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ABSTRACTION OF OXYGEN FROM KETONES BY DECACHLORODINIOBIUM(V) *

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Summary

$[Nb_2Cl_{10}]$ abstracts oxygen from 2-butanone and 9-heptadecanone to yield, after hydrolysis, alkanes, chloroalkanes or arylalkanes, depending upon the solvent employed. Extensive rearrangement of alkyl chains was observed and the extent of rearrangement was consistent with the relative stabilities of proposed alkyl oxide-stabilised carbocationic intermediates. The active species appears to be the $[Nb_2Cl_{10}]$ molecule. When the $[Nb_2Cl_{10}]$/ketone ratio is less than one, formation of inactive mononuclear species is favoured with consequent lower yields of products. Both coordinated ketone and alkyl oxide intermediates were detected in solution. Preliminary results employing $[Mo_2Cl_{10}]$ and $[WCl_6]$ are reported.

Introduction

Halides of the early transition elements in their higher oxidation states have a characteristic ability to abstract an oxo-group from various ligands [1,2] with the formation of a metal—oxo multiple bond which stabilises the higher oxidation state. Specifically, niobium pentachloride (which exists as the binuclear molecule $[Nb_2Cl_{10}]$ in the solid state [3] and in non-coordinating solvents [4]) is reported to form mononuclear adducts (eq. 1) upon reaction with ketones

$$[Nb_2Cl_{10}] + 2n(X{=}O) \rightarrow 2[NbCl_5(X{=}O)_n] \quad (1)$$

$(X = R_2C, R_3P \text{ and } R_2S; n = 1,2)$

$$[NbCl_5(X{=}O)_n] + (m + 1)X{=}O \rightarrow [NbOCl_3(X{=}O)_m] + XCl_2 \quad (2)$$

$(m = 1—3)$

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[*] This paper is dedicated to Professor Joseph Chatt on the occasion of his sixty-fifth birthday.

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[5,6], phosphine oxides [7—11] or sulfoxides [11]. Oxygen abstraction (eq. 2) may follow adduct formation but its observation is dependent upon the exact nature of X and the stoichiometry and conditions employed. In particular, no evidence is available for oxygen abstraction from ketones by $[Nb_2Cl_{10}]$. Solids isolated from benzene and CCl_4 solutions of $[Nb_2Cl_{10}]$ and aromatic and aliphatic ketones ($Nb_2Cl_{10}/R_2CO = 1/2$) have been assigned [5,6] formulae $[NbCl_5(R_2CO)]$.

The mononuclear species $[MeNbCl_4]$ and $[Me_2NbCl_3]$ undergo analogous reactions with oxygen-containing ligands [12—14]. In particular [14], 1/1 complexes were formed with $[Me_2NbCl_3]$ in pentane by aliphatic ketones containing bulky substituent groups, but transfer of methyl groups to coordinated ketone occurred with less sterically-demanding ketones. Reaction 3 was suggested [14] for the case involving acetone:

$$\begin{tikzcd}
{[Me_2NbCl_3] + 2\,Me_2CO} \arrow[r, "25^\circ C", "pentane"'] & {[Me_2NbCl_3(Me_2CO)_2]} \arrow[d, "rapid"] \\
\text{white solid} & {[NbCl_3(Me_3CO)_2]} \arrow[l]
\end{tikzcd} \qquad (3)$$

The white solid was assigned the formula $2[(Me_3CO)NbOCl_2] \cdot Me_2CO$ and its ^1H NMR spectrum contained resonances ascribable to coordinated acetone and *t*-butyl oxide groups.

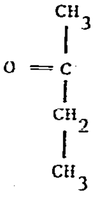
Other reactions relevant to the present study include: (i) the ability of certain reagents [15—18] (presumed to contain low valence state tungsten, iron or titanium species in tetrahydrofuran) to deoxygenate and couple certain ketones, and to deoxygenate epoxides, to yield alkenes in both cases.

(ii) the chlorination of alkenes and alkanes by $[Mo_2Cl_{10}]$ and $[WCl_6]$ in chlorinated solvents to produce chloroalkanes [19—21].

This paper reports the novel abstraction of oxygen from aliphatic ketones by $[Nb_2Cl_{10}]$ to yield, after hydrolysis, alkanes, chloroalkanes or arylalkanes, depending upon the solvent employed. Preliminary observations with $[Mo_2Cl_{10}]$ and $[WCl_6]$ are also mentioned.

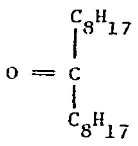
Results

In this study, $[Nb_2Cl_{10}]$ (and other early transition metal chlorides) were treated with the ketones 2-butanone (I) and 9-heptadecanone (II) at various molar ratios:



$CH_3C(=O)CH_2CH_3$

(I)



$C_8H_{17}C(=O)C_8H_{17}$

(II)

$$0 < R = \frac{n(Nb_2Cl_{10})}{n(\text{ketone})} \leqslant 2$$

The course of the reaction was dependent upon the solvent employed and results are reported for benzene, toluene, dichloromethane, chloroform and carbon tetrachloride. The reaction solutions were hydrolyzed after suitable reaction periods and the organic products isolated by techniques suitably adapted to the volatility of those products (see Experimental). Both the reaction solutions and the products were examined by a combination of infrared and ^{1}H NMR spectroscopy and mass spectrometry. In particular, SCOT (support-coated open tubular) column gas chromatography [22] interfaced with chemical ionisation mass spectrometry [23] (CIMS) allowed separation of the components of the complex mixtures formed in the reactions with 9-heptadecanone and the simultaneous examination of those components.

Reaction of [Nb_2Cl_{10}] with 2-butanone in benzene

Table 1 reports the reaction of [Nb_2Cl_{10}] and 2-butanone at various molar ratios, R, in solutions which were 0.125 M in ketone. The organic product was *dl*-2-phenylbutane (III), identified [24] by electron impact mass spectrometry (EIMS) and polarimetry. Yields were determined chromatographically (see Experimental). Hydrolysis with D_2O produced 2-deutero-2-phenylbutane (*vide infra*). Appreciable reaction occurred only for $R > 0.5$ and the reaction was complete for $R > 1$.

Table 2 lists infrared absorptions in the 1600—1800 cm^{-1} region (carbonyl stretching frequency region) at various stages of the reaction. A decrease in frequency relative to the free ketone is indicative [5,6,14] of complexation of the ketone to a niobium centre (IV). The data are consistent with the presence of coordinated and free ketone for $R = 0.25$ and with coordinated ketone for $R = 0.5$. This is in basic agreement with previous work [6] in this system. However, a crystalline product formulated as [$NbCl_5$(2-butanone)] and reported [6] to separate after a few hours, was not observed in the present work (see Experimental). Hydrolysis leads to the recovery of 2-butanone. While coordinated ketone

TABLE 1

REACTIONS OF [Nb_2Cl_{10}] WITH 2-BUTANONE

Solvent	Molar ratio, R [a]	Products (mol%) [b]	
		d,l-2-phenylbutane (III)	Butanes [c]
C_6H_6	0.25	<5	
	0.5	<5	
	0.67	15	
	1	100	
	2	100	
CH_2Cl_2	0.17		25
	0.25		45
	0.5		64
	0.67		75
	1		98
	2		98

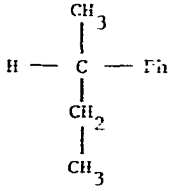
[a] 0.125 M in 2-butanone. [b] Relative to 2-butanone. [c] Mixtures of 2-methylpropane (IX) and butane (X) in the molar ratio of about 4/1.

TABLE 2

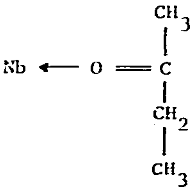
CARBONYL STRETCHING FREQUENCIES (cm^{-1}) FOR REACTIONS OF [Nb_2Cl_{10}] WITH 2-BUTANONE IN BENZENE

Molar ratio, *R* [a]	Initial observation [b]	After 40 h [c]	After hydrolysis [d]
0	1726	1726	1726
0.25	1671,1725	1673,1725	1726
0.5	1670	1672	1727
1	1648	absent	absent

[a] 0.1 *M* in 2-butanone [b] Immediately after mixing the reactants. [c] Immediately prior to hydrolysis. [d] Organic phase after hydrolysis and drying over $MgSO_4$.



(III)



(IV)

is present initially in the reaction with *R* = 1, absorption in this region was absent after 40 h and after hydrolysis, and indicates loss of the carbonyl functional group.

Table 3 collects ^1H NMR chemical shifts for the reaction with *R* = 1. The spectrum of the initial solution is consistent with the presence of coordinated 2-butanone (IV). After 40 h, the spectrum is altered markediy and, coupled with the absence of ν(CO) (Table 2), is consistent with the presence of a tertiary alkyl oxide ligand (V), produced by phenyl substitution at C(2) of a 2-butanone ligand. Hydrolysis with H_2O produces the spectrum of 2-phenylbutane (III) and, with D_2O, the spectrum of 2-deutero-2-phenylbutane which features a characteristic loss of coupling to the α-methylene and α-methyl pro-

TABLE 3

^1H NMR CHEMICAL SHIFT [a] DATA FOR THE REACTION OF [Nb_2Cl_{10}] WITH 2-BUTANONE IN BENZENE (*R* = 1 [b])

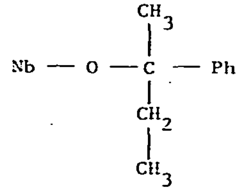
Proton	2-Butanone [b]	Initial Observation [c]	After 40 h [d]	After hydrolysis [e]	
				with H_2O	with D_2O
CH_2CH_3	0.81, t	0.46, t	0.66, t	0.68, t	0.67, t
CH_2	1.80, q	1.48, q	1.15, m	1.34, m	1.30, q
CH	—	—	—	2.38, (br)m	—
CH_3	1.59, s	1.62, s	1.09, s	1.06, d	1.04, s

[a] Chemical shifts, δ (60 MHz) in ppm relative to TMS; benzene lock (7.16 ppm dowfield from TMS). s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet, (br), broad. The coupling constants were about 7 Hz for each multiplet. [b] 0.1 *M* in 2-butanone. [c] Immediately after mixing the reactants. [d] Immediately prior to hydrolysis. [e] Organic phase after hydrolysis and drying over $MgSO_4$.

tons. The latter observation, coupled with satisfactory integration, indicates that deuterium substitution is confined to C(2) of the aliphatic chain.

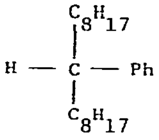
Reactions of [Nb_2Cl_{10}] with 9-heptadecanone in benzene and toluene

Table 4 reports reactions of [Nb_2Cl_{10}] and 9-heptadecanone at various molar ratios, R, in solutions which were 0.125 M in ketone. For $R = 1$ in benzene, the SCOT column gas cromatogram and total ion chromatogram (TIC: a plot of ion current against scan number; Fig. 1a) of the organic product were very similar and show a complex series of components. The CIMS spectrum of each component exhibits a parent peak at *m/e* 315 together with a series of alkyl and phenylalkyl (or tropyl) fragments and consequently *each* is an isomer of 9-phenylheptadecane (VI; M^+, 316; $M - 1^+$, 315). Component α (Fig. 1a) can be assigned to 9-phenylheptadecane itself, but the complex fragmentation patterns exhibited by the other components prevent structural assignments. In addition, it is apparent that complete resolution of components has not been achieved. However, the



$Nb-O-C(CH_3)(CH_2CH_3)-Ph$

(V)



$H-C(C_8H_{17})_2-Ph$

(VI)

TABLE 4

REACTIONS OF [Nb_2Cl_{10}] WITH 9-HEPTADECANONE

Solvent	Molar ratio, R [a]	Products (mol %) [b]			
		9-Heptadecanone	Alkanes	Chloro-heptadecanes	Aryl-heptadecanes
C_6H_6	0.25	95			5
	0.5	85			15
	1.0				100
	2.0				100
$C_6H_5CH_3$	1				100 [d]
CH_2Cl_2	0.25	60	40		
	0.5	50	50		
	1		100		
	2		100		
$CHCl_3$	1 [c]	trace	60	40	
CCl_4	0.25	90		10	
	0.5	95		5	
	1	15		85	

[a] 0.125 M in 9-heptadecanone. [b] Yields (relative to 9-heptadecanone) were determined from chromatographic areas and are accurate to ±5% (see Experimental). See text for exact nature of products. [c] Product ratios are very dependent upon reagent concentration in this system. [d] *Ortho*- and *para*-tolylheptadecanes in approximately equal proportions.

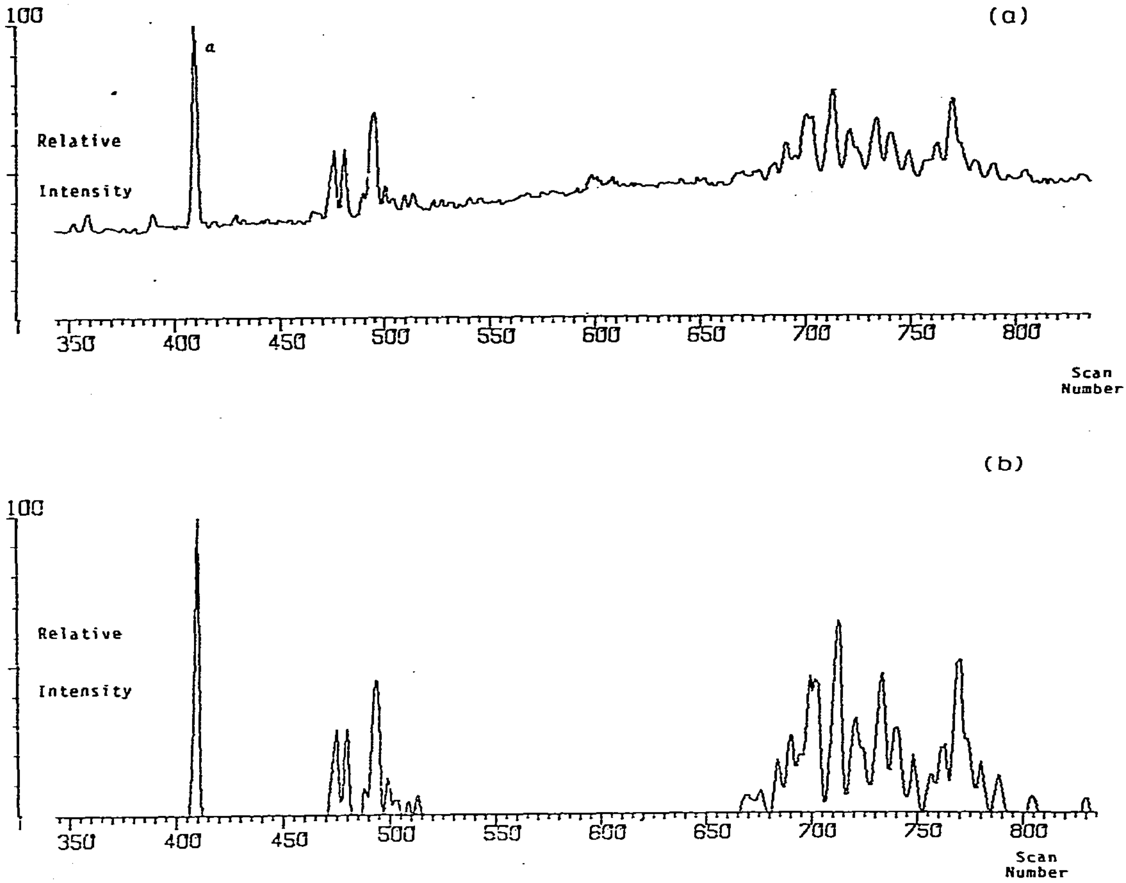


Fig. 1. Reaction product from $[Nb_2Cl_{10}]$ and 9-heptadecanone in benzene ($R = 1$). (a) Total ion chromatogram (TIC); (b) single ion chromatogram ^{a} (SIC) at *m/e* 315; *a*: See Experimental concerning the relative intensities of peaks in TICs and SICs.

isomeric nature of the products is confirmed by the single ion chromatogram (SIC) of *m/e* 315 (Fig. 1b). This is a plot of the normalised ion current for a single *m/e* value against scan number and should be compared to the TIC (Fig. 1a: note footnote a). It can be seen that each component produces an ion of *m/e* 315. Ions of higher mass number were not observed.

Appreciable reaction occurred only for $R > 0.5$ and the reaction was complete for $R > 1$ (Table 4). This is confirmed by the spectroscopic data reported in Table 5 for reaction solutions immediately prior to hydrolysis. Interpretation follows that for the 2-butanone system (Tables 2 and 3). An α-methylene resonance could not be identified in the ^1H NMR spectrum for the case of $R = 1$ and the observation of a complex spectrum is consistent with rearrangement prior to hydrolysis.

Hydrolysis with D_2O leads to an alkane product which exhibits an infrared absorption at 2170 cm^{-1} (aliphatic C—D stretch) which is broad in comparison to the H_2O-hydrolysis product. This is consistent with deuterium incorporation into the alkyl groups of the products.

TABLE 5

SPECTROSCOPIC DATA FOR REACTIONS OF $[Nb_2Cl_{10}]$ WITH 9-HEPTADECANONE IN BENZENE [a]

Molar ratio, R [b]	Carbonyl stretching frequency (cm^{-1}) [c]	δ (CH_2CO) [d] (ppm)
0	1724	2.03, t
0.25	1660, st; 1724, w	2.28, m
0.5	1640	2.30, m
1	absent	[c]

[a] After 24 h and immediately prior to hydrolysis. [b] 0.125 M in 9-heptadecanone. [c] st, strong; w, weak. [d] ^1H NMR (60 MHz); see Table 3, footnote *a*. [e] Could not be identified in the complex spectrum.

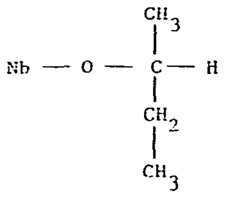
The use of C_6D_6 as solvent produced (perdeuteriophenyl)heptadecanes whose infrared spectra showed absorptions due to aromatic and aliphatic C—D bonds. This again indicates deuterium scrambling into the alkyl chain.

Substitution of toluene for benzene (Table 4) produces *ortho*- and *para*-tolylheptadecanes in approximately equal proportions (estimated from the intensities of the aromatic out-of-plane C—H deformation vibrations [25] in the infrared spectrum).

Reaction of $[Nb_2Cl_{10}]$ with 2-butanone in dichloromethane

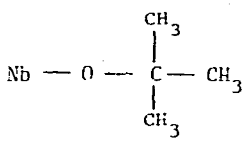
Table 1 lists reactions performed with CH_2Cl_2 as solvent. After hydrolysis, the total yield of the gaseous products was determined manometrically (see Experimental), and for $R > 1$ was the molar equivalent of the 2-butanone initially present. In contrast to the benzene system, appreciable reaction occurs for $R < 0.5$, and the reaction is complete within two minutes.

For the reaction with $R = 1$, about 25% of the observed intensity in the ^1H NMR spectrum of the reaction solution at −20°C (Fig. 2a; δ (CH_2CH_3) 0.69t ppm, δ (CH_2) 0.99m ppm, δ (CH_3) 1.21d ppm) can be ascribed to the presence of a secondary alkyl oxide ligand (VII) [26] formed by H transfer from the solvent to C(2) of a coordinated ketone ligand. The C(2) proton (expected at $\delta \sim$ 4—5 ppm [26]) was not detected presumalby due to the multiplicity of its signal or to overlap with the solvent peak at δ 5.28 ppm. About 75% of the intensity at −20°C is due to a singlet at δ 1.41 ppm assigned to a *t*-butyloxide moiety (VIII) [14,26] formed by rearrangement of the initially formed secondary alkoxide ligand. Intramolecular exchange occurs between the two ligands forms at higher temperatures.



$\mathrm{Nb{-}O{-}CH(CH_3)(CH_2CH_3)}$

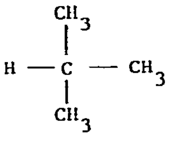
(VII)



$\mathrm{Nb{-}O{-}C(CH_3)_3}$

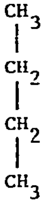
(VIII)

Hydrolysis of the solution by H_2O at room temperature leads to the gaseous products, which were identified by EIMS [27] as a mixture of 2-methylpropane (IX; 80—90 mol%) and n-butane (X; 20—10 mol%). Hydrolysis with D_2O produces a mixture [27] of 2-deuterio-2-methylpropane (75—90 mol%) and 2-deuterio-n-butane (25—10 mol%). The 2-methylpropane/n-butane product ratios could not be defined more exactly because of the similarity of the individual mass spectra. However, the ^1H NMR and EIMS results are convincing evidence that rearrangement occurs prior to hydrolysis, and that the rate of hydrolysis is fast compared to the rate of intramolecular exchange between the two ligand forms.



$H-C(CH_3)_2-CH_3$

(IX)



$CH_3-CH_2-CH_2-CH_3$

(X)

For the reaction with $R = 1$ in CD_2Cl_2, the ^1H NMR spectrum at —20°C (Fig. 2b) is characteristic of a deuterio-*t*-butyloxide ligand (XI) i.e., a triplet (δ 1.47 ppm) overlapped by a septet (δ 1.73 ppm). Signals characteristic of a deuterated secondary alkyl oxide ligand were not detected, presumably due to a destabilising isotope effect which disfavours its formation, or to scrambling of the deuteron along the alkyl chain with consequent spectral complication and apparent loss of intensity. The existance of relatively intense peaks at m/e 59 and 60 in the EIMS of the H_2O- and D_2O-hydrolysis products respectively suggests the presence of mono- and di-deuterobutanes. Further identification was not possible as the mass spectra of a comprehensive selection of mono- and di-deuteriobutanes are not available.

Reaction of [Nb_2Cl_{10}] with 9-heptadecanone in dichloromethane

Table 4 lists the reactions for various molar ratios R. The SCOT column gas chromatograms and the TIC (Fig. 3a) of the organic product are very similar and show an extremely complex series of peaks extending from near the solvent peak. These peaks are assigned to isomers of heptadecane and its lower homologues. For example, the individual CIMS spectra of components of scan numbers 235—295 (Fig. 3a) show each to be an isomer of heptadecane. The spectra are typically paraffinic [28] and each has a parent peak at m/e 239 (corresponding to $C_{17}H_{35}^+$, $M - 1$). The assignments are confirmed by the SIC at m/e 239 (Fig. 3b). The CIMS spectra of other components and SICs corresponding to m/e 225 ($C_{16}H_{33}^+$), 211 ($C_{15}H_{31}^+$), 197 ($C_{14}H_{29}^+$) and 183 ($C_{14}H_{27}^+$) clearly show the homologous and isomeric nature of the products and the presence of C_{13}species at the solvent limit.

The relative concentrations of alkanes were estimated by correlating the integration of the SCOT column gas chromatogram with the TICs and SICs at the various m/e values. The product mixture is composed of about 90 mol% isomeric heptadecanes, about 5 mol% isomeric hexdecanes and smaller proportions of their lower homologues.

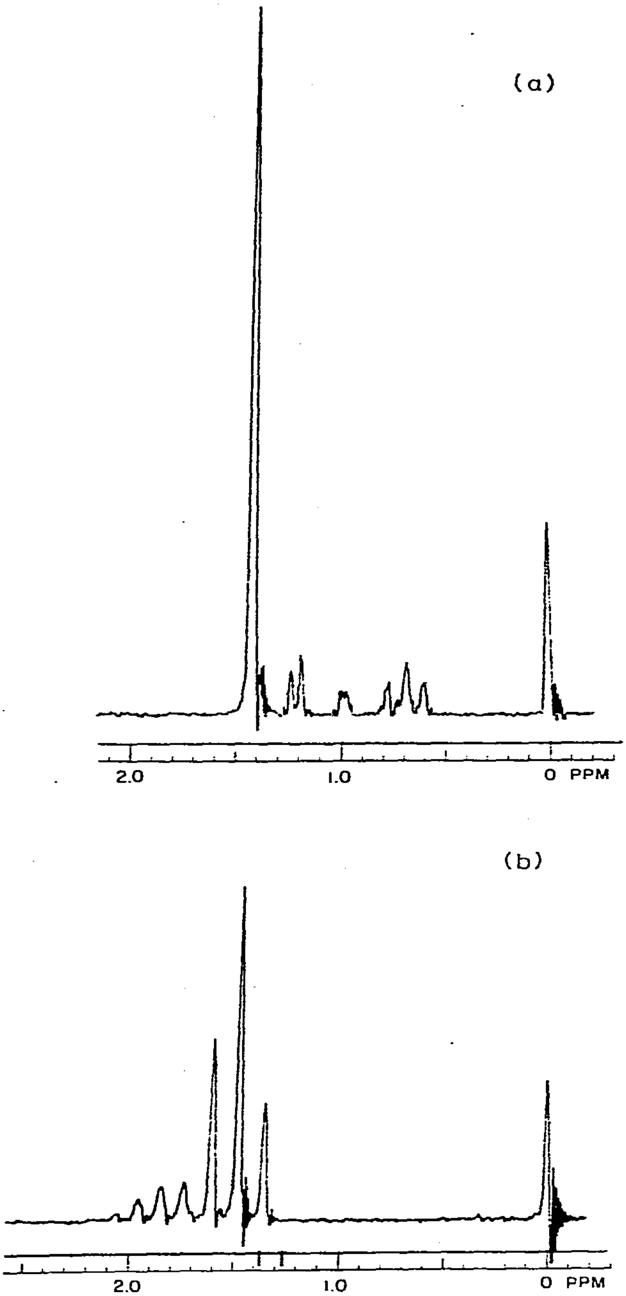


Fig. 2. ^{1}H NMR spectrum at —20°C of the reaction solution from [Nb_2Cl_{10}] and 2-butanone (R = 1). (a) In CH_2Cl_2; (b) in CD_2Cl_2.

Reaction of [Nb_2Cl_{10}] with 9-heptadecanone in chloroform and carbon tetrachloride

In CCl_4, 85% conversion of 9-heptadecanone to isomers of chloroheptadecane was obtained for $R > 1$, but little reaction occurred for $R < 0.5$ (Table 4). Again,

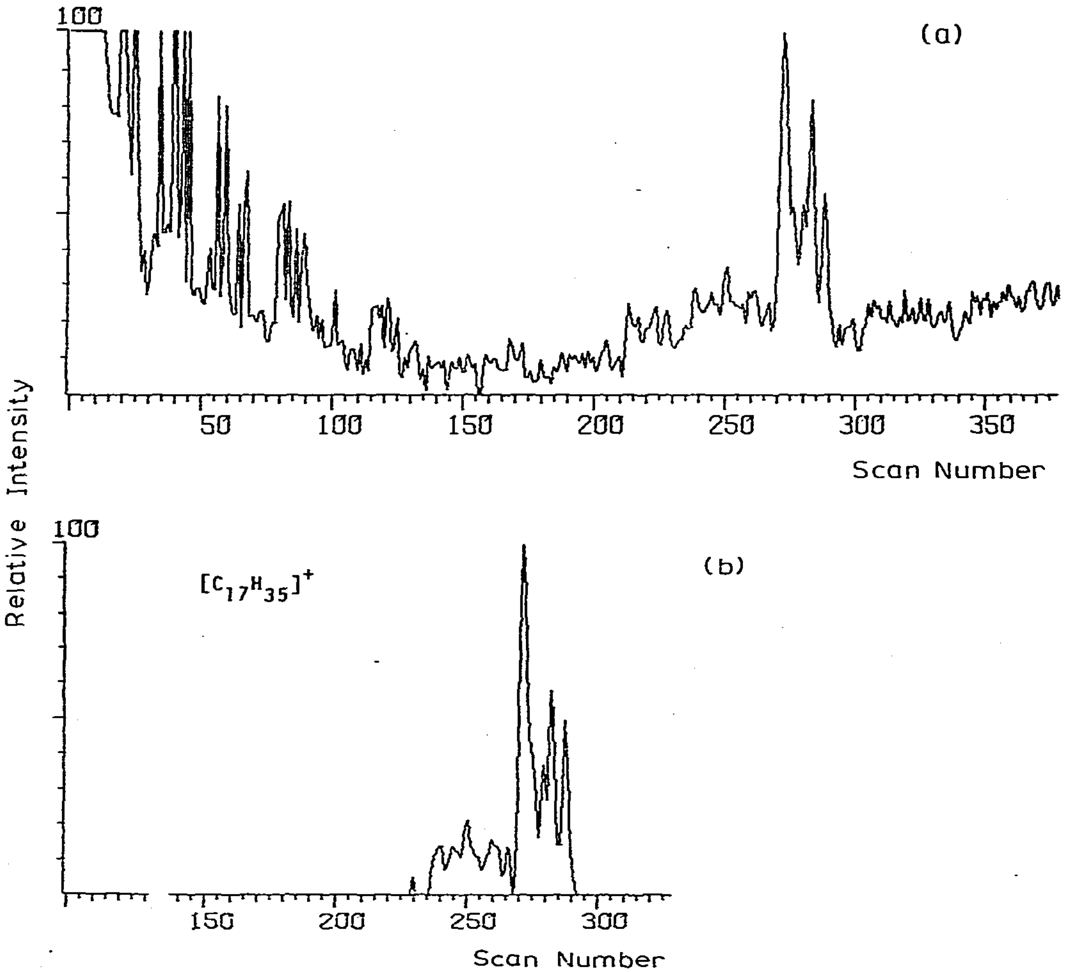


Fig. 3. Reaction product from $[Nb_2Cl_{10}]$ and 9-heptadecanone in dichloromethane ($R = 1$). (a) Total ion chromatogram (TIC); (b) single ion chromatogram ^{a} (SIC) at m/e 239; a: See Experimental concerning the relative intensities of peaks in TICs and SICs.

a broad series of peaks were discernible in the TIC (together with one corresponding to unreacted ketone) and the individual CIMS corresponding to each peak confirmed the presence of isomers of chloroheptadecane. Confirmation of the assignments was given by the SIC of m/e 273 ($C_{17}H_{34}{}^{35}Cl^+$). In contrast to the reaction in CH_2Cl_2, lower homologues of chloroheptadecane were not detected.

In $CHCl_3$ when $R = 1$ (Table 4), a mixture of alkanes and chloroheptadecanes resulted. The SCOT column gas chromatogram and TIC were a resolved superposition of those found for the CH_2Cl_2 and CCl_4 cases.

Effect of change of reaction conditions for $[Nb_2Cl_{10}]$/9-heptadecanone ($R = 1$)

For the reactions in C_6H_6 and CH_2Cl_2, the absolute yields of products and the homologue and isomer distributions were (a) essentially independent of ketone concentration in the range 0.025 to 0.25 M, (b) independent of the mode of

TABLE 6

REACTIONS OF $[Mo_2Cl_{10}]$ [a] AND $[WCl_6]$ [b] WITH 9-HEPTADECANONE IN CHLORINATED SOLVENTS ($R = 1$)

Chloride	Solvent	Products (mol %) [c]		
		9-Heptadecanone	Alkanes	Chloroheptadecanes
$[Mo_2Cl_{10}]$	CH_2Cl_2	—	85	15
	$CHCl_3$	5	65	30
	CCl_4	20		80
$[WCl_6]$	CH_2Cl_2		10	90
	$CHCl_3$		5	95
	CCl_4	5		95

[a] 0.125 *M* in ketone. [b] 0.09 *M* in ketone. [c] Yields were determined from chromatographic peak areas and are accurate to ±5%.

addition of the reactants, and (c) independent of the hydrolysis procedure.

The reactions in $CHCl_3$ and CCl_4 were more sensitive to conditions. For example, the reaction with 9-heptadecanone in CCl_4 barely proceeded at a ketone concentration of 0.025 *M* but gave at least 85% conversion at 0.25 *M* concentration. In the case of $CHCl_3$, the alkane/chloroheptadecane ratio depended upon the mode of addition of the reactions, a fact related to the ability of $CHCl_3$ to transfer either H or Cl groups, or both. However, the homologue and isomer distributions remained unchanged.

Reactions of other early transition metal chlorides with 9-heptadecanone ($R = 1$) in chlorinated solvents.

$[TiCl_4]$ and $[ZrCl_4]$ are not sufficiently reactive to abstract oxygen from 9-heptadecanone, even under reflux.

$[Mo_2Cl_{10}]$ reacts analogously to $[Nb_2Cl_{10}]$, but some chloroheptadecanes are formed in CH_2Cl_2 (Table 6). With $[WCl_6]$, chloroheptadecanes are formed preferentially.

While the total alkane/chloroheptadecane product ratios vary with the specific halide and solvent used (Tables 4 and 6), the homologue and isomer distributions are miantained, i.e., essentially the *same* complex distributions of (a) isomeric and homologous alkanes and (b) isomeric chloroheptadecanes are present in each mixture and the SCOT column chromatograms and TICs are resolved superpositions of those found for the $[Nb_2Cl_{10}]/CH_2Cl_2$ and $[Nb_2Cl_{10}]/CCl_4$ cases (Table 4).

Discussion

Product analysis

The organic products isolated in the reactions of 2-butanone and 9-heptadecanone with $[Nb_2Cl_{10}]$ (Tables 1 and 4) are all formed by deoxygenation of the ketone and incorporation of solvent-derived groups and H from the water employed for hydrolysis. For example, the reaction with 2-butanone hydrolysed with D_2O: (i) in benzene produces 2-deuterio-2-phenylbutane, and (ii) in CH_2Cl_2 produces a mixture of 2-deuterio-2-methylpropane and 2-deuterio-n-butane. The

CIMS detection of $CHCl_3$ in the reaction solution for the latter reaction is further evidence for incorporation of solvent-derived H.

The active niobium species

Irrespective of the solvent employed, the reactions proceed to completion *only* if the molar ratio of $[Nb_2Cl_{10}]$/ketone, R, is greater than or equal to unity. Niobium pentachloride exists as the binuclear, chloro-bridged $[Nb_2Cl_{10}]$ molecule in CCl_4 [4] and probably in CH_2Cl_2, $CHCl_3$ and C_6H_6 as well. It is likely that the $[Nb_2Cl_{10}]$ molecule acts as a template for the present reactions with the ketone being bound to one metal centre and a solvent molecule interacting with the other. This would permit both activation and orientation of the reactants. Apparently for $R < 1$, the equilibrium begins to favour inactive mononuclear species such as $[NbCl_5(R_2CO)_n]$ ($n = 1,2$), formed by the cleavage of bridging Nb—Cl bonds. The previous work [5,6] in this system employed $R = 0.25$ and 0.5 in CCl_4 and C_6H_6 and was interpreted in terms of the existence of such mononuclear species. $[Nb_2Cl_{10}]$ dissolves in coordinating solvents such as RCN, R_2O and R_2S to produce similar mononuclear complexes [29].

Reactions prior to hydrolysis.

The reactions when $R = 1$ in benzene are relatively slow and allow the spectroscopic observation of both coordinated ketone (Tables 2,3 and 5) and, for the 2-butanone case, the tertiary alkyl oxide species (V) produced by phenyl substitution at C(2) of a 2-butanone ligand. The ^{1}H NMR evidence (Fig. 2) for the presence of secondary (VII) and tertiary (VIII, XI) alkyl oxide ligands in the reaction solutions for 2-butanone in CH_2Cl_2 and CD_2Cl_2 is most compelling.

It would appear that the reaction mechanism in the chlorinated and aromatic solvents have features in common. One of the possible scenarios for the reaction in chlorinated solvents CX_2Cl_2 (X = H or Cl) is illustrated in Fig. 4. It features: (i) Interaction of ketone and solvent with, and their activation by, the coordinatively unsaturated $[Nb_2Cl_{10}]$ molecule. The observed CH_2Cl_2 reactions lead to

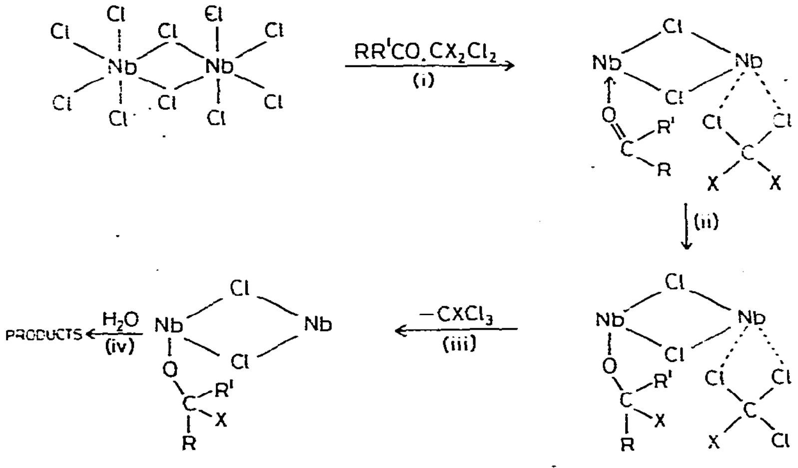
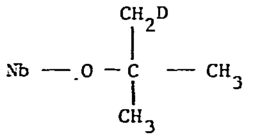


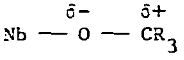
Fig. 4. Reaction scheme for the interaction of $[Nb_2Cl_{10}]$ with ketones in chlorinated solvents CX_2Cl_2 (X = H, Cl). Chloro-ligands are omitted from the niobium species for clarity.

the transfer of H only whilst the $CHCl_3$ reactions allow transfer of both H and Cl (Tables 1 and 4). This is consistent with the two chloro groups in CX_2Cl_2 interacting with one Nb centre. Then, only H can be transferred to the ketone in the case of CH_2Cl_2, but both H and Cl in the case of $CHCl_3$. It is unlikely that solvent H would interact with a Nb centre in preference to solvent Cl; (ii) nucleophilic transfer of solvent X (H or Cl) to an electropositive carbonyl carbon and of Cl (from a niobium centre) to the solvent moiety; (iii) loss of product $CXCl_3$ leaving a stable alkyl oxy-niobium species.

A similar scheme can be devised for the reactions in aromatic solvents, with elimination of HCl. In this case, the solvent molecule might be oriented and activated by interaction of its π-system with the second Nb centre. Niobium pentachloride also promotes [30] Friedel—Crafts acylation (and related electrophilic substitutions) at aromatic centres by acyl halides RCOY and the possibility of a similar reaction scheme involving transient binuclear niobium intermediates containing halo-alkyl oxide ligands, Nb—O—CR(Ar)Y, might be considered. Friedel—Crafts acylations are considered normally to proceed via carbocationic intermediates, but a highly polarised alkyl oxide ligand can be viewed as a stabilised carbocation (XII and *vide infra*).



(XI)



$$\overset{\delta-}{}\qquad\overset{\delta+}{}$$
$$Nb — \overset{\delta-}{O} — \overset{\delta+}{CR_3}$$

(XII)

The presence of both aromatic and aliphatic C—D bonds in the deuteriophenylheptadecanes isolated for the 9-heptadecanone/C_6D_6 system merits some comment. Product DCl or rearrangements (*vide infra*) involving further alkylation of the aromatic nucleus, or both, are most likely responsible for the deuterium incorporation into the alkyl chains.

Rearrangements

The products obtained in the present study are, except for the reaction with 2-butanone in benzene, mixtures of isomers and homologues (Tables 1 and 4). The ^1H NMR and EIMS results for the reaction with 2-butanone in CH_2Cl_2 provide convincing evidence that rearrangement occurs prior to hydrolysis in that system.

Such rearrangement might proceed via carbocationic, radical or carbene mechanisms. A highly polarised alkyl oxide ligand (XII) might be viewed as a stabilised carbocation and the observations are consistent with carbocationic rearrangements [31] involving hydride and alkyl shifts:

(i) n-Butane and isobutane both form the *t*-butyl cation exclusively [31a,32] when dissolved in FSO_3H/SbF_5 solution. However, the equivalent pentanes produce a dynamic equilibrium [32] between the secondary and tertiary cations which mirrors that between the secondary (VII) and tertiary (VIII) alkyl oxide ligands in the 2-butanone/CH_2Cl_2 system of the present study.

(ii) The number of isomers and extent of rearrangement in the various systems can be correlated with the relative stabilities of the anticipated carbocations. Thus, the $[(C_8H_{17})_2CH]^+$ carbocation would not be as stable as the phenyl- and chloro-substituted analogues and so the 9-heptadecanone/CH_2Cl_2 system exhibits more extensive isomerisation (and cracking) than the benzene and CCl_4 systems. At the other extreme, the single product, 2-phenylbutane (III), of the 2-butanone/benzene system is consistent with the stability of the benzylic tertiary carbocation $[CH_3C(Ph)CH_2CH_3]^+$, whose rearrangement would lead to less stable carbocations.

(iii) The observations of the same complex isomer and homologue distributions in the 9-heptadecanone/chlorinated solvent systems (Tables 4 and 6) with $[Nb_2Cl_{10}]$, $[Mo_2Cl_{10}]$ or $[WCl_6]$ correlates with the presence of alkyl oxide-stabilised carbocations whose character is essentially independent of the specific metal centre. Apparently, the metal halide-solvent interactions determine the alkane: chloroheptadecane product ratios but not the isomer distributions. This fact is particularly intriguing in the case of WCl_6 where a different overall mechanism based upon mononuclear species is likely.

Hydrolysis

The organic products obtained after hydrolysis are neither alcohols nor species derived from the dehydration of alcohols. Alkoxides such as $[Nb_2(OR)_{10}]$ hydrolyse to the hydrated metal oxide and corresponding alcohol when treated [34] with an excess of water. However, the observed hydrolysis in any specific case will be the result of competition between the metal and ligand for the oxo function.

The present hydrolysis (see iv, Fig. 4) may involve a similar mechanism to that suggested for the interaction of solvent with the binuclear Nb species (see i—iii, Fig. 4). Thus, interaction of H_2O with one Nb centre of the stable dinuclear alkoxide complex would allow transfer of H to the *vicinal* alkyl oxide ligand and retension of OH by the metal with consequent stabilisation of the high oxidation state.

Experimental

All reactions and handling of air-sensitive materials and solvents were performed [34,35] under strictly anaerobic conditions (under vacuum, or purified argon or dinitrogen atmospheres).

Materials

Analytical reagent grade solvents were purified, dried and rendered oxygen-free by standard techniques. Decachlorodiniobium(V), decachlorodimolybdenum(V) and hexachlorotungsten(VI) (Koch—Light) were refluxed in thionyl chloride, recovered by evaporation under reduced pressure at 40° C and then triply-sublimed *in vacuo*. Zirconium tetrachloride (Alfa) was purified by sublimation in a stream of dihydrogen at 300° C and atmospheric pressure. The crystalline materials were ground finely before use. Titanium tetrachloride (BDH) was used as received.

2-Butanone (BDH) was initially dried over and then fractionated off 3 Å molecular sieves. The distillate was further treated [36] with analytical reagent grade sodium iodide and the fraction boiling at 79—80° C collected under argon. GC-MS indicated >99% purity, the major impurity being acetone (<1%). 9-Heptadecanone (Koch—Light pure) was recrystallised from 60—80° C petroleum ether. The material used in this study was shown to be >98.4% pure by GC-MS and the impurities were 8-hexadecanone (1.1%) and other lower or higher homologues. Heptadecane was prepared [37] by reduction of 9-heptadecanone via 9-heptadecanol and its tosylate.

Analytical techniques

Infrared spectra were recorded on Perkin—Elmer Models 137 and 577 spectrophotometers and calibrated with polystyrene film. Proton NMR spectra were recorded on Varian Model T-60 and HA-100 spectrometers. Electron impact mass spectra (EIMS) at 70 eV were recorded on Hitachi Perkin—Elmer RMU-6D or JEOL DS-100 mass spectrometers.

In the 2-butanone/CH_2Cl_2 system, a mixture of butanes evolved upon hydrolysis. The boiling and freezing points of 2-methylpropane (isobutane) and n-butane (b.p. —10.2 and —0.5° C; f.p. —145 and —138.5° C, respectively) allow their separation from water, CH_2Cl_2, $CHCl_3$ and 2-butanone by exhaustive trap-to-trap distillation and freeze-thaw cycling [35]. The total yields of gas at room temperature were determined manometrically after collection of the butanes in a Toepler pump [35]. Identification of the product and the butane: isobutane ratios were determined by EIMS [27]. The SCOT column gas chromatographic separations in the 9-heptadecanone systems and the 2-butanone-benzene system employed a Perkin—Elmer Model 900 gas chromatograph fitted with a flame ionisation detector. The glass column (50 m; 0.4 mm i.d.) was loaded with SE-30 on Chromosorb P. It is extremely difficult to estimate the percentage loading of the liquid phase due to the method of preparation of the columns [22]. Helium was both the carrier and make-up gas (flow rates 3 and 20 $cm^3\ min^{-1}$, respectively). Temperature programming involved heating at an initial temperature for 5 minutes followed by increasing the temperature to 260—280° C at a rate of 4° /min. The initial temperature employed depended upon the system: CH_2Cl_2 and $CHCl_3$, 60° C; CCl_4, 120° C; benzene, toluene, 200° C. The relative proportions of the various components in each product were calculated from the ratio of peak areas, which were determined by a Hewlett—Packard 3370A electronic integrator. Because of the complex mixtures of products, it was not possible to employ standard compounds for quantitative estimation of yields. Yields relative to 9-heptadecanone were determined from the ratio of peak areas and appear to be accurate to ±5%. In the CH_2Cl_2 and $CHCl_3$ systems, the relative concentrations of the homologous alkanes could be estimated by correlating the chromatographic integration with the total ion chromatogram (TIC) and the single ion chromatograms (SIC) recorded at selected *m/e* values.

The GC-CIMS analyses were determined on a Finnigan 3300E GC-MS instrument using the gaschromatographic conditions outlined above. The reagent gas was methane (flow rate: 20 $cm^3\ min^{-1}$). The SCOT column gas chromatograms and TIC of a product are very similar in appearance. Any differences arise because different methods of detection are used in each technique. Whilst in general, the response of a flame ionisation detector is similar to that of a mass spectrometer, differences can occur because the response of the former is proportional to the number of carbon atoms (to a first approximation), whilst the response of the latter is dependent upon the ease of ionisation. The overall appearance of SICs are similar to the relevant portions of the SCOT column gas chromatogram and the TIC. However the internal relative intensities of the peaks can be quite different as the SICs have been normalised relative to the strongest peak (100%) observed for the selected *m/e* value.

Reactions

The reactions involving metal halides and 9-heptadecanone (Tables 4 and 6) were performed using a standard procedure. The halide and ketone were combined in a Schlenk flask and the solvent (40 cm^3) was added. The solution was stirred for 40 h, hydrolysed (20 cm^3) and the organic phase was separated. The aqueous phase was extracted with fresh solvent (3 × 20 cm^3); the extracts were combined and dried with $MgSO_4$. Gas chromatographic, GC-CIMS and other physical examinations could then be performed. Evaporation of solvent allowed isolation of products. Samples for spectroscopic examination were taken by gastight syringe, prior to hydrolysis.

Reaction conditions were varied in selected cases (see Results) by varying the ketone concentrations, mode of addition of reactants (i.e., adding a solution of one reactant to a solution of the other) and the hydrolysis procedure (i.e., whether water was added to the reaction solution at 25°C or whether the reaction solution was added to a saturated NH_4OOCH_3/NH_4Cl solution at 5°C).

In the niobium pentachloride/2-butanone systems, the ketone was added dropwise to a stirred solution or suspension of the halide. Work-up in the benzene system was similar to that outlines above, but with the CH_2Cl_2 system, careful containment was necessary to avoid loss of gaseous product.

Three specific reactions (Tables 1 and 4) are described as examples:

(a) [Nb_2Cl_{10}]/9-heptadecanone in CH_2Cl_2 ($R = 1$). [Nb_2Cl_{10}] (2.70 g, 5.0 mmol) and 9-heptadecanone (1.27 g, 5.0 mmol) were treated in CH_2Cl_2 (40 cm^3). A light-brown solution was present after stirring for 40 h. Hydrolysis, extraction, drying and evaporation yielded a yellow oil (1.23 g) which crystallised on standing.

(b) [Nb_2Cl_{10}]/2-butanone in benzene ($R = 0.25$). The following experimental conditions mimic those of ref. 6 where crystals, formulated as [$NbCl_5$(2-butanone)] were reported to separate after a few hours. [Nb_2Cl_{10}] (0.81 g, 1.5 mmol) was suspended in benzene (50 cm^3) and stirred. About half of the halide dissolved to produce a yellow-brown solution. The ketone (0.54 cm^3, 6.0 mmol) was added over 5 minutes. The halide dissolved to produce a bright red solution. There was no visible change after four hours and no separation of solid (cf. ref. 6). After stirring for 40 h, the solution was pale yellow with a trace of amorphous solid present. Hydrolysis, extraction, drying and gentle evaporation under vacuum yielded a yellow oil (0.009 g). No characterisation was attempted on this negligible quantity of product. Gas chromatographic analysis on the extracts prior to evaporation indicated >95% recovery of 2-butanone (Table 1).

(c) [Nb_2Cl_{10}]/2-butanone in benzene ($R = 1$). [Nb_2Cl_{10}] (2.70 g, 5 mmol) was suspended in benzene (40 cm^3) and stirred while 2-butanone (0.45 cm^3, 5.0 mmol) was added over 5 minutes. Most of the halide dissolved. Approximately

one minute after the addition was complete, the colour of the supernatant solution was red-orange. After 40 h, the colour was unchanged but a dark red-brown precipirate was present. This was filtered off and worked up separately.

The filtrate was hydrolysed, extracted, dried and evaporated to yield a yellow oil (0.324 g, 64.4%; Found: C, 90.1; H, 10.1; $C_{10}H_{14}$ calcd.: C, 89.5, H, 10.5%). Gas chromatographic analysis of the extracts prior to evaporation indicated 100% conversion to 2-phenylbutane.

The dark-brown precipitate was added to a mixture of saturated NH_4OOCCH_3 (7 cm^3), saturated NH_4Cl (7 cm^3) and diethyl ether (5 cm^3). The mixture was stirred for 1 h. The ethereal phase was separated and the aqueous phase extracted with more ether. The extracts were combined, dried and evaporated to yield a small quantity of yellow oil (0.034 g). Gas chromatographic analysis of the extracts indicated the presence of 2-phenylbutane.

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References

1 D.L. Kepert, The Early Transition Metals, Academic Press, London, 1972.
2 D. Brown in J.C. Bailer (Ed.), Comprehensive Inorganic Chemistry, Vol. 3, Pergamon, Oxford, 1973.
3 A. Zalkin and D.E. Sands, Acta Cryst., 11 (1958) 615.
4 D.L. Kepert and R.S. Nyholm, J. Chem. Soc., (1965) 2871.
5 M.S. Gill, H.S. Ahuja and G.S. Rao, J. Less-Common Metals, 21 (1970) 447.
6 L.V. Surpina, Yu.V. Kolodyazhnyi and O.A. Osipov, Zh. Obshchei Khim., 43 (1973) 1165 (English translation, 43 (1973) 1154).
7 D. Brown, J. Hill and C.E.F. Rickard, J. Less-Common Metals, 20 (1970) 57.
8 R.J. Dorschner, J. Inorg. Nucl. Chem., 34 (1972) 2665.
9 D. Brown, J.F. Easey and J.G.H. du Preez, J. Chem. Soc. (A), (1966) 258.
10 D.B. Copley, F. Fairbrother and A. Thompson, J. Less-Common Metals, 8 (1965), 256.
11 D.B. Copley, F. Fairbrother, K.H. Grundy and A. Thompson, J. Less-Common Metals, 6 (1964), 407.
12 C. Santini-Scampucci and J.G. Riess, J. Chem. Soc., Dalton, (1974) 1433.
13 G.W.A. Fowles, D.A. Rice and J.D. Wilkins, J. Chem. Soc., Dalton, (1972) 2313; (1973) 961.
14 J.D. Wilkins, J. Organometal. Chem., 80 (1974) 357.
15 K.B. Sharpless, M.A. Umbreit, M.T. Nieh and T.C. Flood, J. Amer. Chem. Soc., 94 (1972) 6538.
16 T. Fujisawa, K. Sugimoto and H. Ohta, Chem. Lett, (1974) 883.
17 J.E. McMurry and M.P. Fleming, J. Amer. Chem. Soc., 96 (1974) 4708; J. Org. Chem., 40 (1975) 2555; 41 (1976) 896.
18 A. Ishida and T. Mikaiyama, Chem. Lett., (1976) 1127; D. Lenoir, Synthesis, (1977) 553.
19 S. Uemura, A. Onoe and M. Okano, Bull. Chem. Soc. Japan, 47 (1974) 2131.
20 J. San Filippo, Jr., A.F. Sowinski and L.J. Romano, J. Amer. Chem. Soc., 97 (1975) 1599.
21 J. Marsella and K.G. Caulton. Paper pres. ACS joint Central—Great Lakes Meeting, Butler University, May 24—26, 1978.
22 I. Halász and C. Horváth, Analyt. Chem., 35 (1963) 499.
23 G.W.A. Milne and M.J. Lacey, Crit. Rev. Analyt. Chem., 5 (1974) 45.
24 R.G. Gillis, Organic Mass Spect., 5 (1971) 79.
25 L.J. Bellamy, The Infrared Spectra of Complex Molecules, 3rd ed., Vol 1, p. 84 Wiley, New York, 1975.
26 D.C. Bradley and C.E. Holloway, J. Chem. Soc., A, (1968) 219.
27 E. Stenhagen, S. Abrahamson and F.W. McLafferty, Registry of Mass Spectral Data, Vol. 1, p. 11, Wiley, New York, 1974 and ref. therein.
28 F.H. Field, M.S.B. Munson and D.A. Becker, in R.F. Gould (Ed.), Advances in Chemistry Series, ACS, Washington D.C., 1966, No. 58, p. 167.
29 Ref. 1, p. 161—164.

30 (a) G.A. Olah (Ed.), Friedal—Crafts and Related Reactions, Interscience, 1963; (b) O.C. Dermer and R.A. Billmeir, J. Amer. Chem. Soc., 64 (1942) 464; (c) F. Fairbrother and W.C. Frith, J. Chem. Soc., (1951) 305.
31 (a) G.J. Karabatsos and J.L. Fry in G.A. Olah and P. von R. Schleyer (Ed.), Carbonium Ions, Vol. II, p. 521, 1970; (b) W. Gerrard and H.R. Hudson, Chem. Rev., 65 (1965) 697.
32 G.A. Olah and J. Lukas, J. Amer. Chem. Soc., 89 (1967) 4739.
33 D.C. Bradley, Prog. Inorg. Chem., 2 (1960) 303.
34 D.F. Shriver, The Manipulation of Air-Sensitive Compounds, McGraw-Hill, New York, 1969.
35 H.C. Brown, Organic Syntheses via Boranes, Wiley-Interscience, New York, 1975.
36 A.I. Vogel, Practical Organic Chemistry, 3rd Ed., 1956, Longmans, London.
37 L.F. Fieser and M. Fieser, Reagents for Organic Synthesis, Wiley, New York, 1967, Vol. 1, p. 584, 1179.