C) and even under carbon monoxide pressure. The silica assumes a green colour and the supernatant liquid becomes clear. This colour change and the shift in $\nu(CO)$ absorptions suggests a change in nuclearity from $[Pt_3(CO)_6]_3^{2-}$ to $[Pt_3(CO)_6]_5^{2-}$ on contact with silica. This behaviour is consistent with the known extreme sensitivity of these clusters towards changes in acidic/basic environments [5].

For characterisation of the activated catalysts greatest emphasis has been placed on the use of transmission electron microscopy for the measurement of metal particle size distributions both before and after catalyst testing. For example, typical metal particle size distributions for catalysts prepared by the different methods are summarised in Table 2.

From these results it is clear that the use of cluster compounds as catalyst precursors leads to the formation of particles of smaller crystallite size than those obtained from conventional methods of catalyst preparation. However, it is equally clear that significant aggregation of the initial M_3, M_4 and M_6 cluster units has occurred during the overall supporting/activation process.

TABLE 2

METAL PARTICLE SIZES (Å) OF SILICA-SUPPORTED METAL CATALYSTS MEASURED BY ELECTRON MICROSCOPY

Ruthenium catalysts	Ru (%)	Particle size [a] (Å)	Rhodium catalysts	Rh (%)	Particle size [a] (Å)
$Ru_3(CO)_{12}$	1.7	15—20	$Rh_4(CO)_{12}$	0.3	—
$Ru_6C(CO)_{17}$	1.4	15—20	$Rh_6(CO)_{16}$	0.6	25—30
$[Ru(NH_3)_5N_2]Cl_2$	2.3	25—30	$[Rh(NH_3)_5Cl]Cl_2$	0.5	30—40
$RuCl_3 \cdot xH_2O$	0.5	35—45	$RhCl_3 \cdot xH_2O$	0.4	40—60

[a] Particle sizes quoted are the peaks of the distributions in the samples measured.

Activation of saturated hydrocarbons over supported ruthenium, rhodium and platinum catalysts

The test reaction chosen for study was the activation of saturated hydrocarbons. This is a reaction which is known to be dependent upon metal particle size, i.e. it is structure-sensitive [6], and one which is directly relevant to processes occurring in the catalytic reforming of hydrocarbons, for example, the dehydrocyclisation of n-heptane to aromatic products such as toluene. The reaction is normally carried out in the presence of hydrogen under conditions where hydrogenolysis of the hydrocarbon is also a likely competing reaction. In this section we describe the results of a study of the catalytic activity of silica-supported Ru, Rh and Pt clusters and a comparison with their conventionally prepared counterparts towards the reactions of n-heptane and hydrogen.

Ruthenium catalysts

A nitrogen/hydrogen/n-heptane mixture (volume ratio 100/10/1) at atmospheric pressure was passed over a silica-supported ruthenium catalyst obtained from $Ru_3(CO)_{12}$. The temperature was increased in 50°C increments and the hydrocarbon products monitored by gas chromatography. The results (see Table 3) demonstrate that heptane is completely hydrogenolysed to methane at 250°C with no evidence for the formation of any dehydrocyclisation products.

TABLE 3

REACTIONS OF n-HEPTANE AND HYDROGEN OVER $Ru_3(CO)_{12}/SiO_2$ CATALYST [a]

Temp. (°C)	n-Heptane conversion (%)	Products
100	<1	
150	7	
200	87	$CH_4 + C_2H_6$
250	100	CH_4

[a] Catalyst precursor:	$Ru_3(CO)_{12}$ impregnated from toluene on to Grace Davison 952 silica.
Method of activation:	N_2/H_2 (4/1) at 350°C for 4 h.
Metal content:	1.0%
H_2/n-heptane feed ratio:	10/1 by volume
Pressure:	0 psig.
LHSV:	0.3 vol. substrate/vol. catalyst/h.

A comparison between the activities of various supported ruthenium catalysts derived from $Ru_3(CO)_{12}$, $Ru_6C(CO)_{17}$, $[Ru(NH_3)_5N_2]^{2+}$ and $RuCl_3 \cdot x\ H_2O$ and activated/reduced under the same conditions is presented in Table 4. There is clearly a very significant difference between the cluster derived and conventional catalysts. With the former n-heptane is completely hydrogenolysed to methane at 200—250° C, whereas temperatures greater than 350° C are required to give 78% and 25% conversions over the $[Ru(NH_3)_5N_2]Cl_2$ and $RuCl_3 \cdot x\ H_2O$ based catalysts, respectively.

The new catalysts show a very high selectivity towards methane formation. In the temperature range 200—550° C no unsaturated derivatives, e.g. ethylene, are formed and the only other product observed, in minor amounts, is ethane. In the early stages of this work the gas chromatographic method of analysis did not distinguish C_1—C_3 hydrocarbons and some of the product distributions are therefore quoted in Table 4 as a combined C_1—C_3 fraction. Within this fraction the major GC peak is always methane and C_2, C_3 products appear as shoulders on the side of the methane trace.

With all the ruthenium catalysts studied the dehydrocyclisation activity is low. The only evidence of skeletal isomerisation (to 2- and 3-methylhexanes) or aromatisation (to benzene and toluene) is shown by the $[Ru(NH_3)_5N_2]Cl_2$- and $RuCl_3 \cdot xH_2O$-derived catalysts at temperatures of 300 and 350° C respectively. Here the halide-impregnated catalyst, although with a considerably lower metal content, yields a significantly higher proportion of benzene and toluene. However, the overall selectivity is still low in comparison with the predominant hydrogenolysis reaction to methane. The increased activity for hydrogenolysis to methane observed with the cluster-derived catalysts bears at least a superficial relationship to the decreased metal crystallite size.

Rhodium catalysts

A comparison was also made between silica-supported rhodium catalysts prepared in an analogous manner to the ruthenium series. The measured heptane conversions and product distributions for the various catalysts are summarised in Table 5. Similar overall trends to those noted with the ruthenium catalysts are observed here, although the differences are not so dramatic. For example, catalysts A—C all show some activity towards n-heptane in the temperature range 200—250° C whereas the "conventional" $RhCl_3$-based catalyst D does not promote any reaction below 250° C. Although the conversions over rhodium are considerably lower (10—35% at 250° C, compared with 100% over a ruthenium cluster-based catalyst) the overall product distribution is similar and the predominant reaction hydrogenolysis.

A comparison of the results obtained with catalysts A1 and A2 shows that the higher metal loading is reflected in a considerable increase in conversion of n-heptane. However, the product distribution, measured over catalyst A2 at 300° C and 87% conversion, contains significant proportions of hydrocarbons other than methane, particularly ethane. This contrasts with the behaviour of analogous Ru/SiO_2 catalysts derived from $Ru_3(CO)_{12}$ where, under comparable conditions, methane was the sole product of the reaction.

Small amounts of 2- and 3-methylpentanes and the dehydrocyclisation products benzene and toluene are also observed over all the rhodium catalysts at

(Continued on p. 164)

TABLE 4

HYDROGENOLYSIS OF n-HEPTANE OVER SILICA-SUPPORTED RUTHENIUM CATALYSTS. CONVERSIONS AND PRODUCT DISTRIBUTIONS AS FUNCTIONS OF CATALYST AND TEMPERATURE [a]

Catalyst	Ru (%)	Particle size (Å)	Temp. (°C)	Conversion (%)	Product distribution (%)							
					C_1	C_2	C_3	C_4	C_5	C_6	B	T
A1	1.7	15–20	200	90.0	94.0		1.0	1.0	1.5	2.0	—	—
			250	100	100		—	—	—	—	—	—
A2	2.3	ca. 20	200	100	100		—	—	—	—	—	—
A3	1.2	—	200	90.0	94.0	5.8	—	—	—	—	—	—
			225	95.0	97.0	2.0	tr	tr	—	—	—	—
B	1.4	15–20	250	96.0	← 90.4 →			5.0	2.5	1.3	—	—
			300	100	100		—	—	—	—	—	—
C	2.3	25–30	250	26.0	← 70.0 →			10.0	10.0	12.0	—	—
			350	78.5	← 82.0 →			6.0	4.0	5.0	1.0	0.5
D	0.5	35–45	250	18.0	← 69.0 →			10.5	10.6	8.8	—	—
			350	22.2	← 80.0 →			4.2	2.2	2.3	7.2	3.0

[a] Method of catalyst activation: N_2/H_2 (4/1) at 350°C for 4 h.
H_2/n-heptane feed ratio: 10/1 by volume
Pressure: 0 psig.
LHSV: 0.3 vol. substrate/vol. catalyst/h.

Catalyst precursors: A, $Ru_3(CO)_{12}$; B, $Ru_6C(CO)_{17}$; C, $[Ru(NH_3)_5N_2]Cl_2$; D, $RuCl_3 \cdot xH_2O$.

TABLE 5

HYDROGENOLYSIS OF n-HEPTANE OVER SILICA-SUPPORTED RHODIUM CATALYSTS. CONVERSIONS AND PRODUCT DISTRIBUTIONS AS FUNCTIONS OF CATALYST AND TEMPERATURE [a]

Catalyst	Rh (%)	Particle size (Å)	Temp. (°C)	Conversion (%)	Product distribution (%)												
					C_1	C_2	C_3	C_4	i-C_5	C_5	2MP	3MP	C_6	B	T	2MH	3MH
A1	0.3		250	11.4	51.7	11.1	8.2	—	13.0	tr	tr	16.0			—	—	—
			275	19.0		47.4	13.2	8.4	7.0	12.3	1.3	0.6	9.8	tr	tr	tr	tr
			350	40.0	← 79.0 →			4.6	tr	3.2	—	—	2.4	7.0	3.2	—	—
A2	2.3		250	35.5	59.6	20.7	6.9	5.0	—	4.7	—	—	3.0	—	—	—	—
			300	87.3	71.2	18.2	5.6	2.6	—	1.5	tr	tr	0.7	tr	tr	tr	tr
B	0.6	25—30	250	8.0													
			275	13.4	← 54.1 →			11.6	1.1	10.1	1.0	tr	20.7	1.3	tr	tr	tr
			350	33.0	← 76.2 →			5.0	tr	3.9	tr	tr	4.0	6.9	3.5	tr	tr
C	0.5	30—40	250	12.0	← 69.4 →			5.6	—	8.6	—	—	15.8	—	—	—	—
			275	14.0	← 75.44 →			6.1	1.0	6.9	tr	tr	10.6	tr	—	tr	tr
			350	14.0	← 82.9 →			3.1	0.4	2.0	—	—	2.1	6.5	3.0	—	—
D	0.4	40—60	250	5.5	38.0		8.9	8.9	—	10.5	—	—	33.4	—	—	—	—
			275	7.2	70.0		5.5	3.5	—	6.0	—	—	15.0	—	—	—	—
			350	14.2	← 56.5 →			8.3	1.6	8.3	tr	tr	11.5	7.0	6.8	—	—

[a] Method of catalyst activation: N_2/H_2 (4/1) at 350°C for 4 h.
H_2/n-heptane feed ratio: 10/1 by volume
Pressure: 0 psig
LHSV: 0.3 vol. substrate/vol. catalyst/h

Catalyst precursors: A, $Rh_4(CO)_{12}$; B, $Rh_6(CO)_{16}$; C, $[Rh(NH_3)_5Cl]Cl_2$; D, $RhCl_3 \cdot xH_2O$. MP = methylpentane, MH = methylhexane, B = benzene, T = toluene.

higher temperatures. This contrasts with the ruthenium series where the cluster-derived catalysts gave no detectable dehydrocyclisation products. These products are initially detected at lower temperatures e.g., 275° C, over the rhodium cluster catalysts whereas temperatures of 325° C are required before their formation is observed over catalyst D. The final selectivity of ca. 7% to benzene formation at 350° C is similar throughout the series.

The production of benzene may occur via two alternative mechanistic pathways, viz., hydrogenolysis of heptane to hexane followed by dehydrocyclisation, or dehydrocyclisation of heptane to toluene followed by hydrogenolysis to benzene. The results indicate that both mechanisms are operative. The formation of 2- and 3-methylpentanes seems most likely to occur through dehydrocyclisation followed by ring hydrogenolysis. An alternative direct isomerisation pathway is less probable because it would require acidic sites in order to function via a carbonium mechanism and these are not available on silica. A comparison between rhodium and ruthenium catalysts shows that in the case of the former the overall conversions are significantly lower. Although increased dehydrocyclisation activity is observed with rhodium, the predominant reaction is still hydrogenolysis to lower hydrocarbons. The product spectrum is rather wider and significantly larger quantities of C_2—C_6 fragments are detected than in the case of ruthenium.

Platinum catalysts

A silica-supported platinum catalyst prepared from $(Et_4N)_2[Pt_3(CO)_6]_3$ was activated at 350° C in N_2/H_2 (4/1) for 6 h and tested in the n-heptane/hydrogen reaction. This material, containing 0.5% Pt, gives n-heptane conversions of 24 and 45% at 200 and 250° C, respectively. In contrast to the results obtained from ruthenium and rhodium catalysts, dehydrocyclisation activity is noted at temperatures as low as 200° C and at 250° C benzene (3.5%), toluene (1.5%) and traces of 2- and 3-methylpentanes are observed in the product. However, the predominant reaction is hydrogenolysis with 74 and 65% of the products present as C_1—C_3 saturated hydrocarbons at 200 and 250° C, respectively.

The hydrogenolysis of alkylaromatics over silica-supported ruthenium cluster catalysts

The key point to emerge from the preceding work is that catalysts derived from cluster compounds show significantly higher activity relative to conventionally prepared materials for the hydrogenolysis of hydrocarbons. In the case of ruthenium this effect can provide the opportunity to operate at as much as 150° C below the temperature necessary to give even moderate activity over conventional catalysts.

A potential application of the observed high activity for carbon—carbon bond cleavage lies in the selective hydrogenolysis of ethylbenzene to toluene and methane. In alkylaromatic molecules the strongest bond is the Ar—C bond. This fact gives rise to the possibility that, in addition to the obvious reactions such as partial hydrogenolysis of ethylbenzene to benzene and methane and total hydrogenolysis to methane, it might be possible to obtain high selectivities to toluene. Such a reaction is of interest for the following reasons. The aromatic C_8 fraction obtained from the cracking of crude oil contains the various xylene isomers and ethylbenzene. Separation into individual components is difficult because of the close similarity in boiling points (136—144° C). Some catalysts for the subsequent downstream process — isomerisation of the mixed xylenes to *p*-xylene — are susceptible to poisoning by the presence of ethylbenzene. The selective removal of ethylbenzene from mixed xylene streams is therefore a desirable goal.

Hydrogenolysis of ethylbenzene

In the reaction between ethylbenzene and hydrogen several alternative pathways are possible, ranging between the highly selective hydrogenolysis of the alkyl side chain to toluene and methane and the completely non-selective rupture of the molecule to give methane alone (see Fig. 1). From thermodynamic considerations simple hydrogenation of the aromatic ring is favoured at low temperatures and complete breakdown of the molecule to methane at high temperatures. Selective hydrogenolysis, if at all attainable, is likely to occur at intermediate temperatures.

Table 6 and Fig. 2 summarise and illustrate the ethylbenzene conversions and product distributions measured as a function of temperature, using a silica-supported ruthenium catalyst derived from $Ru_3(CO)_{12}$ and a hydrogen to hydrocarbon feed ratio of 10 : 1. At temperatures of ≤200° C, as predicted, supported ruthenium acts as an effective hydrogenation catalyst for the aromatic ring and the major product observed is ethylcyclohexane. This process is insignificant above 200° C (in fact the reverse reaction becomes predominant) and then hydrogenolysis of the alkyl side chain to toluene and methane becomes the predominant reaction in the temperature range 200—250° C. A maximum

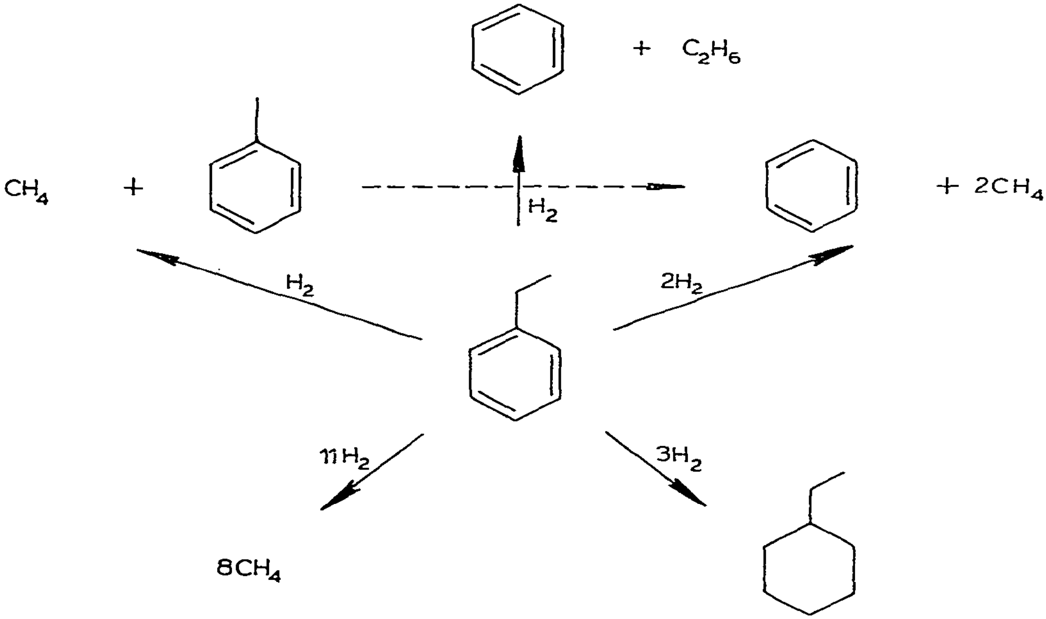

Fig. 1. Ethylbenzene/hydrogen system: possible reaction pathways.

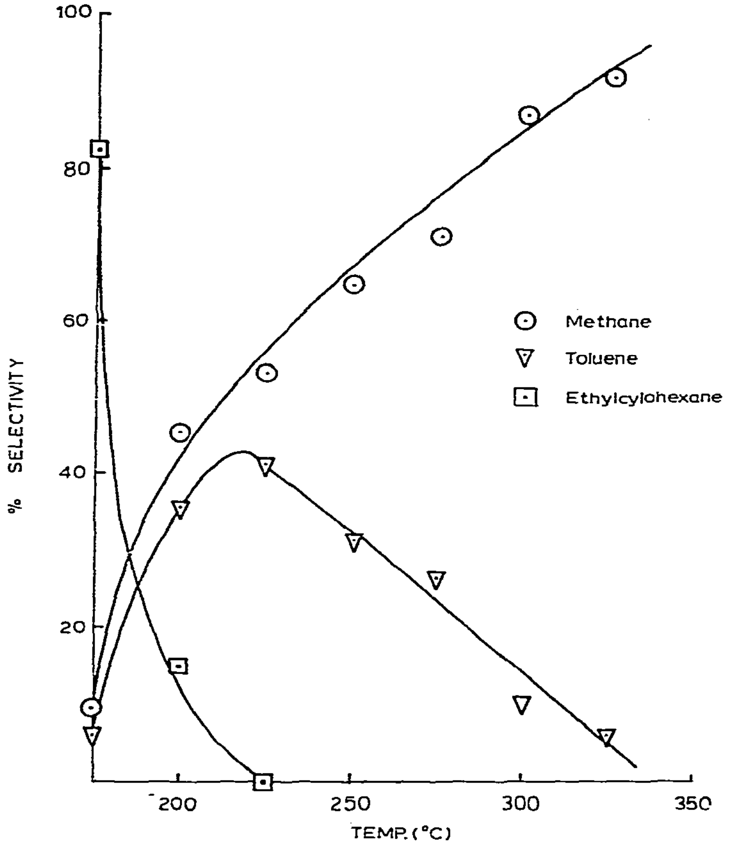

Fig. 2. Ethylbenzene hydrogenolysis: product distribution vs. temperature.

TABLE 6

HYDROGENOLYSIS OF ETHYLBENZENE. CONVERSION AND PRODUCT DISTRIBUTION AS A FUNCTION OF TEMPERATURE [a]

Temp. (°C)	Ethylbenzene conversion (%)	Product distribution (%)				
		Methane	Ethane	Benzene	Toluene	Ethylcyclohexane
175	27.1	9.3	0	0	5.7	82.3
200	16.0	45.2	1.5	0	35.4	15.0
225	30.0	52.9	1.7	0.7	41.0	0
250	31.0	64.8	2.4	1.8	31.0	0
275	—	71.0	1.8	1.8	26.0	0
300	41.0	87.0	1.1	1.5	10.5	0
325	52.7	92.0	0.5	1.1	6.4	0

[a] Catalyst precursor: $Ru_3(CO)_{12}$ impregnated from toluene on to Grace Davison 952 silica.
Method of activation: N_2/H_2 (4/1) at 320°C for 4 h.
Metal content: 2.9%.
Pressure: 0 psig
H_2/ethylbenzene feed ratio: 10/1 by volume.
LHSV: 0.1 vol. substrate/vol. catalyst/h.

toluene/(benzene + toluene) selectivity of 98% at 30% ethylbenzene conversion is observed at 225°C.

Above 250°C the total ethylbenzene conversion increases significantly but with a concomitant decrease in selectivity to products in which the aromatic ring remains intact. However, at all temperatures benzene is only observed as a minor product. Methane formation increases sharply as the selectivity to toluene declines and this is due to fragmentation of both the alkyl side chain and the aromatic ring itself at higher temperatures. At 325°C the product distribution from 53% ethylbenzene conversion contains 92% methane. No other saturated aliphatic hydrocarbons (e.g. C_2—C_6) are formed; this would be expected from the preceding work on the hydrogenolysis of hydrocarbons to methane over the same type of catalyst.

It is clear that, under appropriate reaction conditions, the highly selective hydrogenolysis of ethylbenzene into toluene and methane can be achieved over supported ruthenium cluster catalysts at moderate conversions.

Hydrogenolysis of o-xylene and p-xylene

When *o*-xylene rather than ethylbenzene is used as feed a much lower level of reactivity is immediately apparent, as evidenced by a comparison of the conversions listed in Table 7 with those in Table 6. Only minor (<10%) conversions are noted at 200—250°C with slightly higher activity (18%) at 300°C. The overall selectivity pattern is however similar with the predominance of ring hydrogenation at 200—225°C and non-selective hydrogenolysis to methane at 300°C.

p-Xylene, however, is found to be significantly more reactive than *o*-xylene (see Table 8), and at 225°C the respective conversions for ethylbenzene, *o*-xylene and *p*-xylene are 30.0, <1.0 and 17.9%. There are some selectivity differences, however, and, whereas the 30% conversion of ethylbenzene yields, essentially, just toluene and methane, the product distribution from the 17.9%

TABLE 7

HYDROGENOLYSIS OF *o*-XYLENE. CONVERSION AND PRODUCT DISTRIBUTION AS A FUNCTION OF TEMPERATURE [a]

Temp. (°C)	*o*-Xylene conversion (%)	Product distribution (%)				
		Methane	Ethane	Benzene	Toluene	DMCH
200	9.0	0	0	0	0	99.0
225	<1.0	0	0	0	0	99.0
250	7.6	79.7	0	0	20.3	0
275	—	85.7	0	0	14.2	0
300	18.2	84.4	1.0	3.6	10.4	0

[a] Catalyst precursor:	$Ru_3(CO)_{12}/SiO_2$.
Method of activation:	N_2/H_2 (4/1) at 320°C.
Metal content:	2.9%.
Pressure:	0 psig.
H_2/*o*-xylene feed ratio:	10/1 by volume.
LHSV:	0.1 vol. substrate/vol. catalyst/h.

DMCH = *cis*- and *trans*-1,2-dimethylcyclohexane.

TABLE 8

HYDROGENOLYSIS OF *p*-XYLENE. CONVERSION AND PRODUCT DISTRIBUTION AS A FUNCTION OF TEMPERATURE [a]

Temp. (°C)	*p*-Xylene conversion (%)	Product distribution (%)					
		Methane	Ethane	Propane	Benzene	Toluene	DMCH
200	15.1	4.7	0	0	0	18.9	76.2
225	17.9	17.2	1.3	0	0	45.4	35.8
250	36.6	72.6	2.7	0.8	0.3	20.0	2.0
275	52.9	83.4	2.7	0.9	0.9	12.2	0.8
300		>90					

[a] Catalyst precursor: $Ru_3(CO)_{12}/SiO_2$.
Method of activation: N_2/H_2 (4/1) at 320°C.
Metal content: 2.9%.
H_2/*p*-xylene feed ratio: 10/1 by volume.
LHSV: 0.1 vol. substrate/vol. catalyst/h.

DMCH = *cis*- and *trans*-1,4-dimethylcyclohexane.

conversion of *p*-xylene comprises toluene, methane and 1,4-dimethylcyclohexanes. Thus, as with ethylbenzene, the predominant feature in the low temperature regime is hydrogenation of the aromatic ring but, with *p*-xylene, this pathway (to *cis*- and *trans*-1,4-dimethylcyclohexanes) is still significant at 225° C. At temperatures above 250° C the hydrogenation activity is insignificant and non-selective hydrogenolysis predominates with the product spectrum comprising 90% methane at 300° C. At these temperatures *p*-xylene is more reactive than ethylbenzene. Reduction of the hydrogen : *p*-xylene feed ratio from 10 : 1 to 2 : 1 results in a significant decrease in conversion, particularly at high temperatures, although there is little effect on the product distribution. With *p*-xylene there is a much greater overlap in temperature regimes for ring hydrogenation, selective hydrogenolysis, and non-selective hydrogenolysis to methane than is observed with either *o*-xylene or ethylbenzene.

Hydrogenolysis of ethylbenzene, o-xylene and p-xylene mixtures

From the preceding results it is clear that selective hydrogenolysis of ethylbenzene to toluene and methane is in principle attainable, but the reaction conditions will require careful control to avoid significant destruction of *p*-xylene. It was clearly necessary to perform competitive experiments with mixed feed streams and representative results are summarised in Tables 9 and 10. Catalyst A is $Ru_3(CO)_{12}$-based whereas B is a conventional silica-supported ruthenium catalyst prepared from $RuCl_3 \cdot x\ H_2O$. The two catalysts are directly comparable in terms of metal loading. As is apparent from the table there are both similarities and differences between these two catalysts. For example, at 225° C there is significant conversion of ethylbenzene with little or no reaction of *o*-xylene over both catalysts, although the activity of the cluster-derived catalyst A exceeds that of B by a factor of 3. This relative difference in activity decreases slightly at higher temperatures and this may be associated with greater non-selective hydrogenolysis exhibited by B under these conditions.

With both catalysts at temperatures above 250° C non-selective hydrogenolysis of the alkyl side-chain and the aromatic ring itself combine to yield meth-

TABLE 9

HYDROGENOLYSIS OF ETHYLBENZENE AND *o*-XYLENE MIXTURES. CONVERSIONS AND PRODUCT DISTRIBUTIONS AS A FUNCTION OF TEMPERATURE [a]

Catalyst precursor	Temp. (°C)	Conversion (%)		Product distribution (%)					
		EB	*o*-Xylene	CH_4	C_2H_6	Benzene	Toluene	DMCH	ECH
A	175	37.6	15.1	2.8	0	0	3.3	0	93.4
	200	37.0	7.6	11.7	0	0	8.8	3.4	76.1
	225	30.0	1.0	38.3	0	0	29.6	3.8	28.2
	250	41.6	10.0	58.4	2.0	3.0	36.7	0	0
	275	43.3	11.0	64.6	2.1	2.6	30.7	0	0
B	175	9.2	0						
	200	8.7	2.0	41.0	0	0	58.0	0	0
	225	8.6	0	48.0	0	0	52.0	0	0
	250	16.7	4.5	49.0	0	0	51.0	0	0
	275	18.0	12.0	59.0	0	0	41.0	0	0
	300	25.8	16.7	61.0	0	0	39.0	0	0

[a] H_2/hydrocarbon feed ratio = 10/1.
Ethylbenzene/*o*-xylene feed ratio = 1.2/1.
LHSV: 0.1 vol. (total substrate)/vol. catalyst/h.

DMCH = *cis*- and *trans*-1,2-dimethylcyclohexane, ECH = ethylcyclohexane. Catalyst precursors: A, $Ru_3(CO)_{12}/SiO_2$ (2.2% Ru); B, $RuCl_3 \cdot xH_2O/SiO_2$ (2.1% Ru).

ane as the main reaction product. In addition to the lower overall activity displayed by B, this halide-based catalyst is inactive for hydrogenation of the aromatic ring and no ethyl- or dimethyl-cyclohexanes are observed in the temperature range 200—300° C. In contrast, hydrogenation of ethylbenzene to ethylcyclohexane is the predominant reaction at low temperatures over the $Ru_3(CO)_{12}$-derived catalyst. This difference in hydrogenation/hydrogenolysis activ-

TABLE 10

HYDROGENOLYSIS OF ETHYLBENZENE AND *p*-XYLENE MIXTURES. CONVERSIONS AND PRODUCT DISTRIBUTIONS AS A FUNCTION OF TEMPERATURE [a]

Temp. (°C)	Conversion (%)		Product distribution (%)					
	Ethylbenzene	*p*-Xylene	Methane	Ethane	Benzene	Toluene	ECH	DMCH
200	30.3	12.4	44.7	0	0	28.5	26.8	tr
225	23.4	3.4	64.2	0	0	35.8	tr	tr
250	25.5	3.4	73.8	2.0	0.1	24.0	0	0
275	29.2	8.0	78.5	1.2	1.5	18.8	0	0
300	43.8	28.0	91.5	1.3	0.5	6.7	0	0

[a] Catalyst precursor: $Ru_3(CO)_{12}/SiO_2$.
Method of activation: N_2/H_2 (4/1) at 330°C for 4 h.
Metal content: 1.9%.
Pressure: 0 psig.
H_2/hydrocarbon feed ratio: 10/1 by volume.
Ethylbenzene/*p*-xylene feed ratio: 16/1.
LHSV: 0.1 vol. (total substrate)/vol. catalyst/h.
ECH = ethylcyclohexane, DMCH = *cis*- and *trans*-1,4-dimethylcyclohexane.

ity presumably reflects differences in the respective metal crystallite sizes. Clearly, highly selective hydrogenolysis of ethylbenzene to toluene and methane is attainable over both catalysts at 225° C in the presence of approximately equimolar amounts of *o*-xylene.

Competitive experiments between ethylbenzene and *p*-xylene using a $Ru_3(CO)_{12}/SiO_2$ catalyst (Table 10) show similar trends, although, as noted previously, *p*-xylene displays higher reactivity than *o*-xylene. At 225° C a 23% conversion of ethylbenzene and 3% conversion of *p*-xylene to toluene and methane is observed. The corresponding figures for ethylbenzene and *o*-xylene are 30.0 and 1.0%, respectively. The inclusion of ethylbenzene in the feed stream has completely suppressed the ring hydrogenation activity previously noted with *p*-xylene alone at 225° C. This suggests that ethylbenzene is competing for, and blocking, the active catalytic sites for ring hydrogenation. Although the overall conversions at 250° C are similar to those at 225° C the reaction is less selective, and relatively larger amounts of methane are produced. At higher temperatures the non-selective hydrogenolysis of both ethylbenzene and *p*-xylene to methane predominates. In mixed ethylbenzene/*p*-xylene streams, providing the conditions are carefully controlled, an ethylbenzene/*p*-xylene destruction ratio of 7/1 can be achieved at 225° C.

Conclusions

In this work we have demonstrated that catalysts derived from cluster compounds are significantly more active than their conventionally prepared counterparts for the cleavage of carbon—carbon bonds in saturated hydrocarbons. With ruthenium catalysts, this effect can provide the oppportunity to operate at as much as 150° C below the temperatures necessary to give only moderate activity over conventional catalysts. The ruthenium cluster-derived materials are also considerably more selective for the formation of methane under directly comparable conditions.

The origin of the enhanced catalytic activity displayed by these catalysts is at present uncertain. Superficially it appears to be related to the decreased metal crystallite size reproducibly obtainable with the cluster-derived catalysts. However, other possibilities could also account for the effects. For example, an important factor could be the predominance of different crystal faces from those found in bulk metal catalysts (i.e. of particle sizes >25 Å). Likewise, at the very small metal crystallite sizes we may not be dealing with pure metal but possibly interstitial carbides, nitrides or hydrides. More detailed work is necessary in order to investigate and distinguish between these possibilities.

At this stage it is difficult to assess the mechanistic significance of the results. The commonly accepted mechanism for the hydrogenolysis of alkanes (particularly ethane) involves chemisorption of the hydrocarbon on the metal (with dissociation of C—H bonds) to form an unsaturated surface species, followed by a rate-limiting irreversible rupture of some or all of the carbon—carbon bonds with subsequent rehydrogenation of the fragments to lower hydrocarbons [7—9]. The extremely high specificity for methane production over the cluster-derived catalysts suggests that once chemisorption has occurred the carbon—carbon bond breaking process is extremely rapid. However, on the present data it is not possible to distinguish between selective and sequential terminal attack of the alkane, e.g.,

$$CH_3(CH_2)_5CH_3 + H_2 \rightarrow CH_3(CH_2)_4CH_3 + CH_4 \text{ etc.}$$

and essentially complete rupture of the carbon skeleton with desorption of the fragments as methane. Based on additional evidence from the use of lower hydrogen/n-heptane feed ratios, which show essentially constant selectivity to methane but at very significantly reduced conversions, it seems likely that the latter effect predominates.

We have also shown that the highly specific activity of the ruthenium cluster-derived catalysts for the hydrogenolysis of carbon—carbon bonds in saturated hydrocarbons can be applied to the selective cleavage of carbon—carbon bonds in the alkyl side chains of substituted aromatic hydrocarbons. Thus, with an appropriate choice of reaction conditions, ethylbenzene may be selectively hydrogenolysed to toluene and methane. Such a catalyst system could, in principle, be used to selectively remove ethylbenzene from mixed xylene streams with only minor conversions of the xylenes into toluene (or benzene) and methane. Under more forcing reaction conditions, i.e., higher temperatures, destructive hydrogenolysis of the aromatic rings in ethylbenzene and the xylenes occurs, giving high yields of methane. The metal cluster-derived catalysts are again significantly more active than their conventionally prepared counterparts, lending support to the belief that this could be the general behaviour of such materials. The differences between the relative reactivities of ethylbenzene and *o*- and *p*-xylene towards hydrogenolysis may be rationalised in terms of both the relative bond strengths and steric effects. For example, the strength of the -CH_2—CH_3 bond in ethylbenzene is ca. 72 kcal/mol whereas that of the aromatic—alkyl bond is ca. 100 kcal/mol [10]. Steric effects provide the most likely explanation for the activity differences between *o*- and *p*-xylene. In the former case the presence of adjacent methyl groups on the aromatic ring probably hinder adsorption and reaction on the surface of the catalyst.

At the relatively high catalyst activation temperatures used in the work described here the molecularity of the starting cluster compound is destroyed, aggregation/sintering occurs and at 350°C small metal crystallites of 15—20 Å diameter are obtained. These correspond to aggregates of 100—200 metal atoms. Once formed, the crystallites appear stable to further sintering and little change is noted over long periods (up to one month) under catalytic reaction conditions.

Clearly, considerably more detailed work is necessary to assess such features as (i) the nature of the initial interaction between the cluster compound and the support; (ii) the sequence of events which occurs on ligand removal during the catalyst activation process; (iii) the temperature at which the molecular clusters are transformed into small metal crystallites and (iv) determination of the mildest reaction conditions under which catalytic activity can be detected. Although much detailed information is missing we have clearly demonstrated that metal cluster-derived catalysts display significantly different properties from their conventionally prepared counterparts.

Experimental

Starting materials

The cluster compounds $Ru_3(CO)_{12}$ [11], $Ru_6C(CO)_{17}$ [12], $Rh_4(CO)_{12}$ [13], $Rh_6(CO)_{16}$ [14] and $(Et_4N)_2[Pt_3(CO)_6]_3$ [5] were prepared by literature methods. The coordination complexes, $[Ru(NH_3)_5]Cl_2$ [15]and $[Rh(NH_3)_5Cl]Cl_2$ [16], used in the production of the ion-exchanged catalysts, were prepared from the trichloride salts using published methods. The precious metal starting materials, $RuCl_3 \cdot x\ H_2O$, $RhCl_3 \cdot x\ H_2O$ and Na_2PtCl_6, were used as supplied by Johnson Matthey Limited. Silica (Grace Davison 952) and γ-alumina (Ketjen Grade B) catalyst supports were normally pre-dried either by degassing at 10^{-3} mmHg and 550°C for 4 h or by treatment with a stream of air at 550°C for 4 h, the latter method particularly for the production of γ-alumina.

Preparation of catalyst precursors

A typical method of preparation for the supported cluster compound is illustrated in the following example for $Ru_3(CO)_{12}/SiO_2$. Pre-dried Grace Davison 952 silica (5 g) was added to a stirred solution of triruthenium dodecacarbonyl (0.11 g) in dry toluene (150 ml). The solvent was slowly removed by evaporation under a stream of dry nitrogen to give a yellow, free-flowing powder. Any inhomogeneities in the colour of the powder, e.g., local orange concentrations due to unsupported crystalline $Ru_3(CO)_{12}$, were removed by the addition of further dry toluene and subsequent evaporation with stirring. The pale yellow powder was then transferred to a tubular reactor for activation prior to catalyst testing. Similar methods were used for the preparation of other supported cluster compounds, except that $CHCl_3$ and THF were used as solvents for $Rh_6(CO)_{16}$ and $(Et_4N)_2[Pt_3(CO)_6]_3$, respectively.

Ion-exchanged materials were produced by initial treatment of the support with 0.880 ammonia followed by washing and addition of aqueous solutions of either $[Ru(NH_3)_5N_2]Cl_2$ or $[Ru(NH_3)_5Cl]Cl_2$. In both cases exchange was virtually instantaneous and the supernatant liquid became colourless. Filtration, washing and drying produced either reddish-brown (Ru) or yellow (Rh) powders.

Conventional halide-impregnated catalysts were obtained by dissolving $RuCl_3$ and $RhCl_3$ in the minimum amount of water or acetone followed by the addition of the support material. Evaporation of the solvent on a steam bath produced dry, free-flowing powders containing the impregnated metal halides. With water as a solvent dark red materials were obtained from both ruthenium and rhodium trichlorides, but the use of acetone produced a green solid from $RuCl_3$.

Catalyst activation

The catalyst precursors were transferred to a tubular silica reactor (of length 6 in and diameter $\frac{1}{2}$ in) containing a sintered glass frit and a thermocouple well. Gaseous reactants were passed upwards through the catalyst bed. Activation/reduction of the catalyst took place by first drying the sample at 120°C in flowing nitrogen for 1 h, followed by treatment with a mixture of hydrogen and nitrogen (1/4) at 320—350°C for 4—6 h. Where catalyst test temperatures higher than 300° C were envisaged the catalysts were activated at ca. 550° C for a similar length of time. The activated catalysts were either examined immediately or stored in an inert atmosphere. Catalyst samples were removed from the reactor (via a glove bag) for subsequent analysis and characterisation.

Catalyst characterisation

Infrared spectroscopic studies were carried out on both the starting compounds and the supported metal cluster complexes. The latter were examined as pressed discs both at and above atmospheric pressure using our high pressure infrared cell [17]. Raman spectroscopy was also used to assist in the characterisation of the supported metal cluster compounds (with B.W. Cook and J.D. Louden, Structural Chemistry Group). The supported materials were analysed for metal content both before and after activation (F.S. Frith, Structural Chemistry Group). Many examples of the activated catalysts were examined by transmission electron microscopy, both before and after catalyst testing (R.T. Murray and M.D. Shannon, Structural Chemistry Group). Gas chemisorption measurements were also carried out on selected examples (A.G. Burden and P.B. Wells, University of Hull).

Catalyst testing

The catalyst was contacted with the hydrocarbon feed stream in the following manner. A stream of nitrogen was passed through a thermostatted Drechsel bottle containing the substrate (usually n-heptane) and the resultant N_2/heptane vapour combined with a hydrogen stream in appropriate amounts to provide the required hydrocarbon to hydrogen ratio. This ratio was calculated by comparison with calibrated mixtures. Under the majority of the conditions described here approximately 4% heptane is present in the feed with a gaseous flow rate of $\sim$3 ml min^{-1} and a contact time of $\sim$2 min (which may be reduced to 1 min by increasing the flow and using a smaller sample). In order to obtain sufficient vapour pressures of ethylbenzene and *o*- and *p*-xylene, the Dreschel bottle containing the substrate was maintained at 50° C and subsequent feed lines to the reactor were also heated to avoid condensation.

The mixed feed stream was passed over the catalyst at the desired temperature. After equilibrium had been established (15—30 min), samples were taken from the exit of the reactor and analysed by gas chromatography. Various columns, e.g. squalane, Apiezon L and Porapak Q, were used, depending upon the analysis required.

References

1 P. Chini, J. Organometal. Chem., 200 (1980) 37.
2 R. Whyman in B.F.G. Johnson (Ed.), Transition Metal Clusters, John Wiley, New York, 1980, Chapter 8.
3 S.D. Jackson, P.B. Wells, R. Whyman and P. Worthington, Catalysis, Chem. Soc. Specialist Periodical Report, 4 (1981), in the press.
4 P. Chini, Gazz. Chim. Ital., 109 (1979) 225.
5 G. Longoni and P. Chini, J. Amer. Chem. Soc., 98 (1976) 7225.
6 M. Boudart, A. Aldag, J.E. Benson, N.A. Dougharty and C. Girvan Harkins, J. Catal., 6 (1966) 92.
7 A. Cimino, M. Boudart and H.S. Taylor, J. Phys. Chem., 58 (1954) 796.

8 J.H. Sinfelt, J. Catal., 27 (1972) 468; Adv. Catal., 23 (1972) 91.
9 C.J. Machiels and R.B. Anderson, J. Catal., 58 (1979) 268.
10 Handbook of Chemistry and Physics, 60th Edition, 1979—1980, F 241.
11 B.F.G. Johnson and J. Lewis, Inorg. Synth., 13 (1972) 92.
12 B.F.G. Johnson, J. Lewis and I.G. Williams, J. Chem. Soc. (A), (1970) 901.
13 S. Martinengo, P. Chini and G. Giordano, J. Organometal. Chem., 27 (1971) 389.
14 S.H.H. Chaston and F.G.A. Stone, J. Chem. Soc. (A), (1969) 500.
15 A.D. Allen, F. Bottomley, R.O. Harris, V.P. Reinsalu and C.V. Senoff, Inorg. Synth., 12 (1970) 5.
16 J.A. Osborn, K. Thomas and G. Wilkinson, Inorg. Synth., 13 (1972) 213.
17 W. Rigby, R. Whyman and K. Wilding, J. Phys. E., Sci. Instr., 3 (1970) 572.