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PHOTO-DEGRADATION STUDIES ON DI-η^5-CYCLOPENTADIENYLDIMETHYLTANTALUM AND SOME DEUTERATED ANALOGS

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Summary

The synthesis of $(\eta^5\text{-}C_5H_5)_2Ta(CH_3)_2$ in 61% yield from $(\eta^5\text{-}C_5H_5)_2TaCl_2$ and methyllithium is described. Photo-degradation of $(\eta^5\text{-}C_5H_5)_2Ta(CH_3)_2$ in hydrocarbon solvents results in cleavage of the carbon—tantalum sigma bond. Methane is the major gaseous photo-product. Similar results are obtained in the thermolysis of $(\eta^5\text{-}C_5H_5)_2Ta(CH_3)_2$. Deuterium labelling studies indicate that the methyl ligands, the cyclopentadienyl rings and the solvent are all sources of hydrogen in the photochemically-induced formation of methane. The extent to which each source is active in this process cannot be determined, due to an isotopic preference of hydrogen over deuterium. $(\eta^5\text{-}C_5H_5)_2Ta(CH_3)_3$ and $(C_{10}H_{10}Ta)_x$ are isolated from the photolysis of $(\eta^5\text{-}C_5H_5)_2Ta(CH_3)_2$ in pentane. Irradiation of $(\eta^5\text{-}C_5H_5)_2Ta(CH_3)_2$ in the presence of carbon monoxide results in formation of $(\eta^5\text{-}C_5H_5)_2Ta(CO)CH_3$.

Introduction

In our continuing study of photo-induced reactions of early transition metal—carbon sigma bonds [1—9], we now extend our investigations of the photochemical reactions of Group VB metal—alkyl derivatives [10] to include $(\eta^5\text{-}C_5H_5)_2Ta(CH_3)_2$ (I). We also describe the synthesis of I, as well as detailed photochemical and thermal degradations of I and certain deuterated analogs.

Results and discussion

Synthesis of $(\eta^5\text{-}C_5H_5)_2Ta(CH_3)_2$ (I) * was accomplished in a manner analogous to the preparation of $(\eta^5\text{-}C_5H_5)_2Nb(CH_3)_2$ and $(\eta^5\text{-}C_5H_4CH_3)_2Ta(CH_3)_2$ [12].

$$(\eta^5\text{-}C_5H_5)_2TaCl_2 + 2\ CH_3Li \xrightarrow{Et_2O} (\eta^5\text{-}C_5H_5)_2Ta(CH_3)_2 + 2\ LiCl$$

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* I has been briefly mentioned in the literature, although details are not available [11].

Of the series of Group VB dimethyl metallocene derivatives, I is the most thermally stable, not decomposing until 150°C. The vanadium derivative is reported to decompose at 122°C [13], and the niobium derivative is reported to decompose at 130°C [12].

The ESR spectrum of I is consistent with a d^1 derivative of tantalum (g = 1.993). In toluene solution at room temperature, the spectrum consists of an eight-line pattern (A_{Ta} = 93 G) due to the unpaired electron coupling with the tantalum nucleus (^{181}Ta, I = 7/2, 100% natural abundance), together with super-hyperfine interaction with six methyl protons ($a_H \sim$ 8 G). The super-hyperfine coupling is to a great extent obscured by the large line width of the hyperfine coupling (~30 G). Large line widths appear to be common for the hyperfine coupling constants of d^1 tantalocene derivatives. Line widths of 17, 25 and 28 G have been found for $(\eta^5\text{-}C_5H_4CH_3)_2Ta(CH_3)_2$ [12,14], $(\eta^5\text{-}C_5H_5)_2Ta(C_6H_5)_2$ [14] and $(\eta^5\text{-}C_5H_5)_2TaCl_2$ [15], respectively. The values of g and A_{Ta} for I are identical to those reported for $(\eta^5\text{-}C_5H_4CH_3)_2Ta(CH_3)_2$ [12,14]. The mass spectrum of I indicates a weak molecular ion at m/e = 341, together with stepwise loss of two methyl groups at m/e = 326 and m/e = 311, respectively.

When a pentane solution of I was subjected to photolysis under polychromatic conditions (λ > 300 nm), cleavage of the tantalum—methyl sigma bonds occurred. Gas chromatographic analysis of the gas above the reaction solution indicated the presence of methane (>99%), ethane and ethylene (<1%). A similar gaseous composition was obtained from the thermolysis of I. In contrast, the photolysis of $(\eta^5\text{-}C_5H_5)_2Ta(C_2H_4)CH_3$ in the presence of ligands such as trimethylphosphine does not result in the cleavage of the tantalum—methyl sigma bond [16].

Selective deuteration of the solvent, the methyl groups and the cyclopentadienyl rings illustrates that the hydrogen which is incorporated into the methane produced in the photolysis of I arises from all three possible sources. Similar results are obtained from the photo-degradation of $(\eta^5\text{-}C_5H_5)_2VCH_3$, $(\eta^5\text{-}C_5H_5)_2V(CH_3)_2$ and $(\eta^5\text{-}C_5H_5)_2Nb(CH_3)_2$ [10]. Results of these photolytic studies involving deuterium-labelled derivatives of I are summarized in Table 1.

Selective deuteration of the methyl ligands and the cyclopentadienyl rings demonstrates that the hydrogen which is incorporated into the methane pro-

TABLE 1

DEUTERIUM CONTENT OF METHANE DERIVED FROM THE PHOTOLYSIS OF $(\eta^5\text{-}C_5H_5)_2Ta(CH_3)_2$ AND SPECIFICALLY DEUTERATED DERIVATIVES

Compound	Solvent	Deuterium content, ratio			
		CH_4	CDH_3	CD_3H	CD_4
$(\eta^5\text{-}C_5H_5)_2Ta(CH_3)_2$	C_6D_6	0.98	0.02	—	—
$(\eta^5\text{-}C_5H_5)_2Ta(CD_3)_2$	C_6H_6	—	—	0.92	0.08
$(\eta^5\text{-}C_5D_5)_2Ta(CH_3)_2$	C_6H_6	0.96	0.04	—	—
$(\eta^5\text{-}C_5D_5)_2Ta(CH_3)_2$ + $(\eta^5\text{-}C_5H_5)_2Ta(CD_3)_2$ [a]	C_6H_6	—	—	0.89	0.11
$(\eta^5\text{-}C_5D_5)_2Ta(CD_3)_2$	C_6H_6	—	—	0.20	0.80
$(\eta^5\text{-}C_5D_5)_2Ta(CD_3)_2$	cumene	—	—	0.20	0.80

[a] Equimolar mixture.

TABLE 2

DEUTERIUM CONTENT OF METHANE DERIVED FROM THE THERMOLYSIS OF $(\eta^5\text{-}C_5H_5)_2Ta(CD_3)_2$ AND $(\eta^5\text{-}C_5D_5)_2Ta(CH_3)_2$

Compound	Deuterium content, ratio			
	CH_4	CDH_3	CHD_3	CD_4
$(\eta^5\text{-}C_5H_5)_2Ta(CD_3)_2$	—	—	0.90	0.10
$(\eta^5\text{-}C_5D_5)_2Ta(CH_3)_2$	0.40	0.60	—	—

duced in the solid state thermolysis of I likewise arises from both available sources. The results of the thermal degradation of I are summarized in Table 2.

An aid in the formation of deuterated derivatives of I was the preparation of $(\eta^5\text{-}C_5D_5)_2TaCl_2$. This deuterated metallocene dichloride was prepared in 76% yield from the reaction of C_5D_5Tl [17] and $TaCl_4$ [18] in refluxing 1,2-dimethoxyethane (DME).

$$2\ C_5D_5Tl + TaCl_4 \xrightarrow[\Delta]{DME} (\eta^5\text{-}C_5D_5)_2TaCl_2 + 2\ TlCl$$

The extent to which each source of hydrogen contributes to the abstraction process cannot be exactly determined because of an isotopic preference for hydrogen over deuterium. The photolysis of I in benzene-d_6 resulted in 2% deuterium incorporation into the resulting methane while photolysis of $(\eta^5\text{-}C_5D_5)_2Ta(CD_3)_2$ in benzene resulted in 20% CD_3H. Similar isotope preferences have been observed in the photolysis of $(\eta^5\text{-}C_5H_5)_2VCH_3$ [10], $(\eta^5\text{-}C_5H_5)_2V(CH_3)_2$ [10], $(\eta^5\text{-}C_5H_5)_2Nb(CH_3)_2$ [10], $(\eta^5\text{-}C_5H_5)_2Ti(CH_3)_2$ [5] and $(\eta^5\text{-}C_5H_5)Pt(CH_3)_3$ [19].

The photolysis of an equimolar mixture of $(\eta^5\text{-}C_5D_5)_2Ta(CH_3)_2$ and $(\eta^5\text{-}C_5H_5)_2Ta(CD_3)_2$ in benzene reveals intermolecular hydrogen abstraction from the cyclopentadienyl rings is occurring to some extent. There is a slight increase in the percentage of CD_4 resulting from the photolysis of the equimolar mixture in comparison with the percentage of CD_4 produced in the photo-degradation of $(\eta^5\text{-}C_5H_5)_2Ta(CD_3)_2$.

The photolysis of $(\eta^5\text{-}C_5D_5)_2Ta(CD_3)_2$ in cumene gave the same percentage of CD_3H (20%) as the photolysis of $(\eta^5\text{-}C_5D_5)_2Ta(CD_3)_2$ in benzene. The availability of the solvent hydrogens to abstraction by methyl radicals [20] thus does not affect the formation of methane in the photo-degradation of $(\eta^5\text{-}C_5H_5)_2Ta(CH_3)_2$. The results of photolyzing I in vinyl monomers capable of undergoing free-radical initiated polymerization are summarized in Table 3. Unlike the photolysis of $(\eta^5\text{-}C_5H_5)_2Ti(CH_3)_2$ [21] or homoleptic derivatives of titanium [9], zirconium [22,23] and chromium [8], irradiation of I in the presence of styrene or methyl methacrylate did not result in the polymerization of these vinyl monomers. Rather than initiating the polymerization of styrene or methyl methacrylate, the photolysis of I in fact inhibited this process. More polystyrene and polymethyl methacrylate were obtained when the photo-reactions were run in the absence of I. Photoproducts from the irradiation of $(\eta^5\text{-}C_5H_5)_2Ti(CH_3)_2$ have been postulated to be responsible for the retardation of methyl methacrylate polymerization [21].

TABLE 3

PHOTOCHEMICAL AND DARK REACTIONS OF $(\eta^5\text{-}C_5H_5)_2Ta(CH_3)_2$ WITH METHYL METHACRYLATE AND STYRENE

Compound	Yield of polymer (g)	
	Dark	Photochemical
Methyl methacrylate	0.00	0.21
Methyl methacrylate + $(\eta^5\text{-}C_5H_5)_2Ta(CH_3)_2$	<0.01	0.02
Styrene	<0.01	0.15
Styrene + $(\eta^5\text{-}C_5H_5)_2Ta(CH_3)_2$	<0.01	0.03

The detection of cyclopentadiene in the liquid phase of the photomixture arising from the photolysis of I indicates the photo-induced loss of a cyclopentadienyl ring from I. The photochemical exchange of cyclopentadienyl ligands in $(\eta^5\text{-}C_5H_5)_2TaCl_2$ and related derivatives has been reported [24].

Prolonged photolysis of I in pentane resulted in formation of a precipitate analyzing for $C_{10}H_{10}Ta$. This material is insoluble in organic solvents, does not exhibit terminal metal hydride stretches in its infrared spectrum, and degrades in the presence of HCl to give $(\eta^5\text{-}C_5H_5)_2TaCl_2$. This residue is best formulated as a polymeric form of tantalocene, $(C_{10}H_{10}Ta)_x$, rather than the known dimeric form of tantalocene, $[(C_5H_5)(C_5H_4)TaH]_2$ [25].

Photolysis of I also resulted in formation of $(\eta^5\text{-}C_5H_5)_2Ta(CH_3)_3$ [26]. Unlike the photolysis of dibenzyl cyclopentadienyl-tantalum derivatives [27], carbene derivatives of tantalocene were not isolated from the photolysis of I. $(\eta^5\text{-}C_5H_5)_2Ta(CH_3)_3$ may be the result of a reaction between I with the sixteen-electron species $(\eta^5\text{-}C_5H_5)_2TaCH_3$, generated in the photochemical cleavage of one methyl ligand from I.

$$(\eta^5\text{-}C_5H_5)_2Ta(CH_3)_2 \xrightarrow{h\nu} [(\eta^5\text{-}C_5H_5)_2TaCH_3]$$

$$[(\eta^5\text{-}C_5H_5)_2TaCH_3] + (\eta^5\text{-}C_5H_5)_2Ta(CH_3)_2 \rightarrow (\eta^5\text{-}C_5H_5)_2Ta(CH_3)_3 + 1/x(C_{10}H_{10}Ta)_x$$

The existence of the intermediate $(\eta^5\text{-}C_5H_5)_2TaCH_3$ was substantiated by the photolysis of I in the presence of carbon monoxide. From this reaction, $(\eta^5\text{-}C_5H_5)_2Ta(CO)CH_3$ [26] was isolated in low yield together with $(\eta^5\text{-}C_5H_5)_2Ta(CH_3)_3$. The sixteen-electron intermediate could not be trapped when I was photolyzed in the presence of triethylphosphine, however. This type of intermediate has been successfully trapped in the reaction of $(\eta^5\text{-}C_5H_5)_2Ta(C_2H_4)CH_3$ with trimethylphosphine [16].

$$(\eta^5\text{-}C_5H_5)_2Ta(CH_3)_2 \xrightarrow{h\nu} [(\eta^5\text{-}C_5H_5)_2Ta(CH_3)] \xrightarrow{CO} (\eta^5\text{-}C_5H_5)_2Ta(CO)CH_3$$

The carbon—metal sigma-bonds of I can also be cleaved by HCl. Methane and $(\eta^5\text{-}C_5H_5)_2TaCl_2$ are formed in this process.

$$(\eta^5\text{-}C_5H_5)_2Ta(CH_3)_2 + 2\ HCl \rightarrow (\eta^5\text{-}C_5H_5)_2TaCl_2 + 2\ CH_4$$

Conclusions

$(\eta^5\text{-}C_5H_5)_2Ta(CH_3)_2$ can be prepared by the methylation of $(\eta^5\text{-}C_5H_5)_2TaCl_2$ in diethyl ether solution. Dimethyltantalocene is photo-active and forms methane upon irradiation. Hydrogen is incorporated from the methyl ligands, the cyclopentadienyl rings and the solvent into the photo-generated methane. Similar photochemical results have been found for the vanadium and niobium analogs of $(\eta^5\text{-}C_5H_5)_2Ta(CH_3)_2$. Solid state thermolysis of $(\eta^5\text{-}C_5H_5)_2Ta(CH_3)_2$ also generates methane. Photolysis of $(\eta^5\text{-}C_5H_5)_2Ta(CH_3)_2$ results in formation of $(\eta^5\text{-}C_5H_5)_2Ta(CH_3)_3$ and $(C_{10}H_{10}Ta)_x$. $(\eta^5\text{-}C_5H_5)_2Ta(CO)CH_3$ can be isolated from the photolysis of $(\eta^5\text{-}C_5H_5)_2Ta(CH_3)_2$ in the presence of carbon monoxide.

Experimental

All operations were conducted under argon using Pyrex Schlenk tubes. Argon, solvents and alumina were purified as described previously [5]. Photolyses were conducted with a 450 W Hanovia photochemical lamp located in a Pyrex water-cooled immersion well. This unit was placed 1—2 cm from a water-jacketed Schlenk tube containing the solution to be photolyzed.

Gas chromatographic analyses were performed on a Varian Series 2400 gas chromatograph equipped with a flame ionization detector. Gas analyses were made on a 6 ft Porapak Q column and liquid analyses were made on a 5 ft column of 1.5% OV-101 on Chromosorb. The compositions of various samples were identified by means of a Perkin-Elmer-Hitachi RMU-6L mass spectrometer. IR spectra were obtained on a Beckman IR-10 or a Perkin-Elmer 237-B infrared spectrophotometer. ESR spectra were recorded on a Varian E-9 EPR spectrometer. Proton NMR spectra were obtained on a Varian A-60 spectrometer. UV/Visible spectra were obtained on a Perkin-Elmer 202 ultraviolet-visible spectrometer.

$(\eta^5\text{-}C_5H_5)_2TaCl_2$ was prepared by a literature procedure [18]. C_5D_5Tl (96.5% deuterated) was obtained by a literature method [17]. Deuterated benzene was put through three freeze-thaw cycles after which no gas evolved on melting. Commercial methyllithium was standardized by a published method [28].

Preparation of $(\eta^5\text{-}C_5H_5)_2Ta(CH_3)_2$ (I)

$(\eta^5\text{-}C_5H_5)_2TaCl_2$ (9.00 g, 23.6 mmol) was suspended in 150 ml of diethyl ether at 0°C. Freshly standardized ethereal methyllithium (50 mmol) was added dropwise to the brown slurry. The resulting emerald green mixture was warmed to room temperature and stirred for 1 h. The now brown-red mixture was filtered and the residue washed with pentane until the washings were colorless. The filtrate was taken to dryness under vacuum. The red residue was placed on a frit, extracted with 5 × 25 ml of pentane, and the filtrate was taken to dryness under reduced pressure, yielding 4.89 g (61%) of dark red, air-sensitive $(\eta^5\text{-}C_5H_5)_2Ta(CH_3)_2$, m.p. 150°C (dec). Dimethyltantalocene may be sublimed between 60—80°C at 10^{-3} Torr; however, severe decomposition occurs at the temperatures required for sublimation. Compound I may also be purified by pentane recrystallization at —20°C. Found: C, 41.78; H, 4.70. $C_{12}H_{16}Ta$ calcd.: C, 42.24; H, 4.73%.

The mass spectrum of I exhibited the following major peaks: m/e 341 (2, M^+), 326 (15, $M - CH_3^+$), 311 (1, $M - 2\ CH_3^+$), and 66 (100, $C_5H_6^+$). ESR spectrum (toluene, room temperature): $g = 1.993$, $\langle A_{Ta} \rangle = 93$ G, $\langle a_H \rangle = 8$ G. UV/Visible (n-heptane): 557 ($\epsilon = 61$ cm^{-1} l^{-1} mol), 445 (143), 404 (213), 290 (498), 280 (1.49×10^3), 260 (2.49×10^3) and 254 nm (3.73×10^3).

Preparation of $(\eta^5\text{-}C_5D_5)_2TaCl_2$

To a slurry of 5.78 g (16.1 mmol) of freshly sublimed $TaCl_5$ in 75 ml of diethyl ether at room temperature was added 16.5 mmol of isopropylmagnesium bromide in 60 ml of diethyl ether. The resulting green mixture was stirred for 1 h. The solvent was then removed under vacuum, and the green residue was resuspended in 200 ml of DME. C_5D_5Tl (9.4 g, 34.2 mmol) was added to the mixture and the slurry refluxed for 16 h. The resulting brown mixture was cooled and taken to dryness under vacuum. The black residue was sublimed at 300°C and 10^{-4} Torr, yielding 4.80 g (76%) of $(\eta^5\text{-}C_5D_5)_2TaCl_2$.

Preparation of other deuterated analogs

$(\eta^5\text{-}C_5H_5)_2Ta(CD_3)_2$ and $(\eta^5\text{-}C_5D_5)_2Ta(CD_3)_2$ were prepared by the method used for the synthesis of $(\eta^5\text{-}C_5H_5)_2Ta(CH_3)_2$, utilizing the appropriate tantalocene dichloride and $LiCD_3$. $(\eta^5\text{-}C_5D_5)_2Ta(CH_3)_2$ was prepared from $(\eta^5\text{-}C_5D_5)_2$-$TaCl_2$ and methyllithium in a similar manner.

Gas analysis

Photolysis of $(\eta^5\text{-}C_5H_5)_2Ta(CH_3)_2$ *in pentane*

$(\eta^5\text{-}C_5H_5)_2Ta(CH_3)_2$ (0.50 g, 1.5 mmol) was dissolved in 250 ml of pentane in a water-jacketed Schlenk tube. The red-brown solution was photolyzed for 24 h. Within the first hour of irradiation, the color of the solution changed to green, and a pale yellow precipitate formed. Analysis of the gas above the reaction mixture by gas chromatographic means indicated methane (>99%), ethane and ethylene (<1%) were present.

Photolysis of $(\eta^5\text{-}C_5H_5)_2Ta(CH_3)_2$ *and deuterated analogs in benzene, benzene-*d_6 *and cumene*

Approximately 100 mg of the appropriate dimethyltantalocene derivative was dissolved in 10 ml of the appropriate solvent in a 30 ml Schlenk tube equipped with a rubber septum. The sample was photolyzed overnight in a 15°C waterbath. Gas samples were analyzed by mass spectrometry (18 eV). The results are summarized in Table 1.

Liquid analysis

Photolysis of $(\eta^5\text{-}C_5H_5)_2Ta(CH_3)_2$ *in toluene-free benzene*

A solution containing 10.0 ml of toluene-free benzene, 0.010 ml of mesitylene (internal standard) and 15 mmol of $(\eta^5\text{-}C_5H_5)_2Ta(CH_3)_2$ was photolyzed for 24 h in a 15°C waterbath. The liquid portion of the reaction mixture was analyzed by means of gas chromatography. Cyclopentadiene (11%) was detected.

Insoluble photo-products

Photolysis of $(\eta^5\text{-}C_5H_5)_2Ta(CH_3)_2$ in pentane

A saturated solution of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ta(CH}_3)_2$ in pentane was filtered into a 30 ml water-jacketed Schlenk tube. The red solution was photolyzed for 24 h. The reaction mixture was filtered and the residue washed with pentane. The golden brown solid was vacuum dried. Infrared analysis indicated no absorptions between 2100 cm^{-1} and 1500 cm^{-1}. Found: C, 38.79; H, 3.25; Ta, 56. $\text{C}_{10}\text{H}_{10}\text{Ta}$ calcd.: C, 38.60; H, 3.24; Ta 58.2%.

Addition of HCl-saturated toluene to this residue produced small quantities of hydrogen and methane. A green-brown solid also formed. This precipitate was isolated by filtration, washed with pentane and vacuum dried. Mass spectral analysis indicated that the solid was $(\eta^5\text{-C}_5\text{H}_5)_2\text{TaCl}_2$.

Soluble photo-products

Photolysis of $(\eta^5\text{-}C_5H_5)_2Ta(CH_3)_2$ in pentane

$(\eta^5\text{-C}_5\text{H}_5)_2\text{Ta(CH}_3)_2$ (1.09 g, 3.20 mmol) was dissolved in 250 ml of pentane in a water-jacketed Schlenk tube and photolyzed for 4 h. The solvent was removed under vacuum and the brown-orange residue chromatographed on alumina. Pentane eluted a faint red-brown band. A mixture of 10/1 pentane/benzene eluted a pale yellow band. This band was collected and the solvent removed under reduced pressure, leaving 0.14 g (12% based on Ta) of off-white $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ta(CH}_3)_3$ [26]. NMR (C_6D_6): τ 5.17 (s, 10 H), 9.68 (s, 6 H), 9.73 (s, 3 H): Mass spectrum: $m/e = 356$ (M^+).

Photolysis of $(\eta^5\text{-}C_5H_5)_2Ta(CH_3)_2$ in the presence of carbon monoxide

A solution of 1.56 g (4.57 mmol) of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ta(CH}_3)_2$ in 200 ml of pentane was photolyzed for 2 h in a water-jacketed Schlenk tube as a slow stream of carbon monoxide was bubbled through the mixture. The dark red solution turned green. The solvent was removed under vacuum, and the residue was chromatographed on alumina. A faint red-brown band was eluted with pentane. A 10/1 mixture of pentane/benzene eluted a yellow band immediately followed by a green band. Each band was collected separately. The solvent was removed under vacuum from the yellow band, leaving 80 mg (3% based on Ta) of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ta(CH}_3)_3$. The solvent was removed from the green band under vacuum, leaving 50 mg (3%) of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ta(CO)CH}_3$ [26]. NMR (C_6D_6): τ 5.52 (s, 10 H), 10.38 (s, 3 H); IR (toluene): $\nu(\text{CO}) = 1885\ \text{cm}^{-1}$.

Photolysis of $(\eta^5\text{-}C_5H_5)_2Ta(CH_3)_2$ in the presence of triethylphosphine

A solution containing 1.45 g (4.25 mmol) of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ta(CH}_3)_2$ and 2.0 ml (13.6 mmol) of triethylphosphine in 250 ml of pentane was photolyzed in a water-jacketed Schlenk tube for 4 h. The solvent was removed under vacuum and the residue chromatographed on a column of alumina. Pentane eluted a small red-brown band. Elution with benzene brought down a yellow band. Removal of the solvent from the latter band under vacuum gave 0.13 g (9% based on Ta) of yellow-white $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ta(CH}_3)_3$.

Photolysis of (η^5-C_5H_5)$_2$Ta(CH_3)$_2$ in bulk methyl methacrylate and styrene

A 1.50×10^{-2} *M* solution of $(\eta^5\text{-}C_5H_5)_2Ta(CH_3)_2$ in 20.0 ml of methyl methacrylate or styrene was photolyzed for 1 h at 35°C. The photolysis mixture was then added to 225 ml of methanol containing 5 ml of concentrated hydrochloric acid. The mixture was stirred overnight and the precipitated polymer collected by filtration. Following methanol washings, the white residue was dried in a vacuum oven at 50°C.

In one set of control experiments, the same procedure was repeated, but omitting the organometallic species. Another set of control experiments were run for 1 h in the dark at 35°C with and without $(\eta^5\text{-}C_5H_5)_2Ta(CH_3)_2$ present. The results of these experiments are summarized in Table 3.

Thermal degradation of (η^5-C_5H_5)$_2$Ta(CH_3)$_2$

$(\eta^5\text{-}C_5H_5)_2Ta(CH_3)_2$ (0.30 g, 0.88 mmol) was placed in a thick-walled Schlenk tube and evacuated. The system was immersed in a Wood's metal bath at 200°C for 1.75 h. The reaction vessel was cooled to room temperature. A total of 1.6 equivalents (1.41 mmol) of gas was generated in the thermolysis. Gas chromatographic analysis showed the gas consisted of methane (>99%), ethane and ethylene (<1%).

Thermal degradation of (η^5-C_5H_5)$_2$Ta(CD_3)$_2$ and (η^5-C_5D_5)$_2$Ta(CH_3)$_2$

Solid samples of the appropriate deuterated dimethyltantalocene derivatives were placed in Schlenk tubes and evacuated. The samples were placed in a 200°C bath for 8.5 h, then cooled to room temperature. Gas samples from each vessel were analyzed by mass spectrometry (18 eV). The results are summarized in Table 2.

Degradation of (η^5-C_5H_5)$_2$Ta(CH_3)$_2$ with HCl

To 0.17 g (0.50 mmol) of $(\eta^5\text{-}C_5H_5)_2Ta(CH_3)_2$ was added 5 ml of HCl-saturated toluene. Methane (1.8 equivalents) was evolved and a green-brown precipitate formed. The mixture was filtered and the residue washed with pentane. Following vacuum drying, 0.12 g (63%) of $(\eta^5\text{-}C_5H_5)_2TaCl_2$ was obtained.

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