Multiple Metal–Carbon Bonds. 13.[1] Preparation and Characterization of Monocyclopentadienyl Mononeopentylidene Complexes of Niobium and Tantalum Including the First Details of an α-Abstraction Process

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Abstract: The neopentyl complexes, $Ta(CH_2CMe_3)_2X_3$ (X = Cl or Br), react with TlC_5H_5 or LiC_5Me_5 to give the monocyclopentadienyl complexes, $Ta(\eta^5\text{-}C_5R_5)(CH_2CMe_3)_2X_2$ (R = H or Me). Several of these decompose smoothly to give neopentane and the electron-deficient neopentylidene complexes, $Ta(\eta^5\text{-}C_5R_5)(CHCMe_3)X_2$. In $Ta(\eta^5\text{-}C_5R_5)(CHCMe_3)X_2$ attraction of the CH_α electrons by Ta cooperates with the steric effect of the *tert*-butyl substituent to give large $M{=}C_\alpha{-}C_\beta$ angles (~165°) and low values for $^1J_{CH_\alpha}$ (~75–85 Hz) and ν_{CH_α} (~2500 cm^{-1}). We propose that the electrophilic d^0 metal in $Ta(\eta^5\text{-}C_5R_5)(CH_2CMe_3)_2X_2$ similarly, but more weakly, interacts with a CH_α electron pair in one neopentyl ligand and thereby sets up H_α for abstraction by the second neopentyl ligand. We show that (1) the α-abstraction reaction is intramolecular; (2) the rate of decomposition of $TaCp(CH_2CMe_3)_2Cl_2$ at 309 K varies with solvent in the order ether (1) < pentane (2) < benzene (4) < chloroform (15) ~ dichloromethane; (3) the rate of decomposition of $TaCp(CH_2CMe_3)_2Br_2$ is 200–400 times that of $TaCp(CH_2CMe_3)_2Cl_2$; (4) the rate of decomposition of a $\eta^5\text{-}C_5H_5$ complex is 5×10^3 times that of the corresponding $\eta^5\text{-}C_5Me_5$ complex; (5) the deuterium isotope effect in the rate-determining α-hydrogen abstraction step is approximately 6. Many of the results can be explained adequately if only *cis*-$Ta(\eta^5\text{-}C_5R_5)(CH_2CMe_3)_2X_2$ is prone to α-abstraction and *trans*-$Ta(\eta^5\text{-}C_5R_5)(CH_2CMe_3)_2X_2$ is inert. This postulate is fully supported by studies of the $TaCp(CH_2CMe_3)(CH_2Ph)X_2$ complexes where the cis/trans equilibrium is observable. The yields of analogous Nb neopentylidene complexes are low. $TaCp(CHCMe_3)Cl_2$ reacts quantitatively at 25 °C with acetonitrile or benzonitrile to give imido complexes, $TaCp[N(R)C{=}CHCMe_3]Cl_2$, and with diphenylacetylene quantitatively at 25 °C to give a new alkylidene complex, $TaCp[C(Ph)(PhC{=}CHCMe_3)]Cl_2$.

Introduction

Since the discovery of the first primary alkylidene complex, $Ta(CH_2CMe_3)_3(CHCMe_3)$,[3] we have been trying to prepare one having no potentially reactive alkyl ligands and, like $Ta(CH_2CMe_3)_3(CHCMe_3)$, less than 18 valence electrons. We have now prepared a class of Nb and Ta complexes of this nature with the formula $M(\eta^5\text{-}C_5R_5)(CHCMe_3)X_2$ (R = H or Me; X = halide or alkyl). Since the precursors to several of the neopentylidene complexes can be isolated and characterized we can for the first time describe the α-hydrogen abstraction process in some detail including thermodynamic parameters, the deuterium isotope effect, and how the rate of α-abstraction depends on molecular structure, other ligands, and solvent. These results, as well as the preparation, the characterization, and a few simple reactions of such alkylidene complexes, are reported here.[4]

Results

Reaction of Alkyl Complexes with Cyclopentadienyl Reagents. $Ta(CH_2CMe_3)_2Cl_3$ in toluene reacts rapidly with sparingly soluble TlC_5H_5. The first fleeting purple color changes to red within a few minutes. One mole of neopentane is ultimately given off and monomeric, red, crystalline, sublimable $TaCp(CHCMe_3)Cl_2$ (Cp = $\eta^5\text{-}C_5H_5$) can be isolated from toluene/pentane (1:4) mixtures in 75% yield. Two byproducts of this reaction are sparingly soluble $TaCp_2Cl_2$ and (if excess TlC_5H_5 is present) $TaCp_2(CHCMe_3)Cl$.[6] In ether at 0 °C the same reaction rapidly gives purple $TaCp(CH_2CMe_3)_2Cl_2$ which only slowly evolves neopentane in this solvent (see next section) to give $TaCp(CHCMe_3)Cl_2$:

$$Ta(CH_2CMe_3)_2Cl_3 \xrightarrow{TlC_5H_5} TaCp(CH_2CMe_3)_2Cl_2 \xrightarrow{-CMe_4} TaCp(CHCMe_3)Cl_2 \quad (1)$$

$TaCp(CH_2CMe_3)_2Cl_2$ can also be prepared from $TaCp(CH_2CMe_3)Cl_3$ and 0.5 mol of $Mg(CH_2CMe_3)_2(dioxane)$ in ether. $TaCp(CH_2CMe_3)Cl_3$ is prepared straightforwardly from $Ta(CH_2CMe_3)Cl_4$ and TlC_5H_5 in toluene.

$Ta(CH_2CMe_3)_2Br_3$ reacts more rapidly than $Ta(CH_2CMe_3)_2Cl_3$ with TlC_5H_5 in ether or toluene to give $TaCp(CHCMe_3)Br_2$ in high yield. The suggested intermediate, $TaCp(CH_2CMe_3)_2Br_2$, could not be isolated, but it could be detected by ^1H NMR and its decomposition followed in situ at low temperature (see later section).

The reaction of $Ta(CH_2CMe_3)(CH_2Ph)X_3$ with TlC_5H_5 in toluene gives $TaCp(CH_2CMe_3)(CH_2Ph)X_2$ in high yield (X = Cl or Br). The bromide complex decomposes readily in solution at 25 °C to give $TaCp(CHCMe_3)Br_2$ (see later section).

The reaction between $Nb(CH_2CMe_3)_2Cl_3$ and TlC_5H_5 is comparatively complex. In toluene at 25 °C most of the product is an insoluble, brown powder; purple-red $NbCp(CHCMe_3)Cl_2$ can be isolated easily but only in ca. 5% yield. At lower temperatures the reaction passes through a stage where TlCl is evident before the brown precipitate forms. We have tried other solvents (ether, dichloromethane, THF) and other cyclopentadienyl reagents ($MgCp_2$, NaCp) at −78 to 25 °C. Often (as with $MgCp_2$ in ether) the reaction appears to proceed smoothly to a more orange compound (possibly $NbCp(CH_2CMe_3)_2Cl_2$) which cannot be isolated before it decomposes to the brown powder and traces of (if any) $NbCp(CHCMe_3)Cl_2$. Concomitant decomposition of $Nb(CH_2CMe_3)_2Cl_3$ can also account in part for a low yield since, if more soluble, faster reacting TlC_5H_4Me is used in toluene at 25 °C, $NbCp'(CHCMe_3)Cl_2$ (Cp' = $\eta^5\text{-}C_5H_4Me$) can be isolated in 30% yield.

Neopentyl/halide complexes also react smoothly with LiC_5Me_5 in ether. $Ta(CH_2CMe_3)Cl_4$, $Ta(CH_2CMe_3)_2Cl_3$, $Ta(CH_2CMe_3)_2Br_3$, and $Ta(CH_2CMe_3)(CH_2Ph)Cl_3$ give $TaCp''(CH_2CMe_3)Cl_3$, $TaCp''(CH_2CMe_3)_2Cl_2$, $TaCp''(CH_2CMe_3)_2Br_2$, and $TaCp''(CH_2CMe_3)(CH_2Ph)Cl_2$, respectively, in high yield (Cp'' = $\eta^5\text{-}C_5Me_5$). Only $TaCp''$-

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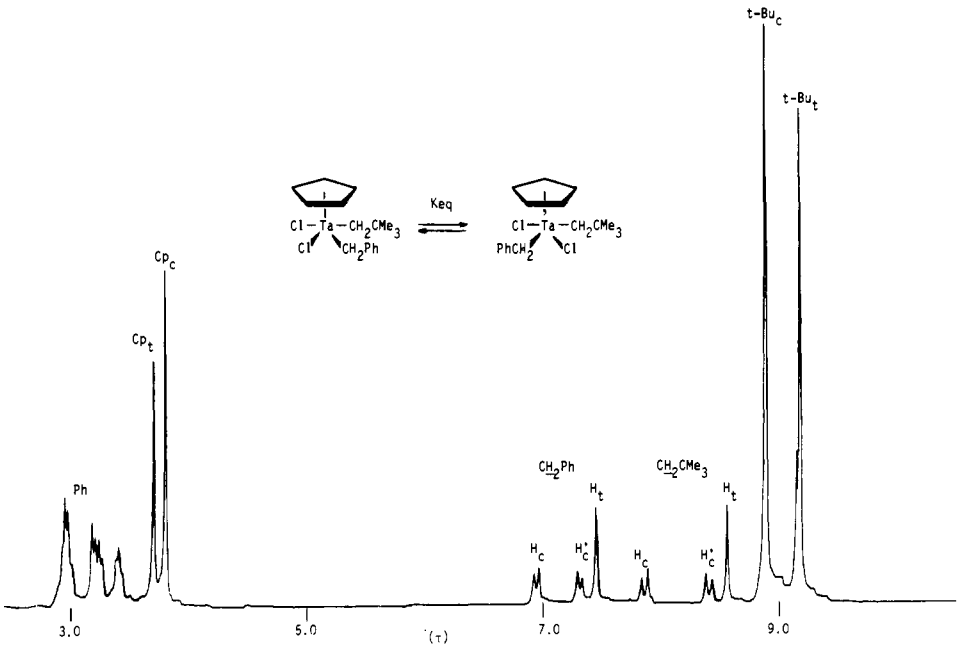


Figure 1. The 270-MHz ^{1}H NMR spectrum of $TaCp(CH_2CMe_3)(CH_2Ph)Cl_2$ at −40 °C in $CDCl_3$: c = cis form; t = trans form.

Table I. Thermodynamic Data for the Cis/Trans Interconversion in $TaCp(CH_2CMe_3)(CH_2Ph)X_2$

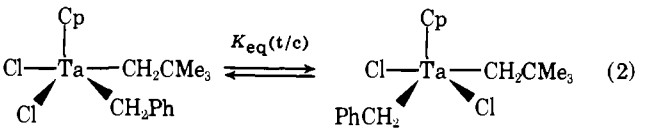
compd	solvent	T, K	K_{eq}(t/c)	ΔH, kcal/mol[a]	ΔS, eu[b]	$\Delta G^{\ddagger}$ kcal/mol[c]
$TaCp(CH_2CMe_3)(CH_2Ph)Cl_2$	ether	251	4.4	2.52	13.3	13.6 ± 0.2
		231	2.1			
		203	1.3			
		333	46[d]			
	toluene	238	1.5	~0.9	~4.7	
		223	1.3			
		207	1.1			
	$CHCl_3$	233	0.7	~1.0	~3.8	
		218	0.6			
$TaCp(CH_2CMe_3)(CH_2Ph)Br_2$	ether	243	0.15	−3.48	−18.1	13.2 ± 0.2
		232	0.25			
		219	0.33			
		333	0.02[d]			

[a] ΔH is the enthalpy of the trans form minus that of the cis form. [b] ΔS is the entropy of the trans form minus that of the cis form. [c] For the interconversion of cis and trans forms at ~260 K (the coalescence point for the two Cp signals in ether). [d] Calculated using the determined values for ΔH and ΔS.

$(CH_2CMe_3)_2Br_2$ decomposes smoothly in chloroform at 31 °C to give $TaCp''(CHCMe_3)Br_2$ (vide infra). Reaction of $Nb(CH_2CMe_3)_2Cl_3$ with LiC_5Me_5 so far has not given an identifiable product.

^{1}H NMR Data for Dialkyl Complexes. The ^{1}H NMR spectrum of $TaCp(CH_2CMe_3)(CH_2Ph)Cl_2$ in $CDCl_3$ at 270 MHz and −40 °C is shown in Figure 1. We assign one set of signals to a trans form of tetragonal pyramidal $TaCp(CH_2CMe_3)(CH_2Ph)Cl_2$ based on the fact that there is one sharp resonance for the neopentyl α protons and one sharp resonance for the benzyl α protons (H_t). (The crystal structure of $TaCp''(PMe_3)_2(CPh)Cl$[7] shows it to be an almost perfect tetragonal pyramid so at this stage any trigonal bipyramidal geometry seems unlikely.) The other set we assign to *cis*-$TaCp(CH_2CMe_3)(CH_2Ph)Cl_2$ based on the fact that each set of α protons now forms a diastereotopic pair which gives rise to a typical AB pattern (H_cH_c'). As the temperature of the sample is raised toward 0 °C the two isomers begin interconverting. At 260 K in ether $\Delta G^{\ddagger} = 13.6 \pm 0.2$ kcal mol^{-1} (from coalescence of the two Cp peaks). Note that the cis and trans forms interconvert at a rate ($k \approx 15$ s^{-1}) which is extremely fast compared to a typical rate ($k \approx 10^{-4}$ s^{-1}) at which a compound of this type decomposes (see later sections).

The equilibrium between the cis and trans forms (eq 2)



(2)

varies with temperature and solvent as shown in Table I. We should first note that more of the cis form (which should have a higher dipole moment than the trans form) is found in chloroform (dielectric constant $\epsilon = 4.8$ at 20 °C) than in toluene ($\epsilon_{20°C} = 2.2$). Ether ($\epsilon_{20°C} = 4.3$) therefore seems out of place but it is also the only one of the three solvents which could coordinate to the metal. Secondly, K_{eq} increases (giving more trans form) as the temperature increases.

From these data one can conclude that $\Delta H_{t/c}$ and $\Delta S_{t/c}$ vary markedly with solvent. In the two relatively noncoordinating solvents both ΔH and ΔS are small compared to their values in ether.

The ^{1}H NMR spectrum of $TaCp(CH_2CMe_3)(CH_2Ph)Br_2$

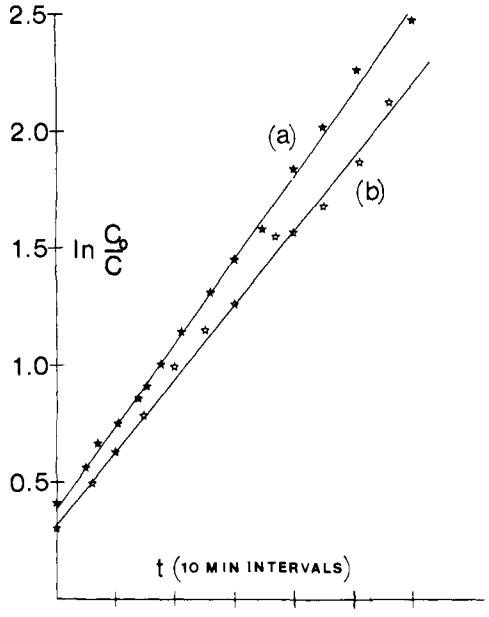


Figure 2. First-order plots of the decomposition of (a) $TaCp(CD_2CMe_3)_2Cl_2$ in $CDCl_3$ at 309 K; (b) $TaCp(CH_2CMe_3)_2Cl_2$ in $CDCl_3$ at 280 K.

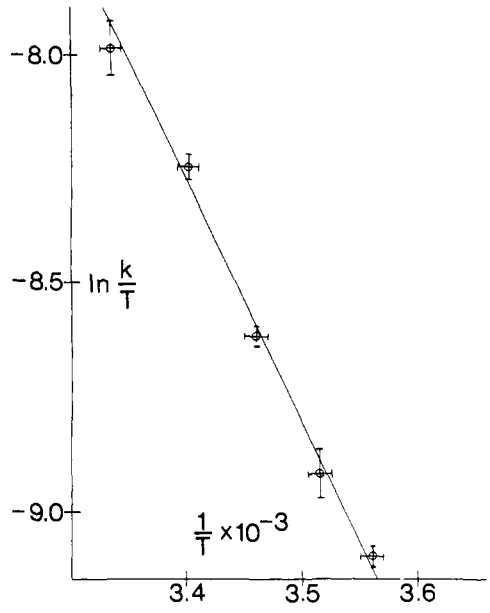


Figure 3. Plot of ln (k/T) vs. $1/T$ for decompositions of $TaCp(CH_2CMe_3)_2Cl_2$ in $CDCl_3$ at five temperatures (see Table II).

in ether at low temperatures is similar to that of $TaCp(CH_2CMe_3)(CH_2Ph)Cl_2$ and $\Delta G^{\ddagger} = 13.2 \pm 0.2$ kcal mol^{-1} for interconverting the two forms (Table I). The main difference is that the cis form is more favored as the temperature increases (K_{eq} decreases). Therefore at 60 °C in ether K_{eq} for $TaCp(CH_2CMe_3)(CH_2Ph)Cl_2$ is 46 (essentially all trans form) while K_{eq} for $TaCp(CH_2CMe_3)(CH_2Ph)Br_2$ is 0.02 (essentially all cis form).

In contrast to the spectra of $TaCp(CH_2CMe_3)(CH_2Ph)X_2$, the ^1H NMR spectrum of $TaCp''(CH_2CMe_3)(CH_2Ph)Cl_2$ shows no evidence for a cis form between −80 and 80 °C. (We believe it unlikely that the cis and trans forms are still interconverting rapidly at −80 °C.) K_{eq}(t/c) must be on the order of 100 or more so that $\Delta G_{t/c}$ is at least 3 kcal mol^{-1}. The most reasonable explanation is that the more sterically demanding η^5-C_5Me_5 group "locks" the alkyls trans. The little cis form which is present would still be forming rapidly from the trans form on the chemical time scale since we have found $\Delta G^{\ddagger}$ for pseudorotation in Cp'' metallacyclopentane complexes of this type (a process which may be closely related to the cis-trans isomerization) to be only 2-3 kcal mol^{-1} higher than in Cp metallacyclopentane complexes.[8a]

Turning now to the Cp and Cp'' dineopentyl complexes we find that cis forms again cannot be observed directly. The reason is clearly steric in the case of $TaCp''(CH_2CMe_3)_2Cl_2$ (cf. $TaCp''(CH_2CMe_3)(CH_2Ph)Cl_2$ above). It is probably steric in origin for $TaCp(CH_2CMe_3)_2Cl_2$ also; a neopentyl and benzyl group can be mutually cis but two neopentyl groups would prefer to be mutually trans. However, we cannot say that *no cis*-$TaCp(CH_2CMe_3)_2Cl_2$ is present at 25 °C; as much as 5% could be present and go undetected by ^1H NMR.

Finally, the ^{13}C NMR spectrum (gated decoupled) of $TaCp(CH_2CMe_3)(CH_2Ph)Cl_2$ could be telling us something about the degree to which α-abstraction is likely in a neopentyl ligand vs. a benzyl ligand. In the cis form the benzyl α-carbon resonance is a clean 1:2:1 triplet ($^1J_{CH_\alpha}$ = 125 Hz) which suggests that $^1J_{CH_\alpha}$ is the same as $^1J_{CH_{\alpha'}}$ (H_α and $H_{\alpha'}$ are diastereotopic). However, what we can see of the neopentyl α-carbon resonance (it overlaps with the cyclopentadienyl resonances) is similar to that found in $TaCp(CHCMe_3)(CH_2CMe_3)Cl$ (for example) where $^1J_{CH_\alpha} \approx 100$ and $^1J_{CH_{\alpha'}} \approx 110$ Hz (see later). We conclude that whatever is causing low values for J_{CH_α} it is more likely to operate in a neopentyl than in a benzyl ligand.

Details of the Thermal Decomposition of $TaCp(CH_2CMe_3)_2X_2$, X = Cl or Br. The decomposition of $TaCp(CH_2CMe_3)_2Cl_2$ in the dark is first order through at least 4 half-lives in ether, pentane, benzene, chloroform (Figure 2), and dichloromethane at several temperatures (Table II). The decomposition product when the reaction is rapid in the dark at <30 °C (dichloromethane or chloroform) is >95% $TaCp(CHCMe_3)Cl_2$ (which is stable under the reaction conditions). However, at higher temperatures, signals which correspond to $TaCp(CH_2CMe_3)Cl_3$ and $TaCp(CHCMe_3)(CH_2CMe_3)Cl$ (vide infra) in about equal amounts, as well as some unidentified signals, are found in the ^1H NMR spectrum. These byproducts amount to 10-20% of the product mixture in a slow reaction (e.g., at 315 K in ether) but only a few percent in a fast reaction (e.g., at 299 K in chloroform). In the few cases where significant byproducts formed k was determined from measurements made early in the reaction. However, even over longer periods (1-2 half-lives) their production did not markedly affect the linearity of the first-order plot for appearance of $TaCp(CHCMe_3)Cl_2$.

Plots of ln (k/T) vs. $1/T$ (see Figure 3 for an example) gave values for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for the decomposition of $TaCp(CH_2CMe_3)_2Cl_2$ in three solvents, and for decomposition of $TaCp(CH_2CMe_3)_2Br_2$ (less accurately) in one (Table III). By comparing the calculated rates in these three solvents at 309 K (Table II) with that in pentane at 309 K we obtain the ordering ether (≡1) < pentane (1.7) < benzene (4.1) < chloroform (14.8). At 268 K the rate in dichloromethane is about the same as that in chloroform. If $\Delta S^{\ddagger}$ in dichloromethane is similar to that in chloroform, they should also be about the same at 309 K. Therefore at 309 K the ordering is roughly ether (≡1) < pentane (~2) < benzene (~4) < chloroform ~ dichloromethane (~15). Of course if $\Delta S^{\ddagger}$ for two solvents are quite different, the relative rates will change markedly with temperature. For example, at 294 K the rate in chloroform is 30 times that in ether (Table II).

In the presence of 1 mol of $Et_4N^+Cl^-$ $TaCp(CH_2CMe_3)_2Cl_2$ decomposed at 268 K in dichloromethane with k = 0.012 (±0.001) min^{-1}, the same result as in the absence of $Et_4N^+Cl^-$ (Table II). In the presence of 5 mol of $Et_4N^+Cl^-$ the rate was again unchanged. Therefore, loss of Cl^- from the

Table II. Kinetic Data for Decomposition of Dineopentyl Cyclopentadienyl Complexes[a]

compd	solvent	T, K	$k \times 10^3$, min^{-1}	$t_{1/2}$, min
$TaCp(CH_2CMe_3)_2Cl_2$	ether	328	81 ± 3	8.5 ± 0.5
		322	38 ± 1	18.0 ± 0.5
		315	24 ± 1	29 ± 1
		309	13[b]	
		308	12.0 ± 0.5	57 ± 2
		304	7.5[b]	
		303	6.3 ± 0.5	110 ± 4
		294	2.5[b]	
		275	0.263[b]	
		262	0.046[b]	
	pentane	309	22 ± 1	32 ± 5
	benzene	309	53[b]	
		304	29 ± 1	24 ± 1
		302	24 ± 1	29 ± 1
		295	9.7 ± 0.5	71 ± 2
	chloroform	309	193[b]	
		304	142[b]	
		299	100 ± 10	7 ± 1
		294	77 ± 5	9 ± 1
		289	52 ± 2	13 ± 1
		285	38 ± 2	18 ± 1
		281	31 ± 1	22 ± 1
		268	12[b]	
	dichloromethane	268	11 ± 1	63 ± 5
$TaCp(CD_2CMe_3)_2Cl_2$	chloroform	309	36 ± 1	20 ± 1
$TaCp(CH_2CMe_3)_2Br_2$	ether	304	1778[b]	
		275	100 ± 10[c]	7 ± 1
		262	22 ± 5[c]	32 ± 4
$TaCp''(CH_2CMe_3)_2Br_2$	chloroform	304	6.0 ± 0.5	115 ± 10
	dichloromethane	304	6.3 ± 0.5	109 ± 10

[a] Data were obtained by ^{1}H NMR integration of Cp or Cp″ resonances in starting material vs. product vs. time through at least 3 half-lives. The rate constant was determined by a least-squares fit of the data; correlation coefficients were always >0.98. See Figure 2 for a plotted example. Errors in k were determined by a standard statistical method based on standard deviations. The exception is $TaCp(CH_2CMe_3)_2Br_2$.[c] [b] Calculated from $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ given in Table III. [c] The rate constant was determined by estimating the half-life by ^{1}H NMR for decomposition of $TaCp(CH_2CMe_3)_2Br_2$ in a mixture of $TaCp(CH_2CMe_3)_2Br_2$ and $TaCp(CHCMe_3)Br_2$ (see Experimental Section).

Table III. Thermodynamic Data for Decomposition of $TaCp(CH_2CMe_3)_2X_2$ (X = Cl or Br)[a]

X	solvent	$\Delta H^{\ddagger}$, kcal mol^{-1} [b]	$\Delta S^{\ddagger}$, eu[b]
Cl	ether	19 ± 1 (18.74)	−16 ± 4 (−15.3)
Cl	benzene	21 ± 2 (21.28)	−4 ± 10 (−4.2)
Cl	chloroform	10.7 ± 0.5 (10.71)	−36 ± 2 (−35.8)
Br	ether	16 ± 2 (16.14)	−13 ± 7 (−12.9)

[a] $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were determined by a least-squares fit of ln (k/T) vs. $1/T$ using the data in Table II (see Figure 3 for an example). The errors were determined by a standard statistical method based on standard deviations except for $TaCp(CH_2CMe_3)_2Br_2$ (only two points), for which extremes were calculated based on the error in $t_{1/2}$ at each temperature. The errors in $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ are the experimental errors. Real errors, especially for $\Delta S^{\ddagger}$, may be somewhat larger owing to the relatively small temperature range (~25 °C) in which rates were measured. [b] The values in parentheses are the exact values obtained from the least-squares plot of ln (k/T) vs. $1/T$. Exact values must be used to calculate k at T.

tantalum complex cannot play a significant role in its decomposition to the neopentylidene complex.

$TaCp(CD_2CMe_3)_2Cl_2$ decomposes significantly more slowly than $TaCp(CH_2CMe_3)_2Cl_2$. In chloroform the rate constant at 309 K is 0.036 min^{-1}; that calculated for $TaCp(CH_2CMe_3)_2Cl_2$ is 0.193 min^{-1}, or $k_H/k_D = 5.4$ (±0.5). This isotope effect can also be measured in a competitive experiment. The product of the reaction of $Ta(CHDCMe_3)_2Cl_3$ and TlC_5H_5 in toluene is largely $TaCp(CDCMe_3)Cl_2$. A careful ^{1}H NMR integration of the neopentylidene α proton in the $TaCp(CHCMe_3)Cl_2$ present in the $TaCp(CDCMe_3)Cl_2$/$TaCp(CHCMe_3)Cl_2$ mixture vs. the Cp signal suggests that $k_H/k_D = 7 \pm 1$ for the α-abstraction step. We conclude that the rate-determining step involves breaking a carbon-H_α (or D_α) bond and $k_H/k_D \approx 6$. (The possibility of a prior equilibrium will be discussed later.)

A sample of $TaCp(CD_2CMe_3)_2Cl_2$ in benzene decomposed essentially completely at 60 °C in 4 h to give a mixture of neopentane-d_3 (94%) and neopentane-d_2 (6%). Up to 2–3% of the neopentane-d_2 probably arises from -$CHDCMe_3$ groups (since $k_H/k_D \approx 6$) but that remaining (3–4%) must arise in some other manner such as formation of free radicals (see later), γ-abstraction, cleavage of a cyclopentadienyl C–H bond, etc. We do not believe that this anomaly is serious enough to prevent our concluding that only an α-deuterium atom is abstracted in this case, or, in general, only an α-hydrogen atom is abstracted when $TaCp(CH_2CMe_3)_2Cl_2$ decomposes.

We can show that the α-abstraction reaction is intramolecular in the following way. A mixture of $TaCp(CH_2CMe_3)_2Cl_2$ (25 mg) and $TaCp(CD_2CMe_3)_2Cl_2$ (150 mg; this ratio negates any intermolecular isotope effect on the order of 6) in $CHCl_3$ at ~22 °C after ~0.5 h decomposed partially to give a mixture of 41% d_3, 7% d_2, 2% d_1, and 50% d_0 neopentane. All volatiles were removed and the remaining dineopentyl complex (mostly $TaCp(CD_2CMe_3)_2Cl_2$) was redissolved in $CHCl_3$; it decomposed essentially completely in the next 5 h to give a mixture of 61% d_3, 16% d_2, 5% d_1, and 18% d_0 neopentane. The formation of almost exclusively neopentane-d_3 and -d_0 in the early part of the decomposition confirms that the α-abstraction reaction is intramolecular. Formation of

much more neopentane-d_2 and -d_1 in the latter part of the decomposition is most likely due either to intermolecular alkyl exchange prior to intramolecular α-abstraction or to intermolecular α-abstraction. We cannot implicate one or the other based on present data.

The reaction between $Ta(CH_2CMe_3)_2Br_3$ and TlC_5H_5 in ether at −40 °C gives a mixture of $TaCp(CH_2CMe_3)_2Br_2$ and $TaCp(CHCMe_3)Br_2$ (by ^1H NMR). Conversion of the former to the latter was followed by ^1H NMR at 2 and −11 °C. Comparing these rate constants (Table II) with those calculated for the decomposition of $TaCp(CH_2CMe_3)_2Cl_2$ at 275 and 262 K (Table II) gives k_{Br}/k_{Cl} = 380 and 480. (At 304 K the calculated ratio is about 240.) Therefore the bromide complex decomposes about 400 times more rapidly than the chloride complex in ether at ca. 0 °C. An isotope effect was obtained (as above) by measuring how much $TaCp(CHCMe_3)Br_2$ formed on decomposition of $TaCp(CHDCMe_3)_2Br_2$. The result, $k_H/k_D = 6 \pm 1$, does not differ measurably from that obtained above for the corresponding chloride complex.

Finally, we should note that the intramolecular α-abstraction step also proceeds smoothly in the solid state. If a sample of $TaCp(CH_2CMe_3)_2Cl_2$ is warmed to 70 °C in a sublimer in vacuo, $TaCp(CHCMe_3)Cl_2$ rapidly sublimes onto the water-cooled probe (94% yield).

Decomposition of Other Dialkyl Complexes and the Role of Light. $TaCp(CH_2CMe_3)(CH_2Ph)Cl_2$ decomposes smoothly on heating in vacuo to 70 °C. Toluene (68%) and neopentane (10%) are found in the liquid N_2 trap (by ^1H NMR vs. internal standard) and $TaCp(CHCMe_3)Cl_2$ (60% yield) is found on the water-cooled probe. In C_6D_6 at 60 °C $TaCp(CH_2CMe_3)(CH_2Ph)Cl_2$ decomposes similarly (57% $TaCp(CHCMe_3)Cl_2$, 59% toluene, 29% neopentane) with a half-life of about 35 min (k = 0.020 min^{-1}). We cannot measure the rate accurately since the reaction is not straightforward. In neither case have we been able to demonstrate that $TaCp(CHPh)Cl_2$ is formed; this species is still unknown.

$TaCp(CH_2CMe_3)(CH_2Ph)Br_2$ decomposes in ether at 25 °C much more cleanly than $TaCp(CH_2CMe_3)(CH_2Ph)Cl_2$. Only about 10% neopentane forms and $TaCp(CHCMe_3)Br_2$ can be isolated in high yield. For this decomposition at 305 K k = 0.029 min^{-1}. If we assume that the rate will approximately double every 10 °C then k at 60 °C will be about 0.23 min^{-1}. The rate of decomposition of $TaCp(CH_2CMe_3)(CH_2Ph)Cl_2$ in ether at 60 °C should be ¼ that in benzene or $k \approx 0.005$ min^{-1}. The bromide complex in this case therefore would decompose about 50 times faster than the chloride complex at 60 °C. This correlates with the relative amounts of the cis forms for each; $TaCp(CH_2CMe_3)(CH_2Ph)Br_2$ is essentially all cis while $TaCp(CH_2CMe_3)(CH_2Ph)Cl_2$ is only ~2% cis or the ratio of cis bromide to cis chloride is about 50. (Note that the relative rates of decomposition of $TaCp(CH_2CMe_3)_2Br_2$ and $TaCp(CH_2CMe_3)_2Cl_2$ (vide supra) would be on the order of 100 at about 60 °C.) Finally, the rate of decomposition of $TaCp(CH_2CMe_3)(CH_2Ph)Br_2$ in chloroform (k = 0.155 min^{-1} at 305 K) is only about five times what it is in ether. (It is essentially all cis in *each* solvent.)

Both $TaCp''(CH_2CMe_3)(CH_2Ph)Cl_2$ and $TaCp''(CH_2CMe_3)_2Cl_2$ are fairly stable thermally. They decompose slowly in C_6D_6 at 70 °C (days), but, like the forced decompositions of $TaCp(CH_2CMe_3)_2Cl_2$, the reaction does not give $TaCp''(CHCMe_3)Cl_2$ cleanly. Signals due to $TaCp''(CH_2CMe_3)Cl_3$ can be seen in the ^1H NMR spectrum in each case, and in the former also signals due to $TaCp''(CHPh)Cl_2$.[8b] In neither case, however, is $Me_3CCH_2CH_2CMe_3$, $PhCH_2CH_2Ph$, or $PhCH_2CH_2CMe_3$ a product. $TaCp''(CHCMe_3)Cl_2$ can be isolated >90% pure by tedious fractional sublimation of the mixture resulting from thermal decomposition of $TaCp''(CH_2CMe_3)(CH_2Ph)Cl_2$ in the solid state. It is an oil under these conditions (cf. $TaCp''(CHCMe_3)Br_2$ below).

We believed that retardation of the α-abstraction reaction on replacing Cp with Cp″ could be counteracted by replacing Cl with Br. Indeed $TaCp''(CH_2CMe_3)_2Br_2$ decomposes significantly more rapidly than $TaCp''(CH_2CMe_3)_2Cl_2$. In chloroform or dichloromethane at 31 °C its half-life is ca. 110 min and k = 0.006 min^{-1} (Table II). Similar data for $TaCp''(CH_2CMe_3)_2Cl_2$ are unavailable for comparison but we might expect the rate of decomposition of $TaCp''(CH_2CMe_3)_2Cl_2$ to be about 240 times slower than that of $TaCp''(CH_2CMe_3)_2Br_2$ at 304 K by comparison with the η^5-C_5H_5 system above. If so we can calculate the consequence of replacing a Cp″ by a Cp ligand: [k($TaCp(CH_2CMe_3)_2Cl_2$, chloroform, 304 K) × 240]/[k($TaCp''(CH_2CMe_3)_2Br_2$, chloroform, 304 K] = 5680. This can also be calculated by extrapolating the $TaCp(CH_2CMe_3)_2Br_2$ data in ether to 304 K and assuming that k(chloroform)/k(ether) = 19 (the ratio of rates for the chloride complex at 304 K) to give $k_{Cp}/k_{Cp''}$ = 5630). Therefore the rate of α-abstraction increases by 5 × 10^3 on replacing a η^5-C_5Me_5 ligand by a η^5-C_5H_5 ligand. $TaCp''(CHCMe_3)Br_2$ can be recovered easily from a typical decomposition in chloroform and recrystallized from pentane (in which it is very soluble) or sublimed at 110 °C (it melts before subliming at 1 μ).

All the α-abstraction reactions we have mentioned are accelerated markedly by light and their sensitivity to light parallels the ease of the thermal reaction. For example, $TaCp''(CH_2CMe_3)_2Cl_2$ must be photolyzed in benzene in a quartz or Vycor tube using 360-nm high-intensity light from a medium-pressure Hg lamp. On the other hand, a benzene solution of $TaCp''(CH_2CMe_3)_2Br_2$ (50 mg in 1 mL) turns cranberry red in bright indirect sunlight in 15–30 min; by ^1H NMR the sample is mostly $TaCp''(CHCMe_3)Br_2$. Finally, solutions of $TaCp(CH_2CMe_3)_2Cl_2$ (the isolable compound most easily converted into $TaCp(CHCMe_3)Cl_2$ thermally) are sensitive even to room fluorescent light. In fact the preparative yield of $TaCp(CHCMe_3)Cl_2$ in toluene can be improved significantly by covering the flask with aluminum foil.

The photochemical reaction is no cleaner than the corresponding thermal reaction, especially if relatively concentrated samples are used. The most important difference is that the photochemical reaction produces significant quantities of 2,2,5,5-tetramethylhexane (dineopentyl), possibly by coupling of neopentyl radicals. Therefore it does seem more complex than the thermal reaction and its use as a preparative technique therefore somewhat limited. We want to stress that these photochemical results are preliminary. More careful, quantifiable studies of the photolysis at low conversion are clearly needed in order to understand exactly how light influences the α-abstraction step.

Other Neopentylidene Complexes. $TaCp(CHCMe_3)Cl_2$ reacts smoothly with first 1 mol of $LiCH_2CMe_3$ in pentane to give $TaCp(CHCMe_3)(CH_2CMe_3)Cl$, then a second to give $TaCp(CHCMe_3)(CH_2CMe_3)_2$. Both products are extremely soluble in pentane and for that reason difficult to isolate on a small scale by crystallization at low temperature. At room temperature, in fact, they are both sublimable, yellow oils. The analogous complexes obtained by replacing one or two chloride ligands in $TaCp(CHCMe_3)Cl_2$ with methyl groups are also extremely pentane-soluble oils (possibly low-melting solids when pure) which we cannot purify beyond 90–95% by crystallization or sublimation.

Two analogous η^5-C_5Me_5 complexes are more tractable and have been fully characterized. Orange $TaCp''(CHCMe_3)(CH_2CMe_3)Cl$ and yellow $TaCp''(CHCMe_3)(CH_2CMe_3)_2$ can be prepared by treating $TaCp''(CH_2CMe_3)Cl_3$ with 2 and 3 mol of $LiCH_2CMe_3$, respectively, in pentane. They are both extremely soluble in pentane but can be isolated crystalline

Table IV. Pertinent ^1H, ^{13}C NMR, and IR Data for Neopentylidene Complexes[a]

compd	$^1H_\alpha$, τ	$^{13}C_\alpha$, ppm	$^1J_{CH_\alpha}$, Hz	ν_{CH_α}, cm^{-1} [b]
$TaCp(CHCMe_3)Cl_2$	3.62	246	84	2510 (2490)[c,d]
$TaCp(CHCMe_3)(CH_2CMe_3)Cl$	4.08	240	81	2520 (2490)
$TaCp(CHCMe_3)(CH_2CMe_3)_2$	5.01	234	80	2515 (2500)
$TaCp''(CHCMe_3)Cl_2$	5.13	242	83	2435
$TaCp''(CHCMe_3)(CH_2CMe_3)Cl$	6.27	232	76	2460
$TaCp''(CHCMe_3)(CH_2CMe_3)_2$	6.87	228	76	2440
$TaCp(CHCMe_3)Br_2$	3.56	254	83	2470 (2510)[d]
$TaCp''(CHCMe_3)Br_2$	5.18	249	77	2420
$TaCp(CHCMe_3)MeCl$	4.12			
$TaCp(CHCMe_3)Me_2$	4.99	231	78	2475 (2510)
$TaCp(CHCMe_3)Cl_2(PMe_3)$	4.01	272	84	2500[e] (2475)[e]
$NbCp'(CHCMe_3)Cl_2$	2.70	254	95[f]	2535[e]
$NbCp(CHCMe_3)Cl_2$	2.75			2520

[a] Cp = η^5-C_5H_5, Cp′ = η^5-C_5H_4Me, Cp″ = η^5-C_5Me_5. Full details can be found in the Experimental Section. NMR solvent = C_6D_6 unless otherwise noted. [b] In Nujol. The minor peak or shoulder, if any, is at the frequency shown in parentheses. [c] ν_{CD_α} = 1855 cm^{-1} in $TaCp(CDCMe_3)Cl_2$. [d] See Figure 4. [e] Comparatively weak. [f] Broad due to coupling of C_α to ^{93}Nb (I = 9/2, 100% abundant).

from concentrated solutions at −30 °C. $TaCp''(CHCMe_3)(CH_2CMe_3)Cl$ sublimes at 60–70 °C and $TaCp''(CHCMe_3)(CH_2CMe_3)_2$ at 100 °C (1 μ) without decomposition.

The reaction of $TaCp(CHCMe_3)Cl_2$ with $LiCD_2CMe_3$ gives $TaCp(CHCMe_3)(CD_2CMe_3)Cl$; no deuterium transfers from the neopentyl to the neopentylidene α-carbon atom in 16 h at 70 °C. $TaCp(CDCMe_3)(CH_2CMe_3)_2$ (prepared from $TaCp(CDCMe_3)Cl_2$ and $2LiCH_2CMe_3$) is also similarly stable toward H transfer. Apparently, therefore, α-hydrogen atom scrambling is slower in these species than in $Ta(CH_2CMe_3)_3(CDCMe_3)$ where $\Delta G^\ddagger \approx 28$ kcal mol^{-1}.[3a]

This finding suggests that we can measure the isotope effect competitively for a reaction involving a lithium reagent. This may be important since k_H/k_D for formation of $Ta(CH_2CMe_3)_3(CHCMe_3)$ (in the presence of $LiCH_2CMe_3$) was found to be ~3, not ~6 as found here for decomposition of $TaCp(CH_2CMe_3)_2X_2$.[3a] $TaCp''(CHDCMe_3)_2Cl_2$ was treated with 2 mol of $LiCHDCMe_3$ in pentane and the resulting mixture of $TaCp''(CHCMe_3)(CHDCMe_3)_2$ and $TaCp''(CDCMe_3)(CHDCMe_3)_2$ examined by 270-MHz ^1H NMR. Integration of $=CHCMe_3$ vs. all Cp″ protons allowed us to calculate $k_H/k_D = 6 \pm 1$ for this reaction. Almost certainly, therefore, the lithium plays no role similar to that it plays in the formation of $Ta(CH_2CMe_3)_3(CHCMe_3)$,[3a] and $TaCp''(CHCMe_3)(CH_2CMe_3)Cl$ (the initial all-protio product) most likely forms by intramolecular decomposition of $TaCp''(CH_2CMe_3)_3Cl$.

NMR and IR Data for Neopentylidene Complexes. Pertinent NMR and IR data for neopentylidene complexes are given in Table IV.

The chemical shift of the neopentylidene α proton varies from about τ 3 to about τ 7. This could be ascribed largely to an electronic effect, i.e., the α-proton resonance moves to higher field on replacing a chloride with a more electron-donating alkyl ligand. The same happens on replacing Cp with the more electron-donating[9] Cp″ group. All the H_α chemical shifts are at higher field than in the biscyclopentadienyl alkylidene complexes of the type $MCp_2(CHR)X$[6] (τ −2 to 0).

The only other notable feature of the ^1H NMR spectra of the neopentylidene complexes is the fact that the neopentyl α protons in $TaCp(CHCMe_3)(CH_2CMe_3)Cl$ and $TaCp(CHCMe_3)(CH_2CMe_3)_2$ (and the Cp″ analogues) are diastereotopic, and differ in chemical shift by up to 2 ppm. In $TaCp(CHCMe_3)(CH_2CMe_3)_2$, for example, one set is found at τ 8.44, the other at τ 10.52 with $^2J_{H_AH_B}$ = 12 Hz. Therefore we can at least say that these molecules are stereochemically rigid, pseudotetrahedral species on the ^1H NMR time scale.

The ^{13}C NMR spectra of the neopentylidene complexes all show a resonance for the neopentylidene α-carbon atom within what is turning out to be the "normal" range for nucleophilic alkylidene complexes, 224–275 ppm downfield of Me_4Si (Table IV). The peak shifts upfield (as does the H_α peak in the ^1H NMR spectrum) on successively replacing the two chloride ligands by alkyl ligands or Cp by Cp″. It shifts downfield on replacing Cl by Br. $^1J_{CH_\alpha}$ is surprisingly and consistently lower than what is found in analogous (and *more* crowded) 18-electron complexes such as $TaCp_2(CHCMe_3)Cl$ (121 Hz) or $NbCp_2(CHCMe_3)Cl$ (131 Hz).[6] The change in $^1J_{CH_\alpha}$ on replacing Cl by Br or Cp by Cp″ is less than that on replacing Ta by Nb; $^1J_{CH_\alpha}$ increases by about 10 Hz (cf. 121 to 131 Hz above). It should be pointed out that $^1J_{CH_\alpha}$ for any *neopentyl* ligand also seems significantly lower than it should be (ca. 125 Hz) for an sp^3-type C–H bond, and $J_{CH_A} \neq J_{CH_B}$; in every case we estimate $J_{CH_A} = 100 \pm 2$ and $J_{CH_B} = 110 \pm 2$ Hz. J_{CH_α} in the methyl group bound to Ta in $TaCp(CHCMe_3)Me_2$ is also slightly lower (118 Hz) than normal (125 Hz).

The IR spectrum of $TaCp(CHCMe_3)Cl_2$ in Nujol is shown in Figure 4a. The peak we want to draw attention to most is at 2510 cm^{-1}; it has a weak shoulder at 2490 cm^{-1}. The IR spectrum of $TaCp(CDCMe_3)Cl_2$ (Figure 4b) shows a similar peak at 1855 cm^{-1}, a shift of the former by 1/1.35. We therefore assign the 2510-cm^{-1} peak to the C–H_α stretch. Other peaks in the spectrum of $TaCp(CHCMe_3)Cl_2$ change on replacing H_α by D, the most prominent being those at 1255 and 1168 cm^{-1}, which *appear* to shift up (to 1285 cm^{-1}) and down (to 1125 cm^{-1}), respectively. At this juncture, however, it would be premature to attempt to assign any of these lower frequency bands or attempt to rationalize why they shift. All are present (with minor changes in intensities and location) in the IR spectrum of $TaCp(CHCMe_3)Cl_2$ in benzene.

Similar low ν_{CH_α} bands are found in the IR spectra of other neopentylidene complexes (Table IV). The band is strongest and sharpest at the lowest frequency (ν_{CH_α} in $TaCp''(CHCMe_3)Br_2$, the lowest, is one of the strongest bands (all medium strength) in the spectrum) and weaker and broader at higher frequencies. Curiously ν_{CH_α} is sometimes doubled, both in Nujol (see Figure 4c for $TaCp(CHCMe_3)Br_2$) and in solution (Figure 4d). The spectrum of $TaCp''(CHCMe_3)Br_2$ again shows only a single, sharper peak.

The IR spectrum of $TaCp_2(CHCMe_3)Cl$[6] in Nujol shows no low-frequency ν_{CH_α} band. In the spectrum of $TaCp_2(CDCMe_3)Cl$ ν_{CD_α} is clearly seen at 2150 cm^{-1}. This suggests that ν_{CH_α} occurs at 2900 cm^{-1} in $TaCp_2(CHCMe_3)Cl$, assuming that $\nu_{CH}/\nu_{CD} = 1.35$ as found above in the monocyclopentadienyl complexes. This does seem slightly low for an "olefinic" C–H stretch; it is more consistent with a C–H bond having a higher percentage p character, e.g., an aliphatic

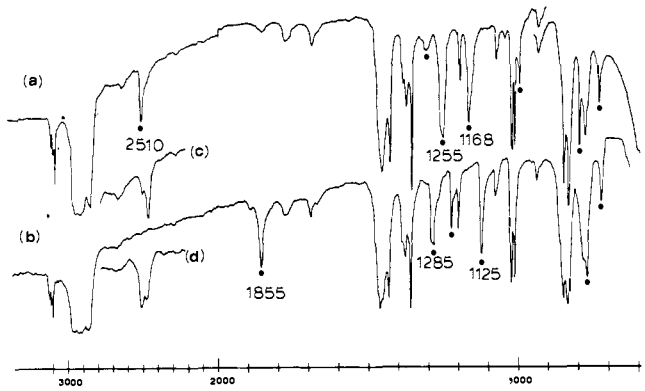
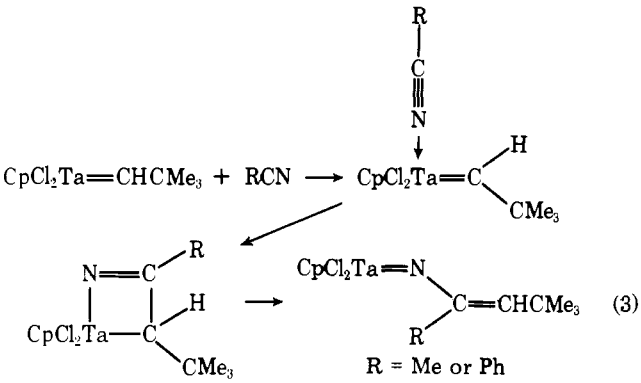


Figure 4. The IR spectra of (a) $TaCp(CHCMe_3)Cl_2$ in Nujol; (b) $TaCp(CDCMe_3)Cl_2$ in Nujol (● denotes the bands which are not common to both spectra); (c) $TaCp(CHCMe_3)Br_2$ in Nujol; (d) $TaCp(CHCMe_3)Br_2$ in benzene.

C-H stretch. The main point, however, is that the ν_{CH_α} band is not nearly so "abnormal" in $TaCp_2(CHCMe_3)Cl$ as in $TaCp(CHCMe_3)Cl_2$.

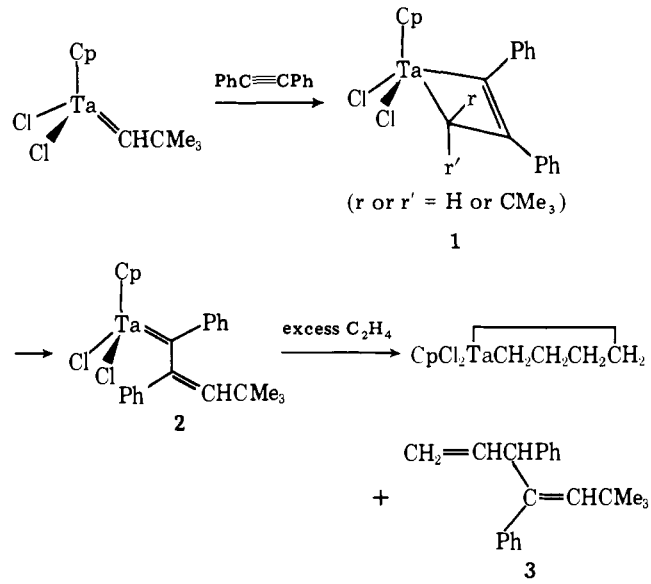
Reaction of $TaCp(CHCMe_3)Cl_2$ with Nitriles, PMe_3, and PhC≡CPh. $TaCp(CHCMe_3)Cl_2$ reacts at 25 °C with acetonitrile or benzonitrile to give (quantitatively) orange, crystalline complexes whose IR, ^1H, and ^{13}C NMR spectra and elemental analyses are entirely consistent with their being a mixture of the *E* and *Z* isomers of the imido complexes formed by inserting RCN into the $Ta{=}CHCMe_3$ bond[3a] (eq 3). This



is consistent with the neopentylidene ligand behaving as a nucleophile. But since 18 valence electron complexes such as $TaCp_2(CHCMe_3)Cl$[6] or $TaCp_2(CH_2)Me$[10] do not react with acetonitrile readily we postulate that RCN must first coordinate to Ta before it is attacked by the nucleophilic neopentylidene ligand. This seems reasonable since the metal is electron deficient (14 valence electrons) and the coordination sphere is not especially crowded. Good evidence that this is the case consists of formation of a PMe_3 adduct.

$TaCp(CHCMe_3)Cl_2(PMe_3)$ contains a neopentylidene ligand in which J_{CH_α} and ν_{CH_α} are virtually the same as in the starting material; the only noteworthy change is a shift of $\delta^{13}C_\alpha$ from 246 to 273 ppm. We therefore believe that PMe_3 adds to the metal and is not in any way associated with H_α or C_α of the neopentylidene ligand. Trimethylphosphine most likely takes up the fourth position in the tetragonal plane of a pseudo-tetragonal-pyramidal molecule, but we do not know if it is cis or trans to the neopentylidene ligand.

The reaction of $TaCp(CHCMe_3)Cl_2$ with PhC≡CPh is analogous to that with RCN (eq 4). Diphenylacetylene probably first coordinates to the metal and is then attacked by the neopentylidene α-carbon atom to give a metallacyclobutene intermediate (**1**) which rearranges to the observed product, blue **2**, which by ^1H and ^{13}C NMR is a single isomer. (The α-carbon atom resonance in **2** is a singlet in the gated decoupled ^{13}C NMR spectrum at 259 ppm.) Apparently a second "insertion" is unfavorable for steric reasons and/or because the α-phenyl group mediates the alkylidene's nucleophilicity. $TaCp(CPh{=}CHCMe_3)Cl_2$ (like $TaCp(CHCMe_3)Cl_2$[5]) reacts smoothly with ethylene to give $Cl_2CpTaCH_2CH_2CH_2CH_2$ and a single organic product which by ^{13}C NMR is *E*- or *Z*-**3** (eq 4). This is the same type of cleavage product (a *terminal* olefin) as that formed on reaction of $TaCp(CHCMe_3)Cl_2$ and ethylene. Internal olefins *can* be the major cleavage product in other types of alkylidene complexes (e.g., $M(CHCMe_3)Cl_3(PMe_3)_2$, M = Nb or Ta[11]). It is somewhat surprising, therefore, that no conjugated diene is formed.



The reaction of $TaCp(CHCMe_3)Cl_2$ with dimethylacetylene is comparatively complex. The initial product is formed from 2 mol of dimethylacetylene per Ta, even at −78 °C. The neopentylidene α-carbon resonance disappears from the ^{13}C spectrum and no other alkylidene α-carbon resonance appears. At low temperature five different methyl groups can be seen. On warming, the sample becomes paramagnetic. Details concerning this reaction and reactions of neopentylidene complexes with other acetylenes will be published separately. However, we might speculate at this time that a simple insertion reaction such as that found above may be the exception rather than the rule.

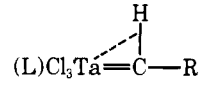
Discussion

We will first discuss the curious spectroscopic and structural features of the neopentylidene complexes reported here (and compare them with others) and then discuss how and why these complexes form; we believe that the former bears an important relationship to the latter. The reactions of $TaCp(CHCMe_3)Cl_2$ with acetonitrile and benzonitrile are similar to those of $Ta(CH_2CMe_3)_3(CHCMe_3)$[3a] and deserve no special comment at this time. The reaction of $TaCp(CHCMe_3)Cl_2$ with PhC≡CPh is interesting[12] but we want to put off any discussion until more examples (in this or another system) are available.

The low values for $^1J_{CH_\alpha}$ and ν_{CH_α} suggest that $TaCp(CHCMe_3)Cl_2$ and analogous molecules differ significantly in some fundamental way from the more crowded, 18 valence electron complex, $TaCp_2(CHCMe_3)Cl$, whose structure is known,[13] and for which $^1J_{CH_\alpha}$ and ν_{CH_α} are not so unusual [121 Hz and 2900 cm^{-1} (ν_{CD} × 1.35, vide supra), respectively]. Structures for two other molecules in this class are known ($TaCp_2(CHPh)(CH_2Ph)$[6] and $TaCp_2(CH_2)Me$[14]). Interestingly, $^1J_{CH_\alpha}$ *decreases* from 132 Hz in $TaCp_2(CH_2)Me$ to 126 Hz in $TaCp_2(CHPh)(CH_2Ph)$ to 121

Hz in $TaCp_2(CHCMe_3)Cl$, while the $M{=}C_\alpha{-}R$ angle (θ) *increases* from 125° (R = H) to 135° (R = Ph) to 150° (R = CMe_3). We might therefore postulate an inverse correlation of $^1J_{CH_\alpha}$ with θ. This seems reasonable since as θ increases (for R = Ph and CMe_3) H_α would necessarily be pushed into a more and more unusual position. When θ = 180° (an extreme which will illustrate the point) the $C{-}H_\alpha$ bond could be described in valence-bond terms as one made with a carbon pure 2p orbital. (A second p orbital would be used to form a π bond to Ta, and the third would be hybridized with s for the σ bonds between C_α and Ta and C_α and R.) Both $^1J_{CH_\alpha}$ and ν_{CH_α} understandably would be unusually low in such a circumstance. We can therefore postulate that intraligand or interligand steric effects which *open up* the $M{-}C_\alpha{-}C_\beta$ angle in an alkylidene complex will contribute to low values for $^1J_{CH_\alpha}$ and ν_{CH_α}.

A recent neutron-diffraction study[15] of an electron-deficient neopentylidene complex, $[Ta(CHCMe_3)Cl_3(PMe_3)]_2$ ($^1J_{CH_\alpha}$ = 101 Hz, ν_{CH_α} = 2605 cm^{-1}), has shown that the $Ta{-}C_\alpha{-}C_\beta$ bond angle is large (161°), the $M{-}C_\alpha{-}H_\alpha$ angle is consequently small (85°), and the $C{-}H_\alpha$ bond is stretched to 1.131 (3) Å, longer than that predicted (1.120 Å) for a pure p-type C-H bond. The electron-deficient Ta is believed to be attracting the CH_α electron pair (**4**), or, alternatively, the α hydrogen as a hydride (H_α^-). A more extreme description is a three-center two-electron (or a total of six electrons) bond in **5**. It would seem that the hydride would not actually transfer to the metal (in this case) since an additional electron pair is needed to form **6** which the metal does not have. (One could



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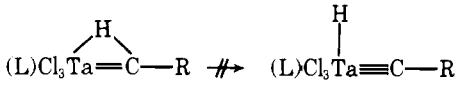
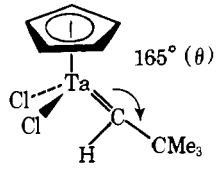


5 **6**

avoid this problem by using descriptions such as $(L)Cl_3(H)\overline{Ta}{=}C^+{-}R$ or $(L)Cl_3(H)Ta{\leftarrow}C{-}R$.) In essence, Ta and C_α are battling for H_α^-. This *electronic* driving force operates synergistically with the steric driving force to open up the $M{-}C_\alpha{-}C_\beta$ angle. This situation should exist in general whenever $^1J_{CH_\alpha}$ and ν_{CH_α} are low (or vice versa). Furthermore, we might expect any increase in the metal's Lewis acidity to encourage M/H_α^- interaction.

Preliminary X-ray structural data[16a] suggest that $TaCp(CHCMe_3)Cl_2$ is a pseudotetrahedral species in which the neopentylidene ligand plane bisects the Cl-Ta-Cl angle (an orientation the same as the isopropylidene ligand in $MnCp(CO)_2(CMe_2)$[16b]). The $Ta{-}C_\alpha{-}C_\beta$ angle is larger still [165 (3)°] and the CMe_3 group points up "*toward*" the Cp ring, presumably in order to allow H_α (not located) to approach the metal from below (**7**). Presumably both the steric and



7

electronic driving forces operate in this case as well. Since $^1J_{CH_\alpha}$ and $\nu_{CH\alpha}$ are even lower than in $[Ta(CHCMe_3)Cl_3(PMe_3)]_2$ we can place some confidence in the inverse correlation of each with the $M{-}C_\alpha{-}C_\beta$ angle, or, alternatively, the direct correlation of each with the $M{-}C_\alpha{-}H_\alpha$ angle. If we take the $Me_3C{-}C{-}H$ angle to be 114° (as in $[Ta(CHCMe_3)Cl_3(PMe_3)]_2$) then the $M{-}C_\alpha{-}H_\alpha$ angle becomes 81° in **7**.

The data in Table IV support the above hypotheses surprisingly well. For example, ν_{CH_α} in $TaCp(CHCMe_3)Br_2$ is 40 cm^{-1} lower than in $TaCp(CHCMe_3)Cl_2$, and in $TaCp''(CHCMe_3)Br_2$ it is 15 cm^{-1} lower than in $TaCp''(CHCMe_3)Cl_2$. Ta in the bromide complexes is probably more electrophilic, for the same reason that $AlBr_3$ is a better Lewis acid than $AlCl_3$[17a] and BBr_3 is better than BCl_3, which is better than BF_3;[17b] Br is a poorer π-electron donor.[17c] Apparently any steric effect on substituting Cl with Br (which would reduce θ) is negligible. Note also that $^1J_{CH_\alpha}$ is relatively insensitive in this range; it is essentially the same in all four complexes.

Replacing Cp with Cp'' decreases ν_{CH_α} from 2510 (in Cl_2). This must be due to steric interaction between CMe_3 and the methyl groups on Cp'' (which increase θ). The electronic effect should be the opposite since Cp'' should donate electron density to the metal.[9] Apparently the steric effect is more important here.

One puzzling result is the effect of replacing a chloride ligand with a neopentyl ligand; θ should decrease ($^1J_{CH_\alpha}$ and ν_{CH_α} should increase) for both steric and electronic reasons. On replacing one chloride ν_{CH_α} does increase slightly but $^1J_{CH_\alpha}$ decreases. On replacing the second chloride, $^1J_{CH_\alpha}$ remains constant but ν_{CH_α} decreases slightly. On replacing both chlorides with methyl groups both $^1J_{CH_\alpha}$ and ν_{CH_α} decrease markedly. The latter data would suggest that the overall result of replacing Cl with CH_3 is to increase θ, i.e., to *decrease* (!) the electron density on Ta. A similar increase in θ on replacing Cl with a neopentyl group would be counteracted by a steric effect to decrease θ. This may be the origin of the small and inconsistent changes in $^1J_{CH_\alpha}$ and ν_{CH_α} in the neopentyl derivatives.

The effect of replacing Ta with Nb is to increase $^1J_{CH_\alpha}$ and ν_{CH_α}, consistent with Nb being a poorer Lewis acid than Ta.[18]

Interestingly, the overall effect on $^1J_{CH_\alpha}$ and ν_{CH_α} of adding PMe_3 to $TaCp(CHCMe_3)Cl_2$ is negligible.

The concept of the metal interacting with the alkylidene CH_α electrons helps explain why H_α in an alkylidene complex can be removed so readily, either by another alkyl ligand[19a] or by an "external base",[19b] to give an alkylidyne complex. One view is that the $C{-}H_\alpha$ bond is long, weak, and susceptible to homolytic cleavage, i.e., "R· abstracts H·." An alternative is that a "semibridging" α-hydrogen atom should be more readily removed by a nucleophile (R^-), since bridging hydrogen atoms in other electron-deficient compounds (boron hydrides, for example) clearly are.[20]

We now go one step further and suggest that intramolecular abstraction of an α-hydrogen atom from an *alkyl* ligand to give an *alkylidene* ligand is a related reaction which is facilitated by steric and electronic effects of the type which we have seen above. There is some evidence that this is the case. $M{-}C_\alpha{-}C_\beta$ angles in bulky alkyl complexes are known to be larger than expected (e.g., 128° for neopentyl in $Ta(CH_2CMe_3)_3[C(CMe_3)(Li{\cdot}dmp)]$[19b]) and $^1J_{CH_\alpha}$ smaller (107 Hz in $Ta(CH_2CMe_3)_3(CHCMe_3)$;[3a] 105 (axial) and 112 Hz (equatorial) in trigonal bipyramidal $Ta(CH_2CMe_3)_4Cl$[3a]). $^1J_{CH_\alpha}$ is also small ($^1J_{CH_A}$ = 100 ± 2, $^1J_{CH_B}$ = 110 ± 2 Hz) in neopentyl/neopentylidene derivatives such as $TaCp(CHCMe_3)(CH_2CMe_3)_2$, and for the neopentyl α protons in *cis*-$TaCp(CH_2CMe_3)(CH_2Ph)Cl_2$. (No reliable data for ν_{CH_α} in such compounds are yet available.) There is no way of knowing a priori whether these effects are essentially all steric or a mixture of steric and electronic (but see below for comparison with phosphorus compounds). In any case we might expect that a methyl ligand would be the least likely (compared to a benzyl or a neopentyl ligand) to give up an

α-hydrogen atom since its H_α atoms would be furthest from the metal and presumably would interact least. Intramolecular elimination of methane from a methyl complex to give a stable methylene complex does seem to be the most difficult in a series of analogous methyl, benzyl, and neopentyl complexes.[6,10]

Another reason why this postulate seems reasonable is that α protons in a neopentylphosphonium salt are unexpectedly acidic compared to those in an ethylphosphonium salt.[21] However, this must be a slight steric effect which is magnified by the overall positive charge since $^1J_{CH_\alpha}$ in phosphonium salts,[22] including $[Ph_3PCH_2CMe_3]^+$,[23] is >125 Hz. Note that $^1J_{CH_\alpha}$ is *larger* in alkylidenephosphoranes,[22] including $Ph_3P{=}CHCMe_3$.[23] Phosphorus(V), unlike Ta(V) or Nb(V), cannot be called electron deficient, and no attraction of the CH_α electrons would be expected. Also, the phosphonium salts and alkylidenephosphoranes which are readily available (including $Ph_3P{=}CHCMe_3$) are not crowded compared to most of the Ta and Nb species which we have prepared. The J_{CH_α} values are therefore "normal".

If we now further postulate that the leaving group must be close to the activated α-hydrogen atom in order to remove it in an essentially concerted process, i.e., that α-abstraction takes place in the cis form of $TaCpR_2Cl_2$ only, then a great many of our findings can be explained. Since cis/trans interconversion is fast relative to the rate of α-abstraction the latter will depend on K_{eq} between the cis and trans forms. K_{eq} can be observed only in the "model" compounds, $TaCp(CH_2CMe_3)(CH_2Ph)X_2$. We must assume that some reasonable amount (say 1%) of *cis*-$TaCp(CH_2CMe_3)_2X_2$ is present (K_{eq} (t/c) $\approx$ 100).

A good example of the importance of cis alkyl groups (we propose) is the substantial decrease in rate on replacing Cp by Cp″. We would not expect (according to our comparison of $TaCp''(CHCMe_3)Cl_2$ with $TaCp(CHCMe_3)Cl_2$) the Cp″ group to differ as markedly from the Cp group electronically as sterically. Since we have found no evidence of a cis form for any $TaCp''R_2X_2$ complex we propose that the bulkier Cp″ group "locks" the alkyl groups into a relative trans orientation and that very little cis form is ever present. It is interesting to note that intermediate $TaCp''(CH_2CMe_3)_3Cl$ (where no "trans" equivalent is possible) must decompose very readily to $TaCp''(CHCMe_3)(CH_2CMe_3)Cl$.

The increase in rate on substituting Br for Cl can also be accounted for in part by a shift in K_{eq} since it varies in the opposite sense in $TaCp(CH_2CMe_3)(CH_2Ph)X_2$ when X = Br (more cis at higher *T*) than when X = Cl (more trans at higher T). Even some of the larger K_{Br}/K_{Cl} ratios (~500) could be explained in this manner. However, we are convinced that there must be a significant electronic difference between Br and Cl which parallels that found in the neopentylidene complexes; an α-hydrogen atom in *cis*-$TaCp(CH_2CMe_3)_2Br_2$ should be more "activated" than that in *cis*-$TaCp(CH_2CMe_3)_2Cl_2$ since the metal should be more electrophilic. This effect could be fairly significant and still be masked by the cis/trans effects. In a case where no isomers are possible ($Ta(CH_2CMe_3)_4X$) we do know that the complex is many times more stable when X = $OCMe_3$ (a better π-electron donor than Cl) than when X = Cl.[3a]

Finally, the solvent effect also is at least qualitatively consistent with a shift in the cis/trans equilibrium toward the more polar cis form in more polar solvents like chloroform. The relative amounts of cis forms in two solvents can easily be 20 or 30. However, in the case where little or no trans form is present ($TaCp(CH_2CMe_3)(CH_2Ph)Br_2$) the solvent effect (chloroform vs. ether) is still significant (≈5). It is interesting to note that little solvent effect (chloroform vs. benzene) was observed in another instance where no isomers are possible.[24]

We prefer to view the abstraction reaction as a concerted process. However, *if* we had to describe $M{-}CH_2R$ cleavage as a separable step it might be best described as a homolytic cleavage for two reasons. First, light dramatically accelerates the α-abstraction reaction. (Light is believed to most characteristically induce homolytic M–R bond cleavage.) Dineopentyl could form from neopentyl radicals generated from the trans isomer since no suitable activated α hydrogen is present. Second, metal reduction is a logical alternative if no suitably activated H_α is close by. ($NbCp(CH_2CMe_3)_2Cl_2$ may be reduced to Nb(IV) since, as we have seen, H_α is not as activated in $Nb{=}CHCMe_3$ complexes as in $Ta{=}CHCMe_3$ complexes.) Of course the $M{-}CH_2R$ bond strength will depend on what other ligands are present, how the CH_2R group is oriented relative to them, and what R is. Interestingly, Lappert found that a $M{-}CH_2CMe_3$ bond was surprisingly weaker than either a $M{-}CH_2Ph$ or $M{-}CH_2SiMe_3$ bond in M(IV) alkyls such as $Zr(CH_2R)_4$.[25] We might also add that one might expect M–alkyl bond strengths in crowded molecules to be weaker, all else being equal.

An intriguing possible partial explanation of the substantial isotope effect is that H prefers to be in the "activated" (possibly "semibridging") position between C_α and Ta much more so than D owing to the greater zero-point energy of the terminal C–H bond (a "thermodynamic" isotope effect).[27] A small energy difference between the two ($\Delta G \approx 0.4$ kcal mol^{-1}) would give $K_{eq} \approx 2$. The true kinetic isotope effect in the α-abstraction step would then only have to be on the order of 3. There is no way of separating the two possible types of isotope effects using the data we have.[28]

We can now understand the importance of structure in dialkyl cyclopentadienyl complexes. $TaCp(CH_2CMe_3)(CH_2Ph)X_2$ can attain the cis form but it is in that form not crowded enough for rapid α-abstraction. $TaCp(CH_2CMe_3)_2X_2$ can still attain the cis form and is crowded enough for α-abstraction. $TaCp''(CH_2CMe_3)_2X_2$ is so crowded that very little cis form is present, and α-abstraction is therefore relatively slow.

When $TaCp(CH_2CMe_3)(CH_2Ph)Br_2$ decomposes it gives primarily toluene and $TaCp(CHCMe_3)Br_2$, exactly the opposite of what one would predict based on the presence of the phenyl ring. A *neopentyl* α hydrogen is more abstractable. For steric reasons the $M{-}C_\alpha{-}C_\beta$ angle in the benzyl ligand will not be as large. In fact $M{-}C_\alpha{-}C_\beta$ angles in known electron-deficient complexes such as $Zr(CH_2Ph)_4$ are abnormally small (as low as 90°) compared to those in $Sn(CH_2Ph)_4$, for example.[29] Interaction of the metal with the ortho C–H bond in the phenyl ring, or with the ring itself (another manifestation of a metal's electron deficiency), was the explanation. This type of interaction could actually be partly or even largely responsible for the apparent relatively slow α-abstraction from a benzyl α-carbon atom under most circumstances; the metal acquires electron density by interacting with the phenyl ring instead of with the α-hydrogen atom.[30]

The obvious question is whether some version of an α-abstraction reaction is possible for other, and in particular later, transition metals. Certainly electron-deficient metals will interact with "hydride" bound to carbon, in Mo pyrazolylborate complexes,[31] in protonated diene–Fe(0) complexes,[32,33] and in $Os_3(CO)_{10}(CH_3)(H)$.[27] [One interesting piece of data should be compared with that which we have presented here; in $[Fe(CO)_3(C_4H_7)]^+$ J_{CH} in the C–"bridging H"–Fe[32a] system is 74 Hz.[32b]] Therefore an electron-deficient metal could in theory set up H_α^- in an alkyl complex to be abstracted or could itself accept H_α to give an alkylidene/hydride complex ("α-elimination"[34]) from which the hydride is subsequently removed; the difference between the two processes may be more formal than real. If this is true then it is peculiar that, although what is overall an α-abstraction is also known for Mo and W neopentyl complexes,[1] neopentyl ligands bound to Ru,[35]

Rh,[35] or Pt[36] lose a γ-hydrogen atom to give β,β-dimethylmetallacyclobutane complexes.

Experimental Section

All manipulations were done under N_2, either in a Vacuum Atmospheres HE43-2 drybox or by standard Schlenk techniques. Ether and toluene were distilled from sodium benzophenone ketyl under nitrogen. Pentane was purified by an acid wash and then distilled from $LiAlH_4$ under nitrogen. Acetonitrile and benzonitrile were distilled from P_2O_5 (the latter at reduced pressure) after refluxing for 2 days. Metal halides and thallium reagents were purchased from standard sources and sublimed prior to use. $LiCH_2CMe_3$,[3a] $Mg(CH_2CMe_3)_2$(dioxane),[3a] $Ta(CH_2CMe_3)_2Cl_3$,[3a] $Nb(CH_2CMe_3)_2Cl_3$,[6] $Zn(CH_2Ph)_2$,[37] and LiC_5Me_5[38] were prepared by published methods. Elemental analyses were done by Alfred P. Bernhardt or by Schwarzkopf. Chloride analyses were usually done in these laboratories by titration of digested samples with $AgNO_3$[39] or $Hg(NO_3)_2$.[40] ^1H NMR spectra were done at 60 and 90 (Perkin-Elmer) or 270 MHz (Brucker) and ^{13}C spectra at 15 (JEOL) or 67.89 MHz (Brucker).

1. Preparation of $Zn(CD_2CMe_3)_2$ and $Zn(CDHCMe_3)_2$. A solution of $LiCD_2CMe_3$ (4.0 g) in 30 mL of ether was added slowly to 5.78 g of $ZnCl_2$(dioxane) in 50 mL of ether with stirring. After 2 days, the mixture was filtered and the ether was removed in vacuo. The residue was extracted into pentane and the solution filtered. The pentane and residual dioxane were removed in vacuo (5 h). The crude yellow liquid was distilled at 76 °C (20 mm) to give 3.16 g (58%) of colorless $Zn(CD_2CMe_3)_2$. This is an improvement of the previously published procedure.[3a] $Zn(CDHCMe_3)_2$ was prepared similarly.

2. Preparation of $Ta(CH_2CMe_3)X_4$. A solution of 3.11 g of $Zn(CH_2CMe_3)_2$ in 25 mL of toluene was added slowly to 16.12 g of $TaCl_5$ (50% excess) in 75 mL of toluene with stirring. The reaction mixture was stirred for 1 week at room temperature. The mixture was filtered and the toluene removed in vacuo. The residue was extracted into pentane and the solution filtered. Removing the pentane in vacuo yielded 10.8 g of yellow, crystalline $Ta(CH_2CMe_3)Cl_4$ (92%). It can be recrystallized from pentane (≥60% recovery). It decomposes at room temperature in several days in absence of $TaCl_5$.

Anal. Calcd for $TaC_5H_{11}Cl_4$: Cl, 36.00. Found: Cl, 35.40. ^1H NMR (τ, C_6D_6): 6.68 (s, 2, CH_2CMe_3), 9.04 (s, 9, CH_2CMe_3).

$Ta(CH_2CMe_3)Br_4$ (τ 7.04, 9.00) is prepared analogously (1 day at 60 °C).

3. Preparation of $Ta(CH_2CMe_3)_2Br_3$. $Zn(CH_2CMe_3)_2$ (1.0 g) in 15 mL of toluene was added slowly to a vigorously stirred suspension of 4.0 g of $TaBr_5$ (excess) in 50 mL of toluene over a period of 1 h. The mixture was filtered and all toluene removed in vacuo leaving a greenish-orange oil. This was dissolved in pentane and the solution was treated with a small amount of activated charcoal and filtered. The yellow solid which remained after removing all pentane from the filtrate in vacuo was pure $Ta(CH_2CMe_3)_2Br_3$ according to its ^1H NMR spectrum in C_6H_6 (τ 6.90 (s), 8.60 (s), 2:9 ratio) compared to mixtures containing $Ta(CH_2CMe_3)_3Br_2$ (τ 7.20 (s), 8.50 (s)) and/or $Ta(CH_2CMe_3)Br_4$ (τ 6.80 (s), 8.70 (s)); the shifts vary somewhat with absolute and relative concentrations of the three. Usually the product is a partially crystalline, yellow-orange oil containing $Ta(CH_2CMe_3)_3Br_2$ as the main contaminant (it is comparatively unreactive) since the result sensitively depends on the purity of the $TaBr_5$, how finely divided it is, the rate of $Zn(CH_2CMe_3)_2$ addition, etc. In that case the purity was determined by ^1H NMR and stoichiometries for subsequent reactions were adjusted accordingly. Little $Ta(CH_2CMe_3)_2Br_3$ is obtained in pentane since $TaBr_5$ is virtually insoluble in this solvent.

4. Preparation of $Ta(CH_2CMe_3)(CH_2Ph)X_3$. A solution of 1.26 g of $Zn(CH_2Ph)_2$ in 20 mL of toluene was added slowly to 4.0 g of $Ta(CH_2CMe_3)Cl_4$ in 30 mL of toluene with stirring. The mixture was stirred for 1 h and the solution filtered. The toluene was concentrated to 5 mL in vacuo and 20 mL of pentane added. Storing the solution at −20 °C for 2 days yielded 3.50 g of red-orange, crystalline $Ta(CH_2CMe_3)(CH_2Ph)Cl_3$ (80%).

Anal. Calcd for $TaC_{12}H_{18}Cl_3$: C, 32.06; H, 4.03; Cl, 23.66. Found: C, 31.69; H, 3.73; Cl, 23.58. ^1H NMR (τ, C_6D_6): 2.53–2.96 (m, 5, C_6H_5), 6.36 (s, 2, CH_2Ph), 7.59 (s, 2, CH_2CMe_3), 8.93 (s, 9, CH_2CMe_3).

$Ta(CH_2CMe_3)(CH_2Ph)Br_3$ was prepared analogously (τ 6.36, 7.40, 8.88).

5. Preparation of $TaCp(CH_2CMe_3)Cl_3$. $Ta(CH_2CMe_3)Cl_4$ (3.25 g) and TlCp (2.22 g) were stirred in 50 mL of toluene for 12 h. The mixture was filtered and the toluene concentrated to 10 mL. Pentane was added and 3.10 g of orange, crystalline $TaCp(CH_2CMe_3)Cl_3$ isolated by filtration (89%).

^1H NMR (τ, C_6D_6): 4.34 (s, 5, Cp), 8.12 (s, 2, CH_2), 8.63 (s, 9, CMe_3).

6. Preparation of $TaCp''(CH_2CMe_3)Cl_3$. $Ta(CH_2CMe_3)Cl_4$ (7.92 g) and LiC_5Me_5 (2.86 g) were stirred in 50 mL of ether for 2 h. The mixture was filtered and the ether removed from the filtrate in vacuo. The residue was extracted into toluene and the solution filtered. The toluene was removed in vacuo and the crude product recrystallized from ether to give 5.54 g of red-orange crystals. The ether was removed from the filtrate in vacuo and the residue was again extracted into toluene. The solution was filtered and the toluene concentrated until crystals were noted. An equal volume of pentane was added and the solution was stored at −20 °C for 24 h to give another 2.0 g of compound (overall yield 76%).

^1H NMR (τ, C_6D_6): 8.03 (s, 15, C_5Me_5), 8.54 (s, 9, CH_2CMe_3), 8.62 (s, 2, CH_2CMe_3).

7. Preparation of $TaCp(CH_2CMe_3)_2Cl_2$ and $TaCp(CD_2CMe_3)_2Cl_2$. A solution of 1.41 g of $Ta(CH_2CMe_3)_2Cl_3$ in 30 mL of ether at 0 °C was treated with 0.88 g of TlCp. The reaction mixture was stirred for 30 min and filtered. Removing the ether in vacuo yielded 1.2 g of dark-red, crystalline $TaCp(CH_2CMe_3)_2Cl_2$ (80%). Recrystallization from pentane yielded 0.80 g (53%).

$TaCp(CD_2CMe_3)_2Cl_2$ was prepared similarly, mol wt (cyclohexane) 433 (calcd, 463).

Anal. Calcd for $TaC_{15}H_{27}Cl_2$: Cl, 15.44. Found: Cl, 15.51. ^1H NMR (τ, C_6D_6): 4.24 (s, 5, Cp), 8.22 (s, 4, CH_2), 8.74 (s, 18, CMe_3).

$TaCp(CH_2CMe_3)_2Cl_2$ was also prepared by reacting 1.0 g of $TaCp(CH_2CMe_3)Cl_3$ with 0.30 g of $Mg(CH_2CMe_3)_2$(dioxane) in 30 mL of ether. After 20 min the solution was filtered and the ether removed in vacuo. The compound was recrystallized from pentane (0.61 g, 56%).^{13}C NMR (ppm, toluene-d_8, ^1H gated decoupled): 117 (t, CH_2CMe_3, $^1J_{CH}$ = 118 Hz), 116 (d, Cp, $^1J_{CH}$ = 175 Hz), 37.2 (s, CH_2CMe_3), 35.1 (q, CH_2CMe_3, $^1J_{CH}$ = 124 Hz).

8. Preparation of $TaCp''(CH_2CMe_3)_2Cl_2$. $Ta(CH_2CMe_3)_2Cl_3$ (2.00 g) and LiC_5Me_5 (0.66 g) were stirred in 30 mL of ether for 2 h. The mixture was filtered and the ether removed in vacuo. The residue was extracted into toluene and the mixture filtered. The toluene was removed in vacuo and the crude product recrystallized from ether to give deep red crystals (1.73 g, 70% yield).

Anal. Calcd for $TaC_{20}H_{37}Cl_2$: C, 45.38; H, 7.05; Cl, 13.40. Found: C, 44.90; H, 7.13; Cl, 13.52. ^1H NMR (τ, C_6D_6): 8.23 (s, 15, C_5Me_5), 8.77 (s, 18, CH_2CMe_3), 9.09 (s, 4, CH_2CMe_3). ^{13}C NMR (ppm, C_6D_6, ^1H gated decoupled): 124 (s, C_5Me_5), 117 (t, CH_2CMe_3, $^1J_{CH}$ = 116 Hz), 37.7 (s, CH_2CMe_3), 36.1 (q, CH_3CMe_3, $^1J_{CH}$ = 123 Hz), 12.8 (q, C_5Me_5, $^1J_{CH}$ = 128 Hz).

9. Preparation of $TaCp''(CH_2CMe_3)_2Br_2$. Pure $Ta(CH_2CMe_3)_2Br_3$ (2.70 g) was dissolved in 50 mL of ether and 0.70 g of LiC_5Me_5 added. The flask was covered with foil and stirred for 1 h. The ether was removed in vacuo and the residue was extracted into 125 mL of pentane. The extract was filtered and stood at −30 °C overnight to give 1.45 g of small, red needles. Decreasing the volume afforded 0.35 g of additional product, total yield 1.80 g (56%). The compound in benzene is red by transmitted light but blue-purple by reflected light.

^1H NMR (τ, C_6D_6): 7.96 (s, 15, C_5Me_5), 8.54 (s, 18, CH_2CMe_3), 9.35 (s, 4, CH_2CMe_3).

10. Preparation of $TaCp(CH_2CMe_3)(CH_2Ph)X_2$. $Ta(CH_2CMe_3)(CH_2Ph)Cl_3$ (3.3 g) and TlCp (1.98 g) were stirred in 50 mL of toluene for 30 min. The mixture was filtered and the toluene removed in vacuo. Pentane was added and 2.62 g of deep-red, crystalline $TaCp(CH_2CMe_3)(CH_2Ph)Cl_2$ isolated by filtration (75%).

Anal. Calcd for $TaC_{17}H_{23}Cl_2$: Cl, 14.80. Found: Cl, 14.80. ^1H NMR (τ, $CDCl_3$, −50 °C): cis isomer 2.68–3.18 (m, 5, C_6H_5), 3.57 (s, 5, Cp), 6.80 (d, 1, CH_AH_BPh, $^1J_{HH}$ = 12 Hz), 7.24 (d, 1, CH_AH_BPh, $^1J_{HH}$ = 12 Hz), 7.74 (d, 1, $CH_AH_BCMe_3$, $^1J_{HH}$ = 14 Hz), 8.37 (d, 1, $CH_AH_BCMe_3$, $^1J_{HH}$ = 14 Hz), 8.82 (s, 9, CH_2CMe_3), trans isomer 2.68–3.18 (m, 5, C_6H_5), 3.46 (s, 5, Cp), 7.35 (s, 2, CH_2Ph), 8.50 (s, 2, CH_2CMe_3), 9.13 (s, 9, CH_2CMe_3). ^{13}C NMR (ppm, $CDCl_3$, ^1H gated decoupled, −50 °C): cis isomer 149.8 (s, C_{ipso}), 127.8, 126.8, 123.9 (d, other phenyl carbons, $^1J_{CH}$ = 159 Hz), 116.4 (d, Cp, $^1J_{CH}$ = 181 Hz), 114.0 (t, CH_2CMe_3, $^1J_{CH} \approx$ 112 Hz), 96.0 (t, CH_2Ph, $^1J_{CH}$ = 126 Hz), 37.1 (s, CH_2CMe_3), 34.2 (q,

CH_2CMe_3, $^1J_{CH}$ = 124 Hz), trans isomer 143.0 (s, C_{ipso}), 130.5, 126.7, 123.7 (d, other phenyl carbons, $^1J_{CH}$ = 159 Hz), 115.6 (d, Cp, $^1J_{CH}$ = 181 Hz), 114.2 (t, CH_2CMe_3, $^1J_{CH} \approx$ 112 Hz), 98.6 (t, CH_2Ph, $^1J_{CH}$ = 128 Hz), 35.1 (s, CH_2CMe_3), 34.0 (q, CH_2CMe_3, $^1J_{CH}$ = 124 Hz).

$TaCp(CH_2CMe_3)(CH_2Ph)Br_2$ was cleanly prepared in situ in ether or $CDCl_3$ at −20 °C for determination of its rate of decomposition at 32 °C. In ether k = 0.029 min^{-1} ($t_{1/2}$ = 24 min). In $CDCl_3$ k = 0.155 min^{-1} ($t_{1/2}$ = 4.5 min). Virtually the only decomposition products were $TaCp(CHCMe_3)Br_2$ and toluene.

^1H NMR (τ, $CDCl_3$, −50 °C): cis isomer 2.54–3.34 (m, 5, C_6H_5), 3.53 (s, 5, Cp), 6.83 (d, 1, CH_AH_BPh, $^1J_{HH}$ = 11 Hz), 7.26 (d, 1, CH_AH_BPh, $^1J_{HH}$ = 11 Hz), 7.83 (d, 1, $CH_AH_BCMe_3$, $^1J_{HH}$ = 15 Hz), 8.59 (d, 1, $CH_AH_BCMe_3$, $^1J_{HH}$ = 15 Hz), 8.80 (s, 9, CH_2CMe_3).

11. Preparation of $TaCp''(CH_2CMe_3)(CH_2Ph)Cl_2$. $Ta(CH_2CMe_3)(CH_2Ph)Cl_3$ (4.85 g) and LiC_5Me_5 (1.53 g) were stirred in 50 mL of ether for 2 h. The mixture was filtered and the ether removed in vacuo. The residue was extracted into toluene and filtered. The toluene was removed in vacuo and the crude product recrystallized from a pentane/ether (25/75) solution. Deep-red crystals (4.6 g) were isolated (78%).

Anal. Calcd for $TaC_{22}H_{33}Cl_2$: Cl, 12.91. Found: Cl, 12.88. ^1H NMR (τ, C_6D_6): 2.42–3.29 (m, 5, phenyl), 7.80 (s, 2, CH_2Ph), 8.13 (s, 15, C_5Me_5), 8.83 (s, 2, CH_2CMe_3), 8.86 (s, 9, CH_2CMe_3).

12. Preparation of $TaCp(CHCMe_3)Cl_2$ and $TaCp(CDCMe_3)Cl_2$. $Ta(CH_2CMe_3)_2Cl_3$ (4.14 g) and TlCp (2.60 g) were stirred in 30 mL of toluene for 24 h. The solution was filtered and the toluene removed in vacuo. The residue was extracted into 25 mL of a pentane/toluene (80/20) solution. Storing the solution at −20 °C for 24 h yielded 2.85 g of red, crystalline $TaCp(CHCMe_3)Cl_2$ (76%).

Anal. Calcd for $TaC_{10}H_{15}Cl_2$: C, 31.03; H, 3.91; Cl, 18.32. Found: C, 31.17; H, 4.05; Cl, 18.30. ^1H NMR (τ, C_6D_6): 3.62 (s, 1, $CHCMe_3$), 3.45 (s, 5, Cp), 9.05 (s, 9, $CHCMe_3$). ^{13}C NMR (ppm downfield from Me_4Si, C_6D_6, ^1H gated decoupled): 246 (d, $CHCMe_3$, $^1J_{CH}$ = 84 Hz), 107 (d, Cp, $^1J_{CH}$ = 180 Hz), 48 (s, $CHCMe_3$), 33 (q, $CHCMe_3$, $^1J_{CH}$ = 126 Hz). Mol wt (cyclohexane): 404 (calcd, 388).

A side product was isolated by extracting the TlCl residue with acetonitrile. Black crystals were obtained by cooling the deep-green acetonitrile solution to −30 °C for 12 h. This compound was identified as $TaCp_2Cl_2$ by analysis and its infrared spectrum.[41] Anal. Calcd for $TaC_{10}H_{10}Cl_2$: C, 31.44; H, 2.64; Cl, 18.57. Found: C, 31.69; H, 2.52; Cl, 18.47.

$TaCp(CDCMe_3)Cl_2$ was prepared as follows. A solution of 0.25 g of $TaCp(CD_2CMe_3)_2Cl_2$ in 5 mL of toluene was stirred for 4 h at 60 °C. The toluene was removed in vacuo and the residue extracted into 5 mL of a pentane/toluene (80/20) solution. Storing the solution at −20 °C for 1 day yielded 0.11 g of red, crystalline $TaCp(CDCMe_3)Cl_2$ (52%).

13. Preparation of $TaCp(CHCMe_3)Br_2$ and Observation of $TaCp(CH_2CMe_3)_2Br_2$. A mixture of 72% $Ta(CH_2CMe_3)_2Br_3$ and 28% $Ta(CH_2CMe_3)_3Br_2$ (2.1 g; 1.52 g of $Ta(CH_2CMe_3)_2Br_3$ = 2.7 mmol) was dissolved in toluene and treated with 0.73 g (2.7 mmol) of TlCp at 25 °C with rapid stirring. The solution turned purple in 10 s, then red within 1 min. After 1 h TlCl was filtered off and all toluene removed in vacuo. The solid was triturated with pentane (5 mL) and 0.72 g of $TaCp(CHCMe_3)Br_2$ was filtered off. Standing the filtrate at −30 °C gave an additional 0.10 g (64% total yield based on $Ta(CH_2CMe_3)_2Br_3$). $TaCp(CHCMe_3)Br_2$ can be recrystallized from 1:4 toluene/pentane mixtures at −30 °C (cf. $TaCp(CHCMe_3)Cl_2$ above).

Anal. Calcd for $TaC_{10}H_{15}Br_2$: C, 25.23; H, 3.17. Found: C, 25.51; H, 3.50. ^1H NMR (τ, C_6D_6): 3.56 (s, 1, $CHCMe_3$), 4.35 (s, 5, Cp), 9.03 (s, 9, $CHCMe_3$). ^{13}C NMR (ppm, C_6D_6, gated ^1H decoupled); 254 (d, $CHCMe_3$, $^1J_{CH}$ = 83 Hz), 106 (d, Cp, $^1J_{CH}$ = 180 Hz), 48.3 (s, $CHCMe_3$), 32.5 (q, $CHCMe_3$, $^1J_{CH}$ = 126 Hz).

Intermediate $TaCp(CH_2CMe_3)_2Br_2$ could be observed by ^1H NMR in the aliquot of a reaction done in ether at ca. −25 °C for 15 min. The Cp signal was located 3.50 ppm downfield of the low-field ether quartet resonance; the Cp resonance in $TaCp(CHCMe_3)Br_2$ is found at 3.27 ppm downfield of the quartet. The rate of decomposition of the former to the latter was obtained at 2 and −11 °C by estimating the half-life of the former at each temperature (7 ± 1 and 32 ± 2 min, respectively).

Reaction of $Ta(CHDCMe_3)_2Br_3$ with TlCp in toluene gave a mixture of 85% $TaCp(CDCMe_3)Br_2$ and 15% $TaCp(CHCMe_3)Br_2$ (by ^1H NMR) or k_H/k_D = 6 ± 1.

14. Preparation of $TaCp''(CHCMe_3)Cl_2$. Four solid samples of $TaCp''(CH_2CMe_3)(CH_2Ph)Cl_2$ (0.25 g each) were heated at 145 °C for 20 min and then sublimed at 0.05 μ for 1 h. Each sublimate was dissolved in 2–3 mL of pentane. These were combined and stored at −20 °C for 2 days. The solution was filtered and the pentane removed in vacuo to give a red oil (0.18 g, 23% yield, >90% pure).

^1H NMR (τ, C_6D_6): 5.13 (s, 1, $CHCMe_3$), 8.01 (s, 15, C_5Me_5), 8.84 (s, 9, $CHCMe_3$). ^{13}C NMR (ppm downfield of Me_4Si, C_6D_6, ^1H gated decoupled): 242 (d, $CHCMe_3$, $^1J_{CH}$ = 83 Hz), 119 (s, C_5Me_5), 47.1 (s, $CHCMe_3$), 33.7 (q, $CHCMe_3$, $^1J_{CH}$ = 127 Hz), 12.3 (q, C_5Me_5, $^1J_{CH}$ = 128 Hz).

15. Preparation of $TaCp''(CHCMe_3)Br_2$. $TaCp''(CH_2CMe_3)_2Br_2$ (0.80 g) was dissolved in minimal $CDCl_3$ and the solution was stood in the dark for 2 days. The solvent was removed and the residue was doubly recrystallized from minimal pentane at −30 °C, yield 0.40 g (57%).

^1H NMR (τ, C_6D_6): 5.18 (s, 1, $CHCMe_3$), 7.88 (s, 15, C_5Me_5), 8.83 (s, 9, $CHCMe_3$). ^{13}C NMR (ppm, C_6D_6, ^1H gated decoupled): 249 (d, $CHCMe_3$, $^1J_{CH}$ = 77 Hz), 119 (s, C_5Me_5), 48.2 (s, $CHCMe_3$), 33.2 (q, $CHCMe_3$, $^1J_{CH}$ = 126 Hz), 13.2 (q, C_5Me_5, $^1J_{CH}$ = 128 Hz).

16. Preparation of $Nb(C_5H_4Me)(CHCMe_3)Cl_2$ and $NbCp(CHCMe_3)Cl_2$. $Nb(CH_2CMe_3)_2Cl_3$ (0.76 g) and TlC_5H_4Me (0.63 g) were stirred in 20 mL of toluene for 10 min. The mixture was filtered and the toluene removed in vacuo. The residue was extracted into pentane and the solution filtered. Storing the filtrate at −20 °C for 24 h yielded 0.23 g of purple, crystalline $NbCp'(CHCMe_3)Cl_2$ (30%).

^1H NMR (τ, C_6D_6): 2.70 (s, 1, $CHCMe_3$), 4.02 (m, 2, $C_5H_2H'_2Me$), 4.42 (m, 2, $C_5H_2H'_2Me$), 8.20 (s, 3, C_5H_4Me), 9.03 (s, 9, $CHCMe_3$). ^{13}C NMR (ppm downfield of Me_4Si, C_6D_6, ^1H gated decoupled): 254 (d, $CHCMe_3$, $^1J_{CH}$ = 95 Hz), 109 (d, $C_2H_2C_2'H_2CMe$, $^1J_{CH}$ = 177 Hz), 105 (d, $C_2H_2C_2'H_2CMe$, $^1J_{CH}$ = 180 Hz), 48.7 (s, $CHCMe_3$), 30.7 (q, $CHCMe_3$, $^1J_{CH}$ = 125 Hz), 14.9 (q, C_5H_4Me, $^1J_{CH}$ = 128 Hz).

$NbCp(CHCMe_3)Cl_2$ was prepared similarly. TlCp reacted slowly compared to TlC_5H_4Me. Reaction times ranged from 4 to 12 h and yields from 7 to 15%.

Anal. Calcd for $NbC_{10}H_{15}Cl_2$: C, 40.17; H, 5.05; Cl, 23.71. Found: C, 40.19; H, 5.16; Cl, 23.66. ^1H NMR (τ, C_6D_6): 2.75 (s, 1, $CHCMe_3$), 4.20 (s, 5, Cp), 9.05 (s, 9, $CHCMe_3$).

17. Preparation of $TaCp(CHCMe_3)(CH_2CMe_3)Cl$. A solution of $LiCH_2CMe_3$ (0.20 g) in 10 mL of pentane was added slowly to 1.0 g of $TaCp(CHCMe_3)Cl_2$ in 30 mL of pentane with stirring. The mixture was filtered and the pentane removed in vacuo to yield 0.72 g of a red-orange oil (66%).

^1H NMR (τ, C_6D_6, 270 MHz): 4.08 (s, 1, $CHCMe_3$), 4.27 (s, 5, Cp), 7.91 (d, 1, $CH_AH_BCMe_3$, J = 13 Hz), 8.90 (s, 9, $CHCMe_3$), 8.95 (s, 9, CH_2CMe_3), 9.28 (d, 1, $CH_AH_BCMe_3$, J = 13 Hz). ^{13}C NMR (ppm downfield from Me_4Si, C_6D_6, ^1H gated decoupled): 240 (d, $CHCMe_3$, $^1J_{CH}$ = 81 Hz), 104 (d, Cp, $^1J_{CH}$ = 177 Hz), 79.1 (dd, $CH_AH_BCMe_3$, $^1J_{CH}$ = 100, 110 ± 2 Hz), 47.3 (s, $CHCMe_3$), 34.8 (s, CH_2CMe_3), 34.6 (q, CH_2CMe_3, $^1J_{CH}$ = 125 Hz), 33.4 (q, $CHCMe_3$, $^1J_{CH}$ = 125 Hz).

18. Preparation of $TaCp''(CHCMe_3)(CH_2CMe_3)Cl$. A solution of 2.68 g of $LiCH_2CMe_3$ was added slowly to 8.50 g of $TaCp''(CH_2CMe_3)Cl_3$ at −78 °C with stirring. The mixture was warmed slowly to room temperature and stirred for 2 h. It was filtered and the pentane was removed from the filtrate in vacuo. The crude compound was recrystallized from pentane and 6.14 g of orange, crystalline $TaCp''(CHCMe_3)(CH_2CMe_3)Cl$ was isolated (71%).

Anal. Calcd for $TaC_{20}H_{36}Cl$: C, 48.73; H, 7.36; Cl, 7.19. Found: C, 48.25; H, 7.51; Cl, 7.40. ^1H NMR (τ, C_6D_6, 270 MHz): 6.27 (s, 1, $CHCMe_3$), 8.12 (s, 15, C_5Me_5), 8.65 (s, 9, $CHCMe_3$), 8.75 (s, 9, CH_2CMe_3), 9.08 (d, 1, $CH_AH_BCMe_3$, J = 14 Hz), 9.25 (d, 1, $CH_AH_BCMe_3$, J = 14 Hz). ^{13}C NMR (ppm downfield from Me_4Si, C_6D_6, ^1H gated decoupled): 232 (d, $CHCMe_3$, $^1J_{CH}$ = 76 Hz), 116 (s, C_5Me_5), 80.8 (dd, $CH_AH_BCMe_3$, $^1J_{CH}$ = 100, 110 ± 2 Hz), 47.3 (s, $CHCMe_3$), 35.2 (q, CH_2CMe_3, $^1J_{CH}$ = 123 Hz), 34.1 (q, $CHCMe_3$, $^1J_{CH}$ = 124 Hz), 12.3 (q, C_5Me_5, $^1J_{CH}$ = 127 Hz).

19. Preparation of $TaCp(CHCMe_3)(CH_2CMe_3)_2$. A solution of 0.71 g of $LiCH_2CMe_3$ in 30 mL of pentane was added slowly to $TaCp(CHCMe_3)Cl_2$ (1.76 g) in 30 mL of pentane with stirring. The mixture was filtered and the pentane removed in vacuo to give 1.75

g of a yellow-orange oil (84%).

^{1}H NMR (τ, C_6D_6, 270 MHz): 4.39 (s, 5, Cp), 5.01 (s, 1, $CHCMe_3$), 8.44 (d, 2, $CH_AH_BCMe_3$, J = 12 Hz), 8.79 (s, 9, $CHCMe_3$), 8.91 (s, 18, CH_2CMe_3), 10.52 (d, 2, $CH_AH_BCMe_3$, J = 12 Hz). ^{13}C NMR (ppm downfield from Me_4Si, C_6D_6, ^{1}H gated decoupled): 234 (d, $CHCMe_3$, $^1J_{CH}$ = 80 Hz), 104 (d, Cp, $^1J_{CH}$ = 175 Hz), 85.4 (dd, $CH_AH_BCMe_3$, $^1J_{CH}$ = 100 ± 2, 110 ± 2 Hz), 47.1 (s, $CHCMe_3$), 35.1 (q, CH_2CMe_3, $^1J_{CH}$ = 125 Hz), 34.8 (s, CH_2CMe_3), 34.0 (q, $CHCMe_3$, $^1J_{CH}$ = 125 Hz).

20. Preparation of Ta(CHCMe$_3$)(CH$_2$CMe$_3$)$_2$. A solution of 0.08 g of $LiCH_2CMe_3$ in 5 mL of pentane was added slowly to 0.50 g of $TaCp''(CHCMe_3)(CH_2CMe_3)Cl$ in 20 mL of pentane with stirring. The mixture was filtered and the pentane was removed in vacuo. The crude product was recrystallized from pentane and 0.32 g of yellow-orange, crystalline $TaCp''(CHCMe_3)(CH_2CMe_3)_2$ was isolated (60%). The compound sublimed readily at 100 °C and 0.05 μ.

Anal. Calcd for $TaC_{25}H_{47}$: C, 56.80; H, 8.96. Found: C, 56.33; H, 8.91. ^{1}H NMR (τ, C_6D_6, 270 MHz): 6.87 (s, 1, $CHCMe_3$), 8.15 (s, 15, C_6Me_5), 8.63 (s, 9, $CHCMe_3$), 8.73 (s, 18, CH_2CMe_3), 8.86 (d, 2, $CH_AH_BCMe_3$, J = 12 Hz), 10.68 (d, 2, $CH_AH_BCMe_3$, J = 12 Hz). ^{13}C NMR (ppm downfield from Me_4Si, C_6D_6, ^{1}H gated decoupled): 228 (d, $CHCMe_3$, $^1J_{CH}$ = 76 Hz), 114 (s, C_5Me_5), 89.5 (dd, $CH_AH_BCMe_3$, $^1J_{CH}$ = 100, 110 ± 2 Hz), 47.7 (s, $CHCMe_3$), 35.4 (q, CH_2CMe_3, $^1J_{CH}$ = 124 Hz), 34.6 (s, CH_2CMe_3), 34.1 (q, $CHCMe_3$, $^1J_{CH}$ = 126 Hz), 12.1 (q, C_5Me_5, $^1J_{CH}$ = 127 Hz).

21. Preparation of TaCp(CHCMe$_3$)MeCl and TaCp(CHCMe$_3$)Me$_2$. A solution of commercially available methyllithium in ether was treated with 1 equiv of dioxane to precipitate the dissolved LiBr. The "halide-free" methyllithium was titrated with propanol using 1,10-phenanthroline as an indicator.[42]

$TaCp(CHCMe_3)Cl_2$ (1.94 g) was dissolved in 30 mL of THF and cooled to −78 °C. A solution of halide-free $LiCH_3$ (1 equiv per Ta) in 20 mL of THF was added dropwise over a period of 30 min. At the end of the addition the solution was allowed to warm slowly to room temperature. The THF was removed in vacuo and the residue was extracted into pentane and filtered. The pentane was removed in vacuo and the resulting orange solid was sublimed at 50 °C and 0.5 μ onto a −78 °C probe to give 0.91 g (50%) of dark-orange crystals (≥90% pure). ^{1}H NMR (τ, C_6D_6): 4.12 (s, 1, $CHCMe_3$), 4.48 (s, 5, Cp), 8.87 (s, 9, $CHCMe_3$), 9.47 (s, 3, TaMe).

$TaCp(CHCMe_3)Me_2$ was prepared similarly using 2 equiv of $LiCH_3$ per Ta. The yield was highly variable (7–69%) and no attempt was made to optimize the procedure. ^{1}H NMR (τ, C_6D_6): 4.40 (s, 5, Cp), 4.99 (s, 1, $CHCMe_3$), 8.82 (s, 9, $CHCMe_3$), 9.88 (s, 6, TaMe). ^{13}C NMR (ppm downfield of Me_4Si, C_6D_6, ^{1}H gated decoupled): 231 (d, $CHCMe_3$, $^1J_{CH}$ = 78 Hz), 104 (d, Cp, $^1J_{CH}$ = 176 Hz), 46.6 (s, $CHCMe_3$), 37.8 (q, TaMe, $^1J_{CH}$ = 118 Hz), 33.3 (q, $CHCMe_3$, $^1J_{CH}$ = 127 Hz).

22. Preparation of TaCp(CHCMe$_3$)Cl$_2$(PMe$_3$). This yellow adduct crystallizes out of benzene or toluene (in which it is slightly soluble) on adding PMe_3 to $TaCp(CHCMe_3)Cl_2$. It is extremely soluble in dichloromethane or chloroform. ^{1}H NMR (τ, CD_2Cl_2): 4.01 (d, 1, J_{HP} = 1.6 Hz, $CHCMe_3$), 4.15 (d, 5, J_{HP} = 2.9 Hz, Cp), 8.40 (d, 9, J_{HP} = 8.6 Hz, PMe_3), 8.87 (s, 9, $CHCMe_3$). ^{13}C NMR (ppm, $CDCl_3$, ^{1}H gated decoupled): 272 (d, $CHCMe_3$, $^1J_{CH}$ = 84, $^2J_{CP}$ = 16 Hz, ^{1}H decoupled), 101 (d multiplet, Cp, $^1J_{CH}$ = 179 Hz), 49.2 (s, $CHCMe_3$), 31.0 (q, $CHCMe_3$, $^1J_{CH}$ = 126, $^4J_{CP} \approx$ 3 Hz, ^{1}H decoupled), 17.0 (dq, PMe_3, $^1J_{CH}$ = 129, $^1J_{CP}$ = 29 Hz).

23. Preparation of TaCp[NC(Me)CHCMe$_3$]Cl$_2$. $TaCp(CHCMe_3)Cl_2$ (1.0 g) was stirred in 5 mL of acetonitrile for 1 day. The acetonitrile was removed in vacuo and the residue was extracted into minimal ether. Storing the solution at −20 °C for 1 day yielded 0.73 g of orange, crystalline $TaCp[NC(Me)CHCMe_3]Cl_2$ (66% yield; ratio of E/Z = 1.6).

Anal. Calcd for $TaC_{12}H_{18}NCl_2$: C, 33.67; H, 4.24; N, 3.27; Cl, 16.56. Found: C, 33.50; H, 4.33; N, 3.21; Cl, 16.61. ^{1}H NMR (τ, C_6D_6): E isomer 4.07 (s, 5, Cp), 5.64 (br s, 1, $CHCMe_3$), 8.32 (d, 3, $NC(Me)$, $J \approx$ 2 Hz), 8.64 (s, 9, $CHCMe_3$), Z isomer 4.05 (s, 5, Cp), 4.93 (br s, 1, $CHCMe_3$), 8.28 (d, 3, $NC(Me)$, $J \approx$ 2 Hz), 8.94 (s, 9, $CHCMe_3$). ^{13}C NMR (ppm, C_6D_6, ^{1}H gated decoupled): E isomer 147 (s, NC(Me)), 130 (d, $CHCMe_3$, J_{CH} = 152 Hz), 112 (d, Cp, $^1J_{CH}$ = 179 Hz), 31.7 (q, $CHCMe_3$, $^1J_{CH}$ = 125 Hz), 31.7 (s, $CHCMe_3$), 26.5 (q, $NC(Me)$, $^1J_{CH}$ = 128 Hz), Z isomer 149 (s, NC(Me)), 134 (d, $CHCMe_3$, $^1J_{CH}$ = 152 Hz), 112 (d, Cp, $^1J_{CH}$ = 179 Hz), 31.7 (q, $CHCMe_3$, $^1J_{CH}$ = 125 Hz), 31.7 (s, $CHCMe_3$), 19.5 (q, $NC(Me)$, $^1J_{CH}$ = 128 Hz).

24. Preparation of TaCp[NC(Ph)CHCMe$_3$]Cl$_2$. A solution of 0.32 g of $TaCp(CHCMe_3)Cl_2$ and 0.10 g of benzonitrile in toluene was left at 25 °C for 2 days. The toluene was removed in vacuo and the residue was extracted into pentane. Cooling the solution at −20 °C for 1 day yielded 0.25 g of orange and yellow crystals (61% yield; E/Z = 1/3.4).

^{1}H NMR (τ, C_6D_6): Z isomer (orange crystals) 2.49–2.98 (m, 5, Ph), 4.38 (s, 5, Cp), 5.18 (s, 1, $CHCMe_3$), 8.57 (s, 9, $CHCMe_3$), E isomer (yellow crystals) 2.88 (m, 5, Ph), 4.41 (s, 5, Cp), 4.55 (s, 1, $CHCMe_3$), 9.10 (s, 9, $CHCMe_3$).

25. Preparation of TaCp[C(Ph)C(Ph)CHCMe$_3$]Cl$_2$. $TaCp(CHCMe_3)Cl_2$ (0.50 g) and 0.23 g of diphenylacetylene were stirred in 50 mL of toluene for 12 h. The toluene was concentrated to ~5 mL in vacuo and 20 mL of pentane was added. Blue, crystalline $TaCp[C(Ph)C(Ph)CHCMe_3]Cl_2$ (0.53 g, 72%) was isolated by filtration.

Anal. Calcd for $TaC_{24}H_{25}Cl_2$: C, 50.99; H, 4.45; Cl, 12.54. Found: C, 50.81; H, 4.54; Cl, 12.44. ^{1}H NMR (τ, C_6D_6): 2.67–3.71 (m, ~10 (olefinic proton buried in phenyl region, even at 270 MHz), Ph), 4.41 (s, 5, Cp), 8.69 (s, 9, $CHCMe_3$). ^{13}C NMR (ppm, C_6D_6, ^{1}H gated decoupled): 259 (s, Ta=CPh), 151 (s, C_{ipso}), 142 (s, C'_{ipso}), 137 (d, $CHCMe_3$, $^1J_{CH}$ = 152 Hz), 131 (s, =CPh), 131–126 (other Ph carbons), 110 (d, Cp, $^1J_{CH}$ = 179 Hz), 36.1 (s, $CHCMe_3$), 32.1 (q, $CHCMe_3$, $^1J_{CH}$ = 126 Hz).

26. Reaction of TaCp[C(Ph)C(Ph)CHCMe$_3$]Cl$_2$ with C$_2$H$_4$. A solution of $TaCp[C(Ph)C(Ph)CHCMe_3]Cl_2$ (0.28 g) in 10 mL of pentane was stirred under 50 psi of C_2H_4 for 12 h. Orange $CpCl_2TaCH_2CH_2CH_2CH_2$ (0.13 g, 72%) was isolated by filtration and identified by comparison of its ^{1}H NMR spectrum with that of an authentic sample.[5] The filtrate was concentrated to ~3 mL and passed through a column of activated alumina. The residual pentane was removed in vacuo and 0.11 g of colorless, liquid CH_2=$CHCH(Ph)C(Ph)$=$CHCMe_3$ was isolated (79%).

^{1}H NMR (τ, C_6D_6): 2.78–3.29 (m, 10, Ph), 3.92 (ddd, 1, =CH–, J = 7, 10, and 18 Hz), 4.47 (s, 1, =$CHCMe_3$), 5.02 (m, 2, =CH_2), 5.96 (d, 1, –CH(Ph)–, J = 7 Hz), 9.13 (s, 9, =$CHCMe_3$). ^{13}C NMR (ppm, $CDCl_3$, ^{1}H off-resonance decoupled): 141.9, 141.5, 140.5 (s, C_{ipso}, C'_{ipso}, –C(Ph)=), 140.1, 139.2 (d, =CH, =$CHCMe_3$), 130–126 (other phenyl carbons), 115.7 (dd, =CH_2), 60.0 (d, –CH(Ph)–), 33.5 (s, $CHCMe_3$), 31.4 (q, $CHCMe_3$).

Decomposition Study of TaCp(CR$_2$CMe$_3$)$_2$Cl$_2$ (R = H or D). A solution of 25 mg of $TaCp(CH_2CMe_3)_2Cl_2$ and 150 mg of $TaCp(CD_2CMe_3)_2Cl_2$ in 1 mL of chloroform was prepared in the dark and left there for 0.5 h. All volatiles were then removed in vacuo and analyzed by GC/mass spectroscopy for deuterated neopentanes as described previously:[3a] 41% d_3, 7% d_2, 2% d_1, and 50% d_0. Another 1 mL of chloroform was added to the residue and the solution left for 5 h in the dark. The volatiles were again analyzed for deuterated neopentanes by GC/MS; 61% d_3, 16% d_2, 5% d_1, and 18% d_0.

A 250-mg sample of $TaCp(CD_2CMe_3)_2Cl_2$ was dissolved in 5.0 mL of benzene and the solution was heated at 60 °C for 4 h. The deuterated neopentanes (by GC/MS) were 94% d_3 and 6% d_2.

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Structural Studies of Organic Silver Complexes in Dimethyl Sulfoxide by ^{13}C and ^{109}Ag NMR

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Abstract: The effects on ^{13}C and ^{109}Ag chemical shifts of complexation of ethylenethiourea, thiazolidine-2-thione, 3-methylthiazolidine-2-thione, dipropylamine, pentamethylene sulfide, and 2-aminothiazole with silver nitrate in dimethyl sulfoxide solution have been examined. Although complexation is reflected via ^{109}Ag chemical shifts of hundreds of parts per million, as compared with only a few parts per million of ligand ^{13}C chemical shifts, both types of NMR data suggest that ligands which bind Ag(I) through sulfur form solutions containing a variety of complex species. By contrast, nitrogen ligands appear to form primarily 2:1 silver-to-ligand complexes. The ^{13}C chemical-shift changes in the unsaturated compounds are discussed in terms of contributions from resonance forms containing different degrees of C=S and C=N bonding in the silver complexes compared to the free ligands.

Introduction

We have shown in an earlier report[1] that a combination of ^{13}C and ^{109}Ag NMR holds promise for determining various structural parameters of organic silver complexes in solution. However, experimental data were obtained only for thiourea and tetramethylthiourea. The apparent structural diversity of the silver-complex systems for these compounds precluded detailed conclusions. Toward a long-term goal of providing a data base which may allow more of the information contained in the ^{13}C and ^{109}Ag spectra of silver complexes to be extracted, we have extended our study to include additional compounds.

The ^{13}C spectra of silver complexes may be useful in providing insight into the effects of complexing of metal ions in general on the ^{13}C chemical shifts of organic ligands. Diamagnetic metal complexes have already been studied. Metal complexes of olefinic and aromatic ligands[2,3] and the shifts caused by metal complexation in carbonyl[4,5] and thiocarbonyl[6,7] compounds have also been studied. A few investigations

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