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PREPARATION AND CHARACTERIZATION OF $M(CH_3)_5$ (M = Nb or Ta) AND $Ta(CH_2C_6H_5)_5$ AND EVIDENCE FOR DECOMPOSITION BY α-HYDROGEN ATOM ABSTRACTION

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Summary

The preparations of $Nb(CH_3)_5$, $Ta(CH_3)_5$, and $Ta(CH_2C_6H_5)_5$ are reported in detail. The $M(CH_3)_5$ complexes decompose autocatalytically to give 3.4 ± 0.1 mol of methane and a non-hydrolyzable residue with approximate composition $MC_{1.5}H$ while $Ta(CH_2C_6H_5)_5$ decomposes in a non-autocatalytic manner to give ca. 2.6 mol of toluene per Ta. Decomposition of $Nb(CD_3)_5$ gave 96% CD_4 in diethyl ether while the toluene produced on decomposition of $Ta(CD_2C_6H_5)_5$ was at least 90%-d_3. An observed kinetic deuterium isotope effect of 2—3 in each case is evidence that an α-C—H(D) bond is broken in a slow step of the decomposition. It is postulated that $M(CH_3)_5$ and $Ta(CH_2C_6H_5)_5$ decompose primarily by α-hydrogen atom abstraction though almost certainly in a complex, possibly intermolecular fashion in the case of $M(CH_3)_5$. In neither case ($R = CH_3$ or $CH_2C_6H_5$) was there evidence for significant homolytic cleavage of the metal—carbon bond to give free alkyl radicals.

Introduction

In the past decade many neutral binary transition metal complexes, MR_x (M mainly metals in Ti or Cr triads), have been isolated and an approximately equal number postulated to exist in solution at low temperatures [1]. Some selected isolable examples are $M(CH_2C_6H_5)_4$ (M = Ti, Zr, Hf), V(1-norbornyl)$_4$, $Cr[CH\{Si(CH_3)_3\}_2]_3$, and $W(CH_3)_6$. The isolated complexes are thought to be thermally stable due to the fact that R usually contains no β-hydrogen atom(s) ($R = CH_3$, $CH_2C_6H_5$, $CH_2C(CH_3)_3$, $CH_2Si(CH_3)_3$, mesityl, etc.) and the well-documented, relatively low energy β-hydride elimination process therefore cannot occur. When decomposition is induced (usually by heating in an appropriate

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"inert" solvent), the alkane ($<x$ mol per M) is the organic product almost exclusively. Intramolecular alkyl coupling, another well-documented decomposition pathway for platinum(IV) and gold(III) methyl complexes, is evidently unfavorable relative to the process which yields RH.

Arguments concerning the formation of alkane have centered about whether RH forms from R· and H abstracted from the solvent or by an "α-hydride elimination" mechanism which leaves carbene, carbyne, or carbide fragments trapped in often intractable residues. The former has been shown to be unlikely in at least one instance, $Ti(CD_3)_4$. Consequently, for this, and many other complexes (not only binary complexes) containing one or more alkyl groups bound to the metal, the latter has been invoked.

Recently, several examples of apparent "α-hydride elimination" (or, in this case, perhaps more accurately, "α-hydrogen atom abstraction") to give stable Nb and Ta complexes containing an alkylidene ligand have been discovered [2]. In each case the hypothetical alkyl complex which had "decomposed" to give the alkylidene complex would have had a crowded coordination sphere; therefore the "decomposition" was postulated to be intramolecular. It was therefore of interest to examine the mode of decomposition of the isolable, less-crowded complexes, $Nb(CH_3)_5$ and $Ta(CH_3)_5$ [3], and a new example, $Ta(CH_2C_6H_5)_5$, in more detail. Their preparation and characterization are also described fully.

Results

Pentamethylniobium and pentamethyltantalum

Preparation and characterization. The entire class of alkyl halides of the type $M(CH_3)_xCl_{5-x}$ (M = Nb or Ta, x = 1, 2, or 3) is known and each member, except $Ta(CH_3)_2Cl_3$, has been isolated in a pure state [1a]. Two members of this class, $Nb(CH_3)_2Cl_3$ (I) and $Ta(CH_3)_3Cl_2$ (II), are obtained nearly pure directly from MCl_5 and 1.0 (M = Nb) or 1.5 mol (M = Ta) of $Zn(CH_3)_2$. $M(CH_3)_xCl_{5-x}$ impurities can be converted to I and II easily by appropriate addition of MCl_5 or $Zn(CH_3)_2$. Both are volatile, monomeric, crystalline, highly soluble complexes which react violently with water or oxygen and decompose slowly at room temperature in a nitrogen atmosphere.

Addition of two moles of halide-free methyllithium in diethyl ether to a solution of II in diethyl ether at −78°C followed by warming to room temperature gives a pale yellow solution of $Ta(CH_3)_5$ (III) and lithium chloride. Routine manipulation (see Experimental Section) gives halide- and solvent-free, volatile, yellow, crystalline III (m.p. ca. 0°C) which can be handled easily by vacuum line techniques. The yield of isolated III is limited by its volatility but the fact that $Ta(CH_3)_5$(dmpe) (IV) can be isolated in nearly quantitative yield by addition of dmpe [1,2-bis(dimethylphosphino)ethane] to the original ether solution suggests that the conversion of II to III is essentially quantitative. Pure, liquid III begins to turn green within a few minutes at 25°C, a grey solid forms, and methane is evolved. $Ta(CH_3)_5$ decomposes violently in air to a black, soot-like material.

Caution — it is dangerous to isolate more than one mmol of $Ta(CH_3)_5$. It should never be stored more than a few hours at −78°C, and never in a partially decomposed state since further decomposition can be sudden and violent.

The instability of III precluded accurate elemental analyses for C and H. It should be noted, however, that analyses for halides (Cl and Br) and lithium were low (<0.2, <0.3, and <0.1%, respectively) while hydrolyses of pure samples with HCl in methanol or ethanol gave 4.5 — 5.0 mol of CH_4 per Ta (3 runs). The highest peak in the mass spectrum of III is due to the $Ta(CH_3)_4^+$ ion. The ^1H NMR spectrum of III in toluene-d_8 at —10° C consists of a single resonance at τ 9.18. The spectrum is unchanged at −90°C.

Pentamethylniobium (V) can be prepared similarly from I (or $Nb(CH_3)_3Cl_2$) and methyllithium in diethyl ether. However, its brilliant yellow ether solutions cannot be warmed above —30° C. Above this temperature they turn green and deposit a black precipitate as methane evolves. It has not yet been isolated as a pure, crystalline solid but techniques similar to those used to isolate pure $Ti(CH_3)_4$ [4] probably would be equally successful for V. A dmpe adduct, yellow $Nb(CH_3)_5$(dmpe) (VI), can be isolated in high yield and has been characterized fully.

Decomposition of neat $Ta(CH_3)_5$ A sample of pure III (ca. 0.5 mmol) can be condensed into a weighed, evacuated flask (V ≈ 200 ml) and allowed to decompose at room temperature. The volatile products can then be examined by Toepler pump techniques and the residue weighed, recovered, and analyzed. Evolved methane can be measured step-wise (cooling the flask in liquid N_2 each time) in order to plot the rate of evolution or to determine the point at which decomposition is complete (usually less than 3 h).

Normally (vide infra) the volatile product mixture consists almost entirely (⩾98%) of CH_4, 3.43 ± 0.10 mol per Ta (7 runs). Traces (1—2%) of ethylene, ethane, and H_2 are the remaining volatile products. The methane accounts for 3.4 carbon atoms and 13.7 hydrogen atoms of the original TaC_5H_{15}.

After decomposition of III the entire inner surface of the flask is coated with a metallic dark grey residue which sometimes falls off the walls as a powder. Its weight is 81 ± 3% (7 runs) that of the starting $Ta(CH_3)_5$. Elemental analyses of one sample showed Ta = 91.7%, C = 10.1%, and H = 1.0%, or roughly $TaC_{1\cdot5}H$. The weight of a residue with this composition would be 78% that of the starting $Ta(CH_3)_5$. Little gas evolves on hydrolysis of this residue with HCl at 25° C in 1 h, in one instance ⩽ 0.3 mol per Ta. This gas was essentially pure H_2 (< 1% ethane).

Usually, therefore, neat $Ta(CH_3)_5$ decomposes as follows (ignoring trace products):

$$Ta(CH_3)_5 \rightarrow 3.43\ CH_4 + TaC_{1\cdot5}H$$

These products account for 4.9 of the original five carbon atoms and 14.7 of the original fifteen hydrogen atoms.

In many cases when III has decomposed about halfway, and the flask is disturbed, a "detonation" takes place within. This sudden and sometimes violent step appears to complete the decomposition process. The major volatile products then consist of 3.10 mol of CH_4 per Ta (2.53 to 3.41 mol in 5 runs) and 0.77 mol of H_2 per Ta (0.20 to 1.52 mol in 5 runs); more H_2 forms (1.52 mol, for example) when less CH_4 is produced (2.53 mol in the same run). The weight of the residue, 77 ± 2% (5 runs) vs. $Ta(CH_3)_5$, is not significantly different than it is in a "normal" decomposition. According to the total number of carbon atoms (3.1) and hydrogen atoms (13.9) accounted for by CH_4 and H_2, the residue's composition should be closer to TaC_2H (unconfirmed). It also does not hydrolyze easily. In one instance 0.14 mol (per Ta) of essentially pure H_2 was evolved on hydrolysis with HCl in methanol at 25°C for 8 h.

The "abnormal" decompositions suggest that the residue itself influences the rate of decomposition of III. Three pieces of evidence confirm that this is the case. The rate at which CH_4 evolves varies widely (vide infra). Secondly, decomposition in a flask filled with ca. 16 g of vacuum-dried glass wool (Owens—Corning Fiberglass No. 3950) was complete in 1 h while $t_{1/2}$ of a "normal" decomposition varied from ca. 90—160 min. Thirdly, decomposition of freshly prepared $Ta(CH_3)_5$ on the residue of a previous decomposition run was complete in ca. 30 min. Significantly, the most H_2 (1.52 mol per Ta) and the least CH_4 (2.53 mol per Ta) were produced in this experiment compared to the other four "abnormal" decompositions starting with a clean flask. Clearly, therefore, the decomposition of neat $Ta(CH_3)_5$ is markedly autocatalytic.

Decomposition of $Nb(CH_3)_5$ in diethyl ether. Bright yellow solutions of V (containing LiCl and LiBr or LiI from preparations of $LiCH_3$) begin to turn green at —30° to —20°C. (Solutions free of LiBr and LiI behave similarly.) A black precipitate forms steadily as the solution warms and gas evolves briskly. When gas evolution ceases the supernatant liquid is colorless.

The evolved gas, 3.40 mol per Nb, is essentially pure CH_4 ($\geqslant$ 98%) containing traces of ethylene, ethane, and H_2. The weight of the insoluble precipitate is not satisfactorily reproducible. Elemental analysis showed it to contain variable amounts of Nb, C, H, Li, halides, and O. In one case, using $LiCH_3$ prepared from CH_3Br (Alfa), the residue analyzed for 35.2% Nb, 38.8% Cl, 9.4% C, 1.4% H, and 3.2% O (this particular sample was not analyzed for Br or Li). As in the case of Ta, the residue yields only small amounts of H_2 on hydrolysis with HCl in methanol.

The fact that $Nb(CH_3)_5$ has not been isolated in a pure state makes studies as detailed as those on decomposition of $Ta(CH_3)_5$ impractical. Note, however, that the amount of CH_4 evolved on decomposition of $Nb(CH_3)_5$ in ether is essentially the same as that on decomposition of neat $Ta(CH_3)_5$. The apparent autocatalytic decomposition of $Nb(CH_3)_5$ has not yet been confirmed. One might infer from the results of labeling studies described below that the gross features of the decomposition of $Nb(CH_3)_5$ in ether are essentially the same as those of neat $Ta(CH_3)_5$.

Labeling studies. The primary purpose of deuterium labeling studies was to confirm what the decomposition of neat $Ta(CH_3)_5$ to give only traces of ethane and ethylene might suggest, that free methyl radicals are probably not sole or even significant primary decomposition fragments.

Labeling experiments depended on mass spectroscopic analysis of the methane evolved on decomposition of $Ta(CH_3)_x(CD_3)_{5-x}$ and $Nb(CH_3)_x(CD_3)_{5-x}$. The method most accurately gave the relative amount of CD_4. The accuracy for CD_3H, CD_2H_2, CDH_3, and CH_4 decreased in that order. Great care was taken to eliminate any interference by adventitious water or O_2 (see Experimental Section for details). A standard prepared by hydrolysis of a 1 : 1 mixture of CD_3MgBr and $LiCH_3$ with a 1 : 1 mixture of CH_3OH and CH_3OD gave results (%) which suggest that any amount or difference on the order of 5% is experimentally significant:

	CH_4	CH_3D	CH_2D_2	CHD_3	CD_4
Found	28	24	4	21	23
Theory	25	25	0	25	25

Evidence against free radical behavior. $Nb(CD_3)_5$ was prepared in ether at —78°C from iodide-free $LiCD_3$ and $Nb(CD_3)_2Cl_3$. The solution was degassed three times by evacuation at —196°C followed by warming to —30°C. It was then allowed to warm to room temperature. After 16 h 2.8 mol of methane per Nb had evolved. Mass spectroscopy showed it to consist of 96% CD_4 and 4% CD_3H. Knowing the ease with which a free methyl radical will abstract a hydrogen atom from diethyl ether [5,6], one must conclude that free CD_3 radicals are not produced during decomposition of $Nb(CD_3)_5$ to any great extent, or if they are, they do not live long enough to diffuse into the bulk solution. (Therefore description of such a fragment as a "free" radical, or even a radical at all, is probably misleading [6].)

The results of decomposition of "mixed" complexes, e.g., "$Ta(CH_3)_3(CD_3)_2$", provide additional evidence against free radical decomposition. Such complexes can be prepared straightforwardly and their empirical formula confirmed by hydrolysis. For example, hydrolysis of "$Ta(CH_3)_3(CD_3)_2$" with DCl in CH_3OD gave the following results (%):

	CH_4	CH_3D	CH_2D_2	CHD_3	CD_4
Found	6	55	1	2	36
Theory	0	60	0	0	40

Unfortunately, no direct evidence suggests that only $Ta(CH_3)_3(CD_3)_2$ is present. Since methyl ligands redistribute in a 1 : 2 mixture of $TaCl_5$ and $Ta(CH_3)_3Cl_2$ in C_6D_6 in a few minutes at 25°C to give $Ta(CH_3)Cl_4$, it is reasonable, but not easily proved, that CH_3 and CD_3 ligands in "$Ta(CH_3)_3(CD_3)_2$" also redistribute to give a statistical mixture of $Ta(CH_3)_x(CD_3)_{5-x}$ species ($x = 0, 1, 2, 3, 4,$ or 5). Yet, whether this is or is not the case does not bear on the results to be described.

The three following decomposition experiments gave identical results (%) within experimental error:

	CH_4	CH_3D	CH_2D_2	CHD_3	CD_4
$Ta(CH_3)_3(CD_3)_2$, neat	39	11	11	31	8
$Ta(CH_3)_3(CD_3)_2$, ether, LiX free	36	13	14	30	7
$Nb(CH_3)_3(CD_3)_2$, ether, LiCl present	39	9	8	34	10

Since the decomposition of $Nb(CD_3)_5$ was just shown to have minimal free radical character, the isotopic distribution in the methane evolved on decomposition of $Nb(CH_3)_3(CD_3)_2$ presumably is the result of an identical non-free radical process. Notably this distribution is essentially identical (within experimental error, ca. 5%) to the isotopic distributions in the methane obtained on decomposition of $Ta(CH_3)_3(CD_3)_2$, neat, or in ether. Therefore, the presence or absence of ether does not significantly affect the ratio of non-free radical to free-radical decomposition, if any of the latter obtains in either situation. Most likely it does not.

The Origin of CH_2D_2

A second interesting result should be noted; the amount of CH_2D_2 is greater than 5% and therefore experimentally significant. Though of course it is not possible at this time to say how CH_2D_2 does form, the results of the two following experiments suggest two ways in which it does not to any major extent.

The first consists of deuterolysis of a sample of $Ta(CH_3)_3(CD_3)_2$ to give essentially only CH_3D and CD_4 within experimental error (vide supra). Therefore H and D do not scramble rapidly among methyl carbon atoms in discrete III, i.e.,

$$Ta(CH_3)_3(CD_3)_2 \not\rightarrow Ta(CH_3)_2(CH_2D)(CD_3)(CD_2H)$$

The second experiment is meant to test whether H and D scramble in a manner which is, overall, that shown above, during decomposition. A solution of 2 mmol of $Nb(CH_3)_2(CD_3)_3$ in ether containing LiI (3 mol per Nb) and LiCl (up to 2 mol per Nb) was allowed to decompose until 2.2 mmol of the expected 6.8 mmol of methane had evolved. The solution was then cooled to −78°C, 1.3 mmol $(CH_3)_2PCH_2CH_2P(CH_3)_2$ added, and 0.18 g (0.57 mmol) of yellow $Nb(CH_3)_5(dmpe)$-d_x (VI-d_x) isolated. Hydrolysis of VI-d_x with HCl in CH_3OH gave 2.31 mmol of the expected 2.78 mmol of methane with the following isotopic composition (%):

	CH_4	CH_3D	CH_2D_2	CHD_3	CD_4
Found	35	0	4	60	1
Theory	40	0	0	60	0

Analysis of the first 0.7 mol (per Nb) of methane and the next 2.4 mol of methane evolved on decomposition of an identical sample of $Nb(CH_3)_2(CD_3)_3$ showed the following (%):

	CH_4	CH_3D	CH_2D_2	CHD_3	CD_4
First 0.7 mol	21	7	8	42	22
Next 2.4 mol	16	8	10	40	26

Hydrolysis of CH_2D and CHD_2 ligands in VI-d_x would give CH_3D and CH_2D_2 respectively. Since CH_2D_2 is present to a significantly greater extent (ca. 8%) in the methane evolved on decomposition of $Nb(CH_3)_2(CD_3)_3$ than in the methane evolved on hydrolysis of VI-d_x, H/D scrambling between CH_3 and CD_3 ligands to give discrete new methyl groups, e.g., CHD_2, in a discrete pentamethylniobium molecule during decomposition would seem remote.

It should also be noted that the ratio of CH_4 to CD_4 in the evolved methane apparently decreases with time. Though the differences here are on the order of experimental error, this is the first hint that CH_4 and CD_4 are not formed at the same rate in "mixed" complexes such as $Nb(CH_3)_2(CD_3)_3$.

The rate of methane evolution. The rate of evolution of methane from samples of neat $Ta(CH_3)_5$ and $Ta(CD_3)_5$ can be followed by periodically freezing the reaction flask in liquid nitrogen and measuring the methane by Toepler pump techniques (vapor pressure ≈ 11 mm at —196° C). The time required to warm the flask back to room temperature is insignificant on the time scale of the decomposition.

Fig. 1 shows four experiments in which the methane evolved on decomposition of ca. 1 mmol samples of $Ta(CH_3)_5$ in a 200 ml Pyrex bulb was measured periodically as described above. The variable results are understandable in view of the autocatalytic nature of the reaction and any differences in the rate of methane evolution in the dark vs. room light, in base-treated flasks vs. untreated flasks *, or on varying the amount of $Ta(CH_3)_5$ from 0.5 to 1.5 mmol are therefore apparently too small to be detected under these conditions. Similar curves for five additional runs fell between the two extremes and to this extent the results of decomposition of neat $Ta(CH_3)_5$ in a given size and type of flask are reproducible. Half the expected 3.4 mol per Ta of methane evolved in ca. 90—160 min ("$t_{1/2}$").

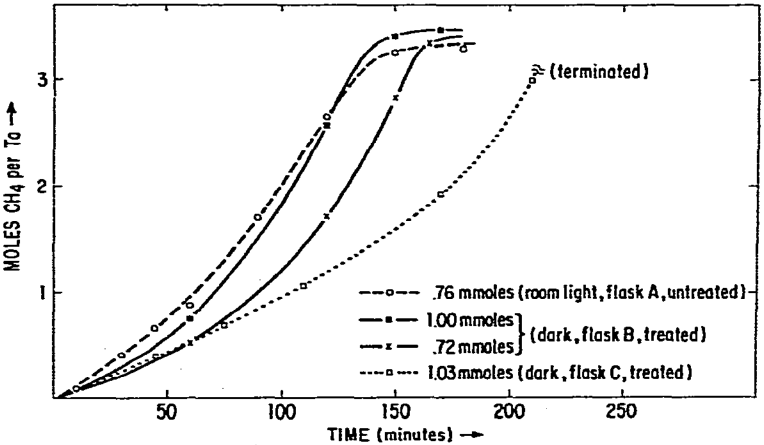

Fig. 1. The rate of evolution of methane on decomposition of ca. 1 mmol samples of neat $Ta(CH_3)_5$ in a 200 ml Pyrex bulb.

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* The same flask was used for several runs. The residue from a previous run was rinsed out with 5% HF solution. The flask was then rinsed out with distilled water, 1 *N* NaOH, more distilled water, then acetone, and finally was dried in vacuo. A fresh sample of $Ta(CH_3)_5$ was then condensed in and the decomposition in the dark or in room light followed as before. These results did not suffer significantly from those in which the 1 *N* NaOH treatment was omitted (an "untreated" flask).

Fig. 2 shows the extreme curves from Fig. 1 plotted on a different time scale with shading between the two, and three curves similarly obtained on decomposition of $Ta(CD_3)_5$. Note that $t_{\frac{1}{2}}$ in the case of $Ta(CD_3)_5$ varies from ca. 230—480 min, significantly longer than $t_{\frac{1}{2}}$ for $Ta(CH_3)_5$. The data is sufficiently consistent to conclude that $Ta(CH_3)_5$ decomposes significantly more rapidly than $Ta(CD_3)_5$, roughly 2—3 times as fast. A difference in their rates of decomposition is evident even on casual examination. For example, $Ta(CD_3)_5$ can be handled for longer periods of time than $Ta(CH_3)_5$ near room temperature with comparatively little decomposition.

Though the decomposition of neat $Ta(CH_3)_5$ is clearly complex, only one explanation for the enhanced stability of $Ta(CD_3)_5$ seems reasonable; at least one relatively slow step in the decomposition must involve breaking a C—D bond. The only pertinent data bearing on the magnitude of this suspected primary kinetic deuterium isotope effect comes from studies of deprotonation of $[Ta(\eta^5\text{-}C_5H_5)_2(CH_3)(CD_3)]^+$ with $(CH_3)_3P(CH_2)$ to give a mixture of $Ta(\eta^5\text{-}C_5H_5)_2(CH_3)(CD_2)$ and $Ta(\eta^5\text{-}C_5H_5)_2(CD_3)(CH_2)$ [2b]; k_H/k_D for the deprotonation is also in the order of 2—3 [7]. That the stability of $Ta(CD_3)_5$ vs. $Ta(CH_3)_5$) is due to a secondary isotope effect, or some other, unknown effect, therefore does not seem likely. Of course, a primary isotope effect is also consistent with the tentative conclusion (vide supra) that slightly more CH_4 forms in the early stages of decomposition of $Nb(CH_3)_2(CD_3)_3$, and slightly more CD_4 in the latter stages.

Pentabenzyltantalum

Preparation and characterization. The reaction between ether-free $Zn(CH_2C_6H_5)_2$ (1.5 mol) and $TaCl_5$ in toluene at 25°C gives red-orange $Ta(CH_2C_6H_5)_3Cl_2$ (VII) in good yield. It is moderately soluble in saturated hydrocarbons. Elemental analysis and its 220 MHz ^1H NMR are consistent with the formulation.

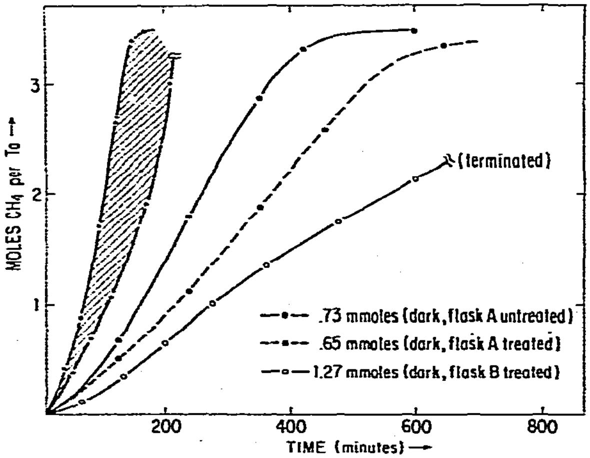


Fig. 2. A comparison of the rates of methane evolution on decomposition of $Ta(CH_3)_5$ (cross-hatched) and $Ta(CD_3)_5$.

Tribenzyltantalum dichloride seems thermally more stable than $Ta(CH_3)_3Cl_2$ but should still be stored under N_2 at 0°C or less. Evidence for $Nb(CH_2C_6H_5)_xCl_{5-x}$ (x probably = 2 or 3) is in hand but so far it has not been isolated in pure form (see Experimental Section).

The reaction between VII and $Mg(CH_2C_6H_5)_2(THF)_2$ in toluene at −78°C followed by warming to 25°C gives a red solution containing a gelatinous white precipitate of $MgCl_2(THF)_2$. Filtration and addition of pentane gives red crystals of $Ta(CH_2C_6H_5)_5$ (VIII) in high yield, the first transition metal complex containing more than four benzyl ligands. Its formulation is supported by elemental analyses, 220 MHz ^1H NMR data, and by the fact that hydrolysis with 12*N* HCl in ether (12 h at 25°C) gives 4.9 mol of toluene per Ta. Molecular weight determinations (cryoscopic in C_6H_6) support the monomeric formulation. Pentabenzyltantalum does not sublime without decomposition and begins to decompose in benzene at 40°C within a few minutes according to ^1H NMR.

Decomposition of pentabenzyltantalum. A 0.5 mmol sample of VIII was heated in ca. 4 ml of C_6D_6 at 80°C for 16 h in a sealed tube. During this period the red solution darkened steadily to red-brown. After several hours some solid had formed but even after 16 h the deep red-brown color remained. The residue which remained after removing all readily volatile products, a red-brown gum, has not been characterized. Quantitative GLC analysis of the C_6D_6 solution of the volatile components showed that the amount of toluene formed per Ta was 2.50 mol. Mass spectral analysis indicated it to be ca. 98% toluene-d_0 and 2% toluene-d_1. (The experimental error in this and similar measurements must be at least ±2%). As in the decomposition of $M(CH_3)_5$, little organic product consists of the dialkyl, in this case, bibenzyl. In one experiment, after hydrolysis of the red-brown residue with 1 *N* HCl/ether, only ca. 0.1 mol per Ta of bibenzyl was found by quantitative GLC analysis. Therefore $\leqslant$ 0.1 mol per Ta of bibenzyl must have been present before hydrolysis.

The failure to form significant quantities of toluene-d_1 by abstraction of D from C_6D_6 by $C_6H_5CH_2^{\cdot}$ would not be at all surprising in view of the very low reactivity of both $C_6H_5CH_2^{\cdot}$ and C_6D_6 (or C_6H_6) in this type of reaction [5,8]. The only reliable indicator of possible free radical-type decomposition would then be the formation of bibenzyl. Since the upper limit on the amount of bibenzyl formed is 0.1 per Ta (some or all may form on hydrolysis of the residue), the decomposition of $Ta(CH_2C_6H_5)_5$ would not seem to give any significant concentration of benzyl radicals.

The reverse of the above experiment consisted of decomposing $Ta(CD_2C_6H_5)_5$ in C_6H_6 for 2 and 6.3 h at 80°C to give 1.1 and 1.6 mol of toluene per Ta respectively. Table 1 lists the peak intensities in the mass spectra of the toluenes from these two experiments along with $C_6H_5CD_3$ and $C_6H_5CD_2H$ standards (from deuterolysis or hydrolysis, respectively, of $Mg(CD_2C_6H_5)_2(THF)_2$), a run in which C_6D_6 was substituted for C_6H_6 (2.0 mol toluene per Ta after 11 h at 80°C), and a calculated spectrum of a mixture of 10% $C_6H_5CD_2H$ and 90% $C_6H_5CD_3$. Unfortunately the data is not sufficiently precise to conclude with certainty that the toluene obtained on decomposition of $Ta(CD_2C_6H_5)_5$ is entirely toluene-d_3 but it must be at least 90% toluene-d_3. Since any possible toluene-d_2 is almost certainly not formed by $C_6H_5CD_2^{\cdot}$ abstraction of H from C_6H_6 (vide supra) these results may indicate that the phenyl ring in α,α-dideu-

TABLE 1

MASS SPECTRAL PEAK INTENSITIES OF LABELED TOLUENES

	m/e					
	91	92	93	94	95	96
$C_6H_5CD_3$	3.1	2.7	46.4	90.1	100.0	7.5
$C_6H_5CD_2H$	3.0	29.6	100.0	92.2	7.0	
Decomposition of $Ta(CD_2C_6H_5)_5$ in C_6H_6 (2 h, 80°C)	13.2	12.6	54.0	100.6	100.0	8.6
Decomposition of $Ta(CD_2C_6H_5)_5$ in C_6H_6 (6.3 h, 80°C)	9.0	7.5	56.7	97.8	100.0	7.5
Decomposition of $Ta(CD_2C_6H_5)_5$ in C_6D_6 (11 h, 80°C)	8.3	8.5	50.5	94.3	100.0	7.5
Calculated for 10% tol-d_2, 90% tol-d_3	3.4	3.0	57.9	100.3	100.0	7.5

terobenzyl ligand is the source of the hydrogen atom. Even if this is the case, however, the predominant mechanism of decomposition clearly involves abstraction of only the α-deuterium atoms to give $C_6H_5CD_3$.

Rate of toluene formation. Separate 0.5 mmol samples of $Ta(CH_2C_6H_5)_5$ and $Ta(CD_2C_6H_5)_5$ were heated in 4 ml of C_6H_6 in sealed vials at 60°C for periods from 0.5 to 11 h. Each vial was opened and the volatiles transferred in vacuo and analyzed quantitatively by GLC for toluene. The results are shown in Fig. 3.

It first should be noted that each set of points falls on a smooth curve. One might expect considerably less reproducible results and a noticeable S-shape to the curves (cf. Figs. 1 and 2) if the decomposition were markedly autocatalytic. Since it apparently is not, the curves represent accurately the rate of formation of toluene in each case, and a comparison of the two therefore is valid.

Clearly $Ta(CH_2C_6H_5)_5$ decomposes significantly faster than $Ta(CD_2C_6H_5)_5$. It is not vitally important that the intimate mechanism of decomposition be known at this stage. The results are meant to illustrate that at least one relati-

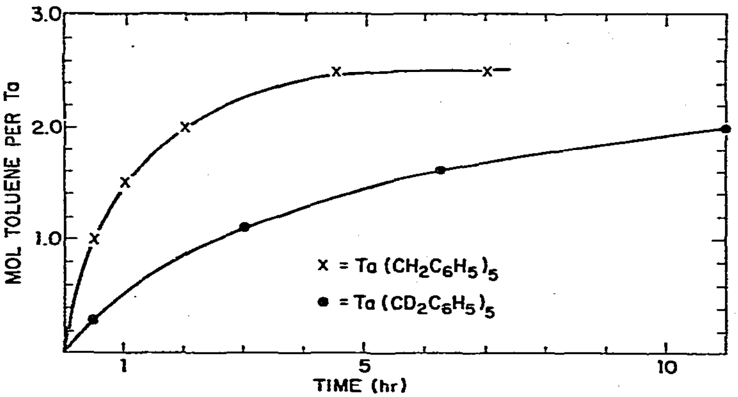


Fig. 3. A plot of the toluene produced on decomposition of individual samples of $Ta(CH_2C_6H_5)_5$ and $Ta(CD_2C_6H_5)_5$ in C_6H_6 at 60°C.

vely slow step of the decomposition of $Ta(CD_2C_6H_5)_5$, like that of $Ta(CD_3)_5$ (vide supra), must consist of breaking a C—D bond. Of course, this result is also consistent with the primary decomposition mode involving abstraction only of α-hydrogen (deuterium) atoms (vide supra).

Discussion

Preparations and properties

The general physical properties of $Nb(CH_3)_5$ and $Ta(CH_3)_5$ appear analogous to those of $Ti(CH_3)_4$ [4,9] and $W(CH_3)_6$ [10] respectively. Both $Ti(CH_3)_4$ and $Nb(CH_3)_5$ decompose at ca. —30° C in ether while $Ta(CH_3)_5$ and $W(CH_3)_6$ are volatile liquids which decompose readily near 25° C. $Ta(CH_3)_5$ is probably monomeric in the vapor phase [11] (symmetry = D_{3h}) according to its He photoelectron spectrum. Like $Ti(CH_3)_4$, $Nb(CH_3)_5$ and $Ta(CH_3)_5$ form relatively stable, well-characterized adducts, e.g., seven-coordinate $M(CH_3)_5$(dmpe) [3]. Details of the preparation of the adducts are given in the Experimental Section.

One report states that several attempts to prepare M-benzyl complexes were as unsuccessful for M = Ta as for M = Nb [12]. The successful preparations of $Ta(CH_2C_6H_5)_3Cl_2$ (VII) and $Ta(CH_2C_6H_5)_5$ (VIII) (and the evidence for $Nb(CH_2C_6H_5)_xCl_{5-x}$) demonstrate that seemingly minor variations in experimental procedure can profoundly effect the outcome of an alkylation experiment. Several authors have reached this conclusion about other transition metal alkyls [1], $Ti(C_6H_5)_4$ probably being most thoroughly studied in this regard [13].

Decomposition of MR_5 complexes — general considerations

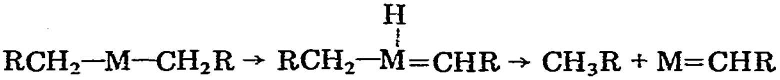
The decompositions of $Nb(CH_3)_5$ and $Ta(CH_3)_5$ closely resemble that of $Ti(CH_3)_4$ [14]. The results are potentially more informative, however, because the stoichiometry, at least that of $Ta(CH_3)_5$ decomposition, can be ascertained more accurately and labeling procedures are more straightforward. The similarities are the following: (i) the decompositions are autocatalytic; (ii) homolytic cleavage of M—CH_3 bonds is minimal in aliphatic hydrocarbons or diethyl ether; and (iii) CH_2D_2 is formed on decomposition in systems containing both CH_3 and CD_3 ligands. The major differences are that (i) significant amounts of H_2 are formed in some instances on decomposition of neat $Ta(CH_3)_5$ and (ii) up to 0.6 mol of methane per Ti evolves on hydrolysis of the Ti residue (the Ta and Nb residues hydrolyze only slightly to give molecular hydrogen).

The decomposition of $Ta(CH_2C_6H_5)_5$ could be compared with that of $Ti(CH_2C_6H_5)_4$ or $Zr(CH_2C_6H_5)_4$. The major difference is that less than the total possible amount of toluene (3.33 mol) was found for Ta, assuming that only α-H(D) atoms are available to form toluene; the maximum, 2.66 mol per metal, was found for $Zr(CH_2C_6H_5)_4$ [15]. An additional informative result in the case of $Ta(CD_2C_6H_5)_5$ is that little (if any) $C_6D_5CD_2H$ is formed by H abstraction from the phenyl ring of a $CD_2C_6H_5$ ligand; primarily α-H (or D) atoms are abstracted.

The observation of kinetic deuterium isotope effects would seem important for three reasons. First, it suggests that a slow step in the decomposition of TaR_5 species consists of breaking an α-C—H or α-C—D bond. That an effect of this magnitude can arise in a decomposition step which consists of homolytic M—C bond cleavage does not seem likely. Therefore, α-abstraction is at least kinetically more favorable than homolytic cleavage. Secondly, it is conceivable that metal alkyls (not containing a β-hydrogen atom) which are of borderline stability under a given set of conditions can be isolated by substituting D for H on the α-carbon atom. This conclusion follows directly from the relative stability of $Ta(CD_3)_5$ and $Ta(CD_2C_6H_5)_5$ vs. $Ta(CH_3)_5$ and $Ta(CH_2C_6H_5)_5$, respectively. Finally, it should be noted that small amounts of protio impurities in deutero sources (e.g., CD_2H in CD_3) will be magnified slightly by the isotope effect. For example, if the ligands in $Nb(CD_3)_5$ are only 98% CD_3 and 2% CD_2H, and $k_H/k_D = 3$, then the methane formed on decomposition by a random α-abstraction process would be 96.7% CD_4 and 3.3% CD_3H. Note that this is approximately the isotopic mixture formed on decomposition of $Nb(CD_3)_5$ in ether in Pyrex glassware (vide supra).

α-Hydrogen atom abstraction

α-Abstraction might be viewed as the analog of "β-hydride elimination" in instances where the alkyl possesses no β-hydrogen atoms, i.e.



$$RCH_2{-}M{-}CH_2R \rightarrow RCH_2{-}\overset{\overset{\displaystyle H}{\vdots}}{M}{=}CHR \rightarrow CH_3R + M{=}CHR$$

There is, in fact, evidence that a metal can "abstract" an α-hydrogen atom [16] and this particular variation has therefore, by analogy, been called "α-hydride elimination". However, a second alkyl ligand may also abstract the α-hydrogen atom directly, a discrete metal hydride not being formed. A distinction between these two processes when more than one alkyl ligand is bound to the metal will be extremely difficult at best. For the present, therefore, we must assume that either, or both versions may obtain in any particular situation.

In contrast, a pattern does seem to be emerging concerning whether an α-abstraction process is inter- or intra-molecular, though, again, conclusive evidence is lacking. Several authors have noted that alkyls such as $Ti(CH_3)_4$ are more stable in dilute solution (diethyl ether for example) [1]. It is also clear that binary complexes containing larger alkyl ligands ($CH_2C_6H_5$, $CH_2C(CH_3)_3$, etc.) are considerably more stable than those containing CH_3 [1]. Finally, adducts of binary methyl complexes (e.g., $Ta(CH_3)_5$(dmpe) and $Ti(CH_3)_4$(dmpe)) are considerably more stable than the binary complexes themselves [1a]. Each of these observations is consistent with the postulate that relatively uncrowded binary alkyls decompose most readily by an intermolecular mechanism. On the other hand, several hypothetical complexes containing bulky ligands apparently decompose by what can only reasonably be an intramolecular α-hydrogen atom abstraction to give stable alkylidene complexes [2]. One can therefore postulate that $Ta(CH_3)_5$ decomposes by an intermolecular α-hydrogen atom abstraction mechanism, one which quite likely is complex * and does not give simple, or at

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* The CH_2D_2 obtained on decomposition of $M(CH_3)_x(CD_3)_{5-x}$ complexes may be characteristic of the apparently complex, autocatalytic nature of the reaction, particularly the violent, "abnormal" decompositions which produce significant amount of molecular hydrogen. However, this need not be the case. For example, it is known that the deuterium in $[(CH_3)_3CCH_2]_3Ta{=}CDC(CH_3)_3$ will scramble among the α-carbon atoms under conditions where the complex does not decompose [2a]. Assuming that this is a first order (intramolecular) reaction, one can show that $\Delta G^{\ddagger}_{348} = 27.5 \pm 0.5$ kcal mol^{-1} [7]. A related, more rapid scrambling process (possibly intermolecular) during decomposition of $M(CH_3)_x(CD_3)_{5-x}$ could therefore be one means of forming (ultimately) CH_2D_2.

least, stable primary products. It is less clear how $Ta(CH_2C_6H_5)_5$ decomposes. If it, in contrast, decomposes by primarily an intramolecular mechanism, then hypothetical $(C_6H_5CH_2)_3Ta{=}CHC_6H_5$ must not be long-lived under the usual reaction conditions. It should be noted in this context that all the known, stable Nb and Ta alkylidene complexes also have sterically crowded coordination spheres and in one case, $Ta(\eta^5\text{-}C_5H_5)_2(CH_3)(CH_2)$, the most reasonable mechanism of decomposition is bimolecular since $Ta(\eta^5\text{-}C_5H_5)_2(CH_3)(CH_2{=}CH_2)$ and the "$Ta(\eta^5\text{-}C_5H_5)_2(CH_3)$" fragment are formed [2b].

The concept of α-abstraction versus homolytic M—C bond cleavage as a primary decomposition process seems particularly attractive in view of the results of recent calorimetric studies aimed at determining M—C bond strengths. Values of $\bar{E}$(M—C) for complexes of the type $M[CH_2C(CH_3)_3]_4$ (M = Ti, Zr, Hf) have been found to be 44, 54, and 58 ± 2 kcal mol^{-1}, respectively [17], while $\bar{D}$(M—C) for $Ta(CH_3)_5$ and $W(CH_3)_6$ similarly have been found [18] to be 62 and 38 ± 2 kcal mol^{-1}, respectively. The larger values are on the order of the metal—carbon bond strengths in main group alkyls like $Pb(CH_3)_4$, and $Pb(CH_3)_4$ decomposes in the gas phase to give free methyl radicals only at high temperatures (ca. 500°C) [19]. It is now perhaps not surprising to find that $Ta(CH_3)_5$ does not decompose at 25°C to give free methyl radicals. The "sterically allowed" intermolecular α-hydrogen atom abstraction process by which it is postulated to decompose therefore must have a relatively low activation energy.

Though details may differ from one situation to another, the concept of α-hydrogen atom abstraction appears sound. The deuterium isotope effects observed here along with other aspects of MR_5 decompositions, as well as isolation of products of apparent intramolecular α-hydrogen atom abstractions [2], should help to more firmly establish the validity of this mode of decomposition for (at least) Nb(V) and Ta(V) alkyl complexes. The possibility that such processes may be more general and alkylidene complexes (even if short-lived) more common, is obviously intriguing.

Experimental section

All manipulations were done in a N_2-filled Vacuum Atmospheres HE43-2 drybox. Solvents were dried by passing them through Linde 4A molecular sieve columns. Metal halides were purchased from standard sources. Dimethylzinc was purchased from Stauffer Chemical Company. Methyllithium was purchased from Alfa and standardized by measuring methane evolved on hydrolysis (Toepler pump). $ZnCl_2$ was dried with $SOCl_2$, then in vacuo for 24 h.

(1) Preparation of $LiCD_3$ in ether

$LiCD_3$ was prepared from 25g CD_3I (Merck Isotopes, > 99 mol%) and 0.2g Li dispersion (1% Na) in 150 ml ether at 0°C followed by warming to room temperature. After filtering, a sample was hydrolyzed with methanol and the evolved methane measured by Toepler pump techniques; yield 73%. One mol dioxane per Li was added to precipitate LiI · dioxane. After filtering, the halide-free $LiCD_3$ solution was again standardized by hydrolysis as above (86% recovered); overall yield 63%.

(2) Preparation of $Zn(CH_2C_6H_5)_2$ and $Zn(CD_2C_6H_5)_2$

A Grignard reagent was prepared by addition of 126 g distilled $C_6H_5CH_2Cl$ over 2 h to 40 g Mg turnings in 1 l ether at 0°C followed by stirring for 5 h at 25°C. Anhydrous $ZnCl_2$ (68 g) was then added slowly as a solid followed by 1 l ether and stirring overnight. The mixture was filtered and the solid rinsed with 1 l ether. The combined filtrates were stripped to a syrup. Toluene (~300 ml) was added, the mixture filtered, and the filtrate distilled at 1 atm. till the head temperature reached 110°C (some Zn metal forms). The mixture in the distillation pot was cooled and filtered. Pentane (ca. 150 ml) was added and the mixture was shaken, then allowed to stand a few minutes till it separated into two layers. The top layer was decanted off and discarded. This process was repeated twice. Exposure of the resulting oil to vacuum caused it to crystallize suddenly; yield 96 g (78%) $Zn(CH_2C_6H_5)_2$. ^1H NMR (τ, C_6D_6): 2.7—7.3 (m), 8.48 (s), 5 : 2 ratio. Reduction of 65 g benzoyl chloride with 10g $LiAlD_4$ gave 47g $C_6H_5CD_2OH$ (91%) which was converted to 46 g $C_6H_5CD_2Cl$ (84%) with 36 ml $SOCl_2$ in 100 ml $CHCl_3$ (stirred overnight then distilled at 27 mm, 80°C). $Zn(CD_2C_6H_5)_2$ was prepared in 61% yield as above.

(3) Preparation of $Mg(CH_2C_6H_5)_2$ and $Mg(CH_2C_6H_5)_2(THF)_2$

Two moles of $C_6H_5CH_2MgCl$ were prepared at 0°C in 1 l ether from 254 g distilled $C_6H_5CH_2Cl$ (b.p. 82°C, 18 mm) and 75 g Mg. The solution was heated to reflux for one hour and 171 ml dioxane added dropwise. $MgCl_2(dioxane)_2$ was filtered off with difficulty and all solvent removed from the filtrate in vacuo leaving 60 g (29%) crude $Mg(CH_2C_6H_5)_2$.

Crude $Mg(CH_2C_6H_5)_2$ (6.55 g) was dissolved in 20 ml THF. Pentane (40 ml) was added and the solution stood at —30°C overnight to give 6.1 g (55%) white, crystalline $Mg(CH_2C_6H_5)_2(THF)_2$. ^1H NMR (τ, C_6D_6): 2.9 (m, 8); 3.3 (m, 2); 6.77 (m, 8, THF); 8.26 (s, 4); 8.83 (m, 8, THF).

$Mg(CD_2C_6H_5)_2(THF)_2$ was prepared similarly from $C_6H_5CD_2Cl$ (see (2)).

(4) Preparation of $Ta(CH_3)_5$

Only ca. 1 mmol of pentamethyltantalum should be isolated at one time. Ether solutions containing larger amounts can be prepared by scaling up the procedure; these should be used soon, not stored. The following procedure is the one used to isolate small quantities of pure $Ta(CH_3)_5$ for analyses, decomposition studies, etc.

$Ta(CH_3)_3Cl_2$ (0.60 g, 2.0 mmol) in 35 ml ether was cooled to —78°C and 2.42 ml of 1.65 M $LiCH_3$ in ether, diluted to 20 ml, was added dropwise with stirring. The mixture was warmed to 25°C to give a pale yellow solution and a fine precipitate of LiCl. LiCl was removed by filtration and the ether was removed in vacuo to give a volatile yellow oil. Pentane was added and residual lithium salts removed by filtration. On removing the pentane in vacuo, $Ta(CH_3)_5$ crystallizes on the cold flask walls, then melts as the flask warms to room temperature. The flask is then frozen in liquid N_2 and evacuated. The last traces of pentane or ether can be removed by warming the flask to room temperature, subliming $Ta(CH_3)_5$ onto the upper half by briefly cooling a small area with a swab dipped in liquid N_2, then opening the flask to vacuum for a few seconds. The sample can then be condensed with liquid N_2 into a weighed flask for further studies; yield ca. 0.30 g.

Samples thus isolated were analyzed after hydrolysis with methanol. Anal.: $Br < 0.3$; $Cl < 0.2$; $Li < 0.1$; CH_4 4.5—5.0 mol per Ta (3 runs). ^1H NMR (τ, tol-d_8, —10° C): 9.18 (s). Mass spectrum: $Ta(CH_3)_4^+$ at m/e 241.

(5) Preparation of $Ta(CD_3)_5$

A 0.6 *M* solution of $LiCD_3$ (33 ml) was added to 1.38 g $ZnCl_2$ (dried with $SOCl_2$) at —78° C. After warming to 25° C, 25 ml of pentane and 2.4 g of $TaCl_5$ were added. After stirring for 5 min, 0.88 g dioxane was added, and stirring continued for 10 min. The mixture was filtered and the solvent removed in vacuo. The residue was extracted with pentane, the mixture filtered, and the pentane stripped from the filtrate in vacuo to give 1.45 g $Ta(CD_3)_3Cl_2$.

$Ta(CD_3)_5$ was prepared from $Ta(CD_3)_3Cl_2$ and $LiCD_3$ as in *(4)*.

(6) Preparation of $Ta(CH_3)_5(dmpe)$; dmpe = $(CH_3)_3PCH_2CH_2P(CH_3)_2$

$Ta(CH_3)_5$ in ether was prepared as in *(4)* from 16.0 g $Ta(CH_3)_3Cl_2$ in 200 ml ether and 50 ml 2.2 *M* $LiCH_3$. The yellow color was discharged on addition of 8.2 g dmpe in 50 ml ether. The solution was filtered, the solvent removed in vacuo, and the residue extracted with toluene (25 ml). After filtering, one volume of pentane was added and the solution stood overnight at —30° C to give 15.4 g of white crystals (pentane wash). The filtrate's volume was reduced to ca. 10 ml in vacuo and an additional 1.5 g isolated by addition of 25 ml pentane and standing at —30° C; total yield 16.9 g (77%) $Ta(CH_3)_5(dmpe)$.

Anal.: Found: C, 32.09; H, 7.62; P, 14.58. $TaC_{11}H_{31}P_2$ calcd.: C, 32.52; H, 7.68; P, 15.24%. The ^1H and ^{13}C NMR spectra are discussed in the preliminary communication [3]. $^{31}P\{^1H\}$NMR (ppm downfield from 85% H_3PO_4, tol-d_8, —30° C); 11.85 (s).

(7) Preparation of $Nb(CH_3)_5$ or $Nb(CD_3)_5$ in ether

This preparation is analogous to *(4)* employing $Nb(CH_3)_2Cl$ and $LiCH_3$ at —78° C in diethyl ether followed by warming to —30° C.

The preparation of $Nb(CD_3)_2Cl_3$ (from $LiCD_3$, $ZnCl_2$, and $NbCl_5$) is analogous to that of $Ta(CD_3)_3Cl_2$ (see *(5)*) and $Nb(CD_3)_5$ analogous to that of $Nb(CH_3)_5$ above.

Since $Nb(CH_3)_5$ is too unstable to be isolated its existence can only be inferred by indirect means (see (*8*)).

(8) Preparation of $Nb(CH_3)_5(dmpe)$

A solution of 6.0 g $Nb(CH_3)_2Cl_3$ in 100 ml of diethyl ether was cooled to —78° C and 18.0 ml of a 2.2 M $LiCH_3$ solution in ether added dropwise over a period of 5 min. followed by a solution of 2.0 g dmpe in 25 ml of diethyl ether. The mixture was warmed to 25° C, stirred for 1 h., and filtered. Solvent was removed from the filtrate in vacuo and the residue was extracted with 50 ml of toluene and filtered. Pentane (40 ml) was added to the filtrate and the solution stood at —30° C overnight to give 5.4 g (67%) brilliant yellow $Nb(CH_3)_5$-(dmpe).

Anal.: Found: C, 41.60; H, 9.60; P, 19.02. $NbC_{11}H_{31}P_2$ calcd.: C, 41.51;

H, 9.84; P, 19.46%. The ^1H and ^{13}C NMR spectra do not differ appreciably from those reported for the Ta analog [3]. The chemical shifts are slightly temperature and concentration dependent.

(9) Preparation of $Ta(CH_2C_6H_5)_3Cl_2$

$TaCl_5$ (5.0 g) and $Zn(CH_2C_6H_5)_2$ (5.2 g) were stirred in 50 ml of a 1 : 1 toluene/pentane mixture for 2 h. The $ZnCl_2$ was removed by filtration and the orange filtrate stripped in vacuo. The residue was dissolved in 50 ml of hexane and filtered. The filtrate was cooled and reduced in volume to give 4.05 g orange, crystalline $Ta(CH_2C_6H_5)_3Cl_2$ (55% yield).

Anal.: Found: C, 47.68; H, 4.10; Cl, 13.46. $TaC_{21}H_{21}Cl_2$ calcd.: C, 48.02; H, 4.13; Cl, 13.50%. ^1H NMR (τ, C_6D_6): 2.7—3.0 (m, 5), 6.80 (s, 2).

$Ta(CD_2C_6H_5)_3Cl_2$ was prepared similarly.

(10) Evidence for $Nb(CH_2C_6H_5)_xCl_{5-x}$

Dioxane (0.36 g, one per Nb) was slowly added to $NbCl_5$ (1.0 g) in 25 ml of ether followed by a solution of 1.40 g $Mg(CH_2C_6H_5)_2(THF)_2$ in 25 ml ether (rapidly). After 5 min the red solution was filtered and the ether removed in vacuo leaving a red oil. The oil was dissolved in 5 ml of pentane and a small amount of activated charcoal added. The mixture was filtered and the pentane was removed in vacuo leaving a red semi-solid (ca. 0.25 g). A ^1H NMR spectrum in C_6D_6 shows phenyl resonances, the characteristic sharp singlet due to bibenzyl, and a broad peak at τ 6.25 which is almost certainly due to α-protons on a benzyl group attached to Nb (cf. benzyl α-proton resonance at τ 6.80 in $Ta(CH_2C_6H_5)_3Cl_2$). The relative amount of bibenzyl and the proposed Nb-benzyl complex varies from one experiment to another. So far the two have not been separated.

(11) Preparation of $Ta(CH_2C_6H_5)_5$

$Ta(CH_2C_6H_5)_3Cl_2$ (4.05 g) was dissolved in 25 ml of toluene and the solution was cooled to —78°C. To this was added dropwise a solution of 2.70 g $Mg(CH_2C_6H_5)_2(THF)_2$ in 25 ml of toluene followed by warming to room temperature. The mixture was filtered and the filtrate stripped to a red-orange syrup. Hexane (20 ml) was added and the mixture stood at —30°C for 2 h to give 4.6 g (93%) $Ta(CH_2C_6H_5)_5$.

Anal.: Found: C, 66.30; H, 5.77; Cl, < 0.3. $TaC_{35}H_{35}$ calcd: C, 66.04; H, 5.54%. ^1H NMR (τ, C_6D_6, 220 MHz): 2.88 (t, 2, $J = 8$, H_{meta}), 3.09 (t, 1, $J = 8$, H_{para}), 3.27 (d, 2, $J = 8$, H_{ortho}), 7.39 (s, 2, CH_2). Mol.wt. (cryoscopic in benzene): found: 572, calcd.: 636. Hydrolysis with a 12 N HCl/ether mixture in a sealed tube for 12 h gave 4.9 ± 0.1 mol of toluene per Ta (quantitative GLC analysis).

$Ta(CD_2C_6H_5)_5$ was prepared in an identical fashion.

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