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MULTIPLE METAL—CARBON BONDS

XIV *. PREPARATION OF ALKYLIDENETANTALUM COMPLEXES BY ALKYLIDENE TRANSFER FROM PHOSPHORANES. THE FIRST ETHYLIDENE COMPLEX AND HOW IT DECOMPOSES

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Summary

The reaction of $TaCp_2(L)Me$ ($L = PMe_3$ or PMe_2Ph) with $R_3P{=}CHR'$ (R = Me, Et, or Ph; R' = H, Me, or Ph) gives L, R_3P, and $TaCp_2(CHR')Me$ in good yield. The ethylidene complex has properties much like other alkylidene complexes in this class, but most importantly, it does not rearrange to the known $TaCp_2(C_2H_4)Me$ complex under conditions where the latter is stable. Instead, it rearranges to $TaCp_2$(propylene)H, possibly by migration of the alkyl to the alkylidene ligand followed by β-hydride elimination.

Introduction

The alkylidene ligand in Nb and Ta complexes such as $MCp_2(CHR)X$ (R = H, Ph, or CMe_3, X = alkyl or chloride) [2,3], $M(CH_2CMe_3)_3(CHCMe_3)$ [4], or $MCp(CHCMe_3)Cl_2$ (M = Nb or Ta) [1,5] appear to be nucleophilic or "ylide-like". Therefore it would seem possible to transfer an alkylidene moiety from a main group ylide to niobium(III) or tantalum(III) under the proper circumstances. One could thereby hope to prepare alkylidene complexes not available by the α-abstraction route [1,4]. Furthermore, if the resulting complex reacts uniquely with (for example) an olefin, and the main group ylide does not, then a catalytic cycle could result [†].

During the study of $TaCp_2(CH_2)(CH_3)$ [2] we discovered the phosphine complexes, $TaCp_2(L)Me$ ($L = PMe_3$ or PMe_2Ph), and saw evidence that phosphine ligand was lost readily. Substituting L with =CHR would regenerate the com-

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[†] A rare example of this type of reaction is the copper(I) catalyzed cyclopropanation of olefins by sulfur ylides [6a]. Other alkylidene sources such as diazoalkanes have been used in this manner for some time, most spectacularly to synthesize asymmetric cyclopropanes of high optical purity [6b].

plex from which they were made (if R = H) or more stable relatives (if R = Ph, etc.). Therefore we chose this type of complex to test the principle of transferring an alkylidene fragment from an ylide to Ta. This paper reports the results employing phosphoranes as the alkylidene source.

Results

The phosphine ligand (L) in $TaCp_2(L)Me$ can be displaced by CO or C_2H_4 to give the known [2] $TaCp_2(L')Me$ complexes (L' = CO or C_2H_4). Since $TaCp_2(L)Me$ is an 18 electron complex, this most likely occurs via loss of L to give the 16 electron complex, " $TaCp_2Me$" (eq. 1). The $TaCp_2(L')Me$ complexes do

$$TaCp_2(L)Me \underset{+L}{\overset{-L}{\rightleftarrows}} \text{“}TaCp_2Me\text{”} \underset{\substack{h\nu \\ (-L')}}{\overset{+L'}{\rightleftarrows}} TaCp_2(L')Me \qquad (1)$$

L' = CO or C_2H_4

not react with L to regenerate $TaCp_2(L)Me$ under similar conditions. However, irradiation of a mixture of $TaCp_2(C_2H_4)Me$ and PMe_3 in C_6D_6 (medium pressure Hg lamp) produces $TaCp_2(PMe_3)Me$ in high yield, presumably via the same "$TaCp_2Me$" complex. Therefore $TaCp_2(L)Me$ can be prepared in good yield in a two stage reaction from $TaCp_2(CH_2)Me$ (eq. 2); the first stage is the thermal

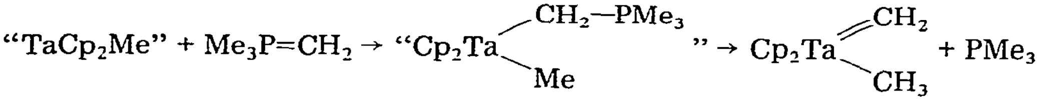
$$TaCp_2(CH_2)Me + L \xrightarrow[2.\ h\nu]{1.\ 40^\circ C} TaCp(L)Me + 0.5\ C_2H_4 \qquad (2)$$

decomposition of $TaCp_2(CH_2)Me$ to $TaCp_2(C_2H_4)Me$ and $TaCp_2(PMe_3)Me$ [2].

$TaCp_2(PMe_3)Me$ reacts slowly at 25°C with $Me_3P{=}CH_2$ (1/5 in benzene) to give $TaCp_2(CH_2)Me$, a process which can be followed easily by ^1H NMR (eq. 3).

$$TaCp_2(PMe_3)Me + Me_3P{=}CH_2 \xrightarrow{25^\circ C} TaCp_2(CH_2)Me + 2\ PMe_3 \qquad (3)$$

Unfortunately, $TaCp_2(CH_2)Me$ decomposes to $TaCp_2(C_2H_4)Me$ and "$TaCp_2Me$", and reacts with $Me_3P{=}CH_2$ to give $TaCp_2(C_2H_4)Me$, not much more slowly than the rate at which it is formed [2]. Under these conditions the final product is $TaCp_2(C_2H_4)Me$, which does not react with $Me_3P{=}CH_2$ in 24 h at 80°C. On irradiation $TaCp_2(C_2H_4)Me$ does react with $Me_3P{=}CH_2$ to give $TaCp_2(CH_2)Me$, C_2H_4, and PMe_3 (by ^1H NMR). [Therefore it is possible to catalyze the decomposition of $Me_3P{=}CH_2$ to Me_3P and ethylene with $TaCp_2(CH_2)Me$ as long as the reaction is irradiated.] Clearly it is necessary to generate "$TaCp_2Me$" either thermally (from $TaCp_2(PMe_3)Me$, eq. 3) or photochemically (from $TaCp_2(C_2H_4)Me$) in order that $Me_3P{=}CH_2$ can coordinate to tantalum(III) to give short-lived I which loses PMe_3 to give $TaCp_2(CH_2)Me$ (eq. 4).



$$\text{“}TaCp_2Me\text{”} + Me_3P{=}CH_2 \rightarrow \text{“}Cp_2Ta{<}\begin{matrix}CH_2{-}PMe_3\\ Me\end{matrix}\text{”} \rightarrow Cp_2Ta{<}\begin{matrix}{=}CH_2\\ CH_3\end{matrix} + PMe_3 \qquad (4)$$

(I)

Treating $TaCp_2(PMe_3)Me$ with $Ph_3P{=}CH_2$ under the same conditions gives similar results. However, this reaction is slightly slower vs. that employing

TABLE 1

STRUCTURAL AND NMR DATA [a]

Compound	$\delta(C_\alpha)$ (ppm)	${}^1J(CH_\alpha)$ (Hz)	θ_{ene}(°)	Φ(°)	$\Delta G^{\ddagger}_{rot}$ (±0.2 kcal mol^{-1})
$TaCp_2(CH_2)Me$ [7,3]	224	132	126(5)	0(3)	⩾21 [b]
$TaCp_2(CHMe)Me$	245	125	[130(est]	[±5(est)]	20.5
$TaCp_2(CHPh)(CH_2Ph)$ [3]	246	127	135.2(7)	−5.7(5)	19.3
$TaCp_2(CHPh)Me$	243	126	—	—	17.9
$TaCp_2(CHCMe_3)Cl$ [8,3]	274	121	150.4(5)	10.3(5)	16.8

[a] Φ is the deviation of the alkylidene plane from an orientation 90° to the C=Ta—X plane (X=Cl, CH_3, etc.; a negative value implies rotation to the "inside"). ϑ_{ene} is the Ta=C—R angle (R = H, Ph, Me). $\Delta G^{\ddagger}_{rot}$ refers to the process in which the alkylidene ligand turns into the C=Ta—X plane, thereby equilibrating the inequivalent cyclopentadienyl groups [3]. [b] This value is estimated based on the inability to see the methylene ligand rotate in $TaCp(\eta^5\text{-}C_5H_4Me)(CH_2)(CH_3)$ under a given set of conditions [3].

$Me_3P{=}CH_2$ (30% complete in 17 h for the former vs. 40% complete in 17 h for the latter).

$TaCp_2(PMe_2Ph)Me$ reacts smoothly with $Me_3P{=}CHPh$ at 60°C to give $TaCp_2(CHPh)Me$, PMe_2Ph, and PMe_3 (eq. 5). $TaCp_2(CHPh)Me$ (like $TaCp_2(CHPh)(CH_2Ph)$ [3]) is thermally stable and does not react with $Me_3P{=}CHPh$ under these conditions. Therefore it can be isolated in good yield. Its ^1H and ^{13}C NMR spectra and dynamic behavior are very similar to those of $TaCp_2(CHPh)(CH_2Ph)$ (vide infra and Table 1). $TaCp_2(PMe_2Ph)Me$ reacts smoothly but more slowly with $Ph_3P{=}CHPh$ under the same conditions to give $TaCp_2(CHPh)Me$; the product is more difficult to isolate in this case due to the presence of PPh_3.

$$TaCp_2(PMe_2Ph)Me + Me_3P{=}CHPh \xrightarrow[\text{benzene}]{60^\circ C} \underset{\text{(40\% isolated)}}{TaCp_2(CHPh)Me} + PMe_3 + PMe_2Ph \quad (5)$$

$TaCp_2(PMe_3)Me$ reacts smoothly with $Et_3P{=}CHMe$ at 60°C to give $TaCp_2(CHMe)Me$ which can be isolated from the reaction mixture in 50% yield as nearly white needles (eq. 6). Its ^1H NMR spectrum shows a quartet at τ — 0.55 ppm ($^3J(HH)$ = 9 Hz) for the ethylidene α-proton, a doublet at τ 7.01 ppm for the ethylidene methyl group, and a singlet at τ 9.85 ppm for the methyl group bound to the metal. The cyclopentadienyl groups are inequivalent and give rise to two singlets (at 25°C, 60 MHz) which suggests the ethylidene ligand is oriented roughly perpendicular to the C—Ta=C plane in this pseudo-tetrahedral molecule, as is found in $TaCp_2(CH_2)Me$ and other members of this class (Table 1). Its ^{13}C NMR spectrum is straightforward. The ethylidene α-carbon atom is found at 245 ppm with ${}^1J(CH_\alpha)$ 125 Hz.

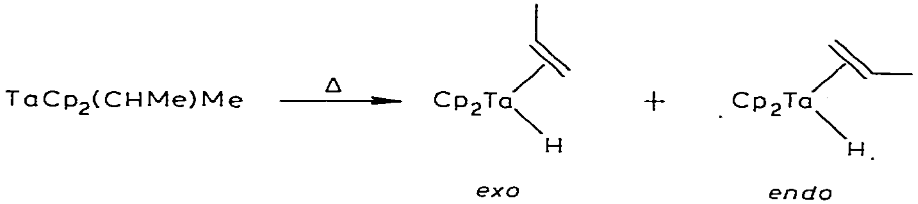
$$TaCp_2(PMe_3)Me + Et_3P{=}CHMe \xrightarrow[\text{benzene}]{60^\circ C} \underset{\text{(50\% isolated)}}{TaCp_2(CHMe)Me} + PMe_3 + PEt_3 \quad (6)$$

The variable temperature ^1H NMR spectra of $TaCp_2(CHPh)Me$ and $TaCp_2(CHMe)Me$ both are characteristic of "rotation" of the alkylidene ligand from its roughly perpendicular orientation into the C—Ta=C plane [3]. The $\Delta G^{\ddagger}$

value for $TaCp_2(CHPh)Me$ (17.9 ± 0.2 kcal mol^{-1} at 331 K) differs only slightly from that for $TaCp_2(CHPh)(CH_2Ph)$ (19.3 kcal mol^{-1} at 349 K). (Differences in the order of 1 kcal mol^{-1} are probably not especially significant.) $\Delta G^{\ddagger}$ for $TaCp_2(CHMe)Me$ is somewhat higher (20.5 kcal mol^{-1}) and the difference between it and $TaCp_2(CHPh)Me$ therefore may be significant; the results would suggest that a methyl group is not as sterically demanding as a phenyl group and the ethylidene ligand therefore is slightly more difficult to tip into the plane.

The structures of $TaCp_2(CHPh)Me$ and $TaCp_2(CHMe)Me$ are probably very similar to that of $TaCp_2(CHPh)(CH_2Ph)$ [3] since $\delta(C_\alpha)$, ${}^1J(CH_\alpha)$, and $\Delta G^{\ddagger}$ are nearly the same for the three, and since there seems to be a definite correlation between these parameters, θ_{ene}, and Φ (Table 1); $\delta(C_\alpha)$, θ_{ene}, and Φ increase as ${}^1J(CH_\alpha)$ and $\Delta G^{\ddagger}{}_{rot}$ decrease. We can therefore predict that the $Ta{=}C_\alpha{-}Me$ angle in $TaCp_2(CHMe)Me$ will be in the order of 130°, and Φ, the amount the ethylidene ligand plane deviates from the perpendicular, will be in the order of $\pm 5°$. We cannot predict which way the ethylidene will be tipped based on these data alone.

$TaCp_2(CHMe)Me$ begins to decompose at 70°C in benzene. The major product which we can see by ${}^1H$ NMR has been isolated (in 32% yield) and identified as $TaCp_2(propylene)H$. One isomer is formed early in the decomposition reaction but the final mixture consists of what we propose is a 1.0/0.8 mixture of the "*exo*" and "*endo*" isomers (eq. 7); we do not know which one is formed



(7)

first. At 100°C little $TaCp_2(propylene)H$ is found since it decomposes readily at this temperature. We should note that $TaCp_2(C_2H_4)Me$, which we believed to be the most likely decomposition product and which is stable under the reaction conditions, was never found at any temperature. We have not been able to identify the insoluble brown precipitate.

$TaCp_2(CHPh)Me$ begins to decompose at ~100°C but no single soluble organometallic product predominates. In the presence of PMe_3 as a trapping agent we can identify $TaCp_2(PMe_3)Me$, toluene, and bibenzyl by ${}^1H$ NMR, a fact which suggests this decomposition is not straightforward. $TaCp_2(CHPh)(CH_2Ph)$ is also more stable thermally than $TaCp_2(CHPh)Me$ and does not decompose to any recognizable soluble product.

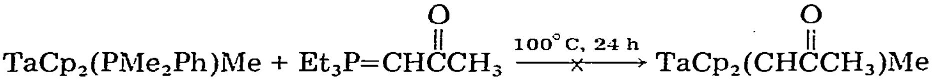
Discussion

Several groups have investigated the reaction of phosphorus ylides with transition metal complexes in the past few years [9]. In no case has any evidence for alkylidene transfer been found. Either the phosphorane attacks a ligand (e.g., CO) in preference to the metal, the alkylidene carbon atom bonds to the metal but the phosphine does not leave, or other reactions of the initial complex (such as loss of a proton from the alkylidene carbon atom between M and P) are faster than loss of the phosphine to give the alkylidenemetal complex. The second would be especially true if the alkylidene α-carbon atom in the hypothetical alkylidenemetal complex would not be nucleophilic (as it is here) but electrophilic, and would therefore remain strongly bound to the phosphine Lewis base.

The initial attack of the ylide on the metal is best described as nucleophilic attack by the electron pair on the alkylidene carbon in $R_3\overset{+}{P}-\overset{-}{C}HR'$ on an empty Ta orbital; the electron pair in another Ta orbital eventually forms the π-component of the double bond. For steric reasons it is reasonable that the reaction slows down as R or R′ becomes larger (rate for $R = Me > Ph$; $R' = H > Et \sim Ph$). Not surprisingly, therefore, we have not been able to transfer neopentylidene from $Ph_3P{=}CHCMe_3$ to $TaCp_2(PMe_3Ph)Me$ (eq. 8). The reaction would also

$$TaCp_2(PMe_2Ph)Me + Ph_3P{=}CHCMe_3 \overset{100^{\circ}\mathrm{C},\ 24\ \mathrm{h}}{\not\longrightarrow} TaCp_2(CHCMe_3)Me \qquad (8)$$

slow if the basicity of the ylide decreases. This (along with the steric arguments) can explain why $Et_3P{=}CHC({=}O)CH_3$ will not react with $TaCp_2(PMe_2Ph)Me$ under similar conditions (eq. 9).



$$TaCp_2(PMe_2Ph)Me + Et_3P{=}CH\overset{\overset{\displaystyle O}{\|}}{C}CH_3 \overset{100^{\circ}\mathrm{C},\ 24\ \mathrm{h}}{\not\longrightarrow} TaCp_2(CH\overset{\overset{\displaystyle O}{\|}}{C}CH_3)Me \qquad (9)$$

The alkylidene transfer reaction was successful not only because the products are known species but probably also because the coordination sphere in this type of complex is severely crowded. The phosphine therefore may be lost more readily from the $Ta{-}CHR'{-}PR_3$ intermediate, but more importantly, CHR′ cannot be deprotonated by additional phosphorane before PR_3 leaves. It would be interesting to know if the alkylidene could be transferred successfully to a relatively uncrowded molecule.

$TaCp_2(CHMe)Me$ is the first example of a terminal ethylidene complex *. The most important feature of an ethylidene ligand is that it has β-hydrogen atoms yet does not rearrange to ethylene. This should be compared with the postulated rearrangement of a =CPhMe ligand to styrene in $(CO)_5W(CPhMe)$ [11] ($t_{1/2} \approx 30$ min at -78°C in ether [11b]). $ReCp(CO)_2(CPhMe)$ [12] and $MnCp(CO)_2(CPhMe)$ [13] have been isolated but no data concerning how they decompose have appeared. The only other complex of an alkylidene ligand which has β-hydrogen atoms is $MnCp(CO)_2(CMe_2)$ [13,14]. Its mode of decomposition likewise is unknown.

Since $(CO)_5W(CPhMe)$, $MCp(CO)_2(CPhMe)$ (M = Re or Mn), $MnCp(CO)_2(CMe_2)$, and $TaCp_2(CHMe)Me$ are all 18 electron complexes, rearrangement may not necessarily depend on the availability of a proper metal coordination site, as is apparently the case for facile β-hydride elimination from an alkyl complex to give an olefin hydride intermediate [15]. This is not unreasonable since, in contrast to β-elimination, an intermediate such as a vinyl hydride [11b] does not involve an increase in the valence electron count of the metal.

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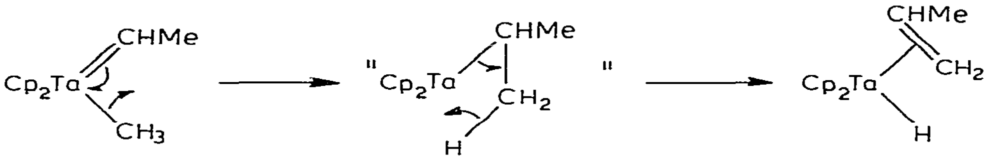
* Hermann has reported the bridging ethylidene complex, $[RhCp(CO)]_2(CHMe)$ [10].

A smooth, facile, perhaps "metal-assisted" H_β to C_α shift may then depend primarily on whether the M=C_α—Me angle is small. In $MnCp(CO)_2(CMe_2)$ [14] the two are 126.2(5)° and 124.1(5)°. In $TaCp_2(CHMe)Me$ it is a ca. 130° (estimated; vide supra). But in a =CPhMe complex the M=C_α—Me angle would probably be less than 125° due to the greater steric demands of the phenyl ring. One might argue that rearrangement to styrene is especially favorable because the double bond is conjugated with the phenyl ring; but this is true in the M=CPhMe complex also and any such stabilizing effects therefore may cancel out.

The way $TaCp_2(CHMe)Me$ does decompose is especially interesting if one makes the analogy between an alkylidene ligand and carbon monoxide. We propose that the methyl group migrates to the alkylidene ligand to give intermediate "$TaCp_2(CHMe_2)$" (which is analogous to "$TaCp_2Me$"; vide supra) which then loses a β-hydrogen atom [15] to give $TaCp_2$(propylene)H * (eq. 10). This is attractive since one would then predict that only one isomer forms first (as we have observed) and that it would be the *exo* isomer (which we, unfortunately, cannot confirm independently). Migration of an alkyl to an alkylidene ligand would seem somewhat unusual, however, since it is apparently unfavorable relative to elimination of alkane to give an alkylidyne ligand in the few cases which have been discovered so far [17]. Either migration of an alkyl to an alkylidene ligand is actually the more general reaction (and loss of alkane to give the alkylidyne the exception) or elimination of alkane is "blocked" because $Cp_2Ta{\equiv}CMe$ is a relatively high energy, unfavorable product. The latter certainly seems reasonable since the available bonding orbitals in the dicyclopentadienyl fragment all lie in the plane which passes between the two rings [18]; i.e., none would be available to form the "out-of-plane" π-type bond. At this time, however, we cannot be certain that benzylidyne and neopentylidyne ligands are not exceptions, and therefore cannot choose between these two possibilities.



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Experimental

All operations were performed under nitrogen in a Vacuum Atmospheres Drybox or by Schlenk techniques. All solvents were dried by standard techniques under nitrogen. Alkylidene phosphoranes were prepared from phosphonium salts employing $NaNH_2$ in THF [19], except $Et_3P{=}CHCOCH_3$, which was prepared from $Et_3\overset{+}{P}CH_2COCH_3$ using $Ph_3P{=}CH_2$ as the base. $TaCp_2(CH_2)Me$ was prepared as before [2].

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* This and similar complexes have recently been prepared by Teuben by treating $TaCp_2Cl_2$ with excess Grignard reagent [16].

Preparation of $TaCp_2(L)Me$ ($L = PMe_3$ or PMe_2Ph; improved method [2])

A toluene solution containing $TaCp_2(CH_2)Me$ (7 g, 20.6 mmol) and PMe_3 (1.88 g, 24.7 mmol) was heated to 60°C for 48 h, then transferred to a Vycor irradiation vessel and irradiated with a Hanovia 450 Watt medium pressure lamp for 24 h. The solution was filtered and the volume reduced to ca. 10 ml to give 3.85 g of deep red crystals of $TaCp_2(PMe_3)Me$. Adding pentane (30 ml) to the first filtrate and standing overnight at —30°C gave an additional 1.4 g of product (63% yield total).

The procedure for preparing $TaCp_2(PMe_2Ph)Me$ was identical and the yield the same. Anal. Found: C, 49.04; H, 5.41. $TaC_{19}H_{24}P$ calcd.: C, 49.15; H, 5.21%.

Alternatively, $TaCp_2(L)Me$ can be prepared in 60% yield by similarly photolyzing a 1/1 mixture of $TaCp_2(C_2H_4)Me$ and L in toluene followed by the isolation procedure described above.

Preparation of $TaCp_2(L')Me$ from $TaCp_2(L)Me$ ($L' = CO$ or C_2H_4)

$TaCp_2(PMe_2Ph)Me$ (0.46 g, 1 mmol) was dissolved in 5 ml of toluene and the solution heated at 60°C for 24 h under 60 psig of CO. The resulting green solution was filtered and the volume reduced to 1 ml. Pentane (4 ml) was added and the solution was left at —30°C overnight to give 0.21 g of blue-green crystalline $TaCp_2(CO)Me$ (60% yield) which was identified by its ^1H NMR and IR spectra [2].

An identical procedure employing C_2H_4 instead of CO gave a 60% yield of yellow $TaCp_2(C_2H_4)Me$ [2].

Observation of $TaCp_2(CH_2)Me$ in the reaction of $TaCp_2(PMe_2Ph)Me$ with $Me_3P{=}CH_2$

$Me_3P{=}CH_2$ (5 mol per Ta) was added to an ^1H NMR sample of $TaCp_2(PMe_2Ph)Me$ in C_6D_6. After 24 h at 25°C peaks corresponding to $TaCp_2(CH_2)Me$ appeared. These grew in the next 24 h but peaks corresponding to $TaCp_2(C_2H_4)Me$ also appeared. After heating 1 day at 60°C the solution contained only $TaCp_2(C_2H_4)Me$, PMe_3, and $Me_3P{=}CH_2$ by ^1H NMR.

Preparation of $TaCp_2(CHPh)Me$.

A toluene solution (30 ml) containing $TaCp_2(PMe_2Ph)Me$ (1.16 g, 2.5 mmol) and $Me_3P{=}CHPh$ (0.52 g, 3.13 mmol) was heated to 60°C for 48 h. The solution was filtered and the solvent and PMe_2Ph removed in vacuo at 50°C. The partially solidified residue was taken up in a minimum volume of toluene (~10 ml) and three volumes of pentane were added followed by a small quantity of activated charcoal. The mixture was filtered and the filtrate cooled to —30°C for 2 days to give 0.42 g of $TaCp_2(CHPh)Me$ as a microcrystalline brown solid (40%). Recrystallization in a similar fashion gave dark gold crystals of analytically pure material.

Anal. Found: C, 52.08; H, 5.04. $TaC_{18}H_{19}$ calcd.: C, 51.93; H, 4.60%. ^1H NMR (τ C_6D_6): -0.67 (s, 1, $C\underline{H}Ph$), 2.80 (m, 5, Ph), 4.92 (s, 5, Cp), 5.08 (s, 5, Cp'), 9.81 (s, 3, Me). ^{13}C NMR (ppm, C_6D_6, ^1H gated decoupled): 243 (d, $^1J(CH)$ 126 Hz, $C\underline{H}Ph$), 160 (s, C_{ipso}), 128 and 126 (each a d, $^1J(CH)$ 157 Hz, C_o and C_m), 123 (d, $^1J(CH)$ 160 Hz, C_p), 101 (d, $^1J(CH)$ 177 Hz, Cp and Cp'), -1 (q, $^1J(CH)$ 123 Hz, Me).

Preparation of $TaCp_2(CHMe)Me$

A benzene solution (50 ml) containing 0.86 g (2.14 mmol) $TaCp_2(PMe_3)Me$ and 0.38 g (2.56 mmol) $Et_3P{=}CHMe$ was heated at 60°C for 24 h. The solution was filtered and the volume reduced to ~2 ml in vacuo. Addition of 6 ml of pentane gave 0.39 g off-white crystalline product. An analytical sample was obtained by cooling to —30°C a saturated toluene solution to which three volumes of pentane had been added.

Anal. Found: C, 43.59; H, 4.81. $TaC_{13}H_{17}$ calcd.: C, 44.08; H, 4.84%. ^1H NMR (τ C_6D_6): —0.55 (q, 1, J(HH) 9 Hz, $C\underline{H}Me$), 4.95 (s, 5, Cp), 5.01 (s, 5, Cp′), 7.01 (d, 3, J(HH) 9 Hz, $CH\underline{Me}$), 9.85 (s, 3, Ta-Me). ^{13}C NMR (ppm, C_6D_6, ^1H gated decoupled): 245 (d, ^1J(CH) 125 Hz, $\underline{C}HMe$), 100 (d, ^1J(CH) 177 Hz, Cp and Cp′), 34 (q, ^1J(CH) 124 Hz, $CH\underline{Me}$), —5 (q, ^1J(CH) 122 Hz, Ta-Me).

Attempted reaction of $TaCp_2(PMe_2Ph)Me$ with $Et_3P{=}CHCOCH_3$ and $Ph_3P{=}CHCMe_3$

A large excess of the phosphorane was added to an ^1H NMR sample of $TaCp_2(PMe_2Ph)Me$ in C_6D_6. The ^1H NMR spectrum of the sample after 24 h at 25°C was identical to the original. Heating at 80°C for 48 h resulted only in decomposition of a portion of the $TaCp_2(PMe_2Ph)Me$.

Decomposition of $TaCp_2(CHMe)Me$ and isolation of $TaCp_2(propylene)H$

A solution of $TaCp_2(CHMe)Me$ (0.95 g) in 5 ml of toluene was heated at 75°C for 24 h. The solution was then filtered and the solvent removed in vacuo. The resulting oil was extracted with 3 × 25 ml pentane leaving 0.40 g of brown solid, a C_6D_6 solution of which gave no ^1H NMR spectrum. The volume of the pale green pentane filtrate was reduced in vacuo to 1 ml. Filtration gave 0.30 g (32%) of greenish-yellow to off-white $TaCp_2(propylene)H$. It was identified by comparison of its ^1H and ^{13}C NMR spectra with those reported by Teuben [16].

^1H NMR (τ C_6D_6, 200 MHz): isomer B; 5.38 (s, 5, Cp), 5.51 (s, 5, Cp′), 7.89 (d, 3, J(HH) 6.6 Hz, $CH_2{=}CH\underline{Me}$), ~8.3—10.0 (m, $C\underline{H}_2{=}C\underline{H}Me$), 13.22 (s, 1, Ta-H): isomer A; 5.47 (s, 5, Cp), 5.51 (s, 5, Cp′), 8.21 (d, 3, J(HH) 5.9 Hz, $CH_2{=}CH\underline{Me}$), ~8.3—10.0 (m, $C\underline{H}_2{=}C\underline{H}Me$), 13.51 ((br)s, 1, Ta-H).

^{13}C NMR (ppm, C_6D_6, ^1H gated decoupled, 67.89 MHz): isomer B; 91.2 (d, J(CH) 170 Hz, Cp), 91.0 (d, J(CH) 170 Hz, Cp′), 28.3 (q, J(CH) 125 Hz, $CH_2{=}CH_2{=}CH\underline{Me}$), 16.1 (d, J(CH) 140 Hz, $CH_2{=}\underline{C}HMe$), 15.1 (t, J(CH) 144 Hz, $\underline{C}H_2{=}CHMe$): isomer A; 90.4 (d, J(CH) 170 Hz, Cp), 89.6 (d, J(CH) 170 Hz, Cp′), 24.9 (q, J(CH) 125 Hz, $CH_2{=}CH\underline{Me}$), 17.0 (d, J(CH) 136 Hz, $CH_2{=}\underline{C}HMe$), 6.6 (t, J(CH) 147 Hz, $\underline{C}H_2{=}CHMe$). IR (cm^{-1}, Nujol): 1570 ((br) s, ν(Ta-H). Isomer A is the one observed during the first half of the decomposition and is believed to have the *exo* configuration. The final ratio of A/B is 1.0/0.8. The NMR isomer assignments are based on relative peak intensities and by comparison with the data in ref. 16.

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