

NIBIUM AND TANTALUM MESITYL COMPLEXES AND THE ROLE OF THE MESITYL LIGAND IN α - AND γ -HYDROGEN ABSTRACTION REACTIONS

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Summary

The Ta and Nb complexes $M(\text{Mes})_nX_{5-n}$ (Mes = Mesityl; X = Cl or Br; $n = 1, 2$ or 3) and several derivatives can be prepared in high yield. They are considerably more stable than their phenyl analogues. ^1H NMR data indicate that a mesityl ligand most likely occupies an equatorial site in a trigonal bipyramidal molecule but cannot rotate freely because its ortho methyl groups cannot pass by the axial chloride ligands. $\text{TaMes}(\text{CH}_2\text{CMe}_3)\text{X}_3$ reacts with PMe_3 (= L) to give the known alkylidene complexes, $\text{Ta}(\text{CHCMe}_3)\text{L}_2\text{X}_3$, but $\text{TaMes}(\text{CH}_3)\text{X}_3$ reacts with PMe_3 to give the benzylidene complexes, $\text{Ta}(\text{CHC}_6\text{H}_3\text{Me}_2)\text{L}_2\text{X}_3$ (by γ -abstraction from the mesityl ligand), instead of the hoped for analogous methylene complex.

Introduction

It is now well-known that complexes containing alkyl ligands which bear one or more β -hydrogen atoms are often unstable with respect to loss of a β -hydrogen atom [1]. Phenyl complexes (especially of early transition metals) fall into this class since an *ortho*-hydrogen atom can be lost from one phenyl ligand to a second (or a different alkyl ligand as the case may be) to give benzyne complexes [2,3], the first stable mononuclear example of which has been isolated recently [4]. This may be part of the reason why early transition metal phenyl complexes † are not nearly as stable as benzyl, neopentyl, or trimethylsilylmethyl

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† The list of relatively stable complexes includes MPh_4 ($M = \text{Ti, Zr, V}$), $\text{ZrPh}_2(\text{ether})_2$, CrPh_3L_x ($x = 2$ or 3), $[\text{TaPh}_6]^-$, and Cp_2MPh_2 ($M = \text{Ti, Zr}$); see [1] and references therein for these and other examples.

complexes [1,5]; for example, $\text{Ta}(\text{CH}_2\text{CMe}_3)_3\text{Cl}_2$ is stable [1] while TaPh_3Cl_2 is not [6].

A mesityl complex cannot decompose similarly *. Therefore, it is perhaps not surprising to find that, although TaPh_2Cl_3 and TaPh_3Cl_2 are thermally unstable [6], the analogous mesityl complexes are comparatively stable. In fact, all six members of the $\text{MMes}_n\text{X}_{5-n}$ class ($\text{M} = \text{Nb}$ or Ta ; $\text{X} = \text{Cl}$ or Br ; $\text{Mes} = \text{mesityl}$; $n = 1, 2, \text{ or } 3$) can be prepared. Mesityl complexes are of interest to us since a mesityl ligand could be the most desirable leaving group in our continuing attempts to prepare a methylene complex by α -hydrogen atom abstraction [11] — a mesityl ligand is bulky (a crowded coordination sphere is required) and has no alternatively abstractable α or β -hydrogen atoms. Here we report the preparation and properties of several mesityl complexes and the results of our initial attempts to induce α -hydrogen abstraction to give a methylene complex.

Results and discussion

Preparation and properties of mesityl complexes

Slow addition of 0.5 equivalents of ZnMes_2 to TaX_5 in pentane or toluene at room temperature gives 0.5 equivalents of ZnX_2 and red, crystalline TaMesX_4 in virtually quantitative yield ($\text{X} = \text{Cl}$ or Br). Adding a second 0.5 equivalents of ZnMes_2 to TaMesCl_4 (or 1.0 equivalent of ZnMes_2 to TaCl_5) in toluene gives the appropriate amount of ZnCl_2 and orange $\text{TaMes}_2\text{Cl}_3$ in good yield. $\text{TaMes}_2\text{Cl}_3$ can be prepared more straightforwardly by adding 2 equivalents of LiMes to TaCl_5 in toluene at -40°C but reduction of Ta^{V} to Ta^{IV} (vide infra) limits the isolated yield of moderately soluble $\text{TaMes}_2\text{Cl}_3$ to $\sim 10\%$.

$\text{TaMes}_2\text{Cl}_3$ does not react further with ZnMes_2 in toluene at 25°C . We might attribute this to the steric bulk of the mesityl groups since $\text{Ta}(\text{CH}_2\text{CMe}_3)_2\text{Cl}_3$ does react with $\text{Zn}(\text{CH}_2\text{CMe}_3)_2$ in toluene or pentane to give $\text{Ta}(\text{CH}_2\text{CMe}_3)_3\text{Cl}_2$. $\text{TaMes}_2\text{Cl}_3$ does react with excess LiMes in toluene to give a good yield of canary yellow $\text{TaMes}_3\text{Cl}_2$ along with pentane-soluble black products. $\text{TaMes}_3\text{Cl}_2$ can be synthesized directly from TaCl_5 and LiMes (5 equivalents) at -40°C in toluene but again the yield is low ($\sim 8\%$ after several recrystallizations from an initially black mixture). Since pentane-soluble black products are also produced from TaMesCl_4 , $\text{TaMes}_2\text{Cl}_3$, or $\text{TaMes}_3\text{Cl}_2$ and Na/Hg in THF they are most likely reduced tantalum containing species; we did not try to identify them.

The reaction of $\text{TaMes}_3\text{Cl}_2$ with LiMes has given only black (presumably reduction) products. Electron transfer must be favored over chloride substitution to give TaMes_4Cl or TaMes_5 . In contrast, $\text{Ta}(\text{CH}_2\text{CMe}_3)_4\text{Cl}$ and $\text{Ta}(\text{CH}_2\text{CMe}_3)_4(\text{OCMe}_3)$ are isolable and $\text{Ta}(\text{CH}_2\text{CMe}_3)_5$ now seems possible (at least sterically) [12]. The difference is that the neopentyl ligand can relieve crowding by opening up the $\text{M}-\text{C}_\alpha-\text{C}_\beta$ angle (usually to around 125° [13,14]), but the mesityl ligand can do nothing to alleviate steric problems except twist about the $\text{M}-\text{C}$ bond.

The corresponding Nb complexes can all be synthesized by similar methods. NbMesCl_4 is deep purple, $\text{NbMes}_2\text{Cl}_3$ is deep red, and $\text{NbMes}_3\text{Cl}_2$ is orange. The

* Examples of early transition metal mesityl complexes are TiMes_3 [7], $\text{VMes}_3\text{THF}_{1.25}$ [8], $\text{CrMes}_2(\text{bipy})\text{THF}$ [9], and MoMes_2O_2 [10].

last can be prepared in only ~30% yield from $\text{NbMes}_2\text{Cl}_3$ and LiMes (1–2 equivalents) in toluene.

The most likely of these species to dimerize [1] is MMesCl_4 but a molecular weight measurement for NbMesCl_4 (cryoscopically in benzene) showed it to be a monomer. Therefore, each of the six members is probably a monomer.

The MMesCl_4 and MMes_2Cl_3 complexes are extremely sensitive to moisture and can be handled successfully only in oven-dried glassware and in rigorously dried solvents. The MMes_3Cl_2 complexes, in contrast, are air-stable in the solid state and apparently also in solution. They do not react with water or even dilute acid in several days. (MMesCl_4 reacts explosively with water.) Normally, MR_3Cl_2 species ($\text{R} = \text{CH}_2\text{Ph}$, CH_2CMe_3) are more resistant to hydrolysis than the lower members of the series (MR_2Cl_3 and MRCl_4) [15]. However, the extraordinary hydrolytic stability of MMes_3Cl_2 must be attributed to an even more crowded coordination sphere in which the ortho methyl groups of what are almost certainly equatorial mesityl ligands (see NMR section) virtually create a cage about the metal.

TaMesCl_4 can be sublimed with only slight decomposition. NbMesCl_4 , on the other hand, decomposes in the solid state at 25°C in several days; at -30°C it can be stored for several months. $\text{NbMes}_2\text{Cl}_3$ also decomposes slowly in the solid state at 25°C . In neither case have we established what the decomposition products are.

We were not always able to prepare mesityl complexes which also contain other alkyl ligands from TaMes_xX_y and alkylating reagents. $\text{TaMes}_2\text{Cl}_3$ does react smoothly with one equivalent of $\text{LiCH}_2\text{CMe}_3$ to give $\text{TaMes}_2(\text{CH}_2\text{CMe}_3)\text{Cl}_2$. However, mixtures resulted when TaMesX_4 ($\text{X} = \text{Cl}$ or Br) was treated with 0.5 equivalents of ZnR_2 or one equivalent of LiR ($\text{R} = \text{Me}$ or CH_2CMe_3). The desired TaMesRX_4 complexes can be prepared in the reverse manner, by adding 0.5 equivalents of ZnMes_2 to TaRX_4 , except when $\text{X} = \text{Br}$ and $\text{R} = \text{Me}$. TaMesMeBr_3 must be prepared by treating TaMesBr_4 with one equivalent of AlMe_3 .

¹H NMR studies

The ¹H NMR spectra of $\text{TaMes}_2\text{Cl}_3$ and $\text{NbMes}_2\text{Cl}_3$ are temperature dependent. At about -40°C (270 MHz) in toluene we see two signals due to *ortho* methyl groups and two signals due to *meta* protons, but only one signal for the two *para* methyl groups (Table 1). The mesityl groups therefore are in the same type of coordination site but cannot rotate freely about their metal– C_α bonds. As the temperature of the sample is raised the two *meta* proton signals coalesce followed by the two *ortho* methyl group signals. From coalescence of the Me_o and Me'_o signals we can calculate ΔG^\ddagger as 14.8 ± 0.2 kcal mol⁻¹ for the fluxional process in each complex (Table 1).

The ¹H NMR spectrum of $\text{TaMes}_2(\text{CH}_2\text{CMe}_3)\text{Cl}_2$ at low temperature shows similar features (Fig. 1). An additional and important observation is that the α -protons on the neopentyl ligand are diastereotopic in the ground state and give rise to an AB quartet ($J_{\text{H}_\alpha\text{H}'_\alpha} = 15$ Hz). We should also note that the tertiary butyl signal at -60°C is broadened significantly compared to the other resonances. The only reasonable explanation is restricted rotation of that tertiary butyl group. As the temperature of the sample is raised, the signals for Me_o and Me'_o coalesce, as do those for H_m and H'_m , and H_α and H'_α .

TABLE 1
¹H NMR DATA FOR MESITYL COMPLEXES ^a

| | H _m | Me _O | Me _P | δν([∞] T _C) (Hz) ^b | T _C (°K) | ΔG [‡] (±0.2 kcal/mol) |
|--|-------------------|-----------------|-----------------|--|------------------------|------------------------------------|
| NbMes ₂ Cl ₃ | 3.58 | 7.09 | 8.09 | 60 | 303 | 14.8 |
| | 3.64 | 7.33 | | | | |
| TaMes ₂ Cl ₃ | 3.38 | 7.15 | 8.08 | 63 | 303 | 14.8 |
| | 3.43 | 7.41 | | | | |
| TaMes ₂ (CH ₂ CMe ₃)Cl ₂ ^c | 3.29 | 7.09 | 8.01 | 101 | 273 | 13.0 |
| | 3.35 | 7.47 | | | | |
| TaMesMeCl ₃ ^d | 3.06 ^e | 7.24 | 7.76 | 48 | 246 | 12.3 |
| | | 7.44 | | | | |
| TaMes(CH ₂ CMe ₃)Cl ₃ ^f | 2.93 | 7.10 | 7.68 | 69 | 284 | 14.0 |
| | 2.99 | 7.39 | | | | |

^a Solvent = tol-*d*₈. Chemical shifts in units of τ at the low temperature limit. ^b δν([∞]T_C) refers to the chemical shift difference between Me_O and Me_O' at T_C (the coalescence temperature) as determined by plotting δν_∞ vs. T and extrapolating to T_C. All variable temperature spectra were run at 270 MHz. ΔG[‡] = -RT ln[kT_C/hk_C] where k_C = (π)(δν([∞]T_C))/√2. ^c τH_α = 6.36; τH_α' = 7.55; τCMe₃ = 8.74; see Fig. 1. ^d Solvent = CDCl₃, τTaMe = 7.79. ^e The H_m and H_m' resonances are essentially coincident in this case. ^f We believe the neopentyl α-hydrogen atoms are magnetically equivalent; see text. Solvent = CDCl₃.

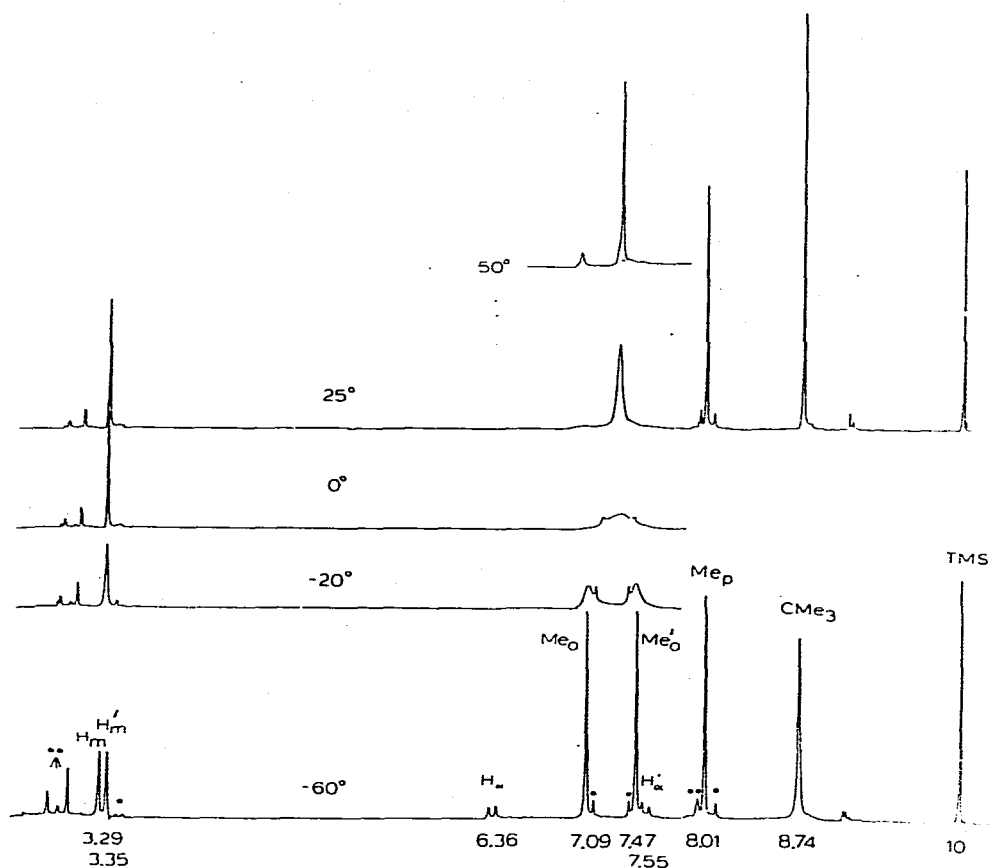


Fig. 1. The variable temperature 270 MHz ¹H NMR spectrum of TaMes₂(CH₂CMe₃)Cl₂ in C₆D₅CD₃ (** is toluene-*d*₇ and * is TaMes₂Cl₃).

The ^1H NMR spectra of $\text{TaMes}(\text{CH}_2\text{CMe}_3)\text{Cl}_3$ and TaMesMeCl_3 are also temperature dependent with ΔG^\ddagger for a similar fluxional process on the same order as those above (14.0 kcal mol $^{-1}$ and 12.3 kcal mol $^{-1}$ in CDCl_3 , respectively; Table 1). In $\text{TaMes}(\text{CH}_2\text{CMe}_3)\text{Cl}_3$ the neopentyl α protons are apparently magnetically equivalent, in contrast to their diastereotopic nature in $\text{TaMes}_2(\text{CH}_2\text{CMe}_3)\text{Cl}_2$. We believe they are not accidentally coincident since the chemical shift difference between H_α and H'_α in $\text{TaMes}_2(\text{CH}_2\text{CMe}_3)\text{Cl}_2$ is quite large (300 Hz).

Finally, the ^1H NMR spectra of the MMesX_4 and MMes_3Cl_2 complexes are not temperature dependent and show only single peaks for *ortho* methyl groups and *meta* protons.

All the above observations can be explained readily if we make two assumptions. First, the alkyl/halide complexes have trigonal bipyramidal structures analogous to their main group organometallic As and Sb cousins [16] in which halide ligands occupy the axial positions and any mesityl or other alkyl ligands occupy equatorial positions. There is some precedent for a mesityl ligand preferring an equatorial site in a five-coordinate tantalum complex in the form of the recently reported structure of $\text{Ta}(\text{CHCMe}_3)_2(\text{PMe}_3)_2(\text{mesityl})$ [17]. Secondly, we must make the reasonable assumption that the mesityl ligands cannot freely rotate about the M—mesityl bond in a structurally rigid complex of the above type due to interaction of their methyl groups with the axial halide ligands.

In complexes of the type MMesRX_3 , then, the mesityl group must be able to lie in the equatorial plane. The neopentyl α -hydrogen atoms would therefore be equivalent, *ortho* methyl groups would be non-equivalent, and *meta* protons would be non-equivalent.

We propose that molecules of the type MMes_2RX_2 no longer contain an equatorial plane of symmetry because the mesityl ligands also cannot rotate past each other and therefore are twisted in a propeller-like fashion. Apparently, rotation past each other is as restricted as rotation past the axial chloride ligands since the diastereotopic neopentyl α -hydrogen atoms appear to coalesce at roughly the same rate as the mesityl ligands' *ortho* methyl groups.

In MMesX_4 and MMes_3X_2 the *ortho* methyl groups are interconvertible by a C_2 or C_3 symmetry operation, respectively. We cannot tell, of course, how the mesityl ligand(s) is (are) oriented in each but would predict it to lie in the equatorial plane in MMesX_4 , and the three to be turned about 45° to the pseudo equatorial plane in MMes_3X_2 . In the latter the *ortho* methyl groups must be packed tightly together to form a "cage" about the metal. This can account for the stability of the MMes_3Cl_2 species to air and water and toward substitution of a chloride by other anionic ligands.

The process which interconverts *ortho* methyl groups (and *meta* protons) in an equatorial mesityl ligand may consist solely of rotation of the mesityl ligands about the M—mesityl bond without any alteration of the trigonal bipyramid itself. It seems more likely, however, that the axial chloride ligands bend back to form a tetragonal pyramidal molecule with a mesityl ligand, which now can rotate more freely, at the apical site. It does not seem likely, nor is it necessary, to postulate any further rearrangement; the chloride ligands simply bend back to again occupy apical sites in a trigonal bipyramidal molecule. One might expect this process to occur most easily in the least crowded molecules of a

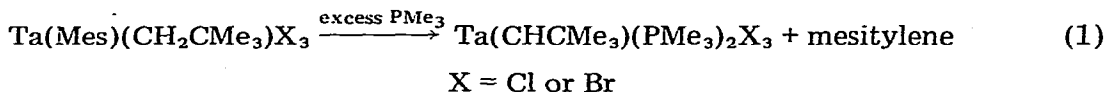
given type. This appears to be true. ΔG^\ddagger increases in the order TaMesMeCl_3 - (12.3) < $\text{TaMes}(\text{CH}_2\text{CMe}_3)\text{Cl}_3$ (14.0) < $\text{TaMes}_2\text{Cl}_3$ (14.8).

The formation of alkylidene complexes by hydrogen abstraction reactions

Adding PMe_3 to TaMesMeCl_3 in toluene yields a red adduct, $\text{TaMesMe}(\text{PMe}_3)_2\text{Cl}_3$. This adduct loses PMe_3 very readily in solution (by ^1H NMR; see Experimental Section) or in the solid state. Therefore, it could be characterized only by NMR methods. It is not stable in toluene. In 4 h at 45°C it is converted into a less soluble green product. This reaction proceeds much more rapidly and cleanly in dichloromethane and on replacing the chlorides with bromides, two effects which were first noticed in the study of how $\text{Ta}(\eta^5\text{-C}_5\text{H}_5)(\text{CH}_2\text{CMe}_3)_2\text{X}_2$ decomposes [11b].

The ^1H and ^{13}C NMR spectra of the green products clearly establish that they are not methylene complexes, but the substituted benzylidene complexes, V (Scheme 1; $\text{L} = \text{PMe}_3$, y and z unknown). They are entirely analogous to the more thoroughly studied unsubstituted benzylidene and neopentylidene complexes of the type $\text{Ta}(\text{CHR})(\text{PMe}_3)_2\text{X}_3$ [18,19]. There are two isomers which interconvert by loss of PMe_3 . In the *trans*, *mer* isomer the alkylidene ligand's $\text{H}_\alpha\text{-C}_\alpha\text{-C}_\beta$ plane contains the Cl-Ta-Cl axis. In the *cis*, *mer* isomer it contains the Cl-Ta-P axis. A complete description of the structure and dynamics of this class of complexes and the role of six and/or seven-coordination in their formation can be found elsewhere [19].

It should be noted that a mesityl ligand can be a leaving group since $\text{Ta}(\text{CHCMe}_3)(\text{PMe}_3)_2\text{X}_3$ can be prepared by adding PMe_3 to $\text{Ta}(\text{Mes})(\text{CH}_2\text{CMe}_3)\text{X}_3$ (equation 1). (This reaction is entirely analogous to the preparation of $\text{Ta}(\text{CHR})$ -

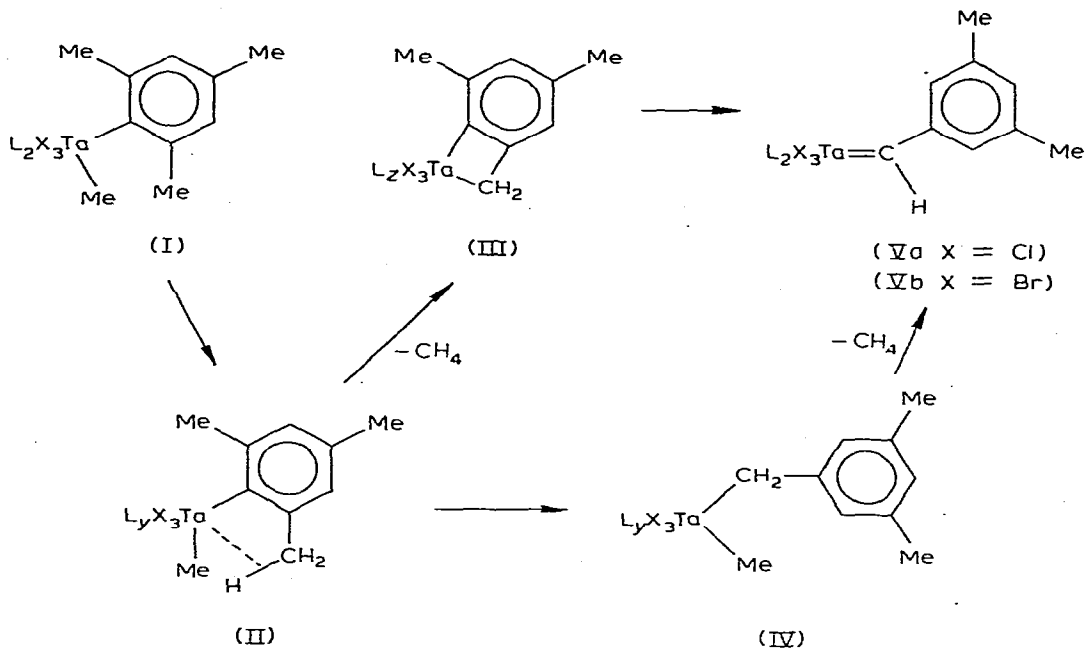


$(\text{PMe}_3)_2\text{X}_3$ from $\text{Ta}(\text{CH}_2\text{R})_2\text{X}_3$ and PMe_3 ($\text{R} = \text{CMe}_3$; Ph) [18,19].) Therefore, it would seem unlikely that the methyl group is converted into a methylene ligand at any point during the decomposition of $\text{TaMesMeX}_3(\text{PMe}_3)_2$. Yet the solvent and halide affect the rate for the γ -abstraction reaction the same as they do an α -abstraction reaction [11b]. Therefore, we believe the two processes are related.

One way of viewing both abstraction reactions is the following. A metal-alkyl bond cleaves homolytically and abstracts the nearest readily abstractable hydrogen atom; this must be essentially a concerted reaction in the most successful abstraction reactions*. If no suitable hydrogen atom source is nearby, the radical escapes the inner coordination sphere and the metal is thereby reduced. (This has so far been the norm in attempts to extend the phosphine induced α -hydrogen abstraction technique to Group IV metals, especially Ti [15].) Therefore, in the case being discussed here we propose that the methyl group abstracts a γ -hydrogen atom more or less directly from the mesityl ligand's

* It is interesting to compare this description with the Cossee mechanism for ethylene polymerization [20]. Addition of ethylene is believed to induce homolytic Ti-R bond cleavage but R^\cdot almost exclusively adds to ethylene to give $\text{TiCH}_2\text{CH}_2\text{R}$.

methyl group. The methyl hydrogen atom may be "activated" by interactions of the C—H electrons with the electrophilic metal (II; Scheme 1) as α -hydrogen



SCHEME 1. Proposed mechanism for the formation of benzylidene complexes V.

atoms are believed to be in certain cases [11b]. This "activation" may also play a role in discriminating between methyl or mesityl as a leaving group. An α -hydrogen atom in a methyl ligand must therefore not be activated as readily (which is in accord with other findings [11a]) and/or the mesityl group is a poorer leaving group (based, perhaps, simply on relative Ta—R bond strengths). We do not believe a mesityl methyl C—H bond actually adds to the metal * since such an intermediate would formally contain "Ta^{VII}".

If the above arguments are correct, then a likely first intermediate is the metallacyclobutene complex, III. Rearrangement of III to V would be a type of α -abstraction reaction [11a] but one for which there is no precedent. However, one cannot entirely exclude the possibility that the "activated" mesityl methyl hydrogen atom is abstracted by the mesityl α -carbon atom to give IV. The benzyl ligand in IV should lose an α -hydrogen atom to the methyl ligand rather than vice versa **. Since we have so far seen no evidence that mesityl ligands rearrange to benzyl ligands, we think the former pathway is more reasonable.

We conclude that abstracting an α -hydrogen atom from a neopentyl ligand is easier than abstracting a γ -hydrogen atom from a mesityl ligand, and each is much easier than abstracting an α -hydrogen atom from a methyl ligand.

* This has been observed recently in an Ir^I mesityl complex to give an Ir^{III} benzometallacyclobutene/hydride complex [21].

** In Ta(η^5 -C₅H₅)(CH₂Ph)(CH₂CMe₃)X₂ [11b], the better α -hydrogen donor is CH₂CMe₃. The complex loses primarily toluene to give Ta(η^5 -C₅H₅)(CHCMe₃)X₂.

Experimental

All reactions were performed under N_2 in a Vacuum Atmospheres dry box or by Schlenk Techniques. Solvents were dried and purified by standard procedures. $TaCl_5$ (Cerac), $TaBr_5$ (Cerac), mesitylbromide and $AlMe_3$ were used as received. $TiCp$ and $NbCl_5$ were sublimed prior to use. $LiCH_2CMe_3$ [12], $TaMe_3Cl_2$ [22], $Ta(CH_2CMe_3)Cl_4$ [11b], $ZnCl_2$ (dioxane) [23], and PMe_3 [24] were prepared as described in the literature.

(1) Preparation of $LiMesityl$ and $Zn(Mesityl)_2$

Mesityl bromide (50 g, 0.25 mol) and a hexane solution of butyllithium (2 M, 125 cm³) were combined and refluxed for 24 h. The pale yellow $LiMesityl$ was filtered off and washed with pentane (quantitative yield). Solid $LiMesityl$ (17.34 g, 140 mmol) was added slowly to a stirred suspension of $ZnCl_2$ (dioxane) (15 g, 70 mmol) in 300 cm³ of ether/toluene (1/1). The mixture was stirred for 1 h and the ether distilled off until and head temperature reached 110°C. The hot toluene solution was filtered and the residue washed with 2 × 150 cm³ of hot toluene. The wash and filtrate were combined, reduced in vacuo to 50 cm³ and 100 cm³ of pentane added. The suspension was cooled to -30°C for 2 h and the snow-like product filtered off. Yield 7.0 g (33%). $ZnMes_2$ is moderately soluble in benzene and toluene nearly insoluble in pentane and may be sublimed at 150°C (1 μ).

¹H NMR (τ, C₆D₆): 3.16(s, 2, H_{meta}), 7.61(s, 6, Me_{ortho}), 7.77(s, 3, Me_{para}).

(2) Preparation of $TaMesX_4$

(a) $X = Cl$. $ZnMes_2$ (1.04 g, 3.42 mmol) was slowly added as a solid to a stirred suspension of $TaCl_5$ (2.45 g, 6.84 mmol) in 50 cm³ pentane. The mixture was stirred for 2 h, $ZnCl_2$ removed by filtration, and the solvent removed in vacuo to yield 2.80 g (93%) of orange-red crystalline $TaMesCl_4$. Found: C, 23.68, H, 2.59; Cl, 32.17, C₉H₁₁Cl₄Ta Calcd.: C, 24.46; H, 2.51; Cl, 32.09. ¹H NMR (τ, C₆D₆): 3.40(s, 2, H_{meta}), 7.30(s, 6, Me_{ortho}), 8.00(s, 3, Me_{para}). ¹³C NMR (ppm from TMS, C₆D₆, ¹H gated decoupled): 231(s, C_α), 145(s, C_δ), 138(s, C_β) 130(d, J(CH) = 153 Hz, C_γ), 26(q, J(CH) = 127 Hz, Me_{ortho}), 22(q, J(CH) = 126 Hz, Me_{para}).

(b) $X = Br$. A procedure virtually identical to that in 2(a) gave a similar yield of dark red crystalline $TaMesBr_4$. Its ¹H NMR spectrum was essentially identical to that of $TaMesCl_4$.

(3) Preparation of $TaMes_2Cl_3$

(a) From $TaCl_5$ and $ZnMes_2$. $TaCl_5$ (6.45 g, 9 mmol) and $ZnMes_2$ (5.45 g, 9 mmol) were mixed in 150 cm³ of toluene at room temperature and stirred for 1 h. $ZnCl_2$ was filtered off and the toluene removed in vacuo to a volume of 40 cm³. An equivalent volume of pentane was added and the resulting cloudy solution was filtered. Orange crystals were filtered off after standing for 2 days at -30°C. An additional quantity was likewise removed from the filtrate after reducing the volume to 20 cm³ of toluene. Total yield 6.83 g (74%).

(b) From $TaCl_5$ and $LiMesityl$. Mesityllithium (2.52 g, 20 mmol) was added as a solid in 20 minutes to a stirred suspension of 3.57 g (10 mmol) $TaCl_5$ in

100 cm³ of toluene at -78°C . The mixture turned black on slowly warming to room temperature over 1 h. Filtration yielded an orange filtrate from which $\text{TaMes}_2\text{Cl}_3$ was obtained as in 3(a); yield 350 mg (9%).

Found: C, 40.80; H, 4.48; Cl, 20.16, $\text{C}_{18}\text{H}_{22}\text{Cl}_3\text{Ta}$ Calcd.: C, 41.13; H, 4.21; Cl, 20.23. See Table 1 and text for ^1H NMR data.

(4) Preparation of $\text{TaMes}_3\text{Cl}_2$

(a) From $\text{TaMes}_2\text{Cl}_3$ and *LiMesityl*. Excess mesityllithium (1.47 g, 11.6 mmol) was added to a toluene solution (50 cm³) of $\text{TaMes}_2\text{Cl}_3$ (2.1 g, 4 mmol) at room temperature. After 3 h the black mixture was filtered and the solvent removed in vacuo. The resulting oil was taken up in warm hexane (30 cm³) and the mixture was filtered. Standing the filtrate overnight at -30°C gave $\text{TaMes}_3\text{Cl}_2$ (1.8 g, 74%) as a yellow powder which could be recrystallized from a 1/1 ether/pentane mixture.

(b) From TaCl_5 and *LiMesityl*. *LiMesityl* (7.2 g, 57 mmol) was added as a solid to TaCl_5 (3.95 g, 11 mmol) in 50 cm³ of toluene. After stirring for 30 minutes the mixture was filtered and toluene was removed from the filtrate in vacuo. The black oil was triturated with 30 cm³ of pentane and cooled to -30°C overnight. The solid was filtered off and washed with 5 cm³ of cold pentane; yield 0.8 g (12% vs. TaCl_5). Recrystallization from pentane gave 0.6 g of $\text{TaMes}_3\text{Cl}_2$.

Found: C, 53.32; H, 5.57; Cl, 11.54, $\text{C}_{27}\text{H}_{33}\text{Cl}_2\text{Ta}$ calcd.: C, 53.22; H, 5.45; Cl, 11.63. ^1H NMR (τ , C_6D_6): 3.13(s, 2, H_{meta}), 7.20(s, 6, *ortho* methyl groups), 7.90(s, 3, *para* methyl group).

(5) Preparation of NbMesCl_4

Solid ZnMes_2 (1.51 g, 5 mmol) was added slowly over 15 min to a vigorously stirred suspension of NbCl_5 (2.71 g, 10 mmol) in 50 cm³ pentane. After stirring for 15 min longer the gelatinous ZnCl_2 was filtered from the intense red-purple solution. The ZnCl_2 was extracted twice with 15 cm³ of pentane and all filtrates were combined and cooled to -30°C for 1 h. Filtration gave 2.0 g of fine, metallic, black-purple plates. The filtrate's volume was halved and 0.6 g additional product filtered off after cooling. This filtrate was halved again and cooled for a third crop (0.3 g); total 2.9 g (85%).

NbMesCl_4 is considerably less stable than TaMesCl_4 in the solid state at room temperature and decomposes after several days. It can be stored indefinitely at -30°C however. Like TaMesCl_4 , it is hydrolyzed violently by water.

Found: Cl, 40.33, $\text{C}_9\text{H}_{11}\text{Cl}_4\text{Nb}$ Calcd.: Cl, 40.07. ^1H NMR (τ , C_6D_6): 3.83-(s, 2, H_{meta}), 7.39(s, 6, Me_{ortho}), 8.17(s, 3, Me_{para}). Mol. wt. Found: 331, Calcd.: 354 (cryoscopically in benzene).

(6) Preparation of $\text{NbMes}_2\text{Cl}_3$

ZnMes_2 (3.04 g, 10 mmol) was added to 2.70 g of sublimed NbCl_5 in 80 cm³ toluene. After 1 h ZnCl_2 was filtered off and the filtrate concentrated to 30 cm³. Pentane (30 cm³) was added, followed by 1 g of activated charcoal. The solution was filtered and the filtrate was stored overnight at -30°C to give $\text{NbMes}_2\text{Cl}_3$ as red needles. The filtrate was concentrated to an oil which was taken up in 30 cm³ of pentane and stored at -30°C overnight. Total yield 3.68 g (84%).

Found: Cl, 24.23, $\text{C}_{18}\text{H}_{22}\text{Cl}_3\text{Nb}$ Calcd.: Cl, 24.30. See Table 1 and text for ^1H NMR data.

(7) Preparation of NbMes₃Cl₂

ZnMes₂ (0.30 g) was added to 0.27 g of sublimed NbCl₅ in 30 cm³ toluene. ZnCl₂ was filtered off after 1 h and 0.22 g LiMesityl was slowly added as a solid at room temperature. The solution was filtered after 1 h and the toluene was removed from the filtrate in vacuo. Pentane (20 cm³) was added and 50 mg (10% yield) of orange NbMes₃Cl₂ isolated by filtration after standing the solution overnight at -30°C.

¹H NMR (τ, C₆D₆): 3.26(s, 2, H_{meta}), 7.09(s, 6, Me_{ortho}), 7.84(s, 3, Me_{para}).

(8) Preparation of TaMesMeX₃ (X = Cl, Br)

(a) X = Cl. TaMe₃Cl₂ (1.63 g, 5.5 mmol) was stirred in pentane (150 cm³) with TaCl₅ (4.33 g, 12.1 mmol) for 20 min. ZnMes₂ (2.5 g, 8.23 mmol) was slowly added as a solid with stirring. The solution was filtered after two hours, reduced in vacuo to 20 cm³, and filtered yielding 4.4 g of orange crystals. Reducing the filtrate to 10 cm³ and cooling to -30°C overnight yielded an additional 1.2 g (81%).

Found: C, 29.04, H, 3.48, C₁₀H₁₄Cl₃Ta Calcd.: C, 28.49; H, 3.35. ¹H NMR (τ, CDCl₃): 3.08(s, 2, H_{meta}), 7.28(s, 6, Me_{ortho}), 7.76, 7.80(s, 3 each, TaMe and Me_{para}).

(b) X = Br. AlMe₃ (0.43 g, 6.08 mmol) in 20 cm³ pentane was added dropwise to a stirred solution of TaMesBr₄ (3.5 g, 6.08 mmol) in 50 cm³ pentane. The orange solution was filtered and the volume reduced to 10 cm³ in vacuo. Orange crystals (1.75 g) were isolated by filtration and washed with cold pentane to remove AlBrMe₂. The wash and filtrate were combined, reduced in volume to 5 cm³ and cooled to -30°C overnight, yielding (after washing) 0.67 g (Total 91%).

The reaction should be worked-up immediately since black precipitates form slowly. The ¹H NMR spectrum is virtually identical to that of the chloride.

(9) Preparation of TaMes(CH₂CMe₃)Cl₃

Solid ZnMes₂ (0.15 g, 0.5 mmol) was slowly added to a stirred solution of Ta(CH₂CMe₃)Cl₄ (0.40 g, 1.0 mmol) in 10 cm³ pentane. The mixture was stirred for 1 h and filtered. The solvent was removed in vacuo leaving 0.44 g (92%) of yellow TaMes(CH₂CMe₃)Cl₃.

¹H NMR (τ, CH₂Cl₂): 3.10(s, 2, H_{meta}), 6.90(s, 2, CH₂CMe₃), 7.40(s, 6, Me_{ortho}), 7.82(s, 3, Me_{para}), 8.90(s, 9, CMe₃).

(10) Preparation of TaMes₂(CH₂CMe₃)Cl₂

A solution of LiCH₂CMe₃ (0.16 g) in 50 cm³ of toluene was added to a solution of TaMes₂Cl₃ (0.526 g) in 50 cm³ of toluene at -78°C. The mixture was warmed to 25°C, filtered and solvent removed in vacuo. The residue was taken up in 50 cm³ of pentane, treated with activated charcoal and filtered. Yellow TaMes₂(CH₂CMe₃)Cl₂ (0.40 g, 70%) was filtered off after standing at -30°C overnight and identified by its ¹H NMR spectrum (see Table 1 and text).

(11) Preparation of TaMesMeX₃(PMe₃)₂ (X = Cl, Br)

(a) X = Cl. PMe₃ (2 cm³, 20.9 mmol) in 5 cm³ pentane was added dropwise with stirring to a saturated solution of TaMesMeCl₄ (4.0 g, 9.5 mmol) in 25 cm³

pentane. The solution became red and cloudy and deposited a red oil which soon crystallized. The crystals (0.40 g) were filtered off. The filtrate slowly deposited more crystals (3.40 g) over a period of about 3 h. Another 0.84 g was obtained by cooling the filtrate to -30°C for 3 h (78% total yield).

(b) $X = \text{Br}$. The procedure was identical to the above. Yield 64%.

^1H NMR (τ , CDCl_3): 3.10(s, 2, H_{meta}), 7.50(s, 6, Me_{ortho}), 7.85, 8.10(s, 3 each, $\text{Ta}-\text{Me}$ and Me_{para}), 8.60(br s, 18, PMe_3). Neither compound could be analyzed due to ready loss of PMe_3 .

(12) Preparation of $\text{TaX}_3(\text{CHC}_6\text{H}_3\text{Me}_2)(\text{PMe}_3)_2$ by decomposition of $\text{TaMesMeX}_3(\text{PMe}_3)_2$

(a) $X = \text{Cl}$. $\text{TaMesMeCl}_3(\text{PMe}_3)_2$ (0.74 g, 1.29 mmol) was dissolved in 10 cm^3 of toluene and heated at 45°C for 5 h. The solution was filtered and the solvent removed in vacuo to yield an oil. Trituration with pentane yielded 0.38 g of grey-green solid. This crude material was ca. 90% pure. The yield ($\sim 50\%$) was erratic and purification attempts were not always successful. The bromide derivative (see below) is much more tractable.

^1H NMR (τ , CDCl_3 , 30°C): 3.20(s, 2, H_{ortho}), 3.50(s, 1, H_{para}), 7.90(s, 6, Me_{meta}), 8.25(br s, 18, PMe_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (ppm, CDCl_3 , 67.89 MHz, -40°C): Major isomer: 242(br s, C_α), 142, 135, 131 and 129(s, C_{phenyl}), 21(s, Me_{meta}), 15(t, $J(\text{PC}) = 13\text{ Hz}$, PMe_3). Minor isomer: 233(m, C_α), 147 and 130(s, C_{phenyl}), 17(d, $J(\text{PC}) = 29\text{ Hz}$, PMe_3), 12(d, $J(\text{PC}) = 16\text{ Hz}$, PMe'_3). Other resonances for the minor isomer were not located; some may overlap with analogous peaks of the major isomer.

(b) $X = \text{Br}$. A red solution of $\text{TaMesMe}(\text{PMe}_3)_2\text{Br}_3$ (0.60 g, 1.0 mmol) in 10 cm^3 of CHCl_3 was stood at 25°C for 16 h. The green solution was filtered and the solvent removed in vacuo yielding green crystals of $\text{Ta}(\text{CHC}_6\text{H}_3\text{Me}_2)(\text{PMe}_3)_2\text{Br}_3$ (97% yield). Green needles were obtained for analysis by cooling a saturated CHCl_3 solution to which one volume of pentane had been added to -30°C overnight.

Found: C, 25.69; H, 4.02, $\text{C}_{15}\text{H}_{28}\text{Br}_3\text{P}_2\text{Ta}$ Calcd.: C, 26.04; H, 4.19. ^1H NMR (τ , CDCl_3 , 270 MHz, -50°C): Major isomer: 6.96(s, 2, H_{ortho}), 6.69(s, 1, H_{para}), 6.63(br s, 1, H_α), 2.20(s, 6, Me_{ortho}), 1.80(t, 18, $^2J(\text{PH}) = 8.1\text{ Hz}$, PMe_3). Minor isomer: 6.90(s, 2, H_{ortho}), 1.67(d, 9, $^2J(\text{PH}) = 7.7\text{ Hz}$, PMe'_3). The other minor isomer peaks are buried or too small to identify. ^{13}C NMR (ppm, CDCl_3 , ^1H gated decoupled, 67.89 MHz, -40°C): Major isomer: 239(d, $J(\text{CH}) = 83\text{ Hz}$, C_α), 142(s, C_{ipso}), 135.1(s, C_{meta}), 131(d, $J(\text{CH}) = 159\text{ Hz}$, C_{para}), 128(d, $J(\text{CH}) = 156\text{ Hz}$, C_{ortho}), 21(q, $J(\text{CH}) = 127\text{ Hz}$, Me_{meta}), 16(q, $J(\text{CH}) = 131\text{ Hz}$, PMe_3). Minor isomer: 227(d, $J(\text{CH}) = 70\text{ Hz}$, C_α). The other minor isomer peaks are not discernible in the gated spectrum.

(13) Observation of $\text{Ta}(\text{CHCMe}_3)(\text{PMe}_3)_2\text{Cl}_3$ from $\text{TaMes}(\text{CH}_2\text{CMe}_3)\text{Cl}_3$ and PMe_3

A two fold excess of PMe_3 was added to an NMR sample of $\text{TaMes}(\text{CH}_2\text{CMe}_3)\text{Cl}_3$ in C_6H_6 . Upon standing overnight the ^{13}C and ^1H NMR spectra showed only peaks corresponding to $\text{Ta}(\text{CHCMe}_3)(\text{PMe}_3)_2\text{Cl}_3$ [18,19] and mesitylene.

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