adecyltrimethylammonium bromide (CTAB) solution (2.5×10^{-3} M); buffer, phosphate–borate (0.01 M) at pH 7; under irradiation for some reactions. In all of these experiments, the products were identical with those obtained without modification; and the thioester of butyric acid, the isomerization product, was not detected in any case. A control reaction, for which only the cobalt complex was absent, yielded the thioester of methacrylic acid, but that of isobutyric acid (**3c**) was not detected.

Reaction of Co^I(BDHC) with Dimethyl Bromomethylmalonate. The reaction was carried out in a similar manner as described above for the one with the bromo thioester (**3a**). At the end of the reaction, the solution was acidified (pH 1) by adding hydrochloric acid. The mixture was continuously extracted with ether (200 mL) for 20 h.[4a] After evaporation of the solvent, the residue was treated wtih diazomethane and analyzed by means of gas chromatography; dimethyl methylmalonate was detected, whereas dimethyl succinate, the isomerization product, was not. A control experiment without the cobalt complex yielded no detectable amount of dimethyl methylmalonate under otherwise identical reaction conditions.

Catalytic and Selective Reduction of Primary Alkyl Bromides. $(CN)_2Co^{III}$(BDHC) (30 mg, 0.05 mmol) in aqueous CTAB solution (2.5×10^{-2} M, 70 mL) was reduced with $NaBH_4$ (60 mg, 1.6 mmol) to the Co(I) state. 1-Dodecyl bromide (250 mg, 1.0 mmol) was added to the solution under nitrogen. The mixture was cooled down with ice water, irradiated with a 250-W tungsten lamp from a distance of 20 cm for 4 h, and extracted with ether (100 mL × 4). The ether extract was washed with water (100 mL × 3), dried over sodium sulfate, and evaporated to dryness. The residue was chromatographed on a column of silica gel (Wako gel C-100) with petroleum ether (300 mL) as eluant: an oil (200 mg), a 1:2.5 mixture of dodecane and 1-dodecyl bromide by gas chromatographic and NMR analyses. The yield of dodecane was 0.25 mmol or 500% based on the amount of the cobalt complex used. The reductive debromination of 1-bromo-3-(bromomethyl)cyclohexane (0.25 mmol) with $NaBH_4$ (0.75 mmol) as catalyzed by $[Co^{II}(BDHC)]ClO_4$ (0.025 mmol) and the competitive debromination of 1-dodecyl bromide (0.13 mmol) and 2-octyl bromide (0.13 mmol) with $[Co^{II}(BDHC)]ClO_4$ (0.025 mmol) and $NaBH_4$ (0.75 mmol) were carried out, and the products were analyzed in a similar manner.

Preparation of Monocyclopentadienyl Benzylidene Complexes of Tantalum and the Crystal Structure of $Ta(\eta^5\text{-}C_5Me_5)(CHPh)(CH_2Ph)_2$[1a]

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Abstract: A benzylidene complex, $Ta(\eta^5\text{-}C_5Me_5)(CHPh)(CH_2Ph)Cl$, can be prepared by adding LiC_5Me_5 to $Ta(CH_2Ph)_3Cl_2$. The analogous $\eta^5\text{-}C_5H_5$ complex apparently is unstable but a relative, $Ta(\eta^5\text{-}C_5H_4Me)(CHPh)(CH_2Ph)_2$, can be prepared by dehydrohalogenating $Ta(\eta^5\text{-}C_5H_4Me)(CH_2Ph)_3Cl$ with $Ph_3P{=}CH_2$ while $Ta(\eta^5\text{-}C_5Me_5)(CHPh)(CH_2Ph)_2$ can be prepared from $Ta(\eta^5\text{-}C_5Me_5)(CHPh)(CH_2Ph)Cl$ and $Mg(CH_2Ph)_2$. Adding LiC_5Me_5 to $Ta(CH_2Ph)_2Cl_3$ gives $Ta(\eta^5\text{-}C_5Me_5)(CH_2Ph)_2Cl_2$ which can be forced to eliminate toluene by pyrolysis or photolysis to give $Ta(\eta^5\text{-}C_5Me_5)(CHPh)Cl_2$ in low yield. An X-ray structural determination of $Ta(\eta^5\text{-}C_5Me_5)(CHPh)(CH_2Ph)_2$ shows a molecule of the expected "three-legged stool" type. The benzylidene ligand's large $Ta{-}C_\alpha{-}C_\beta$ angle (166°) and short $Ta{=}C_\alpha$ bond (1.88 Å) make it seem more like a benzylidyne ligand. We believe this circumstance is due primarily to the metal's need for more electron density (which it acquires from the $C{-}H_\alpha$ bond) and that any contribution to the large $Ta{=}C_\alpha{-}C_\beta$ angle due to steric interaction between the benzylidene's phenyl ring and the $\eta^5\text{-}C_5Me_5$ ring is relatively small.

Introduction

In the past few years, we have found that certain complexes of Ta(V) and Nb(V) which contain at least two neopentyl groups decompose to yield neopentane and neopentylidene complexes by a process which we have called α-hydrogen abstraction.[2] One of the best studied examples is $Ta(\eta^5\text{-}C_5H_5)(CHCMe_3)Cl_2$.[3] This type of species also seems to be more interesting than one of the 18-electron, dicyclopentadienyl variety (e.g., $Ta(\eta^5\text{-}C_5H_5)_2(CHCMe_3)Cl$)[4] since it is electron deficient (14 electrons) and therefore reacts more readily with small molecules such as olefins.[5]

In contrast, the number of analogous benzylidene complexes is small. The only known example is 18-electron $Ta(\eta^5\text{-}C_5H_5)_2(CHPh)(CH_2Ph)$ which is formed when TlC_5H_5 is added to $Ta(CH_2Ph)_3Cl_2$.[4] There is also evidence that $Ta(CHPh)(CH_2Ph)_3$ (cf. $Ta(CHCMe_3)(CH_2CMe_3)_3$[6]) is formed when $Ta(CH_2Ph)_5$ decomposes in a first-order manner,[7] but it is apparently unstable under the reaction conditions.[8] One type of electron-deficient benzylidene complex which should be stable toward intermolecular decomposition reactions is one containing a single cyclopentadienyl ring, e.g., $Ta(\eta^5\text{-}C_5H_5)(CHPh)(CH_2Ph)Cl$, a possible intermediate in the reaction which gives $Ta(\eta^5\text{-}C_5H_5)_2(CHPh)(CH_2Ph)$. Therefore we set out to prepare this or related species by adding a cyclopentadienyl ring to benzyl complexes.

Results

Preparation of $Ta(CH_2Ph)_yCl_{5-y}$ (y = 1, 2, or 4). The only reported benzyl complexes of this type are $Ta(CH_2Ph)_3Cl_2$,[9]

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[1] (a) Multiple Metal-Carbon Bonds. 17. For Part 16 see: Wengrovius, J. H.; Schrock, R. R.; Churchill, M. R.; Missert, J. R.; Youngs, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 4515. (b) MIT; Dow Predoctoral Fellow, 1976–1978. (c) MIT; Camille and Henry Dreyfus Teacher–Scholar Grant Recipient, 1978. (d) Present address: Sandia Laboratories, Alburquerque, New Mexico.

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[8] Further evidence for $Ta(CHPh)(CH_2Ph)_3$ consists of the fact that it can be trapped by acetonitrile to give $Ta(CH_2Ph)_3(N(Me)C{=}CHPh)(MeCN)_x$ (cf. $Ta(CH_2CMe_3)_3(N(Me)C{=}CHCMe_3)$:[6] Fellmann, J. D., unpublished results.

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Table I. Carbon-13 NMR Spectral Data[a] for Benzyltantalum Complexes

compd	T, °C	δ(C$_\alpha$),[b] ppm	$^1J_{\mathrm{CH}_\alpha}$, Hz	δ(C$_\beta$),[b] ppm
Ta(CH$_2$Ph)$_2$Cl$_3$	25	92	139	126
Ta(CH$_2$Ph)$_3$Cl$_2$	25	88	135	131
Ta(CH$_2$Ph)$_4$Cl	−55	117.7[c]	117[c]	138.1[c]
		98.8[d]	131[d]	146.7[d]
Ta(CH$_2$Ph)$_5$[e]	25	105	123	142

[a] CDCl$_3$ solvent. [b] Relative to Me$_4$Si. [c] Axial benzyl group. [d] Equatorial benzyl group. [e] At 25 °C all benzyl groups are equivalent on the NMR time scale.

Ta(CH$_2$Ph)$_5$,[9] and Ta(CH$_2$Ph)Cl$_4$.[10] Therefore we first set out to prepare the other members of this family, especially Ta(CH$_2$Ph)$_2$Cl$_3$.

Ta(CH$_2$Ph)$_2$Cl$_3$ was prepared in 70% yield by adding Zn(CH$_2$Ph)$_2$ to TaCl$_5$ in toluene or benzene/pentane mixtures at room temperature (eq 1). This reaction also generates small

$$\mathrm{TaCl_5 + Zn(CH_2Ph)_2 \rightarrow Ta(CH_2Ph)_2Cl_3 + ZnCl_2} \quad (1)$$

amounts of insoluble Ta(CH$_2$Ph)Cl$_4$ (vide infra), which can be filtered off along with ZnCl$_2$, and Ta(CH$_2$Ph)$_3$Cl$_2$, which can be separated from the less-soluble Ta(CH$_2$Ph)$_2$Cl$_3$ by fractional recrystallization from hexane/toluene or pentane/benzene mixtures. Ta(CH$_2$Ph)$_2$Cl$_3$ of slightly lower purity can be prepared in higher yield (82%) by adding a small amount of ether to the solvent; we believe the ether solubilizes any sparingly soluble Ta(CH$_2$Ph)Cl$_4$ so it can be alkylated further. Ta(CH$_2$Ph)$_2$Cl$_3$ is soluble in aromatic and ethereal solvents and is stable at 25 °C under N$_2$. Like all compounds which we will be talking about here, Ta(CH$_2$Ph)$_2$Cl$_3$ is very sensitive to air and water.

We can prepare Ta(CH$_2$Ph)Cl$_4$ virtually quantitatively by adding 1 mol of HCl to Ta(CH$_2$Ph)$_2$Cl$_3$ in toluene at −78 °C. It is essentially insoluble in toluene but dissolves in ether. We therefore believe it may not be a monomer in nondonor solvents. Unlike other benzyl complexes it sublimes at 100 °C and < 1 μm.

The missing member of this series, Ta(CH$_2$Ph)$_4$Cl, can be prepared similarly by adding HCl to Ta(CH$_2$Ph)$_5$ at −78 °C (eq 2). We could not prepare it directly from either Ta(CH$_2$Ph)$_2$Cl$_3$

$$\mathrm{Ta(CH_2Ph)_5 + HCl \xrightarrow[\text{toluene}]{-78\ ^\circ C} Ta(CH_2Ph)_4Cl\ (81\%)} \quad (2)$$

or Ta(CH$_2$Ph)$_3$Cl$_2$ by using Zn(CH$_2$Ph)$_2$ or Mg(CH$_2$Ph)$_2$(THF)$_2$; we obtained only mixtures of Ta(CH$_2$Ph)$_3$Cl$_2$ and Ta(CH$_2$Ph)$_5$. Since it is slightly unstable thermally, it was characterized only by ^{1}H and ^{13}C NMR methods (vide infra) and by hydrolysis reactions.

The ^{1}H and ^{13}C NMR spectra are all consistent with the formulation of the benzyl complexes. Two findings are noteworthy. First, Ta(CH$_2$Ph)$_4$Cl is a fluxional molecule. At 35 °C the benzyl protons in Ta(CH$_2$Ph)$_4$Cl give rise to a sharp singlet at τ 7.00 (C$_6$D$_6$, 90 MHz), between those for Ta(CH$_2$Ph)$_3$Cl$_2$ (τ 6.82) and Ta(CH$_2$Ph)$_5$ (τ 7.39). By −80 °C this singlet has split into two resonances at τ 6.75 and 8.35 with relative areas of 3:1 (T_c = −25 °C; $\Delta G^\ddagger$ = 11 ± 1 kcal mol^{-1}).[11a] The ^{13}C NMR spectrum varies similarly with temperature. We therefore believe the ground-state molecule is a trigonal bipyramid with the chloride in an axial position.

The second interesting finding is that $^1J_{\mathrm{CH}_\alpha}$ and δ(C$_\beta$) are "normal" for Ta(CH$_2$Ph)$_5$ (123 Hz and 142 ppm, respectively) but increase and decrease (respectively) on replacing benzyl groups with chlorides (Table I). For example, in Ta(CH$_2$Ph)$_2$Cl$_3$, $^1J_{\mathrm{CH}_\alpha}$ (139 Hz) is essentially the same as in Zr(CH$_2$Ph)$_4$ (136 Hz), a molecule in which there is apparently some interaction between Zr and the phenyl ring.[11b] Therefore $^1J_{\mathrm{CH}_\alpha}$ may be a measure of how much the phenyl ring interacts with the metal. The extreme description, a "benzallyl",[12] would account for the relatively large, olefinic-like CH$_\alpha$ coupling constants.

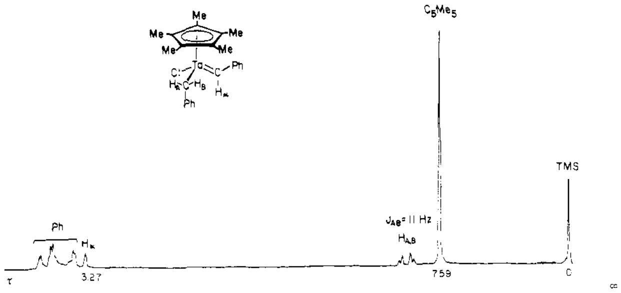

Figure 1. 270-MHz ^{1}H NMR spectrum of Ta(η^5-C$_5$Me$_5$)(CHPh)(CH$_2$Ph)Cl in C$_6$D$_6$.

All attempts to similarly prepare niobium–benzyl complexes have failed. We believe Nb reduces too easily. We encountered similar difficulties in niobium–neopentyl chemistry.[3]

The Formation of Benzylidene Complexes. Ta(CH$_2$Ph)Cl$_4$ and Ta(CH$_2$Ph)$_2$Cl$_3$ react with LiC$_5$Me$_5$ in ether to give Ta(η^5-C$_5$Me$_5$)(CH$_2$Ph)Cl$_3$ and Ta(η^5-C$_5$Me$_5$)(CH$_2$Ph)$_2$Cl$_2$, respectively, in high yield. (Almost always the η^5-C$_5$Me$_4$Et complex can be prepared analogously. We will report it only if we did not prepare the η^5-C$_5$Me$_5$ complex.) However, the product of the reaction between Ta(CH$_2$Ph)$_3$Cl$_2$ and LiC$_5$Me$_5$ is a benzylidene complex, Ta(η^5-C$_5$Me$_5$)(CHPh)(CH$_2$Ph)Cl (eq 3; 70% yield). Its ^{1}H

$$\mathrm{Ta(CH_2Ph)_3Cl_2 + LiC_5Me_5 \rightarrow Ta(\eta^5\text{-}C_5Me_5)(CHPh)(CH_2Ph)Cl + toluene} \quad (3)$$

NMR spectrum in Figure 1 suggests that it is an asymmetric, pseudotetrahedral molecule. In the ^{13}C NMR spectrum, the benzylidene C$_\alpha$ resonance is found at δ 221 ($^1J_{\mathrm{CH}_\alpha}$ = 85 Hz) and the benzyl C$_\alpha$ resonance is an approximate 1:1:1 triplet in the gated proton-decoupled spectrum consistent ($J_{\mathrm{CH_A}} \neq J_{\mathrm{CH_B}}$). Ta($\eta^5$-C$_5Me_5$)(CHPh)(CH$_2$Ph)Cl reacts readily with 1 mol of HCl at −78 °C to give Ta(η^5-C$_5$Me$_5$)(CH$_2$Ph)$_2$Cl$_2$.

A closely related derivative can be prepared by reacting Ta(η^5-C$_5$Me$_5$)(CHPh)(CH$_2$Ph)Cl with $^1/_2$ equiv of Mg(CH$_2$Ph)$_2$ (eq 4). This species must contain a plane of symmetry, but the α-carbon atoms must not lie in this plane since the benzyl α protons are diastereotopic according to the ^{1}H and ^{13}C NMR spectra.

$$\mathrm{Ta(\eta^5\text{-}C_5Me_5)(CHPh)(CH_2Ph)Cl + {}^1/_2Mg(CH_2Ph)_2 \rightarrow Ta(\eta^5\text{-}C_5Me_5)(CHPh)(CH_2Ph)_2} \quad (4)$$

The reaction between Ta(CH$_2$Ph)$_2$Cl$_3$ and TlC$_5$H$_5$ in benzene gave no Ta(η^5-C$_5$H$_5$)(CH$_2$Ph)$_2$Cl$_2$ and gave only oils whose ^{1}H NMR spectra were very broad and featureless. Since GLC analysis of the reaction mixture showed that toluene and stilbenes were formed, Ta(η^5-C$_5$H$_5$)(CH$_2$Ph)$_2$Cl$_2$ probably did form but subsequently decomposed to toluene and Ta(η^5-C$_5$H$_5$)(CHPh)Cl$_2$, which in turn decomposed to give *cis*- and *trans*-stilbene. Apparently, Ta(η^5-C$_5$H$_5$)(CH$_2$Ph)$_2$Cl$_2$ is much less stable than Ta(η^5-C$_5$Me$_5$)(CH$_2$Ph)$_2$Cl$_2$, results which are similar to those obtained in the neopentyl system.[3]

The only product of the reaction between Ta(CH$_2$Ph)$_3$Cl$_2$ and TlC$_5$H$_5$ which we could find was the known Ta(η^5-C$_5$H$_5$)$_2$(CHPh)(CH$_2$Ph).[4] On the other hand, Ta(CH$_2$Ph)$_3$Cl$_2$ did react fairly smoothly with NaC$_5$H$_5$ to give brown Ta(η^5-C$_5$H$_5$)(CH$_2$Ph)$_3$Cl (eq 5). (Black Ta(η^5-C$_5$H$_4$Me)(CH$_2$Ph)$_3$Cl could

$$\mathrm{Ta(CH_2Ph)_3Cl_2 + NaC_5H_5 \xrightarrow[\text{THF}]{-78\ ^\circ C} Ta(\eta^5\text{-}C_5H_5)(CH_2Ph)_3Cl\ (68\%)} \quad (5)$$

be prepared by using LiC$_5$H$_4$Me.) Ta(η^5-C$_5$H$_5$)(CH$_2$Ph)$_3$Cl is not very stable in the solid state, so it had to be characterized by ^{1}H and ^{13}C NMR and by its reaction with HCl. After 1 day in

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benzene, toluene was the only observed product (by ^{1}H NMR) of its rather messy decomposition. It is reasonable to expect the product of this decomposition to be $Ta(\eta^5\text{-}C_5H_5)(CHPh)(CH_2Ph)Cl$. Unlike the $\eta^5\text{-}C_5Me_5$ analogue (see above) it must be thermally unstable. It could be the intermediate in the reaction of $Ta(CH_2Ph)_3Cl_2$ with 2 equiv of TlC_5H_5 if it reacts rapidly enough with TlC_5H_5 to give $Ta(\eta^5\text{-}C_5H_5)_2(CHPh)(CH_2Ph)$.

We decided to try to force a dibenzyl complex to eliminate toluene and give a benzylidene complex analogous to $Ta(\eta^5\text{-}C_5H_5)(CHCMe_3)Cl_2$. This complex would allow us to study reactions of the benzylidene ligand with small molecules without any possible complications caused by other potentially reactive ligands.

We saw little evidence of decomposition of $Ta(\eta^5\text{-}C_5Me_4Et)(CH_2Ph)_2Cl_2$ after a sample was heated in benzene at 80 °C for 6 h. Thermolysis of the solid in vacuo at 135–150 °C gave several products on a dry-ice-cooled probe which we separated by fractional crystallization from hexane and characterized by ^{1}H NMR spectroscopy. $Ta(\eta^5\text{-}C_5Me_4Et)(CHPh)Cl_2$ was obtained in 5–7% yield after painstaking fractional recrystallization. The other organometallic products could not be separated from each other, but they were found by ^{1}H NMR spectroscopy to contain C_5Me_4Et ligands; one of these compounds is believed to be $Ta(\eta^5\text{-}C_5Me_4Et)(CH_2Ph)Cl_3$ on the basis of comparison of its ^{1}H NMR spectrum to that of an authentic sample. No 1,2-diphenylethane was noted among the thermolysis products.

Photolysis was slightly more successful. Photolysis of $Ta(\eta^5\text{-}C_5Me_4R)(CH_2Ph)_2Cl_2$ in benzene (or toluene) with a medium-pressure mercury lamp produced $Ta(\eta^5\text{-}C_5Me_4R)(CHPh)Cl_2$ (R = Me, Et) along with toluene (0.61 mol per tantalum for R = Me) and 1,2-diphenylethane (0.27 mol per tantalum for R = Me). A UV spectrum of $Ta(\eta^5\text{-}C_5Me_4Et)(CH_2Ph)_2Cl_2$ showed absorptions at 460, 340, and <260 nm, the first two being relatively weak. The photochemically active region is believed to be that at <260 nm since photolyses at 366 and 436 nm were unsuccessful and $Ta(\eta^5\text{-}C_5Me_4Et)(CH_2Ph)_2Cl_2$ decomposed more rapidly in quartz than in Vycor or (especially) Pyrex. Higher yields were obtained in smaller scale photolyses (on the order of 0.2 mmol of the starting complexes); all attempts at scaling up the photolyses gave drastically lower yields. By fractional crystallization, 16% (R = Et) of benzylidene complex could be isolated and a byproduct, $Ta(\eta^5\text{-}C_5Me_4Et)(CH_2Ph)Cl_3$, was identified in the mother liquor by ^{1}H NMR. Fractional sublimation of crude photolysis product separated $Ta(\eta^5\text{-}C_5Me_4Et)(CHPh)Cl_2$ (which sublimes at 65–85 °C at 0.01-μm pressure) from the more volatile 1,2-diphenylethane and the less volatile byproducts. $Ta(\eta^5\text{-}C_5Me_5)(CHPh)Cl_2$ was obtained in 17% yeild by fractional sublimation of a crude photolysis product.

The formulation of the $Ta(\eta^5\text{-}C_5Me_4R)(CHPh)Cl_2$ complexes (R = Me or Et) is supported by their ^{13}C and ^{1}H NMR spectra. The gated proton-decoupled ^{13}C NMR spectrum of the C_5Me_5 complex showed a characteristic low-field peak for the benzylidene C_α at δ 225 with $^1J_{CH_\alpha} = 91$ Hz. The benzylidene H_α resonance was obscured by the phenyl resonances in the ^{1}H NMR spectrum of each.

Further support for these species consists of their reactions with olefins. $Ta(\eta^5\text{-}C_5Me_4Et)(CHPh)Cl_2$ reacts readily with ethylene in C_6D_6 to give an orange solution whose ^{1}H NMR spectrum is consistent with formation of a metallocyclopentane complex, $(\eta^5\text{-}C_5Me_4Et)Cl_2\overline{TaCH_2CH_2CH_2CH_2}$,[13] and primarily 3-phenylpropene (eq 6). This is the same type of "cleavage product"

$$Ta(\eta^5\text{-}C_5Me_4Et)(CHPh)Cl_2 + \text{excess } C_2H_4 \rightarrow (\eta^5\text{-}C_5Me_4Et)Cl_2\overline{TaCH_2CH_2CH_2CH_2} + PhCH_2CH{=}CH_2 \quad (6)$$

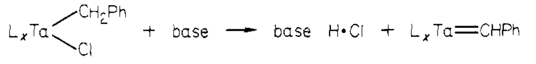
and metallacycle formed when $Ta(\eta^5\text{-}C_5H_5)(CHCMe_3)Cl_2$ reacts with ethylene.[5,13] $Ta(\eta^5\text{-}C_5Me_4Et)(CHPh)Cl_2$ reacts with excess propylene to give (by ^{1}H NMR) primarily 2-methyl-3-phenylpropene as the cleavage product, 2,3-dimethyl-1-butene catalytically,[14] and eventually $Ta(\eta^5\text{-}C_5Me_4Et)(CH_3CH{=}CH_2)Cl_2$[13] (eq 7). This cleavage product is also the same type as that formed

$$Ta(\eta^5\text{-}C_5Me_4Et)(CHPh)Cl_2 + \text{excess } CH_3CH{=}CH_2 \xrightarrow[\text{2 days}]{25\ °C} Ta(\eta^5\text{-}C_5Me_4Et)(CH_3CH{=}CH_2)Cl_2 + PhCH_2(Me)C{=}CH_2 + \underset{\text{catalytically}}{CH_2{=}C(Me)CHMe_2} \quad (7)$$

in the reaction between $Ta(\eta^5\text{-}C_5H_5)(CHCMe_3)Cl_2$ and propylene.[13] Finally, $Ta(\eta^5\text{-}C_5Me_4Et)(CHPh)Cl_2$ reacts with styrene to give (by ^{1}H NMR) $Ta(\eta^5\text{-}C_5Me_4Et)(PhCH{=}CH_2)Cl_2$,[13] 2,3-diphenylpropene (the major product), and 1,3-diphenylpropenes (minor products; eq 8). In the reaction of $Ta(\eta^5\text{-}C_5H_5)(CHCMe_3)Cl_2$ with styrene, the linear product was formed exclusively. This result (eq 8) is then the only one which differs substantially from the results of reactions of $Ta(\eta^5\text{-}C_5H_5)(CHCMe_3)Cl_2$ with olefins.

$$Ta(\eta^5\text{-}C_5Me_4Et)(CHPh)Cl_2 + PhCH{=}CH_2 \xrightarrow[\text{2 days}]{25\ °C} Ta(\eta^5\text{-}C_5Me_4Et)(PhCH{=}CH_2)Cl_2 + \underset{\text{major}}{PhCH_2(Ph)C{=}CH_2} + \underset{\text{minor}}{PhCH{=}CHCH_2Ph} \quad (8)$$

Alkylidene Complexes by Dehydrohalogenation. In seeking a more general route to benzylidene complexes, we thought that dehydrohalogenation of a benzyl halide complex would be plausible (eq 9) since we know that alkylidene complexes can be prepared by deprotonating cationic species.[4,15] This method does work (using an alkylidene phosphorane as the base) but only in special cases.



$$L_xTa(CH_2Ph)(Cl) + \text{base} \rightarrow \text{base H}{\cdot}\text{Cl} + L_xTa{=}CHPh \quad (9)$$

One example is the reaction between $Ph_3P{=}CH_2$ and $Ta(\eta^5\text{-}C_5H_4Me)(CH_2Ph)_3Cl$ in THF (eq 10). $Ta(\eta^5\text{-}C_5H_4Me)(CHPh)(CH_2Ph)_2$ is a red oil which was adequately characterized

$$Ta(\eta^5\text{-}C_5H_4Me)(CH_2Ph)_3Cl + Ph_3P{=}CH_2 \xrightarrow[\text{THF}]{25\ °C} Ta(\eta^5\text{-}C_5H_4Me)(CHPh)(CH_2Ph)_2 + Ph_3P^+MeCl^- \quad (10)$$

by comparison of its ^{1}H and ^{13}C NMR spectra with those for $Ta(\eta^5\text{-}C_5Me_5)(CHPh)(CH_2Ph)_2$ (vide supra). The characteristic features are the diastereotopic benzyl α protons in the ^{1}H NMR spectrum and the benzylidene α-carbon atom at δ 220 ($^1J_{CH_\alpha} = 89$ Hz) in the ^{13}C NMR spectrum.

The second successful dehydrohalogenation gave $Ta(\eta^5\text{-}C_5Me_4R)(CHPh)(CH_2Ph)Cl$ from $Ta(\eta^5\text{-}C_5Me_4R)(CH_2Ph)_2Cl_2$ (R = Me or Et; eq 11). This compound forms essentially quantitatively according to an ^{1}H NMR spectrum of the reaction mixture.

$$Ta(\eta^5\text{-}C_5Me_4R)(CH_2Ph)_2Cl_2 + Ph_3P{=}CH_2 \xrightarrow[-Ph_3P^+MeCl^-]{\text{toluene}} Ta(\eta^5\text{-}C_5Me_4R)(CHPh)(CH_2Ph)Cl \quad (11)$$

Far more commonly, however, dehydrohalogenation is not successful. We usually obtain mixtures of products whose NMR spectra show phenyl resonances and small doublets at τ 4–6. We believe these complexes contain phosphorus–alkylidene ligands of the type obtained when $Ta(\eta^5\text{-}C_5Me_5)(CHPh)(CH_2Ph)Cl$ is treated with $Ph_3P{=}CH_2$ (eq 12). The benzylidene C_α resonance

$$Ta(\eta^5\text{-}C_5Me_5)(CHPh)(CH_2Ph)Cl + Ph_3P{=}CH_2 \rightarrow Ta(\eta^5\text{-}C_5Me_5)(CHPh)(CHPPh_3)Cl + \text{toluene} \quad (12)$$

can be located easily at δ 207 ($^1J_{CH_\alpha} = 85$ Hz), but the C_α resonance for the $CHPPh_3$ ligand must be one of those in the region

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[13] McLain, S. J.; Wood, C. D.; Schrock, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 4558–4571.

[14] McLain, S. J.; Sancho, J.; Schrock, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 5451–5453.

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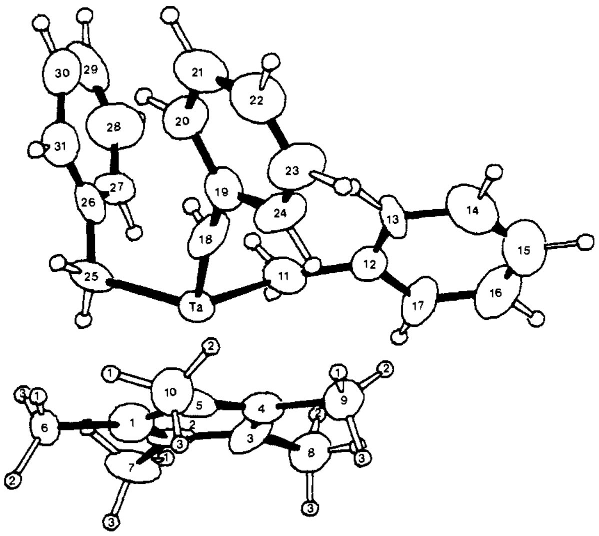

Figure 2. A computer drawing of Ta(η^5-C_5Me_5)(CHPh)(CH_2Ph)$_2$. Carbon atoms are numbered as in Table II. Hydrogen atoms are referred to by the numbers of the associated carbon atoms. Methyl hydrogen atoms are further distinguished by numbers 1–3.

δ 121–135. Therefore the ligand is probably best described as a metal-substituted phosphorus alkylidene (Ta—CH=PPh_3) rather than a phosphorus-substituted metal alkylidene (Ta=CH—P^+Ph_3) even though something between the two may be a more realistic description. The α proton in the Ta—CH=PPh_3 ligand is found at τ 5.13 in the ^1H NMR spectrum. It is strongly coupled to P ($^2J_{HP}$ = 23 Hz) and weakly coupled to the benzylidene H_α ($^4J_{HH} \approx 2$ Hz). In a general reaction of this type a CH_2 proton on the carbon between Ta and P could be removed by any base, presumably also by an additional equivalent of ylide. So far, however, we have not attempted to separate and characterize any of these products.[16]

The X-Ray Structure of Ta(η^5-C_5Me_5)(CHPh)(CH_2Ph)$_2$. The fact that these electron-deficient benzylidene complexes (like electron-deficient neopentylidene complexes[2]) all have low $^1J_{CH_\alpha}$ values prompted us to determine the structure of a representative example (see Experimental Section for details). The structure is shown in Figure 2 and the molecular packing in Figure 3. Table II lists the bond distances and selected interbond angles and Table III the atomic coordinates.

The molecule has a regular "three-legged piano stool" structure. The "top" is a η^5-C_5Me_5 ligand in which each methyl carbon is bent away from the metal by about 5°. This is the normal structure for η^5-C_5Me_5 ligands.[18] The bond distances and interbond angles in the η^5-C_5Me_5 group also are all normal. There are a number of short distances between hydrogen atoms in the cyclopentadienyl ring and atoms in the benzyl or benzylidene groups, the shortest ones being H(9,1)–H(24) = 1.99 Å, H(7,2)–H(25) = 2.16 Å, and H(8,1)–H(17) = 2.31 Å.

The three "legs" are symmetrically placed; the three C_α–Ta–C_α angles all lie in the range 102–105°, and the plane through the three α-carbon atoms is almost parallel to the plane of the η^5-C_5Me_5 ligand (dihedral angle = 2.3°). The space between them is nearly filled by an η^5-C_5Me_5 ring from a second molecule which is translated from the first by the short unit cell axis *b* (Figure 3). This fairly tight molecular packing may help determine the Ta–C_α–C_β angles of the benzyl ligands (see below) and probably also the orientation of the three phenyl rings. The latter is illustrated by the fact that the dihedral angles between the phenyl rings and the η^5-C_5Me_5 plane vary from 89° for C(26)–C(31) to 55° for C(19)–C(24) to 22° for C(12)–C(17). The last appears to be "sandwiched" between the η^5-C_5Me_5 ligand on the same metal to which that benzyl ligand is bound and the encroaching η^5-C_5Me_5 ring in a second molecule.

The Ta–C(11)–C(12) angle in one of the two benzyl ligands is 125.1 (8)°. This somewhat larger than tetrahedral angle may be due to the fact that a η^5-C_5Me_5 ring in another molecule lies nearby, roughly parallel to the phenyl ring of this benzyl ligand. The other benzyl ligand is more "normal", possibly since this phenyl ring can turn away from the η^5-C_5Me_5 ring on the same metal to which it is bound; the Ta–C(25)–C(26) angle therefore can be smaller (114.7 (8)°). Whether the Ta–C(25)–C(26) angle

Table II. Bond Distances and Selected Interbond Angles

atoms	dist/Å	atoms	angle/deg
a. Tantalum Coordination			
Ta–C(1)	2.480 (19)	C(1)–Ta–C(2)	33.4 (6)
Ta–C(2)	2.442 (17)	C(2)–Ta–C(3)	33.1 (6)
Ta–C(3)	2.470 (19)	C(3)–Ta–C(4)	34.4 (5)
Ta–C(4)	2.397 (17)	C(4)–Ta–C(5)	33.9 (6)
Ta–C(5)	2.401 (17)	C(5)–Ta–C(1)	34.5 (6)
Ta–C(11)	2.188 (15)	C(11)–Ta–C(18)	102.8 (6)
Ta–C(18)	1.883 (14)	C(18)–Ta–C(25)	105.2 (6)
Ta–C(25)	2.233 (14)	C(25)–Ta–C(11)	101.8 (5)
b. Pentamethylcyclopentadienyl Ring			
C(1)–C(2)	1.413 (24)	C(5)–C(1)–C(2)	106.4 (17)
C(2)–C(3)	1.401 (25)	C(1)–C(2)–C(3)	109.9 (17)
C(3)–C(4)	1.439 (22)	C(2)–C(3)–C(4)	106.9 (17)
C(4)–C(5)	1.398 (24)	C(3)–C(4)–C(5)	108.4 (16)
C(5)–C(1)	1.448 (25)	C(4)–C(5)–C(1)	108.1 (15)
C(1)–C(6)	1.493 (24)	C(5)–C(1)–C(6)	126.1 (17)
C(2)–C(7)	1.501 (23)	C(2)–C(1)–C(6)	127.5 (18)
C(3)–C(8)	1.477 (24)	C(1)–C(2)–C(7)	122.9 (19)
C(4)–C(9)	1.511 (23)	C(3)–C(2)–C(7)	126.4 (18)
C(5)–C(10)	1.518 (23)	C(2)–C(3)–C(8)	126.4 (18)
		C(4)–C(3)–C(8)	126.6 (19)
		C(3)–C(4)–C(9)	122.8 (17)
		C(5)–C(4)–C(9)	128.4 (16)
		C(4)–C(5)–C(10)	127.0 (18)
		C(1)–C(5)–C(10)	123.5 (18)
c. Benzyl and Benzylidene Groups			
C(11)–C(12)	1.548 (15)	Ta–C(11)–C(12)	126.1 (8)
C(12)–C(13)	1.409 (23)	C(11)–C(12)–C(13)	118.2 (5)
C(13)–C(14)	1.381 (26)	C(11)–C(12)–C(17)	119.0 (5)
C(14)–C(15)	1.391 (30)	C(17)–C(12)–C(13)	122.8 (18)
C(15)–C(16)	1.357 (30)	C(12)–C(13)–C(14)	114.6 (18)
C(16)–C(17)	1.405 (27)	C(13)–C(14)–C(15)	124.2 (21)
C(17)–C(12)	1.376 (23)	C(14)–C(15)–C(16)	119.2 (22)
		C(15)–C(16)–C(17)	119.5 (22)
		C(16)–C(17)–C(12)	119.5 (20)
C(18)–C(19)	1.494 (14)	Ta–C(18)–C(19)	166.0 (10)
C(19)–C(20)	1.424 (25)	C(18)–C(19)–C(20)	119.8 (5)
C(20)–C(21)	1.395 (23)	C(18)–C(19)–C(24)	122.9 (5)
C(21)–C(22)	1.401 (27)	C(24)–C(19)–C(20)	117.3 (17)
C(22)–C(23)	1.337 (27)	C(19)–C(20)–C(21)	121.1 (18)
C(23)–C(24)	1.404 (26)	C(20)–C(21)–C(22)	119.4 (20)
C(24)–C(19)	1.384 (24)	C(21)–C(22)–C(23)	119.7 (19)
		C(22)–C(23)–C(24)	122.1 (20)
		C(23)–C(24)–C(19)	120.5 (19)
C(25)–C(26)	1.464 (13)	Ta–C(25)–C(26)	114.7 (8)
C(26)–C(27)	1.417 (26)	C(25)–C(26)–C(27)	124.3 (6)
C(27)–C(28)	1.285 (29)	C(25)–C(26)–C(31)	120.7 (6)
C(28)–C(29)	1.358 (35)	C(31)–C(26)–C(27)	114.9 (19)
C(29)–C(30)	1.328 (32)	C(26)–C(27)–C(28)	125.5 (24)
C(30)–C(31)	1.448 (32)	C(27)–C(28)–C(29)	120.1 (28)
C(31)–C(26)	1.380 (27)	C(28)–C(29)–C(30)	120.1 (26)
		C(29)–C(30)–C(31)	120.8 (26)
		C(30)–C(31)–C(26)	118.5 (23)

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(16) We have shown that this type of reaction can occur cleanly in some Zr complexes. For example, $ZrCp_2(CH_2CMe_3)Cl$ reacts with 2 equiv of Me_3P=CH_2 to give yellow, sublimable $ZrCp_2(CH_2CMe_3)(CH$=$PMe_3)$. An analogous reaction of $ZrCp_2MeCl$ with Me_3P=CH_2 gives $ZrCp_2Me(CH$=$PMe_3)$. The α-carbon resonances are found at 114 ($^1J_{CH}$ = 116, $^1J_{CP}$ = 28) and 107 ppm, respectively, and the H_α resonances at τ 5.19 ($^2J_{HP}$ = 13) and τ 4.23 ($^2J_{HP}$ = 11), respectively. W. C. Kaska[17] has also been studying reactions of this sort for Zr and has done the X-ray structure of one of the products.

(17) Kaska, W. C., private communication.

(18) See, for example: (a) Churchill, M. R.; Youngs, W. C. *Inorg. Chem.* **1979**, *18*, 171–176. (b) Sanner, R. D.; Duggan, D. M.; McKenzie, T. C.; Marsh, R. E.; Bercaw, J. E. *J. Am. Chem. Soc.* **1976**, *98*, 8358–8365. (c) Freyberg, D. P.; Robbins, J. L.; Raymond, K. N.; Smart, J. C. *Ibid.* **1979**, *101*, 892–897.

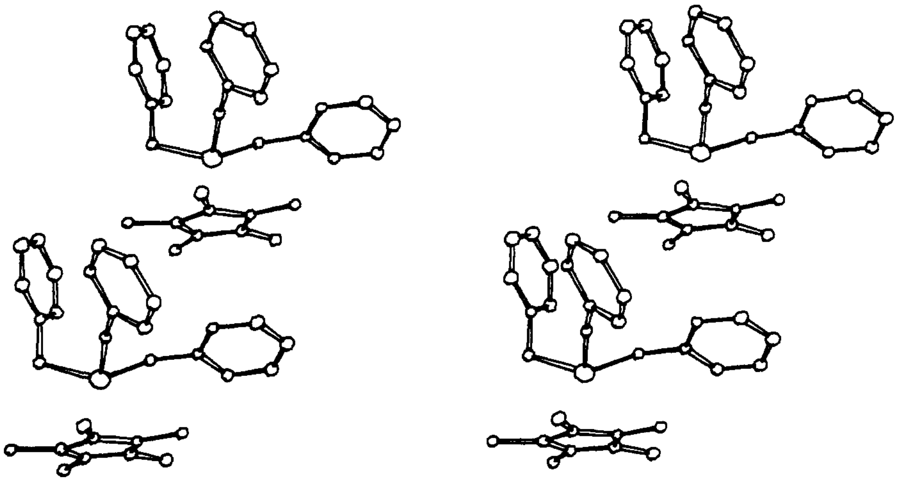

Figure 3. Stereopair showing snug fit between molecules. The orientation is the same as in Figure 2. The Cp ring of one molecule is situated between the three "Phenyl-legs" of the molecule translated by *b*.

Table III

a. Atomic Coordinates (×10^4) and Thermal Parameters (×10^3) for Nonhydrogen Atoms

atom	*x*	*y*	*z*	*U*(11)	*U*(22)	*U*(33)	*U*(23)	*U*(13)	*U*(12)
Ta	2470.2 (5)	4039.6 (9)	6065.7 (3)	40.8 (4)	31.1 (5)	44.1 (5)	−0.7 (5)	11.1 (3)	1.4 (4)
C(1)	2726 (13)	950 (22)	6135 (6)	62 (13)	42 (11)	52 (12)	2 (11)	−1 (11)	38 (11)
C(2)	1866 (12)	1274 (19)	5720 (7)	60 (12)	22 (11)	56 (12)	−20 (10)	16 (11)	16 (19)
C(3)	2199 (13)	2092 (25)	5292 (7)	51 (13)	87 (15)	41 (13)	−18 (12)	7 (10)	1 (11)
C(4)	3291 (11)	2431 (20)	5460 (7)	31 (10)	31 (10)	61 (13)	−9 (10)	14 (9)	2 (18)
C(5)	3615 (12)	1743 (20)	5972 (8)	38 (11)	26 (19)	82 (16)	−9 (10)	−7 (11)	10 (9)
C(6)	2728 (14)	22 (21)	6648 (6)	102 (14)	27 (10)	45 (12)	8 (10)	35 (11)	16 (10)
C(7)	806 (12)	552 (21)	5718 (8)	46 (11)	42 (12)	108 (16)	−21 (11)	9 (11)	−21 (9)
C(8)	1560 (13)	2462 (24)	4760 (7)	78 (13)	58 (13)	43 (13)	2 (11)	2 (10)	7 (11)
C(9)	3945 (12)	3222 (22)	5094 (7)	50 (11)	53 (12)	58 (12)	0 (10)	24 (9)	2 (9)
C(10)	4726 (13)	1488 (23)	6264 (7)	68 (13)	68 (15)	58 (13)	10 (11)	14 (11)	0 (11)
C(11)	1598 (14)	5844 (26)	5503 (8)	64 (10)	33 (10)	63 (11)	15 (10)	16 (8)	3 (9)
C(12)	2017 (14)	6822 (21)	5059 (7)	64 (12)	33 (10)	47 (14)	6 (10)	28 (11)	24 (10)
C(13)	2954 (13)	7722 (21)	5205 (7)	57 (12)	40 (11)	56 (13)	24 (10)	20 (10)	−7 (10)
C(14)	3277 (15)	8551 (24)	4786 (11)	56 (13)	61 (15)	124 (21)	12 (15)	35 (15)	9 (10)
C(15)	2764 (20)	8478 (29)	4253 (11)	87 (18)	89 (19)	100 (21)	27 (16)	52 (16)	30 (15)
C(16)	1854 (17)	7623 (30)	4131 (8)	78 (16)	99 (18)	61 (15)	7 (15)	23 (13)	47 (14)
C(17)	1480 (14)	6742 (24)	4538 (7)	77 (13)	74 (14)	34 (12)	14 (11)	11 (11)	35 (11)
C(18)	3642 (10)	5290 (20)	6389 (5)	47 (9)	75 (13)	27 (9)	1 (9)	5 (7)	14 (9)
C(19)	4706 (13)	6005 (23)	6566 (7)	45 (11)	56 (12)	48 (12)	17 (12)	−6 (10)	−10 (10)
C(20)	4934 (12)	6959 (23)	7050 (7)	46 (12)	69 (13)	52 (13)	−5 (11)	2 (9)	−6 (10)
C(21)	5916 (14)	7664 (23)	7221 (8)	58 (13)	56 (13)	83 (16)	−5 (12)	1 (12)	−11 (11)
C(22)	6687 (15)	7429 (27)	6911 (9)	61 (14)	81 (17)	87 (17)	−4 (15)	0 (13)	−30 (12)
C(23)	6468 (15)	6566 (27)	6451 (9)	56 (13)	104 (18)	85 (17)	−33 (14)	27 (12)	−30 (12)
C(24)	5490 (15)	5832 (27)	6271 (8)	86 (15)	87 (16)	73 (14)	−35 (14)	40 (13)	−35 (14)
C(25)	1477 (11)	3848 (17)	6692 (8)	76 (10)	17 (9)	85 (12)	−3 (11)	50 (9)	12 (8)
C(26)	1160 (14)	5466 (22)	6887 (8)	56 (12)	48 (14)	59 (14)	17 (11)	34 (11)	−11 (11)
C(27)	231 (16)	6322 (24)	6664 (8)	90 (17)	36 (13)	73 (14)	−11 (12)	41 (13)	−8 (11)
C(28)	−68 (20)	7734 (36)	6831 (12)	112 (20)	75 (22)	138 (27)	−18 (18)	64 (19)	4 (17)
C(29)	500 (28)	8493 (28)	7269 (14)	198 (34)	25 (15)	153 (31)	17 (17)	144 (28)	28 (19)
C(30)	1387 (24)	7810 (36)	7515 (10)	169 (28)	79 (22)	72 (18)	−4 (17)	67 (19)	−20 (19)
C(31)	1745 (17)	6225 (29)	7333 (9)	106 (17)	70 (17)	67 (16)	1 (14)	43 (14)	−25 (15)

b. Atomic Coordinates for Hydrogen Atoms

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
H(61)	3379	589	6912	H(13)	3386	7768	5612
H(62)	2936	−1229	6540	H(14)	3977	9297	4874
H(63)	2072	−47	6851	H(15)	3077	9105	3940
H(71)	196	1445	5574	H(16)	1418	7606	3725
H(72)	864	380	6146	H(17)	776	6007	4443
H(73)	627	−638	5515	H(20)	4337	7152	7287
H(81)	1923	3414	4552	H(21)	6077	8384	7589
H(82)	755	2786	4747	H(22)	7454	7947	7044
H(83)	1607	1259	4567	H(23)	7063	6420	6210
H(91)	4706	3636	5290	H(24)	5344	5138	5897
H(92)	3587	4188	4821	H(27)	−268	5725	6329
H(93)	4018	2081	4871	H(28)	−769	8324	6620
H(101)	4738	1963	6665	H(29)	226	9646	7421
H(102)	5156	2328	6051	H(30)	1848	8458	7852
H(103)	5077	253	6288	H(31)	2446	5639	7544

is small also in part due to long-range interaction of the phenyl ring with the electron-deficient metal[11b] is something we cannot say for certain. Interestingly, although the two Ta–C_α(benzyl) bond lengths (2.188 (15) and 2.233 (14) Å) are in the range of normal Ta^{5+}–C(alkyl) bond lengths,[19] the shorter of the two (Ta–C(11)) is found in the ligand with the larger Ta–C_α–C_β angle.

Two important features of the benzylidene ligand are the short Ta=C bond length (1.883 (14) Å) and the large Ta—C(18)—C(19) bond angle (166.0°). These values are in fact closer to those observed for the benzylidyne ligand in $Ta(\eta^5\text{-}C_5Me_5)(CPh)(PMe_3)_2Cl$[18a] (Ta≡$C_\alpha$ = 1.849 (8) Å, Ta—C_α—C_β = 171.8 (6)°) than the benzylidene ligand in 18-electron $Ta(\eta^5\text{-}C_5H_5)_2(CHPh)(CH_2Ph)$[4] (Ta=$C_\alpha$ = 2.07 (1) Å, Ta=C_α—C_β = 135.2 (7)°). The two other important facts are that the Ta—C(18)—C(19) plane forms a large dihedral angle (78°) with the $\eta^5\text{-}C_5$ plane and that the phenyl ring points *toward* the $\eta^5\text{-}C_5Me_5$ ring, thereby placing H_α in the "hole" created by C(11), C(18), and C(25). A fifth pertinent fact is that the phenyl ring is not far from lying in the Ta—C(18)—C(19) plane (smallest dihedral angle = 24°), thereby placing H(24) 1.99 Å from H(9,1).

Discussion

There is no reason to suggest that the mechanism of forming monocyclopentadienyl benzylidene complexes is any different than that for forming the corresponding neopentylidene complexes.[3] It was found in that case that substituting the $\eta^5\text{-}C_5H_5$ ring with an $\eta^5\text{-}C_5Me_5$ ring slowed the rate of elimination of neopentane from $Ta(\eta^5\text{-}C_5R_5)(CH_2CMe_3)_2X_2$ drastically. The suggested reason was that a cis configuration was necessary to generate the neopentylidene ligand by α-hydrogen atom abstraction but the larger $\eta^5\text{-}C_5Me_5$ ring "locked" the two neopentyl groups relatively trans. In hypothetical $Ta(\eta^5\text{-}C_5Me_5)(CH_2Ph)_3Cl$, however, one benzyl ligand is always cis to another, and since the molecule is apparently crowded enough for facile α abstraction,[2] $Ta(\eta^5\text{-}C_5Me_5)(CHPh)(CH_2Ph)Cl$ is formed.

There is an important practical difference between the benzyl and the neopentyl systems. Benzyl and benzylidene ligands are smaller than neopentyl and neopentylidene ligands so that the situations which are conductive to α abstraction and which give benzylidene complexes which are stable toward what we believe to be the major mode of decomposition, a bimolecular decomposition[2] to give stilbenes, are fewer. For example, $Ta(\eta^5\text{-}C_5H_5)(CH_2Ph)_3Cl$ decomposes readily, but the likely product $Ta(\eta^5\text{-}C_5H_5)(CHPh)(CH_2Ph)Cl$ could not be isolated. $Ta(\eta^5\text{-}C_5Me_5)(CHPh)(CH_2Ph)Cl$ could be, however. In contrast, both $Ta(\eta^5\text{-}C_5H_5)(CHCMe_3)(CH_2CMe_3)Cl$ and $Ta(\eta^5\text{-}C_5Me_5)(CHCMe_3)(CH_2CMe_3)Cl$ form easily and are stable toward bimolecular decomposition.[3]

The reason why $Ta(\eta^5\text{-}C_5Me_4Et)(CHPh)Cl_2$ reacts with propylene and styrene to give largely the branched product of rearrangement of an intermediate tantallacyclobutane complex while $Ta(\eta^5\text{-}C_5H_5)(CHCMe_3)Cl_2$ reacted with styrene to give solely the linear product could be ascribed to the more crowded circumstances favoring formation of the β-substituted tantallacyclobutane complex. However, more detailed experiments are necessary with these and other compounds (such as $Ta(\eta^5\text{-}C_5Me_5)(CHCMe_3)Cl_2$) before we can draw any firm conclusions.

Now let's go back to a discussion of how and why the "benzylidene" ligand bonds to Ta the way it does. We should first note that short Ta=C bond lengths and large Ta=C_α—C_β angles have been found recently for neopentylidene ligands in several tantalum complexes.[20] The hypothesis is that the electron-deficient metal attracts electron density from the CH_α bond and thereby opens up the Ta=C_α—C_β angle and shortens the Ta=C_α bond.[2,20a] This process may be assisted in a synergistic manner by steric crowding between the *tert*-butyl group and some other part of the molecule. One important question then was whether an alkylidene ligand with a smaller substituent would be distorted similarly. If so, a steric effect in general would seem to be a relatively unimportant factor in producing such a distortion. We contend that is the case in $Ta(\eta^5\text{-}C_5Me_5)(CHPh)(CH_2Ph)_2$. Some interactions (e.g., H(24)···H(1,9)) encourage or reinforce this distortion, but these should not be significant enough to produce it. The phenyl ring appears to have enough room to alleviate any steric interactions by twisting about the C(18)–C(19) bond. That it does not could be ascribed to a preferred orientation approximately coplanar with the Ta—C(18)—C(19) plane which would allow some conjugation of the phenyl ring's π system with the Ta=C(18) double bond.

It is not surprising for two reasons that the benzylidene ligand plane is oriented roughly perpendicular to the $\eta^5\text{-}C_5Me_5$ plane. First, an X-ray structural study of $Ta(\eta^5\text{-}C_5Me_5)(C_2H_4)Cl_2$ shows that the C=C axis lies roughly parallel to the $\eta^5\text{-}C_5Me_5$ ring;[21] an alkylidene ligand therefore should orient perpendicular to the ring in order to utilize the same π-type metal orbital. Second, several X-ray structural studies of monocyclopentadienyl complexes containing a carbene-type ligand show it to be oriented essentially perpendicular to the cyclopentadienyl ring.[22] Perhaps a more surprising feature is that the phenyl substituent points toward the $\eta^5\text{-}C_5Me_5$ ring rather than away from it. (The latter would appear to be more likely for steric reasons.) As in the case of $Ta(\eta^5\text{-}C_5H_5)(CHCMe_3)Cl_2$,[3,20c] we believe this orientation allows maximum donation of electron density from the C–H_α bond to the metal. In $[Fe(\eta^5\text{-}C_5H_5)(CO)_2(CHPh)]^+$[23] the authors postulated that the phenyl ring pointed away from the $\eta^5\text{-}C_5H_5$ ring while in $[Re(\eta^5\text{-}C_5H_5)(NO)(PPh_3)(CHPh)]^+$[24] the two isomers were postulated to be that in which the phenyl ring pointed toward the ring and that in which it pointed away. (In the latter case the authors postulated that the benzylidene ligand plane was tipped so that it more nearly contained the Re–NO axis.) X-ray structural studies for the Fe and Re compounds should help establish whether the preferred orientation for an alkylidene ligand bound to Fe or Re does indeed differ from that for an alkylidene ligand bound to Ta.

Experimental Section

All experiments were conducted under nitrogen by using standard procedures for air- and moisture-sensitive compounds.[3] Solvents were purified by standard methods and checked periodically for protic impurities by titration with a lithium reagent.[25a] ^{13}C NMR spectra were done at 67.89 MHz in the ^1H-decoupled and ^1H-gated-decoupled mode at probe temperature (ca. 30 °C) unless otherwise noted. Preparations for benzylzinc and -magnesium reagents can be found elsewhere.[9] ^1H NMR spectra were taken at 60 or 90 MHz unless otherwise noted. LiC_5Me_5 was prepared by Bercaw's method[25b] while the LiC_5Me_4Et had been prepared by Whitesides' method.[25c] Compounds were analyzed by A.P. Bernhardt or Schwartzkopf by using drybox techniques. Samples were routinely burned with V_2O_5.

Crystal Preparation and Data Collection. Dark red, air-sensitive needles of $Ta(\eta^5\text{-}C_5Me_5)(CHPh)(CH_2Ph)_2$ were grown by slowly cooling a hot toluene solution to room temperature; the room-temperature solution is supersaturated and must not be disturbed. The air-sensitive crystals were transferred in a Vacuum Atmosphere drybox (H_2O and O_2 < 1 ppm) into thin-glass capillaries by using a glass rod and a small amount of beeswax. The capillaries were closed with beeswax and sealed by melting. The crystal chosen for the investigation measured 0.43 × 0.18 × 0.10 mm and exhibited the faces (100), (010), (001) and (−1,0,2).

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The needle axis coincided with [010]. Systematic absences, diffraction symmetry, and approximate cell dimensions were determined from zero-layer precession and zero- and first-layer Weissenberg photographs. The cell dimensions were refined by least squares to fit data from eight reflections automatically centered on a Picker FACS four-circle diffractometer equipped with a graphite monochromator for Mo Kα radiation: $a = 13.093$ (5) Å, $b = 7.946$ (4) Å, $c = 25.299$ (13) Å, $\beta = 100.64$ (4)°, space group $P2_1/c$, $Z = 4$, $V = 2587$ Å^3.

X-ray intensity data were collected in the ω–2θ scan mode with a scanning speed of 2°/min and a scanning interval of 2 ± (0.7 + 0.346 *tan θ). The background intensity was measured for 10 s at each end of the scanning interval. Three reflections 040, 517, and −1,0,12 were measured as standards after every 50 reflections. A total of 2884 reflections with $2.5° < 2\theta < 40°$ were collected ($k \geq 0$, $l \leq 0$) of which 501 with negative or zero intensities were rejected. Corrections for absorption factors were applied with $\mu = 40.62$ cm^{-1}. Extreme transmission factors were 0.73 and 0.55. After a few equivalent reflections were averaged, the data set contained 2190 unique reflections.

Calculations. All calculations were performed on the MRL DEC 2040 computer, using a local program for intensity calculations and the program SHELX[26] for absorption correction, structure solution, refinement, and calculations of bond distances and interbond angles. ORTEP II was used for structure plots.

Structure Solution. The tantalum atom was found in an E map. The remaining nonhydrogen atoms were found in successive difference syntheses. Initially, 74 parameters were refined with isotropic temperature factors for all but the tantalum atom and with three rigid phenyl rings and one rigid pentamethylcyclopentadienyl [$R = 0.079$ and $R_w = 0.069$ (1)]. The constraints were then removed and the temperature factors converted to anisotropic form for all the atoms. [$R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = \sum w^{1/2}||F_o| - |F_c||/\sum w^{1/2}|F_o|$.] The overall scale factor and the 288 positional and thermal parameters were refined to $R = 0.071$ and $R_w = 0.065$. The methyl and phenyl hydrogen atoms were then inserted at the expected positions. Continued refinement with rigid methyl groups and constant phenyl carbon–hydrogen distances converged at $R = 0.067$ and $R_w = 0.061$. The strongest peak in the resulting difference synthesis is situated close to a reasonable position for the hydrogen atom on C(18). The distance to C(18) is 1.64 Å and to Ta 2.25 Å. Two hydrogen atoms on C(11) and two on C(25) were also found.

Preparation of $Ta(CH_2Ph)_2Cl_3$. $TaCl_5$ (11.28 g, 31.5 mmol, 5% excess) was suspended in a mixture of toluene (125 mL) and ether (10 mL) at −10 °C. $Zn(CH_2Ph)_2$ (7.45 g, 30 mmol) in toluene (30 mL) was added dropwise over 1.5 h. The mixture was warmed to 25 °C, and the solvent was removed in vacuo. The resulting solid was extracted with benzene (3 × 20 mL) and filtered (3.10 g of white $ZnCl_2$; theory = 4.09 g). The filtrate was concentrated in vacuo to ca. 40 mL, and ca. 80 mL of pentane was added. After 10 min, red crystals were filtered off, washed with pentane (2 × 5 mL), and dried in vacuo. The first crop equals 5.60 g. After 0.5 h at −20 °C a second crop of 4.84 g was filtered off, washed, and dried. The filtrate was concentrated in vacuo to ca. 20-mL volume, and 80 mL of pentane was added. After the solution was filtered and stood overnight at −20 °C, a third crop of 1.18 g was isolated (total = 11.62 g, 82% of theory). Analytically pure samples may be obtained by recrystallization from benzene/pentane mixtures.

Anal. Calcd for $TaC_{14}H_{14}Cl_3$: C, 35.81; H, 3.01; Cl, 22.65. Found: C, 35.30; H, 3.07; Cl, 21.92. ^{1}H NMR (C_6D_6): τ 6.77 (s, 2, CH_2), 3.03–2.75 (m, 5, Ph). ^{13}C NMR ($CDCl_3$, 15 MHz): δ 92.3 (t, $^1J_{CH}$ = 139 Hz, C_α), 126.1(s, C_β), 128.7, 129.1, 138.9 (d, $^1J_{CH}$ = 162–163 Hz, Ph C_o, C_m, C_p). Mol wt (cryoscopic in cyclohexane): calcd 470; found, 423. Hydrolysis of 0.469 g (1.00 mmol) of $Ta(CH_2Ph)_2Cl_3$ with excess gaseous HCl (later neutralized with NH_3) in C_6H_6 containing 0.101 g (1.01 mmol) of C_7H_{16} (internal standard) gave 1.80 mmol of toluene by GLC.

Preparation of $Ta(CH_2Ph)Cl_4$. Gaseous HCl (9.60 mmol, 235 mL at 25 °C) was added in 50-mL aliquots via syringe over 2 h to a stirred, cooled solution (−78 °C) of $Ta(CH_2Ph)_2Cl_3$ (4.69 g, 10 mmol) in toluene (125 mL). Brown, insoluble $Ta(CH_2Ph)Cl_4$ formed slowly during the course of addition. The mixture was stirred at −78 °C for 1 h and then warmed to room temperature. The product was isolated by filtration, washed with benzene (5 mL) and then pentane (15 mL), and dried in vacuo. The product weight equals 3.94 g (95% yield). Analytically pure samples can be obtained by sublimation at 100 °C (<1 μm Hg pressure).

Anal. Calcd for $TaC_7H_7Cl_4$: C, 20.31; H, 1.71; Cl, 34.26. Found: C, 20.48; H, 1.80; Cl, 33.99. ^{1}H NMR (CD_3CN): τ 2.5–2.9 (m, Ph), 6.00 (s, CH_2). Hydrolysis of 0.358 g (0.865 mmol) of $Ta(CH_2Ph)Cl_4$ with excess gaseous HCl in C_6H_6 containing 0.87 g (0.86 mmol) of C_7H_{16} (internal standard) gave 1.00 mmol of toluene by GLC (1.16 mol of toluene/mol of tantalum).

Preparation of $Ta(CH_2Ph)_4Cl$. $Ta(CH_2Ph)_5$ (9.37 g, 14.7 mmol) in toluene (250 mL) at −78 °C was stirred and treated with gaseous HCl (14.7 mmol, 356 mL at 25 °C injected in 50-mL aliquots via syringe). The stirred reaction mixture was slowly warmed to 0 °C over 1 h, and the solvent was removed in vacuo. Benzene (ca. 30 mL) and pentane (ca. 90 mL) were added, the resulting deep red solution was filtered, and the filtrate was cooled to −30 °C for ca. 20 h. Deep red crystals of $Ta(CH_2Ph)_4Cl$ (5.80 g) were isolated by filtration, washed with pentane, and dried in vacuo. Removal of solvent from the filtrate in vacuo and recrystallization from benzene/pentane gave 1.12 g of additional product (total = 6.92 g, 81% yield). An ethereal solution of dry HCl can be substituted for gaseous HCl in the above cleavage reaction. The product recrystallizes best from benzene/pentane mixtures.

Anal. Calcd for $TaC_{28}H_{28}Cl$: Cl, 6.10. Found: Cl, 5.91. ^{1}H NMR (C_6D_6): τ 2.67–3.10 (m, 5, Ph), 7.00 (s, 2, CH_2). ^{1}H NMR ($C_6D_5CD_3$, 270 MHz, −80 °C): τ 8.35 (s, 2, CH_2 (axial)), 6.75 (s, 6, CH_2 (equatorial)), 2.86–3.48 (m, 20, Ph). T_c = −25 °C. $\Delta G^‡$ was obtained from coalescing singlets of unequal area.[27] ^{13}C NMR ($CDCl_3$, −55 °C): δ 98.8 (t, $^1J_{CH}$ = 131 Hz, C_α(equatorial)), 117.7 (t, $^1J_{CH}$ = 117 Hz, C_α(axial)), Ph region complex (two types of Ph groups), 138.1 (s, C_β(axial)), 146.7 (s, C_β(equatorial)). Coalescence temperature for methylene carbons equals −12 °C. Hydrolysis of 0.228 g (0.393 mmol) of $Ta(CH_2Ph)_4Cl$ with excess gaseous HCl in C_6H_6 containing 0.166 g (1.66 mmol) of C_7H_{16} (internal standard) gave 1.45 mmol of toluene by GLC (3.68 mmol of toluene/mol of tantalum).

Preparation of $Ta(\eta^5\text{-}C_5Me_5)(CH_2Ph)Cl_3$. $Ta(CH_2Ph)Cl_4$ (1.24 g, 3.00 mmol) dissolved in ether (100 mL) at −15 °C was stirred with LiC_5Me_5 (0.43 g, 3.0 mmol) for 30 min while the mixture was warmed to 25 °C. Ether was removed in vacuo and toluene (100 mL) used to extract the product from insoluble LiCl and unreacted $Ta(CH_2Ph)Cl_4$ (total insolubles = 0.30 g; theory for LiCl = 0.13 g). Cooling the filtrate to −20 °C gave 0.28 g of bronze crystals. Removing toluene from the filtrate in vacuo gave 0.39 g of additional product (total = 0.67 g, 43% yield).

Anal. Calcd for $TaC_{17}H_{22}Cl_3$: C, 39.75; H, 4.33; Cl, 20.70. Found: C, 39.72; H, 4.53; Cl, 20.48. ^{1}H NMR (C_6D_6): τ 8.01 (s, 15, C_5Me_5), 7.57 (s, 2, CH_2), 2.30–2.75 (m, 5, Ph).

Preparation of $Ta(\eta^5\text{-}C_5Me_5)(CH_2Ph)_2Cl_2$. $Ta(CH_2Ph)_2Cl_3$ (4.69 g, 10.0 mmol) was dissolved in ether (90 mL) and the solution cooled to −15 °C. LiC_5Me_5 (1.80 g, 12.5 mmol, 27% excess) was then added and the mixture stirred 90 min at room temperature. Solvent was removed in vacuo, the residue taken up in toluene, and the solution filtered to remove LiCl. Removal of toluene in vacuo left 4.95 g (87% yield) of black, crystalline product.

Anal. Calcd for $TaC_{24}H_{29}Cl_2$: C, 50.62; H, 5.14. Found: C, 48.40, 52.12; H, 4.92, 5.66. ^{1}H NMR (C_6D_6): τ 8.15 (s, 15, C_5Me_5), 7.78 (s, 4, CH_2), 2.67–3.34 (m, 10, Ph). ^{13}C NMR ($CDCl_3$, 15 MHz): δ 12.8 (q, $^1J_{CH}$ = 129 Hz, Me), 97.3 (t, $^1J_{CH}$ = 123 Hz, C_α), 123.5 (d, $^1J_{CH}$ = 158 Hz, C_p), 124.8 (s, C_5Me_5), 126.4 (dd, $^1J_{CH}$ = 157 Hz, $^2J_{CH}$ = 6 Hz, C_o), 130.5 (doublet of m, $^1J_{CH}$ = 160 Hz, C_m), 145.1 (s, C_β).

Preparation of $Ta(\eta^5\text{-}C_5Me_4Et)(CH_2Ph)_2Cl_2$. $Ta(CH_2Ph)_2Cl_3$ (1.70 g, 3.62 mmol) in ether (50 mL) was stirred with LiC_5Me_4Et (0.57 g, 3.7 mmol) for 15 min. White solid (0.12 g; theory for LiCl = 0.15 g) was filtered from the black reaction mixture (deep red to transmitted light), and the filtrate was cooled to −30 °C. Black crystals were later obtained by filtration, washed with ether, and dried in vacuo (first crop = 1.27 g, second crop = 0.33 g, third crop = 0.15 g; total = 1.75 g, 83% yield).

^{1}H NMR (C_6D_6): τ 9.26 (t, 3, $^3J_{HH}$ = 8 Hz, CH_2CH_3), 8.05 and 8.14 (s, 12, $C_5Me_2Me'_2$Et), 7.78 (s, 4, CH_2Ph), 7.73 (q, 2, $^3J_{HH}$ = 8 Hz, CH_2CH_3), 2.6–3.3 (m, 10, Ph). UV (hexane): 460, 340, <260 nm.

Preparation of $Ta(\eta^5\text{-}C_5H_5)(CH_2Ph)_3Cl$. A stirred solution of $Ta(CH_2Ph)_3Cl_2$ (5.00 g, 9.52 mmol) in tetrahydrofuran (50 mL) at −78 °C was treated dropwise over 30 min with a solution of NaC_5H_5 (0.96 g, 10.9 mmol, 15% excess) in tetrahydrofuran (5 mL). The mixture was stirred while being allowed to warm to room temperature. After 15 min, all volatiles were exhaustively removed in vacuo and the resulting solid was extracted with CH_2Cl_2 (50 mL) and filtered (0.76 g of insolubles; theory for NaCl and unreacted NaCp = 0.68 g). Pentane (75 mL) was added slowly to the filtrate and the solution cooled to −30 °C. A first crop (3.23 g) was isolated by filtration; the second crop equals 0.38 g (68% yield). The product should be stored at <0 °C.

Anal. Calcd for $TaC_{26}H_{26}Cl$: Cl, 6.39. Found: Cl, 6.21. ^{1}H NMR (C_6D_6): τ 7.15 (s, 6, CH_2), 4.65 (s, 5, C_5H_5), 2.65–3.3 (m, 15, Ph). ^{13}C NMR ($CDCl_3$, 15 MHz): δ 88.1 (t, $^1J_{CH}$ = 127 Hz, C_α), 113.4 (d of m, $^1J_{CH}$ = 190 Hz, C_5H_5), 124.0 (d of t, $^1J_{CH}$ = 152 Hz, C_p), 127.7 and 128.5 (overlapping doublets, $^1J_{CH}$ = 158 and 157 Hz, respectively, C_o and C_m), 146.9 (s, C_β). Cleavage of benzyl groups from (C_5H_5)Ta-

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$(CH_2Ph)_3Cl$ with 2.5 M anhydrous HCl in ether in the presence of C_8H_{18} (internal standard) followed by GLC analysis showed 2.73 mol of toluene/mol of tantalum.

Preparation of $Ta(\eta^5\text{-}C_5H_4Me)(CH_2Ph)_3Cl$. $Ta(CH_2Ph)_3Cl_2$ (5.00 g, 9.52 mmol) was dissolved in tetrahydrofuran (50 mL) and the solution cooled to −78 °C. LiC_5H_4Me (0.82 g, 9.53 mmol) in tetrahydrofuran (30 mL) was added dropwise over 30 min to the stirred solution. The mixture was warmed to room temperature and stirred for 60 min, and then all solvent was removed in vacuo. The crude black solid was extracted with CH_2Cl_2 (125 mL), the solution was filtered (0.36 g of white solid; theory for LiCl = 0.40 g), and the filtrate was cooled to −30 °C. After 24 h, 2.46 g of black crystals were obtained by filtration. A second crop was later isolated (0.54 g) to give a total of 3.00 g of product (55% yield).

Anal. Calcd for $TaC_{27}H_{28}Cl$: Cl, 6.23. Found: Cl, 6.23. ^1H NMR (CD_2Cl_2): τ 8.00 (s, 3, Me), 7.25 (s, 6, CH_2), 4.20–4.30 and 3.95–4.05 (m, 4, $C_5H_2H'_2Me$), 2.80–3.40 (m, 15, Ph).

Preparation of $Ta(\eta^5\text{-}C_5Me_4Et)(CHPh)(CH_2Ph)Cl$. $Ta(CH_2Ph)_3Cl_2$ (4.00 g, 7.62 mmol) and LiC_5Me_4Et (1.19 g, 7.63 mmol) were placed in a 60-mL glass bomb with magnetic stirbar. Tetrahydrofuran (50 mL) was added, and the mixture was stirred at 60 °C for 1 h. The oil obtained by removing all solvent in vacuo was extracted with hexane, and the solution was filtered and all solvent removed in vacuo to give an oil. The oil was dissolved in a minimum volume of 25% (v/v) ether in hexane and the solution placed in a flask whose walls were then scratched. Cooling the solution to −30 °C gave a microcrystalline powder (0.52 g, 13%) which was removed by filtration and dried. This compound commonly oils out of solution.

Anal. Calcd for $TaC_{25}H_{30}Cl$: C, 54.89; H, 5.54; Cl, 6.48. Found: C, 54.30; H, 5.40; Cl, 6.37. ^1H NMR (C_6D_6, 270 MHz): τ 9.174 (t, 3, $^3J_{HH}$ = 7.5 Hz, CH_3CH_2), 8.197 and 8.204 (s, 6, Me and Me′), 8.144 (s, 6, Me″ and Me‴), 7.741 (q, 2, $^3J_{HH}$ = 7.7 Hz, CH_2CH_3), 7.549 and 7.889 (AB q, 2, $^2J_{H_AH_B}$ = 12 Hz, CH_AH_BPh), 3.251 (s, 1, =CH), 2.64–3.15 (m, Ph and Ph′). $^{13}C\{^1H\}$ NMR (C_6D_6, 22.63 MHz): δ 11 (four Me groups of C_5Me_4Et), 15 (CH_3CH_2), 20 (CH_2CH_3), 64 (CH_2Ph), 117 and 116 (C_5Me_4Et, methyl-bearing ring carbons), 122 (C_5Me_4Et, unique ring carbon), 124, 125, 127, 129, and 130 (Ph and Ph′, excluding C_β of benzylidene), 148.9 (C_β of benzylidene), 222 (benzylidene C_α). Multiplicities were confirmed by off-resonance proton decoupling.

GLC analysis of the reaction mixture volatiles with the use of heptane as an internal standard showed that 0.86 mol of toluene/mol of tantalum was generated in the reaction.

Preparation of $Ta(\eta^5\text{-}C_5Me_5)(CHPh)(CH_2Ph)Cl$. $Ta(CH_2Ph)_3Cl_2$ (7.88 g, 15.0 mmol) and LiC_5Me_5 (2.35 g, 16.5 mmol, 10% excess) were stirred in tetrahydrofuran (30 mL) overnight. All volatiles were removed in vacuo, and the resulting solid was extracted with toluene (30 mL) for several days. The mixture was filtered (0.68 g of white powder; theory for LiCl plus unreacted LiC_5Me_5 = 0.85 g) and all solvent removed from the filtrate in vacuo. The resulting oil was exhaustively triturated with pentane (120 mL) and filtered to yield 3.98 g of brick-red powder. Cooling the filtrate to −30 °C overnight afforded, upon filtration, 1.59 g of additional product (total = 5.57 g, 70% yield).

The yield of toluene formed in the reaction was determined by adding octane (2.28 g, 19.9 mmol) as an internal standard to the trap-to-trap distilled volatiles from a 20-mmol preparation. GLC analysis showed that 18.6 mmol of toluene (0.93 mol of toluene/mol of $Ta(CH_2Ph)_3Cl_2$) was produced in the reaction.

^1H NMR (C_6D_6): τ 8.18 (s, 15, CH_3), 7.55 and 7.89 (AB q, 2, $^2J_{H_AH_B}$ = 12 Hz, CH_AH_BPh), 3.27 (s, 1, =CH), 2.62–3.15 (m, 10, Ph and Ph′). ^{13}C NMR (C_6D_6): δ 11.4 (q, $^1J_{CH}$ = 128 Hz, CH_3), 64.4 (ca. 1:1:1 t, $J_{CH_A} \approx J_{CH_B} \approx$ 120 Hz, CH_AH_BPh), complex phenyl region suggests two inequivalent phenyl groups, 148.4 (s, C_β of =CHPh), 221.5 (d, $^1J_{CH_\alpha}$ = 85 Hz, =CHPh).

Thermal Preparation of $Ta(\eta^5\text{-}C_5Me_4Et)(CHPh)Cl_2$. $Ta(\eta^5\text{-}C_5Me_4Et)(CH_2Ph)_2Cl_2$ (1.00 g) was placed in a sublimer (dry-ice–acetone-cooled probe). Glass wool was placed over the dibenzyl compound to prevent splattering of the melted material onto the probe, and a small beaker was placed under the probe to catch any liquid or oil from the probe. The sample was heated to 140 °C on the vacuum line (~0.1 μm) until all sublimed. A small amount of oil fell into the beaker when the probe was warmed to room temperature. The probe and beaker were rinsed with hexane, the solution was filtered (insoluble material = 0.18 g), and the solvent was removed from the filtrate in vacuo to give an oil whose ^1H NMR spectrum showed it to be impure $Ta(\eta^5\text{-}C_5Me_4Et)(CHPh)Cl_2$. Fractional crystallization from hexane afforded crystalline $Ta(\eta^5\text{-}C_5Me_4Et)(CHPh)Cl_2$, 60 mg (7%).

^1H NMR (C_6D_6, 270 MHz): τ 9.22 (t, $^3J_{HH}$ = 7.6 Hz, CH_2CH_3), 8.13 (s, Me), 8.06 (s, Me′), 7.63 (q, $^3J_{HH}$ = 7.6 Hz, CH_2Ph), 3.10–3.17, 2.83–2.88, and 2.72 (m, m, and s, respectively, Ph and =CH). Integration to the expanded phenyl region suggested that the δ 3.10–3.17 region corresponded to H_p plus 2 H_o, the δ 2.83–2.88 region to 2 H_m, and the δ 2.72 resonance to =CH.

Photochemical Preparation of $Ta(\eta^5\text{-}C_5Me_4Et)(CHPh)Cl_2$. Two samples of $Ta(\eta^5\text{-}C_5Me_4Et)(CH_2Ph)_2Cl_2$ (150 mg each), each in benzene (10 mL) in a Vycor test tube with stirbar, were photolyzed with a medium-pressure mercury lamp for 1 h. The solutions were combined, and the benzene was removed in vacuo. The oil was dissolved in a minimum volume of hexane, and the solution was cooled to −30 °C. After several days a single crystal of the product (identified by ^1H NMR) was isolated by filtration and dried in vacuo; mol wt = 40 mg (16%).

Photochemical Preparation of $Ta(\eta^5\text{-}C_5Me_5)(CHPh)Cl_2$. $Ta(\eta^5\text{-}C_5Me_5)(CH_2Ph)_2Cl_2$ (1.40 g, 2.46 mmol) was dissolved in benzene (14 mL). The solution was photolyzed in 5-mm quartz tubes (thirty 0.5-mL samples, each for 45 min) with a medium-pressure mercury lamp. Volatiles were removed in vacuo at 60 °C. The residue was transferred to a sublimer and slowly heated to 140 °C. A deep red solid (0.20 g) sublimed onto the −78 °C probe in 2 h. It was identified as $Ta(\eta^5\text{-}C_5Me_5)(CHPh)Cl_2$, (17% yield) by ^1H and ^{13}C NMR.

^1H NMR (C_6D_6): τ 8.10 (s, 15, CH_3), 2.79–3.15 (m, 6, =CHPh). ^{13}C NMR (C_6D_6): δ 11.7 (q, $^1J_{CH}$ = 128 Hz, CH_3), 225.3 (d, $^1J_{CH_\alpha}$ = 91 Hz, =CHPh). The sample was too dilute for accurate phenyl carbon assignments.

Heptane was added to the volatiles for GLC analysis. They contained toluene (0.61 mol/mol of tantalum) and 1,2-diphenylethane (1.27 mol/mol of tantalum).

Preparation of $Ta(\eta^5\text{-}C_5Me_5)(CHPh)(CH_2Ph)_2$. $Ta(C_5Me_5)(CHPh)(CH_2Ph)Cl$ (5.9 g, 11.1 mmol) was dissolved in 50 mL of toluene, and 1.94 g of solid $Mg(CH_2Ph)_2(THF)_2$ was added slowly at 25 °C. Magnesium salts were filtered off after 1 h, and the solution volume was halved in vacuo to give red microcrystals (3.65 g). This solution was filtered and stripped again to ~10 mL, then warmed until all crystals dissolved, and left undisturbed overnight to give 1.5 g of larger, deep red crystals (total = 5.29 (80%)). This compound usually crystallizes as fluffy, fine needles. Solutions of it appear to supersaturate, and slow crystallization is rarely successful.

^1H NMR (C_6D_6): τ 2.6–3.2 (phenyl resonances), 4.20 (s, 1, benzylidene H_α), 6.85 (d, 2, $J_{H_AH_B}$ = 12 Hz, CH_AH_BPh), 8.15 (s, 15, C_5Me_5), 8.45 (d, 2, $J_{H_AH_B}$ = 12 Hz, CH_AH_BPh). ^{13}C NMR (C_6D_6): δ 220 (d, $^1J_{CH}$ = 82 Hz =CHPh), 149 (s, benzylidene C_β), phenyl region complex, 114 (s, C_5Me_5), 71.8 (ca. 1:1:1 t, $J_{CH_A} \approx J_{CH_B} \approx$ 120 Hz), 11.2 (s, C_5Me_5).

Reaction of $Ta(\eta^5\text{-}C_5H_4Me)(CH_2Ph)_3Cl$ with $Ph_3P{=}CH_2$ To Give $Ta(\eta^5\text{-}C_5H_4Me)(CHPh)(CH_2Ph)_2$. $Ta(\eta^5\text{-}C_5H_4Me)(CH_2Ph)_3Cl$ (1.14 g, 2.00 mmol) and $Ph_3P{=}CH_2$ (0.55 g, 2.0 mmol) were each dissolved in tetrahydrofuran (50 mL and 200 mL, respectively) and the solutions cooled to −15 °C. The latter was added to the former, and the cloudy mixture was stirred 1 h while being warmed to room temperature. A white solid (0.38 g) was filtered off and all solvent removed from the filtrate in vacuo. The resulting oil was extracted with toluene (75 mL) and the mixture was filtered to give 0.21 g of tan insolubles (total insolubles = 0.59 g; theory for $Ph_3(CH_3)P^+Cl^-$ = 0.63 g). The solvent was removed in vacuo to give an oil which was dissolved in 200 mL of pentane. Filtration removed a small amount of gummy solid. The pentane was then removed in vacuo to give an oil. [The white insoluble solid was shown to be $Ph_3(CH_3)P^+Cl^-$ by ^1H NMR in $CDCl_3$.]

^1H NMR (C_6D_6): τ 8.20 (s, 3, Me), 7.80 and 8.30 (AB q, 4, $^2J_{H_AH_B}$ = 10 Hz, CH_AH_BPh), 4.70 (m, 4, C_5H_4Me), 4.35 (s, 1, =CH), 2.70–3.15 (m, 15, Ph and Ph′). ^{13}C NMR (C_6D_6, 67.89 MHz): δ 14.3 (q, $^1J_{CH}$ = 128 Hz, Me), 55.7 (ca. 1:1:1 t, $J_{CH_A} \approx J_{CH_B} \approx$ 128 Hz, CH_AH_B), 103.0 and 104.7 (d, $^1J_{CH}$ = 183 and 171 Hz, respectively, C_5H_4Me proton-bearing ring carbons), 123.2 (s, C_5H_4Me unique ring carbon), 142.7 (s, benzylidene C_β), 219.9 (d, $^1J_{CH}$ = 89 Hz, =CHPh). The phenyl region is complex but consistent with inequivalent Ph groups.

Reaction of $Ta(\eta^5\text{-}C_5Me_4Et)(CH_2Ph)_2Cl_2$ with $Ph_3P{=}CH_2$. $Ta(\eta^5\text{-}C_5Me_4Et)(CH_2Ph)_2Cl_2$ (0.19 g, 0.33 mmol) in hexane (30 mL) was treated with $Ph_3P{=}CH_2$ (0.09 g, 0.33 mmol) in hexane (20 mL) with stirring. The mixture was stirred 15 min and filtered, leaving 0.10 g of a white precipitate (theory for $Ph_3(CH_3)P^+Cl^-$ = 0.10 g). Hexane was removed in vacuo to give a red oil whose ^1H NMR spectrum showed it to be $Ta(\eta^5\text{-}C_5Me_4Et)(CHPh)(CH_2Ph)Cl$.

With $Ta(\eta^5\text{-}C_5Me_5)(CH_2Ph)_2Cl_2$, the analogous reaction in toluene gave a nearly quantitative yield of $Ph_3(CH_3)P^+Cl^-$ (identified by ^{31}P NMR in Me_2SO) and $Ta(\eta^5\text{-}C_5Me_5)(CHPh)(CH_2Ph)Cl$ (identified by ^1H NMR in C_6D_6).

Preparation of $Ta(\eta^5\text{-}C_5Me_5)(CHPh)(CH{=}PPh_3)Cl$. $Ta(\eta^5\text{-}C_5Me_5)(CHPh)(CH_2Ph)Cl$ (0.91 g, 1.71 mmol) was dissolved in benzene (15 mL), and $Ph_3P{=}CH_2$ (0.47 g, 1.70 mmol) in benzene (10 mL) was added. The clear solution was stirred 2 h at room temperature, and then all volatiles were removed and trapped in vacuo. The residue was triturated with a minimal amount of pentane/benzene and filtered to give 0.78 g of yellow $Ta(\eta^5\text{-}C_5Me_5)(CHPh)(CH{=}PPh_3)Cl$ (64%). It can be recrystallized from toluene/pentane mixtures. Heptane (110 mg, 1.11 mmol) was added to the volatiles from the reaction, and toluene (1.21 mmol, 0.71 mmol/mmol of tantalum) was measured by GLC.

Anal. Calcd for $TaC_{36}H_{37}ClP$: C, 60.29; H, 5.21; P, 4.32. Found: C, 60.24; H, 5.43; P, 4.42. ^1H NMR (C_6D_6): τ 7.87 (s, 15, Me), 5.13 (dd, 1, $^2J_{HP}$ = 23 Hz, $^4J_{HH}$ = 2 Hz, $CH{=}P$), 3.39 (d, 1, $^4J_{HP}$ = 8 Hz, coupling to $CH{=}P$ unresolved, $={C}H$Ph), 2.78–3.15 and 2.15–2.38 (m, 20, PPh_3 and Ph). ^{13}C NMR (C_6D_6): δ 12.1 (q, $^1J_{CH}$ = 127 Hz, Me), 114.1 (s, C_5Me_5), 121.4–134.7 (complex, contains correct number of resonances for PPh_3, Ph, and $CH{=}P$ carbons), 149.9 (s, C_β in $=CHPh$), 206.6 (d, $^1J_{CH_\alpha}$ = 85 Hz, $=CHPh$).

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Photoelectron Study of the Interaction of CO with ZnO[1]

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Abstract: Ultraviolet photoelectron spectroscopy (UPS) has been used to study the chemisorption of CO on four low-index surfaces of ZnO, an active methanol catalyst. These surfaces have significant differences with respect to their coordination unsaturation; thus, a correlation between the adsorption behavior and the surface structure enables the geometric requirements for chemisorption to be determined. The He II photoelectron peak associated with the 4σ molecular orbital of the CO molecule serves as a probe of the amount of adsorbed CO. The adsorption is found to be reversible, and measurements of the equilibrium coverage as a function of temperature and pressure demonstrate that the bonding interactions are very similar on all four surfaces, with an initial heat of adsorption of 12.0 ± 0.4 kcal/mol, which decreases approximately linearly with coverage. Chemisorbed CO is readily displaced by NH_3, indicating the involvement of zinc ions in the bonding of CO to the surface. This is strongly supported by the relative CO coverage of the four surfaces under equivalent conditions, which generally correlates with the availability of unsaturated zinc sites. Angle-resolved measurements of the 4σ intensity are used to confirm this binding mode. The bonding of CO to ZnO is dominated by the σ donor interaction of the carbon end of the molecule with the zinc ion as determined from the observed decrease in the splitting of the energies of the 4σ and 5σ molecular orbitals. The lack of significant π back-bonding is supported by the increase of the dipole moment of the coordinated CO molecule to ~0.6 D as determined from He I photoelectron work function measurements. This mode of binding of CO is consistent with the observed increase in the CO stretching frequency relative to the gas-phase value and suggests possible relevance to catalysis.

Introduction

Studies of the interactions between CO and a variety of materials have been spurred by an interest in the electronic structure of CO complexes as well as in the reactivity of coordinated CO, since CO is the basic feedstock in a number of catalytic processes. While the interaction of CO with metals is currently the subject of intense study, the metal oxides are also extremely relevant as heterogeneous catalysts,[2] and their interactions with CO are somewhat unusual compared to those of known inorganic complexes.

One important system in which CO interacts with a metal oxide catalyst is the methanol synthesis reaction[3] (1). The earlier

$$CO + 2H_2 \xrightarrow[\substack{200\text{ atm}\\400\text{ C}}]{ZnO\text{-}CrO_3} CH_3OH \qquad (1)$$

industrial catalysts employed a mixture of zinc and chromium oxides, where it is believed that the active component in the catalyst is ZnO, which is prevented from sintering by the formation of a zinc chromite spinel, acting as an intercrystalline promoter.[4,5] Newer low-temperature, low-pressure Cu–Zn–Cr oxide catalyst mixtures have been developed,[6,7] in which the active material has been suggested to be Cu substituted for Zn in ZnO surface sites.[8] The mechanism of the reaction has not been clarified for any of these catalysts. A number of reaction intermediates have been proposed and a variety of "rate-determining" steps have been suggested.[9-21] In particular, there has been much speculation

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